Mechanism of carrier-induced ferromagnetism in magnetic semiconductors

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(Received 25 March 2002; revised 20 June 2002; published 4 October 2002)

Taking into account both random impurity distribution and thermal fluctuations of localized spins, we have performed a model calculation for the carrier (hole) state in $Ga_{1-x}Mn_xAs$ by using the dynamical coherent potential approximation. The result reveals that carriers are nearly bound to magnetic impurity sites and that the carrier spin strongly couples to the localized *d* spins on Mn ions. The hopping of carriers among Mn sites causes the ferromagnetic ordering of the localized spins through the double-exchange mechanism. The Curie temperature obtained by using conventional parameters agrees well with the experimental result for $Ga_{1-x}Mn_xAs$.

DOI: 10.1103/PhysRevB.66.153202 PACS number(s): 75.50.Pp, 71.23.−k, 71.70.Gm

Although a considerable amount of experimental results has already been accumulated,[1] the origin of the ferromagnetism in III-V-based diluted magnetic semiconductors (DMS's) has still not been clarified theoretically.[2–8] Since the magnetic interactions between Mn impurities in III-V semiconductors have been shown to be antiferromagnetic, the ferromagnetic interactions in III-V-based DMS's are most likely hole induced.[1] The ferromagnetism is considered to be caused by the exchange interactions between delocalized carriers (holes originating from the valence band) and the localized spins on the Mn ions. Matsukura *et al.*[2] referred to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction as the origin of the ferromagnetism. The RKKY mechanism explains some characteristic magnetic and transport properties of the DMS's, while the application of the RKKY theory to this system is somewhat questionable, as pointed out by various authors.[3–5,9] The RKKY theory is applicable when the exchange interaction is small compared to the Fermi energy of the carriers, but this is not the case in DMS's because the hole density is low. Furthermore, recent studies of the infrared optical conductivity[10,11] revealed the absence of the low-frequency Drude peak, which suggests that the carriers are not in a simple metallic state. In contrast to the RKKY picture, Akai stressed the *d* character of the holes based on his band calculations and invoked a double-exchange mechanism.[3] The band calculations by other authors,[12,13] however, showed that holes at the Fermi level have mainly the As $4p$ character and originate from the host valence band. The results of photoemission spectroscopy studies[14–16] suggested that the states split off the valence band may be responsible for the ferromagnetism.

In this paper, we propose a theory of carrier-induced ferromagnetism, which consistently accounts for essential features of the above experimental observations. We adopt a simple one-band model for valence-band holes in DMS's. We assume that a mole fraction x of host cations (denoted by A) is replaced at random with magnetic ions (denoted by M). Since we focus our attention on the case of $Ga_{1-x}Mn_xAs$, $A(M)$ is regarded to be a Ga (Mn) ion in the following. The present model is described by[17,18]

$$H=\sum_{m,n,\mu}\varepsilon_{mn}a^{\dagger}_{m\mu}a_{n\mu}+\sum_{m}U_m, \tag{1}$$

where $a^{\dagger}_{m\mu}$ ($a_{m\mu}$) creates (annihilates) a carrier (or *p*-hole) with spin μ at the mth site. Here, U_m denotes either $E_A\Sigma_\mu a^{\dagger}_{m\mu}a_{m\mu}$ or $E_M\Sigma_\mu a^{\dagger}_{m\mu}a_{m\mu}-I\Sigma_{\mu\nu}a^{\dagger}_{m\mu}\boldsymbol{\sigma}_{\mu\nu}\cdot\mathbf{S}_m a_{m\nu}$, depending on whether the site m is occupied by A or M. E_A (E_M) denotes the spin-independent potential of a Ga (Mn) ion; $-I\boldsymbol{\sigma}\cdot\mathbf{S}_m$ represents the exchange interaction between the carrier and the localized spin $\mathbf{S}_m$ of Mn at site m. Thus we take into account that a Mn^{2+} ion in GaAs acts as both an acceptor and a magnetic impurity. We use an attractive short-range potential E_M instead of a realistic long-ranged one as the potential due to Mn^{2+} and assume that ε_{mn} does not depend on the species of ions at sites m and n. In the following, we show that this simple model can account for essential features of the carrier-induced ferromagnetism in DMS's, though the short-range potential may not necessarily be justified, particularly in the case of low carrier density.

