PHYSICAL REVIEW B VOLUME 53, NUMBER 8 15 FEBRUARY 1996-II

High-pressure effects on high-field magnetophotoluminescence in $Cd_{1-x}M_xSe$ (M=Mn,Co)

Y. Matsuda and N. Kuroda
Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai 980-77, Japan

(Received 12 June 1995; revised manuscript received 30 October 1995)

Photoluminescence measurements have been performed in the diluted magnetic semiconductors $Cd_{1-x}M_xSe$(M=Mn,Co) at 4.2 K under combined extreme conditions of high hydrostatic pressure up to 2 GPa and high magnetic field up to 27 T. The field-induced shift of the energy of the A exciton is enhanced significantly by pressure in $Cd_{0.988}Co_{0.012}Se$ and $Cd_{0.95}Mn_{0.05}Se$, while it is rather reduced in $Cd_{0.75}Mn_{0.25}Se$. The former effect arises from strengthening of the p-d exchange interaction by pressure, and the latter effect shows that pressure strengthens not only the p-d exchange interaction but also the antiferromagnetic coupling among magnetic ions. The anisotropy energy of the trigonal crystal field is sensitive to pressure, as well. When magnetic field is applied perpendicular to the c axis of the wurtzite structure, the pressure effect on the exciton energy depends strongly on the external magnetic field, demonstrating that the transverse exchange field critically competes with the trigonal crystal field and the spin-orbit coupling.

I. INTRODUCTION

Pressure exerts an influence on the chemical bonds of a substance directly to modify the electronic structure as well as the crystal structure, while magnetic field quantizes the electronic states to cause various quantum effects, especially at high fields and low temperatures. Consequently, one may envisage that combination of high pressure, high magnetic field, and low temperature would induce a variety of novel properties of solids. To perform such experiments, however, one has to overcome the difficulty that the bore space of a magnet is usually too tight to set a high-pressure apparatus. In this respect optical experiment has an advantage because nowadays miniature diamond anvil cell (DAC), which is as small as 30 mm in diameter, is available. In fact the combination of a miniature DAC and fiber optic technique has enabled us to make optical measurements of various solids under pressures higher than 10 GPa at liquid-He temperatures in the presence of magnetic field up to 23 T.[1–9]

Photoluminescence in $Cd_{1-x}Mn_xSe$ and $Cd_{1-x}Co_xSe$, which are typical substances of diluted magnetic semiconductors (DMS), has been a subject for studies under combined extreme conditions.[5–8] In these compounds spins of electrons and holes of the host substance strongly couple with spins of magnetic ions through the exchange interaction. To date a number of experimental studies have been reported on the optical properties related to this exchange interaction.[10,11] According to the recent theoretical studies the exchange constant of a hole is much greater than that of an electron and it is dominated by the hybridization between the p-like valence band and the 3d states of the transition-metal ions.[12–16] This kinetic-exchange scheme claims that the strength of the hybridization is directly related to the electron-electron correlation of transition-metal ions as well as the transfer integral between the anion p and transition-metal d orbitals. Hence the exchange constants obtained from magneto-optical measurements in various DMS have been interpreted in connection with the on-site Coulomb repulsion energies.[17] However, as pointed out by Hamdani *et al.*,[17] the interpretation has not been well established yet because there remain considerable uncertainties in the estimated values of the on-site Coulomb repulsion energies and the p-d transfer integrals.

In this context optical properties of DMS under combined extreme conditions are of particular interest. Within the framework of the kinetic-exchange theory the magnitude of the exchange interaction should be in proportion to the squared p-d transfer integral V_{pd}. According to Harrison,[18] V_{pd}^2 scales with the bond length l between a magnetic ion and an adjacent anion of the host substance as l^{-7}. Namely, the pressure coefficient of the exchange constant should be an order of magnitude greater than the linear compressibility of the lattice. Nevertheless our experiment on the magnetophotoluminescence has proved that in $Cd_{0.90}Mn_{0.10}Se$ the p-d exchange constant is rather insensitive to pressure.[6] Experimentally, however, it is uncertain if the pressure dependence of the exchange constant is generally so small. Our preliminary experiments for the substances other than $Cd_{0.90}Mn_{0.10}Se$ have suggested that the exchange constant is indeed sensitive to pressure, but its pressure coefficient varies with the content x of transition-metal ions.[7,8] To examine the validity of the kinetic-exchange theory, therefore, it is required to systematically examine the pressure dependence in $Cd_{1-x}Mn_xSe$ and $Cd_{1-x}Co_xSe$ of various values of x. The study will also allow us to search for new electronic properties induced by the combined extreme conditions.

In this paper we present a systematic study on the properties of the magnetophotoluminescence due to the A exciton in $Cd_{0.95}Mn_{0.05}Se$, $Cd_{0.75}Mn_{0.25}Se$, and $Cd_{0.988}Co_{0.012}Se$ under the combination of high magnetic field up to 27 T and high pressure up to 2 GPa at 4.2 K. [Hereafter the substances are referred to as $Cd_{1-x}Mn_xSe$ or $Cd_{1-x}Co_xSe$ with the content x of metal ions specified in parentheses in such a way as $Cd_{1-x}Mn_xSe$ (x=0.05).] The results are analyzed with weight given to evaluating the pressure dependence of the p-d exchange constant and its dependence on x. The experimental details are described in Sec. II. The results are presented in Sec. III and discussed in Sec. IV with the previous results on $Cd_{1-x}Mn_xSe$ (x=0.10) taken additionally into account. Section V summarizes the results of this study.

