Pressure Dependence of Hole-Mn and Mn-Mn Exchange Interactions in $Cd_{0.95}Mn_{0.05}Se$

Noritaka Kuroda and Yasuhiro Matsuda

Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai 980-77, Japan
(Received 4 December 1995)

Magnetophotoluminescence due to the A exciton has been studied in a diluted magnetic semiconductor $Cd_{0.95}Mn_{0.05}Se$ under hydrostatic pressures of $0-2$ GPa at 1.4 K. The experimental data on the pressure dependencies of the hole-Mn p-d and Mn-Mn d-d exchange interactions suggest that in concurrence with an increase in the p-d transfer integral the on-site Coulomb energy U and p-d charge-transfer energy Δ decrease with increasing pressure. The deduced value, $d \ln U/dP = -2.5 \times 10^{-2}$ GPa^{-1}, of the relative pressure coefficient of U is about 4 times in magnitude as great as the linear compressibility of lattice. [S0031-9007(96)00840-X]

PACS numbers: 71.45.Gm, 75.30.Et, 75.50.Pp, 78.20.Ls

Electron correlation is one of the most important matters in understanding the nature of transition-metal (TM) compounds. In the case of diluted magnetic semiconductors (DMSs), TM ions are substituted for cations of the host semiconductors. The holes of the topmost valence band consisting of anion p orbitals have a strong antiferromagnetic exchange interaction with the d electrons of TM ions, giving rise to enormous magneto-optical effects. In addition, TM ions settled on the nearest-neighbor cation sites couple one another antiferromagnetically. Taking account of the d-d Coulomb interaction, Larson *et al.* [1] and Bhattacharjee and co-workers [2] have made perturbative approaches to these exchange interactions. They have shown that the p-d and d-d exchange interactions are second and fourth order perturbations, respectively, by the transfer, viz., real-space hopping, of an electron between p and d orbitals. The hopping of an electron causes a change in the number of electrons of TM ions. Results of the perturbative approaches show that such charge fluctuations, whether real or virtual, bring about strong correlation effects.

As emerged from magnetophotoluminescence experiments on the A exciton in $Cd_{1-x}Mn_xSe$ and $Cd_{1-x}Co_xSe$, the p-d exchange interaction is strengthened markedly by hydrostatic pressure. A large part of this change arises from a change in the transfer integral caused by the contraction of the Mn(Co)-Se bonds [3–5]. However, the degree of the observed enhancement of the p-d exchange interaction is too large to be explained in terms of the transfer integral alone [6]. It is suggested, therefore, that the on-site Coulomb energy U and the charge-transfer energy Δ are also changed by pressure. Since an inequality relationship of $U > \Delta$ holds, in Zaanen-Sawatzky-Allen's classification of TM compounds [7] II-VI DMSs belong to the same regime as semiconductors such as CuO. Many of those compounds are antiferromagnetic. MnTe, for instance, is an antiferromagnetic semiconductor with Néel temperature T_N of 307 K and an energy gap of 1.3 eV. Interestingly, T_N increases with pressure [8]. To understand this phenomenon, knowledge

of the behavior of U and Δ under pressure would be crucial. However, in neither DMSs nor TM compounds is reliable experimental information available on the pressure dependencies of U and Δ.

In this Letter we report on experimental studies of the magnetophotoluminescence due to the A exciton in $Cd_{0.95}Mn_{0.05}Se$ under high hydrostatic pressures at 1.4 K. If the mole fraction of TM ions is raised to the order of 0.05, a significant amount of the ions is settled on the nearest-neighbor cation sites to form antiferromagnetic spin pairs. These ions manifest themselves as a series of weak and stepwise anomalies of magnetization under high magnetic fields and low temperatures. In $Cd_{0.95}Mn_{0.05}Se$ the stepwise anomalies are known to appear around 13 and 24 T at 1 atm [9]. The present study focuses attention on the pressure dependence of these stepwise anomalies as well as the paramagnetic background due to isolated Mn ions. The results show that the anomalies shift rapidly toward higher magnetic fields with increasing pressure. This observation permits us for the first time to look closely into the variation of U and Δ caused by a change in the bond lengths in a highly correlated material.

