RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 58, NUMBER 8 15 AUGUST 1998-II

Core-level photoemission study of $Ga_{1-x}Mn_xAs$

J. Okabayashi
Department of Physics, University of Tokyo, Bunkyou-ku, Tokyo 113-0033, Japan

A. Kimura
Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8666, Japan

O. Rader,* T. Mizokawa, and A. Fujimori
Department of Physics, University of Tokyo, Bunkyou-ku, Tokyo 113-0033, Japan

T. Hayashi and M. Tanaka
Department of Electronic Engineering, University of Tokyo, Bunkyou-ku, Tokyo 113-0033, Japan

(Received 16 April 1998)

We have studied the electronic structure of Mn impurities in GaAs by Mn $2p$ core-level photoemission spectroscopy. From cluster-model analysis assuming the neutral (Mn^{3+}) or negatively ionized (Mn^{2+}) ground state, electronic structure parameters have been obtained. In either case, the Mn d electron number is evaluated to be ~ 5 using the obtained parameters, meaning that the neutral Mn^{3+} impurity, if it exists, consists of the Mn $3d^5$ configuration and a valence hole bound to it through p-d hybridization and/or Coulomb interaction. We discuss the exchange interaction between the Mn local spin and the valence hole as well as the stability of the neutral impurity against the ionization of the valence hole. [S0163-1829(98)52532-5]

The recent success of doping III-V semiconductors with magnetic impurities using the molecular-beam epitaxy technique has opened up, to the best of our knowledge, a new field in the research of diluted magnetic semiconductors (DMS).[1,2] Because one can introduce both magnetic moments and charge carriers in DMS, they have the possibility of combining magnetics and electronics. So far, II-VI based DMS such as $Cd_{1-x}Mn_xTe$, in which magnetic ions, particularly Mn^{2+}, can be doped up to high concentration, have been extensively studied.[3,4] $Cd_{1-x}Mn_xTe$ is now used as optical isolators because of their strong magneto-optical effects.[5] In II-VI based DMS, Mn impurities substituting 2+ cations are stable as 2+ ions and therefore there are few carriers, making them insulators. Owing to the presence of conducting carriers, III-V based DMS show ''carrier-induced ferromagnetism'' in p-type samples.[6,7] In recent years, a III-V based DMS system $Ga_{1-x}Mn_xAs$ has attracted considerable interest because of its relatively high Curie temperature ($T_c \sim 110$ K).[8] Also, magnetotransport properties such as anomalous Hall effect and large magnetoresistance,[9,10] as well as photoinduced ferromagnetism,[11] have been reported for the GaAs-based DMS.

In order to understand those anomalous properties associated with the strong coupling between the magnetism and the charge transport in the III-V based DMS, we must first characterize their electronic structure, especially interaction between the localized Mn d electrons and the delocalized band electrons of the host semiconductor. In order to understand such a system, theoretical framework beyond a one-electron band picture is necessary because electron correlation at the Mn site should be quite substantial. Different models have been suggested for the III-V based DMS,[12,13] and there has been no consensus on their electronic structure. Photoemission spectroscopy is a powerful technique in the investigation of the electronic structure of solids, especially of correlated-electron systems such as $3d$ transition-metal compounds.[14] Indeed, the electronic structure of II-VI based DMS, including $Cd_{1-x}Mn_xTe$, has been studied by photoemission spectroscopy combined with configuration-interaction (CI) cluster-model calculation and their optical properties, p-d exchange interactions and donor and acceptor ionization energies have been explained on a unified ground.[4,15,16] In this paper, we present a study of the electronic structure of the Mn impurity in $Ga_{1-x}Mn_xAs$ by core-level photoemission spectroscopy and subsequent cluster-model calculations. We discuss the p-d exchange interaction between the Mn impurity and the host semiconductor as well as the stability of the neutral impurity A^0 (Mn^{3+}) against the negatively ionized state A^- (Mn^{2+}).