0163-1829/96/53(8)/4471(8)/$06.00

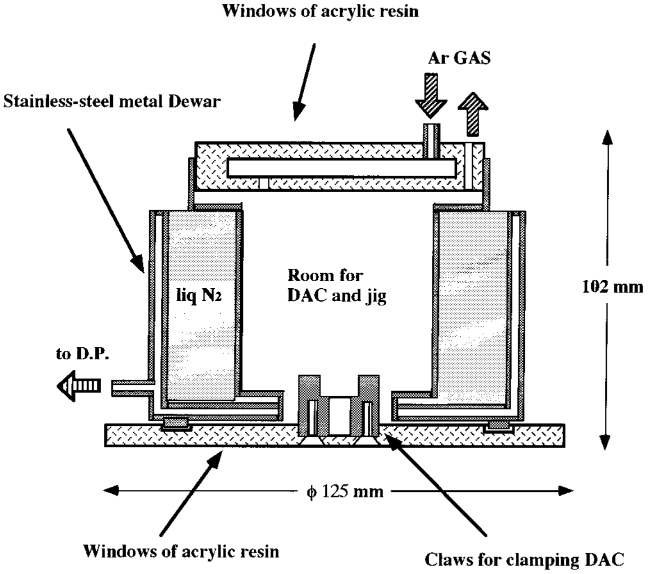

FIG. 1. Schematic diagram of an apparatus to liquefy argon in a clamp-type diamond anvil cell.

II. EXPERIMENT

A miniature DAC that has an outer diameter of 30 mm is used for generating hydrostatic pressure. This DAC is a modification of the Merrill-Bassett cell, which is of clamp-type, and can generate pressure up to about 10 GPa rather easily. Single crystals of $Cd_{1-x}Mn_xSe$ ($x=0.05$, 0.25) and $Cd_{1-x}Co_xSe$ ($x=0.012$) are cut into platelets with the typical area of 200 μm×200 μm and thickness of 30–100 μm such that the platelet surfaces are parallel or perpendicular to the c axis of the wurtzite structure. Condensed argon is used as the pressure-transmitting medium. To load the DAC with liquid argon we have constructed an apparatus with reference to the method developed by Grimsditch, Loubeyre, and Polian for the lever-type DAC.[19] Figure 1 shows the outline of the apparatus. The apparatus consists of a jig of a DAC and a stainless-steel metal Dewar. In operation, we cool the DAC down to about 77 K by using liquid N_2. Ar gas flows through the space between the upper diamond anvil and the gasket of the DAC. The dewar has a window of acrylic resin, which enables us to watch liquefied Ar by using an optical microscope. When the sample cell is filled with liquid Ar, the cell is closed by clamping the diamond anvils. The DAC is taken out of the jig after the whole system is warmed up to room temperature, and then pressure is raised to an appropriate value. Since the substances studied here undergo the structural phase transition to a rock-salt phase at 2–3 GPa,[20] the pressure range is limited to 0–2 GPa in the present work.

The value of pressure at 4.2 K is deduced from the pressure-induced energy shift of the exciton luminescence band itself at zero magnetic field on the basis of the pressure versus energy gap relationship that was obtained from the absorption measurement at room temperature. In the absorption measurement the value of pressure was obtained by the ruby fluorescence method. The pressure dependence of the fundamental absorption spectrum at room temperature shows that the shift of the energy gap below 2 GPa can be expressed well with a quadratic function of pressure P as $\Delta E_g = bP + cP^2$ in all the three materials examined. The values of the coefficients b and c are listed in Table I.

TABLE I. The values of the pressure coefficients b and c of the energy gap in $Cd_{0.95}Mn_{0.05}Se$, $Cd_{0.75}Mn_{0.25}Se$, and $Cd_{0.988}Co_{0.012}Se$.

Material	b (10^{-2} eV GPa^{-1})	c (10^{-3} eV GPa^{-2})
$Cd_{1-x}Mn_xSe$ ($x=0.05$)	5.5±0.16	−2.1±0.63
$Cd_{1-x}Mn_xSe$ ($x=0.25$)	4.4±0.14	−1.1±0.64
$Cd_{1-x}Co_xSe$ ($x=0.012$)	5.7±0.13	−3.1±0.60

Magnetic field is generated with a hybrid magnet or Bitter-type electromagnet.[21] The former can generate static magnetic fields up to 28 T in a bore of 52 mm, and the latter can generate static magnetic fields up to 15 T in a bore of 82 mm. We employ a homemade cryogenic optical fiber system.[5] The system is directly immersed in liquid He at 4.2 K in a metal Dewar. The 514.5-nm radiation of an Ar-ion laser is used as the excitation light source. The sample surface irradiated by the laser beam is mounted perpendicular to the external magnetic field and the photoluminescent light is detected in the reflection geometry.

III. RESULTS AND DATA ANALYSIS

Hydrostatic pressure widens the energy gap and thus causes a blueshift to the photoluminescence spectrum due to the A exciton. As the external magnetic field H increases, on the other hand, the spectrum shifts rapidly toward lower energies under any pressure. Figure 2 shows the field dependence of the photoluminescence spectrum in $Cd_{1-x}Mn_xSe$ ($x=0.05$) for $H \parallel c$ at 1 atm and 1.2 GPa. The observed luminescence spectrum is comprised of two bands; with increasing field the intensity of the lower-energy band is reduced significantly compared to the higher-energy band. The higher-energy band is attributable to the luminescence due to free excitons, while the lower-energy band to the luminescence due to bound excitons.[22]

Figures 3 and 4 show the plot of the energy shift of the free exciton luminescence band in $Cd_{1-x}Mn_xSe$ ($x=0.05$) and $Cd_{1-x}Co_xSe$ ($x=0.012$), respectively, at several pressures as a function of magnetic field. The exciton energy shift depends strongly on the field orientation, reflecting a strong magnetic anisotropy of the A valence band in II-VI wurtzite-type semiconductors. We see that in contrast to the case of $Cd_{1-x}Mn_xSe$ ($x=0.10$) (Ref. 6) pressure enhances the shift not only for $H \perp c$ but also for $H \parallel c$ in both $Cd_{1-x}Mn_xSe$ ($x=0.05$) and $Cd_{1-x}Co_xSe$ ($x=0.012$). In addition the shift is saturated almost completely above 15 T in $Cd_{1-x}Co_xSe$ ($x=0.012$) and thus the diamagnetic effect that leads to a blueshift proportional to H^2 can be clearly seen above 15 T. In Fig. 5 is shown the result of $Cd_{1-x}Mn_xSe$ ($x=0.25$) for $H \parallel c$. Interestingly in this substance the field-induced shift is rather suppressed by pressure.