We apply the dynamical coherent potential approximation (dynamical CPA)[19–21] to the above model. In the present model, carriers are scattered by the randomness arising from both substitutional disorder and the thermal fluctuations of the localized spins. In the dynamical CPA,[21] the carriers are described as independent particles moving in an effective medium of spin-dependent coherent potentials $\Sigma_\uparrow$ and $\Sigma_\downarrow$. We determine the coherent potentials so that the t matrix for a carrier at an arbitrarily chosen site embedded in the effective medium vanishes on average. This condition (the dynamical CPA condition) is given by

$$(1-x)t^{A}_{\uparrow\uparrow}+x\langle t^{M}_{\uparrow\uparrow}(S_z)\rangle_{\mathrm{av}}=0, \tag{2a}$$

$$(1-x)t^{A}_{\downarrow\downarrow}+x\langle t^{M}_{\downarrow\downarrow}(S_z)\rangle_{\mathrm{av}}=0. \tag{2b}$$

The t-matrix element $t^{A}_{\mu\mu}$ ($\mu=\uparrow$ or $\downarrow$) represents the multiple scattering of a μ-spin carrier by an A ion and $t^{M}_{\mu\mu}(S_z)$ by an M ion, where S_z stands for the z-component of the localized spin. The thermal average over the fluctuating localized spin is taken as

$$\langle t^M_{\mu\mu}(S_z)\rangle_{\rm av} = \sum_{S_z=-S}^{S} t^M_{\mu\mu}(S_z)\exp\left(\frac{hS_z}{k_BT}\right) \Big/ \sum_{S_z=-S}^{S} \exp\left(\frac{hS_z}{k_BT}\right), \tag{3}$$

where h denotes the effective field felt by the localized spins. Off diagonal t-matrix elements $t^M_{\uparrow\downarrow}$ and $t^M_{\downarrow\uparrow}$ vanish after the thermal average operation because the magnetization is assumed to be along the z axis. Since there is one-to-one correspondence between $\langle S_z\rangle_{\rm av}$ and the parameter $\lambda \equiv h/k_BT$, we can express the carrier states in terms of $\langle S_z\rangle_{\rm av}$ instead of λ. In this work, we treat the localized spins classically, though the extension to the case of $S=5/2$ is straightforward. We took a semicircular density of states (DOS) with the half-bandwidth Δ for the host valence band. Note that the present theory takes the spin flipping processes into account and therefore a single t-matrix element $t^M_{\mu\mu}(S_z)$ depends simultaneously on both $\Sigma_\uparrow$ and $\Sigma_\downarrow$.[21] Thus we solved Eqs (2a) and (2b) and obtained $D_\uparrow(\omega)$ and $D_\downarrow(\omega)$, the DOS per site, for an up- and down-spin carrier, respectively.

We set E_A as the origin of the energy, and adopted the parameters $\Delta = 2$ eV,[12,13] $IS/\Delta = -0.4$ and $E_M/\Delta = -0.3$ for $Ga_{1-x}Mn_xAs$. These parameters lead to an impurity level at the energy of $E_a = -1.057\Delta$ in the dilute limit ($x \to 0$), which is consistent with an acceptor energy of 0.113 eV ($=0.057\Delta$).[22] With increase in x, an impurity band forms, and for $x \gtrsim 0.02$ it merges into the host valence band. The results consistently explain the experimental observation of impurity-band-like states[16] and the insulator-metal transition at $x \sim 0.03$.[23] We may determine the magnetization and the carrier states self-consistently for a given carrier density and a temperature by minimizing the free energy with respect to λ (or $\langle S_z\rangle_{\rm av}$). However, first we examine the effect of the magnetization on the carrier states treating $\langle S_z\rangle_{\rm av}$ as a free parameter and clarify the mechanism of carrier-induced ferromagnetism.