The sample was prepared by molecular-beam epitaxy at low growth temperature as follows. We grew a $Ga_{1-x}Mn_xAs$ (001) single-crystal thin film on the GaAs (001) surface at the growth temperature of 250 °C. The Mn concentration was estimated to be $x = 0.074$ by x-ray diffraction. We estimated the Curie temperature to be $T_c = 55$–60 K from anomalous Hall effect, the details of which are reported in Refs. 17 and 18.

We performed x-ray photoemission spectroscopy (XPS) experiments using a VG CLAM hemispherical analyzer and a Mg x-ray source. The measurements were made in an ultrahigh vacuum of 10^{-11} Torr at room temperature. The resolution of XPS was estimated to be ~ 0.7 eV from the Au $4f$ core-level spectrum. For sample cleaning, we repeated Ar ion sputtering (1 kV) and annealing at 200 °C. It is known that if $Ga_{1-x}Mn_xAs$ samples are heated above 400 °C after the growth, ferromagnetic MnAs clusters appear. Therefore, we took caution by controlling the annealing temperature below 240 °C so that MnAs did not appear. We obtained an

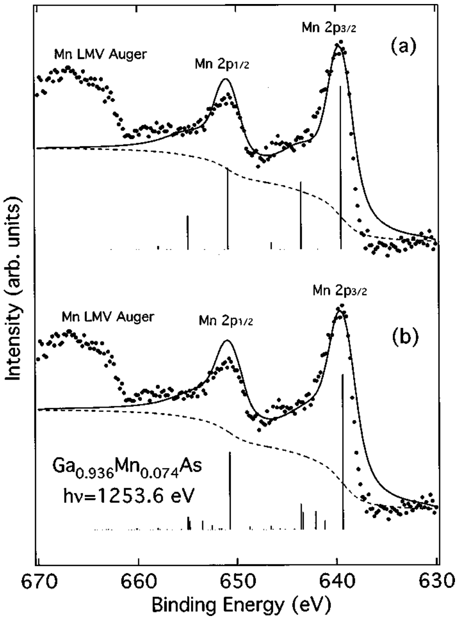

FIG. 1. Photoemission spectrum of the Mn $2p$ core level (dots) and its cluster-model analysis (solid curves) assuming the negatively ionized Mn^{2+} (a) and neutral Mn^{3+} (b) ground states. The vertical bars are unbroadened spectra. The calculated background is shown by dashed curves.

ordered surface as confirmed by a clear 1×1 low-energy electron diffraction (LEED) pattern. We presume that on the energy scale of the core-level photoemission spectroscopy, the spectra are not affected by magnetic ordering and therefore that they do not depend on the temperature appreciably.

Figure 1 shows the XPS spectrum of the Mn $2p$ core level in $\mathrm{Ga_{0.93}Mn_{0.07}As}$. The spectrum shows a spin-orbit doublet $(j=\frac{3}{2},\frac{1}{2})$, each component of which shows a charge-transfer satellite on the higher binding energy side of the main peak. The broad peak at 667 eV is due to the Mn $L_{2,3}M_{2,3}M_{4,5}$ Auger emission and is not considered here. The presence of the satellite structure indicates strong Coulomb interaction between the Mn $3d$ electrons and hybridization between the Mn $3d$ and other valence orbitals. One can see from Fig. 1 that the satellite intensity is weak compared with those of the II-VI based DMS.[19] We have analyzed the satellite structure using the CI cluster model to obtain the electronic structure parameters as described below.