The influence of the exchange interaction on the energies of the valence bands near the zone center of wurtzite-type DMS has been treated by Komarov *et al.*,[23] Gubarev,[24] and Aggarwal *et al.*[25] The dominant part of the Hamiltonian is

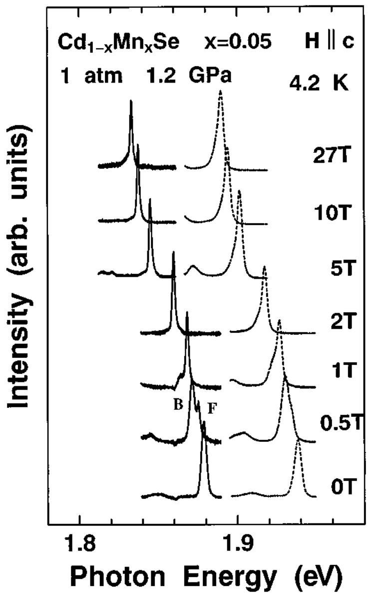

FIG. 2. Photoluminescence spectra due to the *A* exciton in $Cd_{0.95}Mn_{0.05}Se$ under various magnetic fields at 1 atm and 1.2 GPa. The features due to free and bound excitons are denoted as *F* and *B*, respectively.

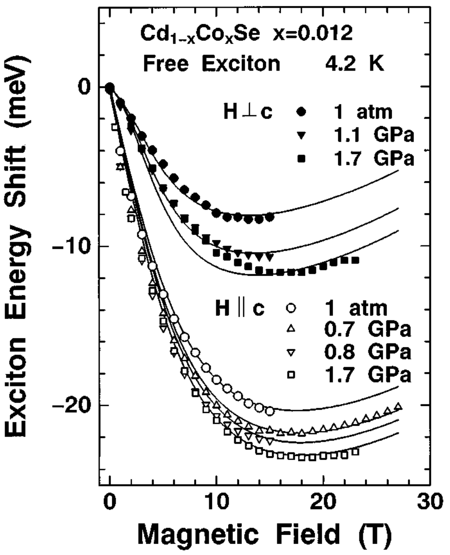

FIG. 4. Field-induced energy shift of the *A* exciton photoluminescence line in $Cd_{0.988}Co_{0.012}Se$ under several pressures. Experimental and theoretical values are shown by markers and solid lines, respectively.

given by the crystal field, spin-orbit interaction, and *p*-*d* exchange interaction:

$$\mathscr{H}_0=\mathscr{H}_c+\mathscr{H}_{so}+\mathscr{H}_{ex}. \tag{1}$$

One may espouse Hopfield's quasicubic model for $\mathscr{H}_c+\mathscr{H}_{so}$. The *p*-*d* exchange interactions of the spin **s** of a hole with spins **S** of magnetic ions are nearly isotropic and thus $\mathscr{H}_{ex}$ can be written as

$$\mathscr{H}_{ex}=N_0\beta x\langle\mathbf{S}\rangle\cdot\mathbf{s}, \tag{2}$$

where N_0 is the density of cations, β is the exchange constant, x is the mole fraction of magnetic ions, and $\langle\mathbf{S}\rangle$ is the thermal average of the spins of magnetic ions. Let the crystal c axis be the z axis and the angle between the c axis and $\langle\mathbf{S}\rangle$ be θ. Then putting $\frac{1}{2}N_0\beta x\langle S\rangle=\delta$, the Hamiltonian $\mathscr{H}_0$ can be written in a matrix form as

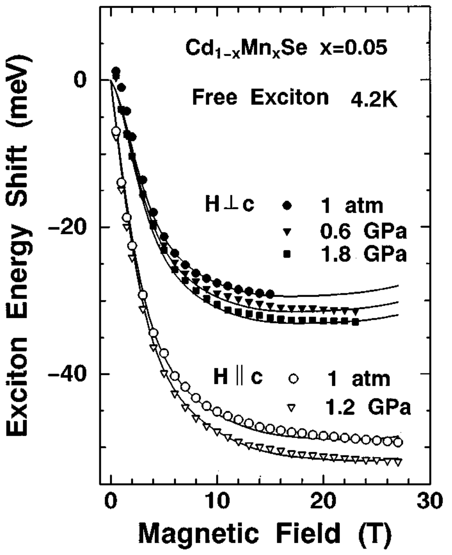

FIG. 3. Field-induced energy shift of the *A* exciton photoluminescence line in $Cd_{0.95}Mn_{0.05}Se$ under several pressures. Experimental and theoretical values are shown by markers and solid lines, respectively.

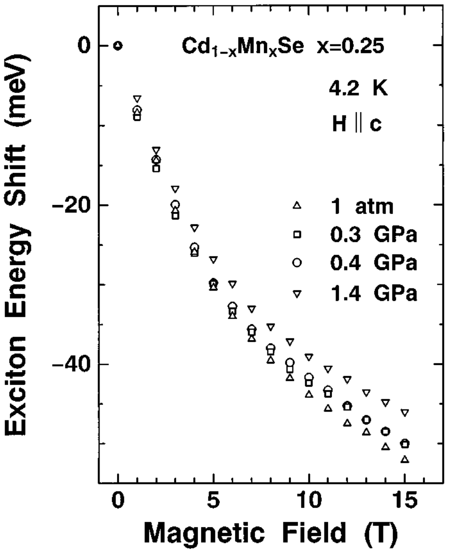

FIG. 5. Field-induced energy shift of the *A* exciton photoluminescence line in $Cd_{0.75}Mn_{0.25}Se$ under several pressures.