The result of the carrier DOS for $x=0.05$ is shown in Fig. 1(a) for various values of $\langle S_z\rangle_{\rm av}/S$. The band tail arising from the magnetic impurity band is strongly affected by the magnetization; the lower edge of the DOS is slightly shifted to lower energy with an increase of $\langle S_z\rangle_{\rm av}$ and simultaneously, $D_\uparrow(\omega)$ is strongly suppressed in the band tail. We show the relative local DOS at Mn sites defined by $R(\omega) = [D^M_\uparrow(\omega) + D^M_\downarrow(\omega)]/[D_\uparrow(\omega) + D_\downarrow(\omega)]$ in Fig. 1(b), which shows that $R(\omega)$ hardly depends on $\langle S_z\rangle_{\rm av}$. The result for $R(\omega)$ shows that the majority of carriers in the band tail remain at Mn sites [$R(\omega) \sim 0.6$] in spite of small x; this is consistent with the nearly bound-hole picture suggested by the results of experiments.[10,11]

In order to examine how strongly the carrier spin couples to the localized spins, we calculated the carrier spin polarization $P(n) \equiv (n_\downarrow - n_\uparrow)/(n_\downarrow + n_\uparrow)$ as a function of the total carrier density n. We assume that the carriers are degenerate throughout this study. We show the results of $P(n)$ for $x=0.01$ and $x=0.05$ in Figs. 2(a) and 2(b), respectively. In the case of $x=0.01$, the impurity band is separated from the host band and carriers stay mainly at Mn sites as long as $n \lesssim x$. Figure 2(a) shows that $P(n) \approx \langle S_z\rangle_{\rm av}/S$ for $n \lesssim x$, which we can deduce assuming that the carrier spin is always antiparallel to the localized spin. This result suggests that a carrier spin at a Mn site faithfully follows the fluctuations of the localized spin at the site. When $x=0.05$, the magnetic impurity band merges into the host band and the Fermi level (ε_F) reaches the bottom of the host band at $n=n_1 \sim 0.035$. Accordingly, $P(n) \approx \langle S_z\rangle_{\rm av}/S$ for $n \lesssim n_1$, as shown in Fig. 2(b). When $n \gtrsim n_1$, carriers with the energy higher than $-\Delta$ seep out of the Mn sites and wander among nonmagnetic sites.

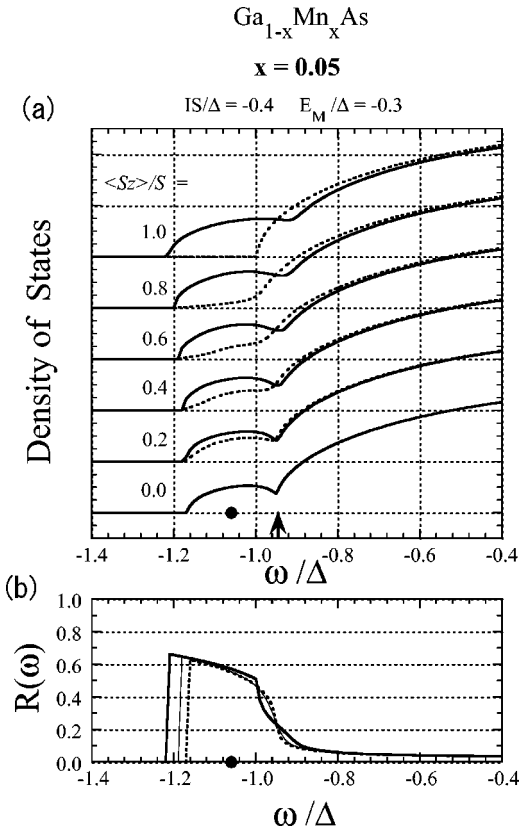

FIG. 1. (a) The carrier (hole) density of states for $x=0.05$ are depicted for various values of magnetization. The solid and dotted lines represent $D_\downarrow(\omega)$ and $D_\uparrow(\omega)$, respectively. The impurity level $E_a = -1.057\Delta$ is indicated by a dot on the line of $\langle S_z\rangle_{\rm av}=0$. The arrow indicates the Fermi level for $n=x(=0.05)$, which is about -0.95Δ and is almost independent of $\langle S_z\rangle_{\rm av}$. (b) The ratio $R(\omega)$ of the local DOS at Mn site to the total DOS for $\langle S_z\rangle_{\rm av}/S = 1.0$ (thick full line), 0.5 (thin full line), and 0.0 (dotted line).