A homemade cryogenic optical system [10] consisting of a clamp-type diamond anvil cell and optical fibers is used to measure the photoluminescence. Condensed argon is employed as the pressure-transmitting medium. The maximum pressure is limited to 2.0 GPa because a pressure-induced phase transition to a rocksalt structure occurs irreversibly around 2.5 GPa. A magnetic field up to 23 T is generated with a hybrid magnet and is applied parallel to the c axis of the wurtzite structure of the sample. The 514.5 nm line of an Ar-ion laser is used to excite photoluminescence. The optical system is immersed in pumped superfluid He. All the measurements are performed at 1.4 K.

Figure 1 shows the photoluminescence spectra due to the A exciton under various magnetic fields at a pressure of ~ 0.02 GPa. If the external magnetic field is lower than 0.1 T, the spectrum is dominated by a rather broad line (B) due to excitons bound by lattice defects. As the
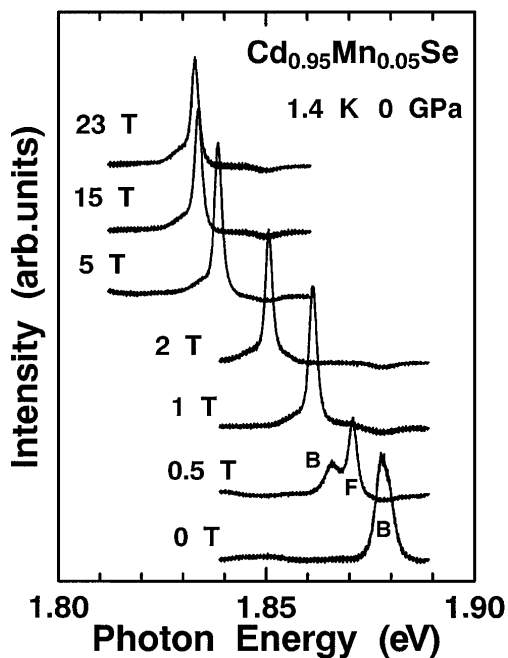
FIG. 1. Photoluminescence spectra in $Cd_{0.95}Mn_{0.05}Se$ under various magnetic fields at 1.4 K and 0 GPa. The magnetic field is applied parallel to the c axis of the crystal. The features denoted as B and F are due to bound and free excitons, respectively.

FIG. 2. Energy shift of the free exciton line in $Cd_{0.95}Mn_{0.05}Se$ induced by the external magnetic field under 0 ($\bigcirc$), 0.7 ($\bigtriangledown$), 1.3 ($\square$), and 1.9 ($\triangle$) GPa at 1.4 K. The inset shows the derivative of the exciton energy with respect to the external magnetic field under 0 ($\bigcirc$), 0.7 ($\bigtriangledown$), 1.3 ($\square$), and 1.9 ($\triangle$) GPa. Solid lines are guides for the eye. Arrows show the field positions H_1 and H_2.

magnetic field increases the bound exciton line is rapidly suppressed and a sharp free exciton line (F) appears. This behavior of the photoluminescence is almost identical with the behavior observed at 2 K [11] and 4.2 K [3,6].

The free exciton line appearing under a magnetic field is due to the radiative recombination of excitons in the lower Zeeman sublevel formed by an electron in the lower magnetic sublevel of the lowest conduction band and a hole in the upper magnetic sublevel of the A valence band. Figure 2 shows a plot of the field-induced shift δE_A of the peak energy E_A of the free exciton line at several pressures: The value of E_A at 0 T is obtained from the energy of the bound exciton line assuming that the binding energy of 4 meV is independent of magnetic field. At any pressure the magnitude of δE_A increases rapidly with increasing external magnetic field but almost levels off above about 6 T.