$$\mathscr{H}_0=\left(\begin{array}{cccccc|c}
\delta\cos\theta & \delta\sin\theta & 0 & 0 & 0 & 0 & (X_+\uparrow)\\
\delta\sin\theta & -2\Delta_2-\delta\cos\theta & \sqrt{2}\Delta_3 & 0 & 0 & 0 & (X_+\downarrow)\\
0 & \sqrt{2}\Delta_3 & -\Delta_1-\Delta_2+\delta\cos\theta & 0 & 0 & \delta\sin\theta & (Z\uparrow)\\
0 & 0 & 0 & -\delta\cos\theta & \delta\sin\theta & 0 & (X_-\downarrow),\\
0 & 0 & 0 & \delta\sin\theta & -2\Delta_2+\delta\cos\theta & \sqrt{2}\Delta_3 & (X_-\uparrow)\\
0 & 0 & \delta\sin\theta & 0 & \sqrt{2}\Delta_3 & -\Delta_1-\Delta_2-\delta\cos\theta & (Z\downarrow)
\end{array}\right) \tag{3}$$

where Δ_1 is the crystal-field anisotropy energy and Δ_2 and Δ_3 are constants of the spin-orbit interaction. In addition, the linear Zeeman energy is important at high fields not only for $H\parallel c$ but also for $H\perp c$ because for $H\perp c$ the strong transverse exchange field due to a large value of $\langle S\rangle$ induces a transverse component of hole spin; besides, the large Zeeman energy causes mixing of spin states of low-lying B and C valence bands with the A valence band. To treat these effects in the present study we incorporate the Zeeman term

$$\mathscr{H}_Z=\mu_B(L_x+2s_x)H_x+\mu_B(L_y+2s_y)H_y+g_h\mu_B s_z H_z \tag{4}$$

in the total Hamiltonian, where μ_B is the Bohr magneton, $\mathbf{L}$ is the orbital angular momentum, and g_h is the effective g parameter of a hole for $H\parallel c$.

The A exciton consists of the electron of the conduction band and the hole of the A valence band. Since for $H>5$ T the exchange field due to magnetic ions reaches the order of 100 T at 4.2 K, the effects of the electron-hole exchange interaction are negligible regardless of the direction of the external field. The photoluminescence observed is due to the 1s exciton consisting of the electron of the lower magnetic sublevel of the conduction band and the hole of the upper magnetic sublevel of the A valence band. Under high magnetic fields the exciton executes a significant diamagnetic shift, as it is clearly seen above 15 T in $\mathrm{Cd}_{1-x}\mathrm{Co}_x\mathrm{Se}$ ($x=0.012$). Writing this shift as σH^2, the field-induced energy shift ΔE_A of the observed exciton is given by

$$\Delta E_A=-\tfrac{1}{2}N_0\alpha x\langle S\rangle-\tfrac{1}{2}g_e\mu_B H-E_v+\sigma H^2, \tag{5}$$

where α and g_e are the s-d exchange constant and the g parameter of the electron, respectively; the energy E_v is the highest eigenvalue of the sum of the Hamiltonians $\mathscr{H}_0$ and $\mathscr{H}_Z$.

The value of $\langle S\rangle$ is controlled by the external magnetic field. If the content of magnetic ions is sufficiently low, $\langle S\rangle$ comes mainly from isolated ions and the nearest-neighbor pairs of ions. The isolated ions are paramagnetic, while a pair of the nearest-neighbor ions couple antiferromagnetically to one another. Then if the magnetic ion occupies a cation site in isolation at a probability P_1 and if two magnetic ions form the nearest-neighbor pair at a probability P_2, we have[26]

$$\langle S\rangle=SP_1\mathscr{B}_i\left[S\,\frac{g_M\mu_B H}{k_B(T+T_0)}\right]+\frac{1}{2}P_2\sum_n\left[1+\exp\left\{\frac{g_M\mu_B}{k_BT}(H_n-H)\right\}\right]^{-1}. \tag{6}$$

The function $\mathscr{B}_i$ of the first term on the right-hand side of Eq. (6) is the Brillouin function of index i, which equals to S, i.e., the Brillouin function relevant to $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ and $\mathrm{Cd}_{1-x}\mathrm{Co}_x\mathrm{Se}$ is $\mathscr{B}_{5/2}$ and $\mathscr{B}_{3/2}$, respectively; g_M is the g parameter of a magnetic ion, k_B is the Boltzmann constant, T is the temperature of the sample, and T_0 is an effective temperature representing the exchange mean field due to magnetic ions except for the pairs. The second term on the right-hand side of Eq. (6), which represents the contribution from the nearest-neighbor pairs, is important if the content of magnetic ions is significantly larger than 1% in such a case as $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ ($x=0.05$). The energy of the pair is quantized into states with the total spin of $S_P=0,1,2,\ldots,2S$. At zero field these states are energetically unequally separated depending on the exchange constant J_{NN}. Consequently the ground state, which at zero external field is the state $S_P=0$, is replaced successively by the lowest Zeeman sublevel of the state $S_P=1,2,\ldots$, and $2S$ as the external magnetic field increases: At the field

$$H_n=\frac{2n|J_{\mathrm{NN}}|}{g_M\mu_B} \tag{7}$$

the lowest Zeeman sublevel of the state of $S_P=n$ crosses downward over that of the state of $S_P=n-1$ to become the ground state of a pair of magnetic ions.

As evident from Eqs. (3) and (4), the magnitude of the spin splitting of the A valence band in the configuration $H\parallel c$ is simply given by $2\delta+g_h\mu_B H$. Thus the field-induced energy shift $\Delta E_{A\parallel}$ in this configuration is expressed as

$$\Delta E_{A\parallel}=-\tfrac{1}{2}N_0(\alpha-\beta)x\langle S\rangle-\tfrac{1}{2}|g_e-g_h|\mu_B H+\sigma_\parallel H^2. \tag{8}$$

Since pressure dependencies of $|g_e-g_h|$ and $\sigma_\parallel$ are expected to be very weak, the effect of pressure on $\Delta E_{A\parallel}$ would be dominated by the exchange interactions. We see from Figs. 3 and 4 that the exchange constant $\alpha-\beta$ is enhanced significantly by pressure in both $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ ($x=0.05$) and $\mathrm{Cd}_{1-x}\mathrm{Co}_x\mathrm{Se}$ ($x=0.012$). In the case of the configuration $H\perp c$, on the other hand, the theoretical value of the field-induced shift $\Delta E_{A\perp}$ of the exciton is obtained by numerically diagonalizing the sum of the Hamiltonians $\mathscr{H}_0$ and $\mathscr{H}_Z$ given by Eqs. (3) and (4), respectively.