In the CI picture, the wave functions are given as linear combinations of d^n, $d^{n+1}\underline{L}$, $d^{n+2}\underline{L}^2,\ldots,$ configurations, where $\underline{L}$ stands for a hole in the ligand orbitals. We have considered a $\mathrm{MnAs_4}$ cluster with the central Mn atom, concentrating on energy levels arising from the hybridized Mn $3d$ and ligand As $4p$ orbitals. The cluster contains the following parameters: The ligand-to-$3d$ charge-transfer energy is defined by $\Delta=E(d^{n+1})-E(d^n)$. The on-site $3d$-$3d$ Coulomb interaction energy is defined by $U=E(d^{n-1})+E(d^{n+1})-2E(d^n)$, where $E(d^n\underline{L}^m)$ is the center of gravity of the $d^n\underline{L}^m$ multiplet. The multiplet splitting is expressed using Racah parameters B and C, which are fixed at the values of the free Mn ion.[15] One-electron transfer integrals between the Mn $3d$ and As ligand p orbitals are expressed in terms of Slater-Koster parameters $(pd\sigma)$ and $(pd\pi)$. We have utilized the relationship between $(pd\sigma)$ and $(pd\pi)$: $(pd\sigma)\simeq-2(pd\pi)$.[20]

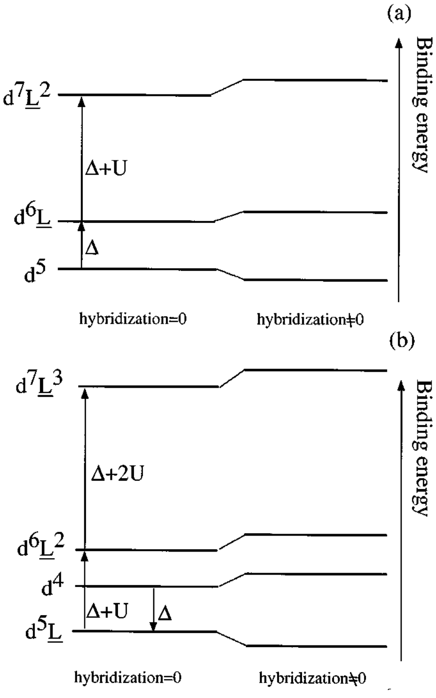

FIG. 2. Schematic energy-level diagrams of the $\mathrm{MnAs_4}$ cluster in the initial states for the negatively ionized Mn^{2+} (a) and neutral Mn^{3+} (b) models.

In the analysis, we have assumed the ground state of formally Mn^{2+} or Mn^{3+} configuration. For the Mn^{3+}, i.e., neutral impurity ground state, the wave function is expanded by a linear combination d^4, $d^5\underline{L}$, $d^6\underline{L}^2,\ldots,$ configuration as shown in Fig. 2. We also consider the case where the Mn impurity is negatively ionized (A^-) and becomes Mn^{2+} as in the II-VI compounds. In this case, the ground state is given by a linear combination of d^5, $d^6\underline{L},\ldots,$ configurations. We have fitted the XPS spectrum by varying Δ, $(pd\sigma)$ and U, as shown by solid curves in Fig. 1. The Coulomb interaction Q between the core hole and the d electron is assumed to be $Q=1.25U$ as usual.[19] The Gaussian and Lorentzian broadening was applied with full width at half maximum (FWHM) of 1.5 and 1.0 eV, respectively, to simulate the measured spectra. The integral background is shown by dashed curves in Fig. 1. The $j=\frac{3}{2}$ part of the spectrum was used for the fitting because the $j=\frac{1}{2}$ part is broadened by a Coster-Kronig decay into the $j=\frac{3}{2}$ and is also obscured by the overlapping Auger feature and the high background level.

The parameters thus obtained are listed in Table I and are compared with those of II-VI based DMS.[15] The U value

TABLE I. Electronic structure parameters for substitutional Mn impurities in semiconductors. Δ, U, and $(pd\sigma)$ are given in units of eV. Error bars are ±0.5 eV for Δ and U and ±0.1 eV for $(pd\sigma)$.