The shift of the exciton energy is proportional to the strength of the mean exchange field due to TM ions [12]. The external-field dependence shown in Fig. 2 indicates that the magnetization of isolated Mn ions is saturated above about 6 T. Moreover, the saturated value of δE_A is enlarged by hydrostatic pressure. This is due to the enhancement of the exchange interaction between TM ions and the A exciton by pressure [3–6]. One may also note that the shift undulates slightly over the field region between 6 and 23 T. The inset of Fig. 2 shows the derivative $-dE_A/dH$ of the peak energy with respect to the external magnetic field H. At 0 GPa the derivative curve exhibits peaks at 13 T and around 24 T, showing
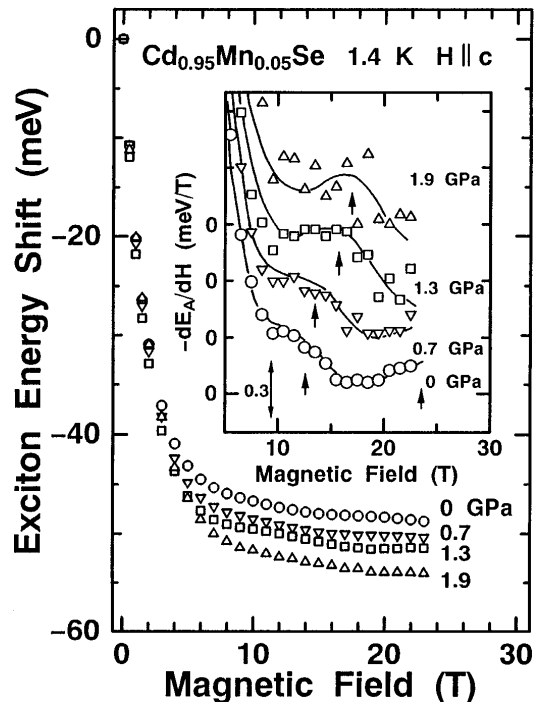
that E_A undergoes a stepwise shift at these magnetic fields. (We have confirmed by other experiments with magnetic fields increased to 25 T that the second peak occurs at 24 T.) This observation agrees well with the magnetization data at 1.4 K reported by Foner et al. [9]. There is no doubt that the peaks of $-dE_A/dH$ are due to the magnetization of paired Mn ions. Furthermore, the present observation shows that the peak positions shift toward higher magnetic fields with increasing pressure.

Figure 3 shows the single-particle scheme of the density of states of electrons in $Cd_{1-x}Mn_xSe$. The ground state of the d electron of Mn ions is the so-called lower Hubbard state. It consists of three $d\varepsilon$ and two $d\gamma$ electrons, of which the $d\varepsilon$ electrons hybridize with the Se $4p$ electrons of valence band [13]. In this state every Mn is ionized into Mn^{2+}. The valence band edge is located below the upper Hubbard state, since the Mott-Hubbard gap U is greater than the energy Λ required to promote an electron from a Mn^{2+} ion to an anion to annihilate a hole in the valence band. In this scheme the charge-transfer energy Δ, which is the energy for a reverse process to the Λ transfer and has been introduced by Zaanen, Sawatzky, and Allen [7], equals $U - \Lambda$. The present situation, where $U > \Delta$, corresponds to the charge-transfer-semiconductor regime of Zaanen, Sawatzky, and Allen's classification of TM compounds. Here we consider the p states near the topmost edge of the valence band
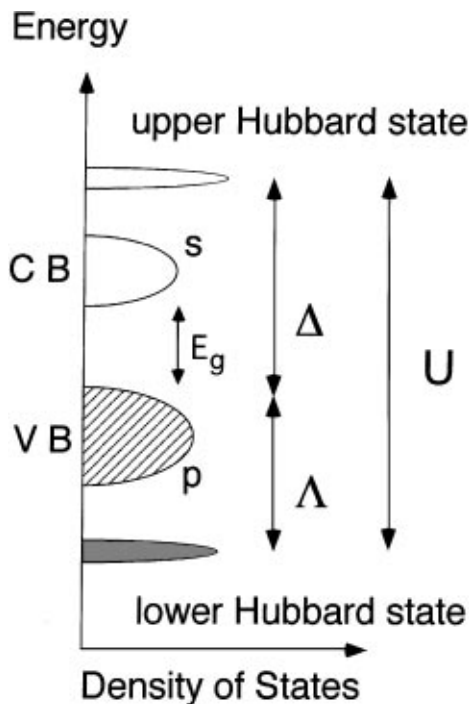
FIG. 3. Schematic representation of the single-particle density of states in II-VI DMSs. CB and VB denote the conduction and valence bands, respectively. The density of states of the lower and upper Hubbard states are exaggerated.