To analyze the experimental results we take the exchange constant $N_0\beta$ and the crystal field anisotropy energy Δ_1 as the adjustable parameters dependent on pressure, whereas the quantity T_0 is treated as a parameter being adjustable but independent of pressure; besides, the electron g parameter, g_e, is assumed to be equal to 2 independent of pressure. Of course, from definition the effective temperature T_0 should

TABLE II. Valence-band parameters, exchange constants, g parameters, diamagnetic coefficients, and magnetization parameters P_1, P_2, and T_0 in $Cd_{0.95}Mn_{0.05}Se$ and $Cd_{0.988}Co_{0.012}Se$ at 1 atm. The marks ∥ and ⊥ denote the field configurations $H \| c$ or $H \perp c$, respectively.

Material	Δ_1 (eV)	Δ_2 (eV)	Δ_3 (eV)	$N_0\alpha$ (eV)	$N_0\beta$ (eV)	$\lvert g_e - g_h \rvert$	$\sigma_\parallel$ (10^{-5} eV/T^2)	$\sigma_\perp$ (10^{-5} eV/T^2)	P_1	P_2	T_0 (K)	g_{Mn}	g_{Co}	J_{NN}/k_B (K)
$Cd_{1-x}Mn_xSe$ ($x=0.05$)	0.048	0.124	0.125	0.26	−1.11	1.76	1.45	1.24	0.54(∥) 0.54(⊥)	0.35(∥) 0.29(⊥)	2(∥) 2(⊥)	2		−7.5
$Cd_{1-x}Co_xSe$ ($x=0.012$)	0.048	0.124	0.125	0.27	−2.25	1.76	0.68	0.68	1(∥) 1(⊥)		6(∥) 3(⊥)		2.3	

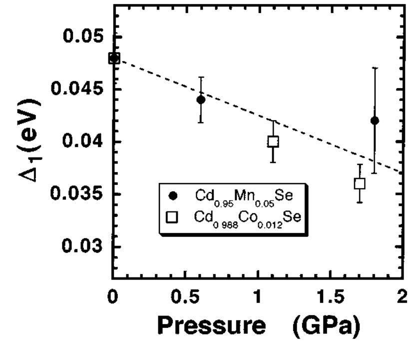

FIG. 6. Pressure dependence of the crystal field anisotropy energy Δ_1 in (●) $Cd_{0.95}Mn_{0.05}Se$ and (□) $Cd_{0.988}Co_{0.012}Se$. The dotted line shows the linear least-squares fit to the experimental data.

depend on pressure. However, our main concern is the high-field regime satisfying $g_M \mu_B H \gtrsim 2k_B(T+T_0)$. Since $\langle S \rangle$ is almost saturated in this regime, the influence of the pressure dependence of T_0 on the exciton energy can be neglected. For Δ_2, Δ_3, α, g_M, and $\sigma_\perp$, as well as $\lvert g_e - g_h \rvert$ and $\sigma_\parallel$, we employ the experimental values at 1 atm and assume them independent of pressure because they are essentially insensitive to pressure. The values of the parameters used for calculating $\Delta E_{A\parallel}$ and $\Delta E_{A\perp}$ are listed in Table II. They are all consistent with previous studies at 1 atm.[25,27–30] The contribution from magnetic ion pairs to $\langle S \rangle$ is significant in $Cd_{1-x}Mn_xSe$ ($x=0.05$). In principle, the parameter J_{NN}, as well as β, must be sensitive to pressure. An increase of J_{NN} functions to reduce ΔE_A through a change in the field H_n given by Eq. (7). However, if J_{NN} is enhanced by 10%, the amount of the reduction estimated from Eq. (8) is merely 1 meV at 20 T. Therefore J_{NN} is also assumed to be constant, as shown in Table II, in the present analysis. The validity of this assumption is discussed later.

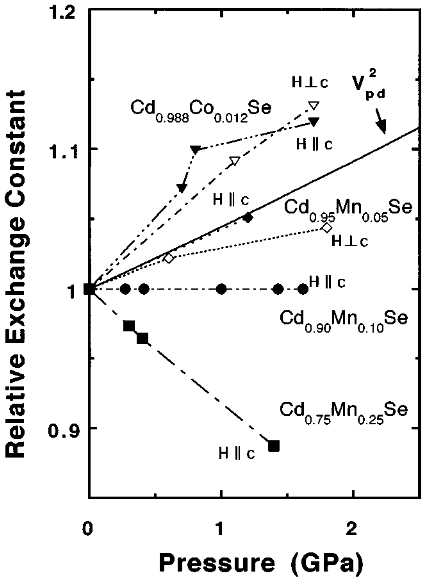

FIG. 7. Pressure-induced change of the exchange constant $\lvert N_0\beta_{hyb} \rvert$ in $Cd_{0.95}Mn_{0.05}Se$, $Cd_{0.75}Mn_{0.25}Se$, and $Cd_{0.988}Co_{0.012}Se$. Previous experimental results for $Cd_{0.90}Mn_{0.10}Se$ (Ref. 6) are also shown for comparison. The continuous line shows the pressure dependence of the squared p-d transfer integral V^2_{pd}.

Figures 3 and 4 show the theoretical curves of ΔE_A in $Cd_{1-x}Mn_xSe$ ($x=0.05$) and $Cd_{1-x}Co_xSe$ ($x=0.012$), respectively, along with the experimental data. We see that in both substances the calculated curves reproduce the experimental data very well at all pressures examined. In Fig. 6 is shown the pressure dependence of the crystal-field anisotropy energy Δ_1 deduced from this analysis. It is found that Δ_1 decreases at a rate of $d \ln \Delta_1/dP = -(11\pm1)\times10^{-2}$ GPa^{-1} in $Cd_{1-x}Mn_xSe$ ($x=0.05$) and $Cd_{1-x}Co_xSe$ ($x=0.012$), in good accord with the case of $Cd_{1-x}Mn_xSe$ ($x=0.10$).[6]