Next we calculate the Curie temperature. The total energy is given by

$$E(\langle S_z\rangle_{\rm av}) = \int_{-\infty}^{\varepsilon_F} \omega[D_\uparrow(\omega) + D_\downarrow(\omega)]d\omega. \tag{4}$$

Note that $E(\langle S_z\rangle_{\rm av})$ is the sum of the kinetic and exchange energies. We show in Fig. 3(a) the energy difference between the ferromagnetic and paramagnetic states as a function of n. The free energy of the present model per site is given as

$$F(\langle S_z\rangle_{\rm av}) = E(\langle S_z\rangle_{\rm av}) - T\mathcal{S}, \tag{5}$$

where the entropy due to the localized spins is given by

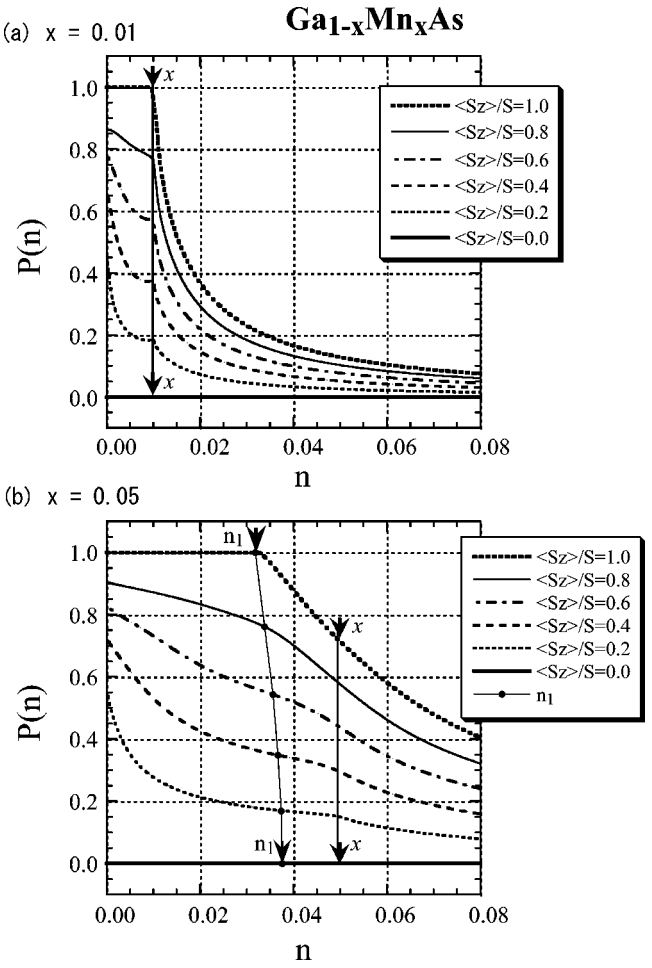

FIG. 2. The carrier spin polarization $P(n)$ for various values of magnetization for $x=0.01$ (a) and $x=0.05$ (b). The arrows indicate $n=x$ and $n=n_1$; n_1 is the carrier density where the Fermi level (ε_F) reaches the bottom of the host band.

$$\mathcal{S}=xk_B\ln\sum_{S_z=-S}^{S}\exp(\lambda S_z)-xk_B\lambda\langle S_z\rangle_{\mathrm{av}}. \tag{6}$$