according to the three-level model of Larson et al. [1]. Then at 1 atm we have $U = 7.6$ eV, $\Lambda = 3.4$ eV [1], and $\Delta = 4.2$ eV.

In general, the ordinary potential term of the exchange interaction of the electron of an exciton with Mn ions almost cancels that of the hole, and therefore the exciton-Mn exchange is dominated by the hole-Mn kinetic spin interaction. Thus according to the scheme shown in Fig. 3, the exciton-Mn exchange constant is given to a good approximation by [1,2]

$$J_{pd} = -16t_{pd}^2 U/S\Lambda(U - \Lambda), \qquad (1)$$

where $S = 5/2$ is the total spin of the lower Hubbard state ^6S of a Mn ion and t_{pd} is the transfer integral between the p and d orbitals. The field position H_1 of the first peak of $-dE_A/dH$, on the other hand, is related to the nearest-neighbor d-d exchange constant J_{NN} of a Mn-Mn pair and the g parameter, $g = 2.0$, of the Mn spins by $H_1 = 2|J_{NN}|(g\mu_B)^{-1} + H_d$ [9], where μ_B is the Bohr magneton and $H_d \approx 1.5$ T is a correction due to the distant-neighbor interactions. The d-d interaction is dominated by the kinetic superexchange interaction mediated by p-d bonds. In light of the treatments of Larson et al. [1] and Gorska and Anderson [14], J_{NN} is given by

$$J_{NN} = -t_{pd}^4(2U - \Lambda)/2S^2 U(U - \Lambda)^3. \qquad (2)$$

An identical expression has been obtained by Zaanen and Sawatzky [15] from a configuration-interaction approach to T_N in TM mono-oxides.

In Fig. 4 $\delta E_A(P)/\delta E_A(0)$ are plotted, obtained from experimental values of δE_A at 10 T and $J_{NN}(P)/J_{NN}(0)$

determined from H_1 as a function of pressure P. The values of δE_A at 10 T are chosen because, as evident from Fig. 2, they function as a good probe for the pressure dependence of J_{pd}. We see from Fig. 4 that both $|J_{pd}|$ and $|J_{NN}|$ increase with increasing pressure. Their increasing rates are found to be $d\ln|J_{pd}|/dP = (7.0 \pm 1) \times 10^{-2}$ and $d\ln|J_{NN}|/dP = (21.0 \pm 5) \times 10^{-2}$ GPa^{-1}. As a test of the universality of this value of $d\ln|J_{pd}|/dP$ we have measured $\delta E_A(P)/\delta E_A(0)$ for $Cd_{0.99}Mn_{0.01}Se$, in which the Mn content is so small that Mn ions are mostly isolated. The result agrees well with that for $Cd_{0.95}Mn_{0.05}Se$, as shown in Fig. 4.