IV. DISCUSSION

A. Exchange constant

Figure 7 shows the pressure dependence of $|N_0(\beta-\alpha)|$ in $Cd_{1-x}Mn_xSe$ ($x=0.05$) and $Cd_{1-x}Co_xSe$ ($x=0.012$); the data in $Cd_{1-x}Mn_xSe$ ($x=0.10$) obtained by our previous study are also shown for comparison. We have seen in Fig. 5 that in $Cd_{1-x}Mn_xSe$ ($x=0.25$) pressure suppresses the field-induced energy shift significantly. In the case of $Cd_{1-x}Mn_xSe$ ($x=0.25$), however, the probabilities P_1 and P_2 should be lower than 0.03 and 0.02, respectively. This fact means that most Mn^{2+} ions form clusters rather than pairs. Therefore in this case Eq. (6) is not appropriate for describing the magnetization of magnetic ions. Hence for $Cd_{1-x}Mn_xSe$ ($x=0.25$) the mean value of the relative exciton energy shift is taken as a measure of the relative exchange constant $|N_0(\beta-\alpha)|$. The result is also plotted in Fig. 7. It appears from this plot that the pressure coefficient of the exchange constant $d \ln|N_0(\beta-\alpha)|/dP$ is as large as about 8×10^{-2} and 4×10^{-2} GPa^{-1} in $Cd_{1-x}Co_xSe$ ($x=0.012$) and $Cd_{1-x}Mn_xSe$ ($x=0.05$), respectively. Moreover, one may note that the quantity $\langle S\rangle$, i.e., the magnetization of transition-metal ions, is largely suppressed by pressure in the substances $Cd_{1-x}Mn_xSe$ ($x=0.10$) and $Cd_{1-x}Mn_xSe$ ($x=0.25$).

The exchange constant β may be written in terms of two parts as $\beta=\beta_{\mathrm{pot}}+\beta_{\mathrm{hyb}}$,[11] where β_{pot} and β_{hyb} are the contributions from the potential (ferromagnetic) and p-d hybridization, respectively. Since the value of β_{pot} is approximately equal to α,[31] we have

$$|N_0(\beta-\alpha)| \approx |N_0\beta_{\mathrm{hyb}}|. \tag{9}$$

In the kinetic-exchange theory[13] $N_0\beta_{\mathrm{hyb}}$ is given by the generalized Schrieffer-Wolff formula

$$N_0\beta_{\mathrm{hyb}} = -\left(\frac{1}{2S}\right)32V_{pd}^2[(E_\nu-\varepsilon_d)^{-1}+(\varepsilon_d+U_{\mathrm{eff}}-E_\nu)^{-1}], \tag{10}$$

where ε_d and U_{eff} are the mean energy and the effective on-site Coulomb energy, respectively, of the d state. As mentioned in Sec. I, the squared transfer integral V_{pd}^2 scales with the Mn(Co)-Se bond length l as l^{-7}. The compressibility of the lattice constant in CdSe can be evaluated to be 0.62×10^{-2} GPa^{-1} from the data of elastic constants,[32] which yields $d \ln V_{pd}^2/dP \approx 4.3\times10^{-2}$ GPa^{-1} as shown by the solid line in Fig. 7. Consequently, from the above-mentioned experimental result $d \ln|N_0\beta_{\mathrm{hyb}}|/dP \approx 8\times10^{-2}$ GPa^{-1}, the value of $d \ln[(E_\nu-\varepsilon_d)^{-1}+(\varepsilon_d+U_{\mathrm{eff}}-E_\nu)^{-1}]/dP$ is estimated to be $\sim3.7\times10^{-2}$ GPa^{-1} in $Cd_{1-x}Co_xSe$ ($x=0.012$), the most diluted entity of the substances studied here. It is conceived that $U_{\mathrm{eff}}\approx5.9$ eV and $E_v-\varepsilon_d=3.5$ eV at 1 atm in $Cd_{1-x}Co_xSe$ ($x=0.012$).[13,33] The present result suggests that the quantities U_{eff} and/or $E_v-\varepsilon_d$ depend significantly on hydrostatic pressure.

A good agreement between the values of $d \ln|N_0\beta_{\mathrm{hyb}}|/dP$ and $d \ln V_{pd}^2/dP$ in the case of $Cd_{1-x}Mn_xSe$ ($x=0.05$) could be rather accidental. In the present analysis J_{NN} is assumed independent of pressure. However, our experimental results suggest that this assumption is not necessarily valid. Since the spins of the nearest-neighbor ions are coupled to one another by a superexchange interaction, within the framework of the kinetic-exchange theory the coefficient J_{NN} is proportional to V_{pd}^4 and thus scales with the bond length as l^{-14}. Hence, even if the energy denominator terms,[12,34] which are also given by U_{eff} and $E_v-\varepsilon_d$, are assumed unaffected by pressure, one may expect $d \ln J_{\mathrm{NN}}/dP \approx 9\times10^{-2}$ GPa^{-1}. As mentioned in Sec. III, in $Cd_{1-x}Mn_xSe$ ($x=0.05$) the increase in J_{NN} by 10% leads to a reduction of the exciton energy shift by about 1 meV at 20 T for $H\parallel c$. Since this effect is neglected in the present analysis, the value of $d \ln|N_0(\beta-\alpha)|/dP$ should be significantly underestimated in $Cd_{1-x}Mn_xSe$ ($x=0.05$). Similarly, in the case of substances with comparatively large values of x the magnetization of clusters is expected to decrease rapidly with pressure. The effect of the decrease of magnetization of clusters on the exciton energy might almost cancel or even predominate over the effect of enhancement of the p-d exchange interaction. It may be for this reason that the apparent pressure coefficient of $|N_0(\beta-\alpha)|$ is almost null in $Cd_{1-x}Mn_xSe$ ($x=0.10$) and is negative in $Cd_{1-x}Mn_xSe$ ($x=0.25$).

B. Spin state under transverse magnetic fields

Here we look at the properties of spins under transverse magnetic fields. The spin and orbital angular momentum of a hole of the A valence band are forced to align parallel to the c axis by the spin-orbit interaction and the trigonal crystal field. As a consequence the spin of the hole in II-VI compounds with wurtzite structure has an almost ideal Ising character. In fact the A exciton exhibits no intrinsic Zeeman splitting in CdSe in the configuration $H\perp c$ up to 12 T.[27]

A distinctive feature of DMS is that the exchange interaction between an electron and magnetic ions is strong enough to break down the electron-hole exchange coupling, which rules the spin state of the exciton if magnetic ions are absent, even if the external magnetic field is very low. Therefore the exciton undergoes a large paramagnetic splitting in both of the configurations $H\parallel c$ and $H\perp c$. Moreover the p-d exchange energy 2δ of a hole reaches 0.14 eV, which corresponds to an exchange field of 1200 T, under the external magnetic field of 20 T in $Cd_{1-x}Mn_xSe$ ($x=0.05$), for example.