The parameter λ is determined so as to minimize $F(\langle S_z\rangle_{\mathrm{av}})$ through the condition $(d/d\lambda)F(\langle S_z\rangle_{\mathrm{av}})=0$. If we can expand $F(\langle S_z\rangle_{\mathrm{av}})$ in terms of $(\langle S_z\rangle_{\mathrm{av}})^2$, T_c is determined as the temperature where the coefficient of $(\langle S_z\rangle_{\mathrm{av}})^2$ vanishes. However, the calculations for small magnetizations that are accurate enough to estimate the coefficient of $(\langle S_z\rangle_{\mathrm{av}})^2$ are rather difficult. Since $E(\langle S_z\rangle_{\mathrm{av}})-E(0)$ is approximately proportional to $(\langle S_z\rangle_{\mathrm{av}})^2$ up to full polarization at a fixed n, as is shown in Fig. 3(a), we fitted the data of $[E(\langle S_z\rangle_{\mathrm{av}})-E(0)]/\Delta$ with $(\langle S_z\rangle_{\mathrm{av}}/S)^2=0.4$ and 1.0 to the expansion $E(\langle S_z\rangle_{\mathrm{av}})-E(0)]/\Delta=-a(\langle S_z\rangle_{\mathrm{av}}/S)^2+b(\langle S_z\rangle_{\mathrm{av}}/S)^4$ and estimated a and b. Then we obtained T_c as $k_BT_c=2a/3x$. Figure 3(b) displays T_c as a function of n for $x=0.05$. The obtained T_c is in good agreement with the value of 110 K observed in $Ga_{1-x}Mn_xAs$ for $x=0.053$ and $n\simeq 0.3x$.[1]

In order to obtain further insight into the mechanism of the ferromagnetism in DMS's, we examine a case where the exchange interaction is so strong that the carrier spins remain almost antiparallel to the fluctuating localized spins. We

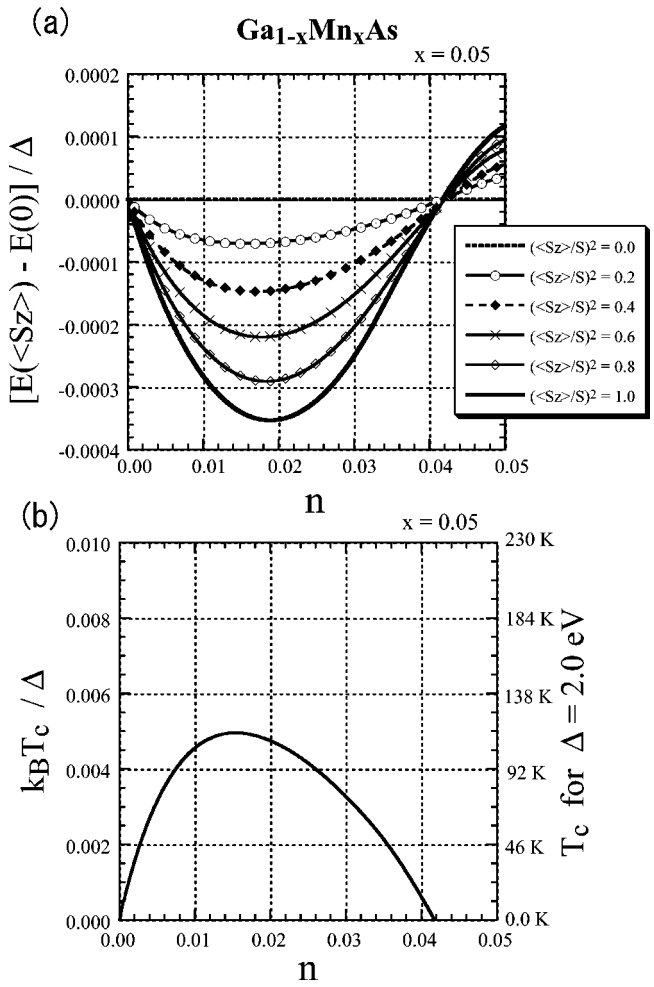

FIG. 3. (a) $[E(\langle S_z\rangle_{\mathrm{av}})-E(0)]/\Delta$ is depicted for $x=0.05$ as a function of n, for various values of $(\langle S_z\rangle_{\mathrm{av}}/S)^2$. (b) The Curie temperature T_c for $x=0.05$ as a function of n.

show in Fig. 4 the result for $IS/\Delta=-1.0$ and $E_M/\Delta=0$ where the impurity band is separated from the host band. The total number of states in the impurity band per site is equal to x irrespective of the value of $\langle S_z\rangle_{\mathrm{av}}$. When $\langle S_z\rangle_{\mathrm{av}}=S$, all states in the impurity band are down-spin states, while when $\langle S_z\rangle_{\mathrm{av}}=0$, the impurity band is composed of the same num-