Material	Δ	U	$(pd\sigma)$	n_d	
$\mathrm{Cd_{1-x}Mn_xTe}$	2.0	4.0	1.1		Ref. 15
$\mathrm{Cd_{1-x}Mn_xSe}$	2.5	4.0	1.2		Ref. 15
$\mathrm{Cd_{1-x}Mn_xS}$	3.0	4.0	1.3		Ref. 15
$\mathrm{Ga_{1-x}Mn_xAs}$ (A^-: Mn^{2+})	1.5	3.5	1.1	5.3	
$\mathrm{Ga_{1-x}Mn_xAs}$ (A^0: Mn^{3+})	−1.5	3.5	1.0	5.1	

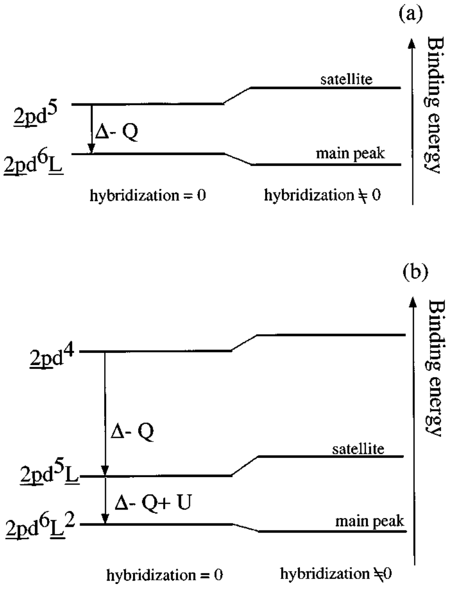

FIG. 3. Schematic energy-level diagrams of the $MnAs_4$ cluster with a Mn $2p$ core hole for the negatively ionized Mn^{2+} (a) and neutral Mn^{3+} (b) models.

$(=3.5$ eV) is a little smaller than those of the II-VI compounds, probably due to the stronger screening effect in the III-V compound. For the Mn^{2+} (A^-) state, Δ was found to be positive [see Fig. 2(a)]. For the Mn^{3+} (A^0) state, on the other hand, Δ is found to be negative. The negative Δ means that the ground state is not dominated by the d^4 configuration but by the $d^5\underline{L}$ configuration [Fig. 2(b)]. That is, the stable $d^5\underline{L}$ state is formed by charge transfer from the ligand As $4p$ orbitals to the impurity Mn $3d$ orbitals. This is analogous to the case of Cu^{3+} in the ''negative-Δ insulator'' $NaCuO_2$, where the ground state is dominated by the $d^9\underline{L}$ configuration rather than the d^8 configuration.[21] The Mn $3d$ electron count from the present analysis is found to be 5.3 in the case of the Mn^{2+} and 5.1 in the case of the Mn^{3+} ground states. It is not clear, however, whether the Mn^{3+} (A^0) state is stable, i.e., whether the hole created on the As $4p$ orbitals behaves as a bound hole around the Mn^{2+} impurity to form the Mn^{3+} state or is extended throughout the crystal leaving the Mn^{2+} state. The great similarity between the two calculated spectra is attributed to the fact that the Mn impurity has five d electrons in either case because the difference between $\Delta(Mn^{2+})$ and $\Delta(Mn^{3+})$ nearly equals the d-d Coulomb interaction U. Figure 3 shows the energy diagram of the XPS final state in the CI picture. Because of the core-hole potential, the $2\underline{p}d^6\underline{L}$ state is pulled down below the $2\underline{p}d^5$ state with the separation $\Delta-Q$, where $2\underline{p}$ denotes a hole in the $2p$ core level. The main peak is composed of $2\underline{p}d^6\underline{L}$ in the Mn^{2+} state and $2\underline{p}d^6\underline{L}^2$ in the Mn^{3+} state. Excited states, which correspond to the satellite, consist of $2\underline{p}d^5$ and $2\underline{p}d^5\underline{L}$ configurations for the Mn^{2+} and Mn^{3+} cases, respectively.