Because of the difference in the tetrahedral radius between Mn and Cd ions, there should be a local distortion of lattice around Mn ions. The nonhydrostaticity of pressure due to freezing of argon, which is used as the pressure medium, might cause additional distortion. However, the distortion would be random since Mn ions are substituted for Cd ions randomly in the crystal. The present study deals with the mean value of δE_A and the central position of the anomaly of $-dE_A/dH$. Therefore, in the following discussion the compression of $MnSe_4$ configurations is assumed to be uniform, with the bond angles unchanged, throughout the crystal.

According to Harrison, the transfer integral t_{pd} scales with the Mn-Se bond length l as $l^{-7/2}$ [16]. At 1 atm, since we have $J_{pd} = -1.37$ eV and $J_{NN} = -6.4 \times 10^{-4}$ eV, Eqs. (1) and (2) give $t_{pd} = 0.64$ and 0.79 eV, respectively, which agree rather well with one another. On account of the isostructural and isovalent nature of CdSe and MnSe, it may be reasonable to expect that the compressibility of the Mn-Se bond is similar to the compressibility of the host CdSe lattice. In fact the bulk modulus of $Cd_{1-x}Mn_xTe$ obtained by Strössner et al. [17] indicates that the compressibility of the Mn-Se bonds is almost equal to the compressibility
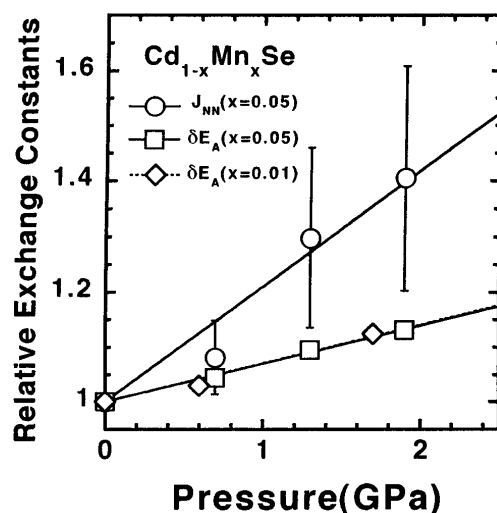

FIG. 4. Pressure dependencies of δE_A at 10 T ($\square$) and J_{NN} ($\circ$) in $Cd_{0.95}Mn_{0.05}Se$, and of δE_A at 10 T ($\diamond$) in $Cd_{0.99}Mn_{0.01}Se$. All data are normalized by the values at 0 GPa. The solid lines are the linear fits to the experimental data.
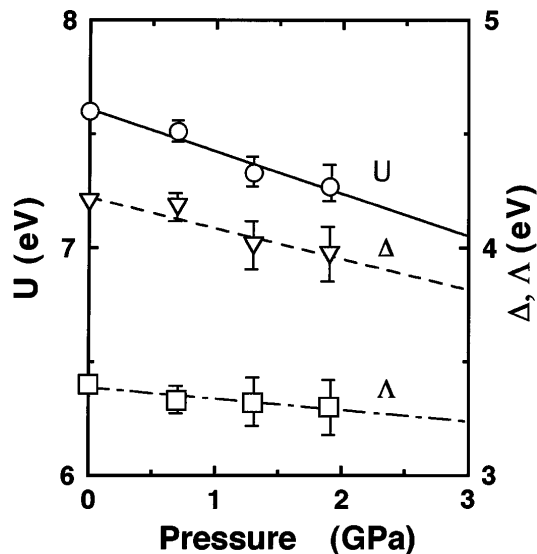
FIG. 5. Pressure dependencies of U ($\bigcirc$), Δ ($\triangledown$), and Λ ($\square$) in $Cd_{0.95}Mn_{0.05}Se$. The solid, dashed, and dot-dashed lines are the linear fits to the experimental data of U, Δ, and Λ, respectively.