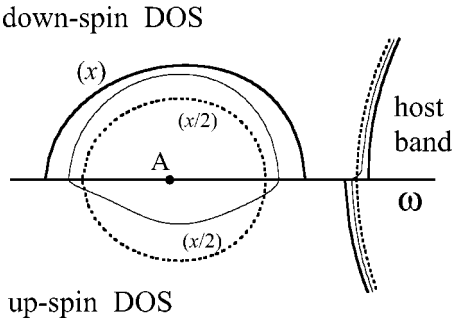

FIG. 4. The DOS of the impurity band in the case of $IS/\Delta=-1.0$ and $E_M=0$. The thick, thin, and dotted lines represent the cases of $\langle S_z\rangle_{\mathrm{av}}/S=1.0$, 0.5 and 0.0, respectively. The dot A indicates the impurity level for $x\to 0$.

ber of up- and down-spin states. The impurity band has a larger bandwidth in the ferromagnetic state than in the paramagnetic state. Hence the ferromagnetic state has lower energy than the paramagnetic one when n is small. The energy gain increases initially with the increase of n and reaches a maximum at $n \sim x/2$. Then it gradually decreases and finally vanishes at $n \sim x$. The gain of kinetic energy causes the ferromagnetism under a certain temperature. This implies that the double-exchange mechanism[24] for ferromagnetism is operative in the impurity band. The result for $Ga_{1-x}Mn_xAs$ shown in Fig. 3(a) has a similar n dependence to the case discussed above. Therefore we expect that the same mechanism causes ferromagnetism in $Ga_{1-x}Mn_xAs$, although the impurity band is not separated in the case of $x \simeq 0.05$.

Here we discuss the model and parameters used in the present work. We have taken the value of 2Δ according to the valence bandwidth estimated by band calculations.[12,13] We have assumed that $IS/\Delta = -0.4$, which is a conventional value for II-VI-based DMS's (Ref. 17) and is consistent with the recently obtained p-d exchange coupling constant of III-V-based DMS's,[16] although there are still controversies concerning the magnitude (and even the sign) of the exchange constant.[1] Since the impurity level E_a is given by $E_a/\Delta = [(E_M + IS)/\Delta] + \frac{1}{4}[\Delta/(E_M + IS)]$ in the present model, we introduced the attractive potential $E_M = -0.3\Delta$ so as to reproduce the experimental value of the acceptor level.[14,22] We emphasize that the attractive potential strongly assists the occurrence of the ferromagnetism. If we take $E_M/\Delta = 0$ together with $IS/\Delta = -0.4$, T_c is calculated to be, at highest, 40 K for $x = 0.05$. In this case, the carrier spreads over many nonmagnetic sites, which reduces the effective exchange coupling. This result explains why Mn-doped III-V-based DMS's exhibit appreciable ferromagnetism while those based on II-VI semiconductors exhibit negligible ferromagnetism. If we assume a more attractive potential than that used in the present work, i.e., $E_M/\Delta = -0.6$ together with $IS/\Delta = -0.4$, the magnetic impurity band separates from the host band, and T_c increases to 140 K for $x = 0.05$. In this case, the carrier is strongly bound to magnetic impurity sites so that the double-exchange mechanism works more efficiently.

In summary, we have shown that the carriers in the band tail of $Ga_{1-x}Mn_xAs$ have such a high local carrier density at Mn sites that the carrier spins couple strongly to the fluctuating localized spins. The double-exchange mechanism in the impurity band causes the ferromagnetism. The attractive local potentials at impurity sites strongly assist the occurrence of ferromagnetism in III-V-based DMS's. Experimental observation of T_c as a function of the carrier density for a fixed Mn concentration will be useful in clarifying the validity of the present theory.

The authors would like to thank Professor Y. Kayanuma for informing them of the work of his group before publication. One of the authors (M.T.) is grateful to Professor W. Nolting for his instructive comments on the carrier-induced ferromagnetism. This work was supported in part by Grants-in-Aid for Scientific Research Nos. 14540311 and 14540362 from the Ministry of Education, Culture, Sports, Science and Technology of Japan. K. K. was partially supported by Center for Science and Engineering Research, Research Institute of Aoyama Gakuin University.

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