Using the above parameter values, one can estimate the exchange constant $N\beta$ between the Mn^{2+} ion and the electron at the top of the valence band of the host semiconductor.[22] We treated the hybridization as a perturbation in the CI picture. In the second-order perturbation, with respect to the charge transfer, the $N\beta$ is given by

$$N\beta=-\frac{16}{S}\left(\frac{1}{-\delta_{eff}+U_{eff}}+\frac{1}{\delta_{eff}}\right)\times\left(\frac{1}{3}(pd\sigma)-\frac{2\sqrt{3}}{9}(pd\pi)\right)^2.$$

Here, Δ_{eff} and U_{eff} are defined with the respect to *the lowest term of each multiplet.* Actual energies for the processes $d^n\rightarrow d^{n+1}\underline{L}$ and $d^n+d^n\rightarrow d^{n+1}+d^{n-1}$ are given by Δ_{eff} and U_{eff}, respectively, rather than Δ and U.[4,22,23] δ_{eff} is obtained by subtracting the valence-band width from Δ_{eff}. To deduce Δ_{eff} and U_{eff} from Δ and U, we have used Kanamori parameters j, j', and u evaluated from Racah parameters $B=0.119$ eV and $C=0.412$ eV as described elsewhere.[24] The details of the calculation are given in Ref. 22. The value thus evaluated is $N\beta=-1.2\pm0.2$ eV (for $S=\frac{5}{2}$). This means that the p-d interaction is antiferromagnetic, consistent with the recent magnetic circular dichroism (MCD) measurement of the interband transition for $x=0.074$.[25] In another MCD study of very dilute $(x\leqslant0.001\%)$ samples, however, $N\beta$ has been estimated to be positive and large, $+2.5$ eV.[13] It has also been reported that $|N\beta|$ is 3.0 eV from magnetotransport measurements.[8]

It should be noted here that the $N\beta$ value depends on whether the Mn impurity is 2+ or 3+. For the Mn^{2+} state, the spin-up states are fully occupied and only the valence electrons which have spins antiparallel to the Mn d spins can be transferred to the empty Mn $3d$ states, so that the p-d exchange interaction becomes antiferromagnetic. In the case of Mn^{3+}, valence electrons with parallel spin can also be transferred to the Mn $3d$ orbitals, making ferromagnetic p-d exchange interaction possible. Unfortunately, our experimental results are consistent with both the Mn^{2+} (A^-) and Mn^{3+} (A^0) ground states and one cannot make a definite prediction about the sign of $N\beta$.

Whether the ground state of the Mn ion is 3+ or 2+ depends on whether the Mn^{2+} ion binds a hole to form a neutral impurity A^0 or is ionized to become A^-. In order to answer this question, the Anderson impurity model was used to see whether a bound state exists within the energy gap due to the p-d hybridization. Using the parameter set obtained from the CI cluster calculation, we found that a bound state is not formed for the A^0 state. However, the limitation of this model is the absence of the long-range Coulomb interaction between electrons. If the long-range Coulomb interaction were introduced, it may lead to a bound state within the energy gap. If the origin of the bound state formation in the very dilute sample[12,13] is the long-range Coulomb interaction, then it will be screened out in samples with higher Mn, and hence hole concentrations. This may explain why neutral impurities (A^0) exist only in the very dilute samples.[25] The same proposal was made in Ref. 25.

In summary, we have studied the electronic structure of $Ga_{1-x}Mn_xAs$ $(x=0.074)$ by core-level photoemission spectroscopy and analyzed the spectrum using the CI cluster model and the Anderson impurity model. Using the estimated electronic structure parameters, the d electron count of Mn in the GaAs is found to be ~5, so that if the Mn impurity is in the A^0 state, it does not have d^4 configuration but d^5 plus a valence hole. The hole induces the ferromagnetism and drives the remarkable magnetotransport properties. We find no bound state within the band gap of GaAs using these parameters within the Anderson impurity model and propose that the bound-state formation is made possible by the long-range Coulomb interaction.

The authors would like to thank Professor A. Kakizaki for continuous support and useful advice, and A. Harasawa, N. Kamakura, K. Kobayashi, J. Matsuno, and M. Satake for technical support. This work was supported by a Grant-in-Aid for Scientific Research in the priority area ‘‘Spin Controlled Semiconductor Nanostructures’’ from the Ministry of Education, Science, Sports, and Culture, and was performed under the approval of the Photon Factory program Advisory Committee (Grant Nos. 95G398 and 97G335).