In the $H\perp c$ configuration the exchange energy critically competes with the anisotropy energy of the crystal field and the spin-orbit coupling to induce a large transverse component of the hole spin. Figure 8 shows this situation schematically. The effect of pressure on the exciton spectrum in this situation cannot be a simple sum of the changes in the exchange energy and the crystal-field anisotropy energy. The relative exciton energy shift obtained by calculation shown in Fig. 3 is plotted as a function of magnetic field in Fig. 9,

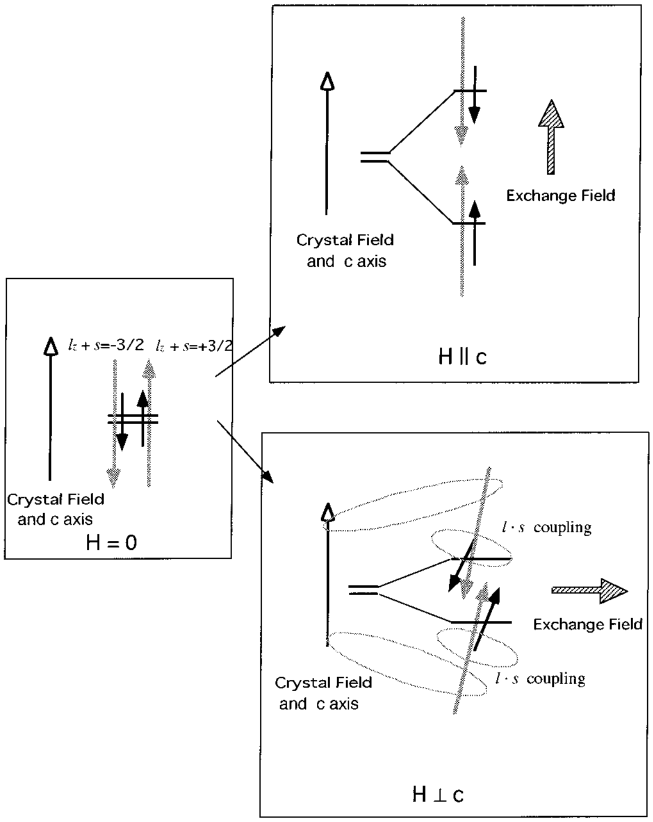

FIG. 8. A schematic representation of the orientation of spin (solid arrows) and angular (shaded arrows) momentum of the A valence band under magnetic field relative to the rotation axis (open arrows) of the trigonal crystal field.

where the linear Zeeman and diamagnetic energy terms are omitted for simplicity. Evidently the pressure-induced enhancement of the exciton energy shift depends strongly on the external field if $H \perp c$, although it does not if $H \| c$. This phenomenon may be regarded as a kind of combined effect of high pressure and high magnetic field.

V. CONCLUSIONS

Magnetophotoluminescence due to the A exciton in $Cd_{1-x}M_xSe$ (M=Mn, Co) has been measured under magnetic fields up to 27 T at 4.2 K in the presence of high hydrostatic pressure up to 2 GPa. It is found from the magnetic-field-induced giant shift of the luminescence energy that pressure enhances the strength of the p-d exchange interaction between holes and magnetic ions at a rate of about 8% GPa^{-1} and 4% GPa^{-1} in $Cd_{0.988}Co_{0.012}Se$ and $Cd_{0.95}Mn_{0.05}Se$, respectively. These experimental results have been interpreted consistently in terms of the kinetic-exchange theory. It has turned out that a major part of those pressure coefficients comes from an increase in the p-d hybridization due to the compression of the bond length.

Within the framework of the kinetic-exchange theory, the exchange constant $N_0\beta$ depends on the electronic correlation, particularly the effective on-site energy U_{eff} of the Coulomb repulsion. The results of the present study suggest that U_{eff} is also affected by pressure. This is reasonable because U_{eff} may depend on the p-d hybridization through the screening by the p electrons. As argued in Refs. 12 and 34, the metal-metal exchange constant J_{NN} should be very sensitive to U_{eff}. Therefore if we can measure the pressure dependence of the magnetization steps at a lower temperature, it will enable us to study the pressure dependence of U_{eff} and thus to experimentally explore the mechanism of the correlation effects in DMS. The study is now in progress.

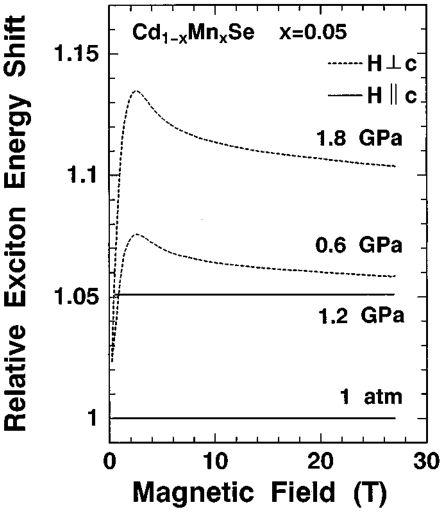

FIG. 9. Theoretical field-induced shift of the energy of the A exciton at several pressures relative to the shift at 1 atm in $Cd_{0.95}Mn_{0.05}Se$ for $H \| c$ (solid lines) and $H \perp c$ (dashed lines).

In $Cd_{0.75}Mn_{0.25}Se$, on the other hand, the giant shift of the luminescence energy is suppressed by application of pressure, suggesting that if the content of magnetic ions is large the effect of suppression of magnetization due to the enhancement of antiferromagnetic coupling among magnetic ions predominates over the effect of enhancement of the exchange interaction between holes and magnetic ions.

When magnetic field is applied perpendicular to the c axis of the wurtzite structure, the p-d interaction competes with the anisotropy of the trigonal crystal field, which also depends on pressure, and the spin-orbit interaction. As a result, the pressure effect on the energy of the A exciton depends strongly on the external field.