0.62×10^{-2} GPa^{-1} of the Cd-Se bonds. Hence Harrison's formula gives $d \ln t_{pd}^2 / dP \approx 4.3 \times 10^{-2}$ GPa^{-1} and $d \ln t_{pd}^4 / dP \approx 8.7 \times 10^{-2}$ GPa^{-1}. Note that these values can explain only halves of the experimental values $d \ln |J_{pd}|/dP \approx 7 \times 10^{-2}$ and $d \ln |J_{NN}|/dP \approx 21 \times 10^{-2}$ GPa^{-1}, respectively. Moreover, $d \ln |J_{NN}|/dP$ is 3 times as large as $d \ln |J_{pd}|/dP$. These facts suggest that U, Δ, and/or Λ depend on pressure.

Substituting the pressure coefficients of t_{pd}^2, t_{pd}^4, J_{pd}, and J_{NN} into Eqs. (1) and (2) one may evaluate the pressure dependencies of U, Δ, and Λ. The results are shown in Fig. 5. We see from Fig. 5 that U, Δ, and Λ decrease pronouncedly with increasing pressure. Their pressure coefficients are -0.19 ± 0.04, -0.13 ± 0.04, and -0.06 ± 0.04 eV/GPa, respectively. It is worth noting that the relative pressure coefficient $|d \ln U/dP| = 2.5 \times 10^{-2}$ GPa^{-1} of U is about 4 times as great as the linear compressibility of lattice. This is the same order as the increasing rate of the transfer integral, that is, $d \ln t_{pd}/dP \approx 2.2 \times 10^{-2}$ GPa^{-1}. Concerning the quantity U/t_{pd}, which is a key parameter for characterizing the effects of electron correlation in a substance [7], a half of its reduction can be attributed to U in the present substance. The positive value of $d \ln t_{pd}/dP$ means that the p-d hybridization is enhanced by compression of lattice. Presumably, therefore, the observed reduction of U is induced by the enhancement of the screening effect due to the valence electrons. The changes of Δ and Λ are the results of the reduction of U and relative shifts of the lower Hubbard state and valence band.

In conclusion, the magnetophotoluminescence due to the A exciton in $Cd_{0.95}Mn_{0.05}Se$ under high hydrostatic pressures at 1.4 K has been interpreted in terms of the kinetic exchange theory. The results suggest that the on-site Coulomb repulsion energy U of Mn ions and the p-d charge-transfer energy Δ are *reduced* by pressure. The relative pressure coefficient $|d \ln U/dP|$ is about 4 times as great as the linear compressibility of lattice and is comparable to the pressure coefficient for the increase in the transfer integral. Therefore, not only the transfer but also the electron correlation in solids should generally depend on bond lengths. This finding will give us an insight into various electronic properties of correlated systems, particularly under high pressures.

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

[2] A. K. Bhattacharjee, Phys. Rev. B **46**, 5266 (1992); F. Hamdani, J. P. Lascaray, D. Coquillat, A. K. Bhattacharjee, M. Nawrocki, and Z. Golacki, Phys. Rev. B **45**, 13 298 (1992).

[3] 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.

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

[5] R. Meyer, M. Dahl, G. Schaack, A. Waag, and R. Boehler, Solid State Commun. **96**, 271 (1995).

[6] Y. Matsuda and N. Kuroda, Phys. Rev. B **53**, 4471 (1996).

[7] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[8] H. Sugiura, A. Sawaoka, S. Saito, and K. Inoue, J. Phys. Chem. Solids **40**, 701 (1979).

[9] S. Foner, Y. Shapira, D. Heiman, P. Becla, R. Kershaw, K. Dwight, and A. Wold, Phys. Rev. B **39**, 11 793 (1989).

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

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

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

[13] S. H. Wei and A. Zunger, Phys. Rev. B **35**, 2340 (1987).

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

[15] J. Zaanen and G. A. Sawatzky, Can. J. Phys. **65**, 1262 (1987).

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

[17] K. Strössner, S. Ves, W. Dieterich, W. Gebhardt, and M. Cardona, Solid State Commun. **56**, 563 (1985).