---

*Present address: BESSY, Lenzeallee 100, D 14195 Berlin, Germany.

[1] H. Ohno, H. Munekata, T. Penny, S. von Molnar, A. Segmüller, and L. L. Chang, Phys. Rev. Lett. **68**, 2664 (1992).

[2] H. Munekata, H. Ohno, S. von Molnar, A. Segmüller, L. L. Chang, and L. Esaki, Phys. Rev. Lett. **63**, 1849 (1989).

[3] *Diluted Magnetic Semiconductors, Semiconductors and Semimetals*, edited by J. K. Furdya and J. Kossut (Academic Press, Boston, 1986), Vol. 25.

[4] A. Fujimori and T. Mizokawa, in *II-VI Semiconductor Compounds*, edited by M. Jain (World Scientific, Singapore, 1993), p. 103.

[5] K. Onodera, T. Matsumoto, and M. Kimura, Electron. Lett. **30**, 1954 (1994).

[6] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye, Appl. Phys. Lett. **69**, 363 (1996).

[7] If free holes can be introduced into II-VI compounds, ferromagnetism can be induced as demonstrated for a quantum-well system Cd$_{0.976}$Mn$_{0.024}$Te/Cd$_{0.66}$Mg$_{0.27}$Zn$_{0.07}$Te:N. [A. Haury *et al.*, Phys. Rev. Lett. **79**, 511 (1997).]

[8] F. Matsukura, H. Ohno, A. Shen, and Y. Sugawara, Phys. Rev. B **57**, 2037 (1998).

[9] A. Oiwa, S. Katsumoto, A. Endo, M. Hirasawa, Y. Iye, H. Ohno, F. Matsukura, A. Shen, and Y. Sugawara, Solid State Commun. **103**, 209 (1997).

[10] A. Van Esch, J. De Boeck, L. Van Blockstal, R. Bogaerts, F. Herlach, and G. Borghs, J. Phys.: Condens. Matter **9**, L361 (1997).

[11] S. Koshihara, A. Oiwa, M. Hirasawa, S. Katsumoto, Y. Iye, C. Urano, H. Takagi, and H. Munekata, Phys. Rev. Lett. **78**, 4617 (1997).

[12] J. Schneider, U. Kaufmann, W. Wilkening, M. Baeumler, and F. Kohl, Phys. Rev. Lett. **59**, 240 (1987).

[13] J. Szczytko, W. Mac, A. Stachow, A. Towadowski, P. Becla, and J. Tworzydlo, Solid State Commun. **99**, 927 (1996).

[14] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985); M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. (to be published).

[15] T. Mizokawa and A. Fujimori, Phys. Rev. B **48**, 14 150 (1993).

[16] L. Ley, M. Taniguchi, J. Ghijsen, R. L. Johnson, and A. Fujimori, Phys. Rev. B **35**, 2839 (1987).

[17] T. Hayashi, M. Tanaka, T. Nishinaga, H. Shimada, H. Tsuchiya, and Y. Otuka, J. Cryst. Growth **175/176**, 1063 (1997).

[18] T. Hayashi, M. Tanaka, T. Nishinaga and H. Shimada, J. Appl. Phys. **81**, 4865 (1997).

[19] A. E. Bocquet, T. Mizokawa, T. Saitoh, H. Namatame, and A. Fujimori, Phys. Rev. B **46**, 3771 (1992).

[20] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1989).

[21] T. Mizokawa, A. Fujimori, H. Namatame, K. Akeyama, and N. Kosugi, Phys. Rev. B **49**, 7193 (1994).

[22] T. Mizokawa and A. Fujimori, Phys. Rev. B **56**, 6669 (1997).

[23] S. Sugano, Y. Tanabe, and H. Kaminura, *Multiplets of Transition Metal Ions in Crystals* (Academic Press, New York, 1970).

[24] J. Kanamori, Prog. Theor. Phys. **30**, 275 (1963).

[25] K. Ando, T. Hayashi, M. Tanaka, and A. Twardowski, J. Appl. Phys. **53**, 6548 (1998).