ACKNOWLEDGMENTS

The authors are grateful to J. R. Anderson and W. Giriat for providing single crystals of $Cd_{0.95}Mn_{0.05}Se$ and $Cd_{0.75}Mn_{0.25}Se$ and to I. Mogi for providing a single crystal of $Cd_{0.988}Co_{0.012}Se$. The authors acknowledge J. R. Anderson also for the critical reading of the manuscript. The experiments were performed at the High Field Laboratory for Superconducting Materials, Tohoku University, with technical assistance by M. Kamiko. This work was supported in part by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture. One of the authors (Y.M.) was supported by the Fellowships for Junior Scientists of the Japan Society for Promotion of Science.

[1] D. Heiman, X. L. Zheng, S. Sprunt, B. B. Goldberg, and E. D. Isaacs, Proc. SPIE-Int. Soc. Opt. Eng. **1055**, 96 (1989).

[2] Y. Oeda, M. Takeda, N. Kuroda, G. Kido, Y. Nishina, and Y. Nakagawa, in Advances in Mageto-Optics, Proceedings of the International Symposium on Magneto-Optics, edited by K. Tsushima and Shinagawa [J. Magn. Soc. Jpn. **11**, Suppl. S1 157 (1987)].

[3] N. Kuroda, Y. Oeda, G. Kido, M. Takeda, Y. Nishina, and Y. Nakagawa, High Press. Res. **2**, 65 (1989).

[4] N. Kuroda, H. Kanda, G. Kido, M. Takeda, Y. Nishina, and Y. Nakagawa, Jpn. J. Appl. Phys. **31**, L700 (1992).

[5] Y. Matsuda, N. Kuroda, and Y. Nishina, Rev. Sci. Instrum. **63**, 5764 (1992).

[6] Y. Matsuda, N. Kuroda, I. Mogi, G. Kido, Y. Nishina, Y. Nakagawa, J. R. Anderson, and W. Giriat, Jpn. J. Appl. Phys. Suppl. **32-1**, 270 (1993).

[7] Y. Matsuda, N. Kuroda, I. Mogi, G. Kido, and Y. Nishina, Physica B **201**, 411 (1994).

[8] Y. Matsuda, N. Kuroda, and I. Mogi, in *Proceedings of the 22nd International Conference on the Physics of Semiconductors, Vancouver, 1994*, edited by D. J. Lockwood (World Scientific, Singapore, 1995), Vol. 3, p. 2513.

[9] W. Zhou, C. H. Perry, and J. M. Worlock, Phys. Rev. B **42**, 9657 (1990).

[10] See *Diluted Magnetic Semiconductors, Semiconductors and Semimetals*, edited by J. K. Furdyna and J. Kossut (Academic, Boston, 1988), Vol. 25.

[11] J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988).

[12] B. E. Larson, K. C. Hass, H. Ehrenreich, and A. E. Carlsson, Phys. Rev. B **37**, 4137 (1988).

[13] A. K. Bhattacharjee, Phys. Rev. B **46**, 5266 (1992).

[14] J. Blinouski and P. Kacman, Phys. Rev. B **46**, 12 298 (1992).

[15] Su-Huai Wei and Alex Zunger, Phys. Rev. B **35**, 2340 (1987).

[16] J. Masek, Solid State Commun. **78**, 351 (1991).

[17] F. Hamdani, J. P. Lascaray, D. Coquillat, A. K. Bhattacharjee, M. Nawrocki, and Z. Golacki, Phys. Rev. B **45**, 13 298 (1992).

[18] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980), p. 451.

[19] M. Grimsditch, P. Loubeyre, and A. Polian, Phys. Rev. B **33**, 7192 (1986).

[20] S. Jiang, S. C. Shen, Q. G. Li, H. R. Zhu, and G. L. Ju, Phys. Rev. B **40**, 8017 (1989).

[21] Y. Nakagawa, K. Noto, A. Hoshi, K. Watanabe, S. Miura, G. Kido, and Y. Muto, Physica **155B**, 69 (1989).

[22] D. Heiman, P. Becla, R. Kershaw, D. Ridgley, K. Dwight, A. Wold, and R. R. Galazka, Phys. Rev. B **34**, 3961 (1986).

[23] A. V. Komarov, S. M. Ryabchenko, Yu. G. Semenov, B. D. Shanina, and N. I. Vitrikhovskii, Zh. Eksp. Teor. Fiz. **79**, 1554 (1980) [Sov. Phys. JETP **52**, 783 (1980)].

[24] S. I. Gubarev, Zh. Eksp. Teor. Fiz. **80**, 1174 (1981) [Sov. Phys. JETP **53**, 601 (1981)].

[25] R. L. Aggarwal, S. N. Jasperson, J. Stankiewicz, Y. Shapira, S. Foner, B. Khazai, and A. Wold, Phys. Rev. B **28**, 6907 (1983).

[26] R. L. Aggarwal, S. N. Jasperson, P. Becla, and R. R. Galazka, Phys. Rev. B **32**, 5132 (1985).

[27] H. Venghause, S. Suga, and K. Cho, Phys. Rev. B **16**, 4419 (1977).

[28] M. Inoue, N. Adachi, I. Mogi, G. Kido, Y. Nakagawa, and Y. Oka, Physica B **184**, 441 (1993).

[29] N. Adachi, G. Kido, Y. Nakagawa, T. Onishi, Y. Oka, J. R. Anderson, M. Gorska, and W. Giriat, Physica B **177**, 453 (1992).

[30] E. D. Isaacs, D. Heiman, P. Becla, Y. Shapira, R. Kershaw, K. Dwight, and A. Wold, Phys. Rev. B **38**, 8412 (1988).

[31] A. K. Bhattacharjee, G. Fishman, and B. Coqblin, Physica B+C **117&118**, 449 (1983).

[32] *Elastic, Piezoelectric, Pyroelectric, Electrooptic Constants and Nonlinear Dielectric Susceptibilities of Crystals*, edited by K. H. Hellwege and A. M. Hellwege, Landolt-Borstein, New Series, Group III, Vol. II (Springer, Berlin, 1979), p. 40.

[33] K. Kopalko, B. J. Kowalski, B. A. Orlowski, A. Mycielski, and V. Chab, Acta Phys. Pol. A **77**, 403 (1990).

[34] M. Gorska and J. R. Anderson, Phys. Rev. B **38**, 9120 (1988).