Ferromagnetism and Its Stability in the Diluted Magnetic Semiconductor (In, Mn)As

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(Received 5 June 1998)

Carrier-induced ferromagnetism in the doped diluted magnetic semiconductors $(\mathrm{In}, \mathrm{Mn}\uparrow, \mathrm{Mn}\downarrow, A)\mathrm{As}$, where A is As or Sn and Mn↑ (Mn↓) denotes Mn atoms whose local magnetic moment is parallel (antiparallel) to the magnetization, are investigated using the Korringa-Kohn-Rostoker coherent-potential approximation and local density approximation first-principles calculation. The result shows that (i) the ferromagnetic state is stable due to the double exchange at low concentrations of A, and (ii) a spin-glass-like local-moment disordered state, which stems from the superexchange, is more favorable when the Mn d holes are nearly compensated. [S0031-9007(98)07222-6]

PACS numbers: 75.50.Dd, 71.23.–k, 71.55.Eq, 75.30.–m

The first fabrication of (In, Mn)As diluted magnetic III-V compound semiconductors reported by Munekata *et al.* [1] brought to light a new class of magnetic materials, namely, carrier-controllable magnetic semiconductors. These materials are some of the most physically interesting, and promising from the point of view of potential applications, to emerge in the last few years. Both (In, Mn)As and (Ga, Mn)As have been studied intensively as prototypes of such systems [2–7]. The important features of these materials are that (i) the concentration of Mn can be as high as several tenths of a percent, and (ii) the carrier density can be controlled over a wide range between n and p type. These features open up the possibility that the magnetic behavior of the materials can be controlled simply by changing the carrier density. This sort of control over magnetic properties has already been successful for both (In, Mn)As and (Ga, Mn)As. In those experiments the carrier density was controlled at heterojunctions [4] as well as by irradiation of light [6]. Giant negative magnetoresistance has also been reported [7], which further enhances the interest of these systems as candidates for useful devices. Through these experimental studies, it has become clear that the III-V based diluted magnetic semiconductors are very different from the classical II-VI based magnetic semiconductors such as CdMnTe and ZnMnSe which show no magnetic ordering.

Though a considerable amount of experimental data has been already accumulated, the theoretical understanding of diluted III-V semiconductors is still at a preliminary stage. Most attempts to understand the magnetic behavior of these systems are based on models in which the Mn local magnetic moments interact with each other via RKKY-type (Ruderman-Kittel-Kasuya-Yoshida) interactions [2]. Under the assumption that only the ferromagnetic component survives due to the low carrier density, this picture explains the temperature dependence of the magnetization and the hole resistivity of the diluted magnetic semiconductors. Some people, however, question this explanation. If the carriers in such systems originate from the Mn d states, which are far from free-electron-like, the RKKY picture may not be realistic. Another less convincing argument is that ferromagnetism due to the RKKY-type interactions has never been observed in any real systems, irrespective of the carrier density. It has also been suggested that magnetic polaron effects may be important [8–10]. It is very likely that magnetic polarons play a role in these systems as they do in II-VI magnetic semiconductors. However, there is as yet no quantitative discussion of polaron effects for III-V magnetic semiconductors.

On the other hand, first-principles calculations have been carried out by Shirai *et al.* on systems that roughly approximate the diluted magnetic semiconductors [11]. They studied hypothetical ordered alloys $\mathrm{Ga}_{1-x}\mathrm{Mn}_x\mathrm{As}$ of zinc blende structure, where $x = 1/2, 1/4$, and performed band structure calculations in the framework of the local density approximation (LDA). They showed that these ordered alloys were all ferromagnetic. They also showed that the equilibrium lattice constants extrapolated to the low Mn concentration region were in good agreement with the experimental lattice constants. The fact that the band structure calculation based on LDA produces a reasonable description of at least ordered GaMnAs alloys implies that a large part of the ground state properties of the diluted random alloys might also be explained in the framework of the LDA.

This Letter reports the results of KKR-CPA-LDA (Korringa-Kohn-Rostoker coherent-potential and local density approximation) calculations [12–14] of the electronic structure of doped (In, Mn)As alloys and propose a mechanism for the carrier-induced ferromagnetism based on these calculations. KKR-CPA-LDA is applied to the multicomponent partially disordered system $(\mathrm{In}_{1-x-y-z}\mathrm{Mn}\uparrow_x\mathrm{Mn}\downarrow_y A_z)\mathrm{As}$, where Mn↑ or Mn↓, respectively, denote the Mn atoms whose local magnetic moment is parallel or antiparallel to the magnetization. To control the carrier density $A =$ As or Sn, which serves as an electron donor, is introduced. The Mn atoms themselves behave as electron acceptors in (In, Mn)As. In, Mn↑, Mn↓, and A, are supposed to occupy the same, say, the first, sublattice of the zinc blende-type lattice,

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and form a random quaternary alloy within the sublattice. The second sublattice is then occupied entirely by As atoms. Thus, the disorder arises only in the first sublattice and the system is only partially disordered.

The configurational averaged Green's function is described by a set of coherent t matrices, t_1 and t_2, each being associated with one of the two sublattices. The site off-diagonal coherent t matrix t_{12}, which connects the two sublattices, and which might be included in nonsingle site treatments such as the molecular CPA, is omitted in the present calculation so as to be consistent with the single-site approximation. The effect of including t_{12}, however, would be negligible. In such a treatment, and when no disorder exists in the second sublattice as here, the coherent t matrix t_2 is nothing but the atomic t matrix of the atoms on the second sublattice. The self-consistency that is required by the Kohn-Sham equation of the density functional theory is treated in the framework of the local (spin) density approximation with the parametrization given by Moruzzi, Janak, and Williams [15]. The experimental lattice constant of $a = 11.45$ (a.u.) is assumed throughout the calculations since the lattice constant seems not to be essential for the present discussion. Two extra empty muffin-tin potentials on the antibond sites of the zinc blende-type lattice are used in addition to those for the normal atomic sites.

Figure 1 shows the total density of states (DOS) and the Mn d density of states (d-DOS) of $(\mathrm{In}_{1-x-y-z} \times \mathrm{Mn}\uparrow_x \mathrm{Mn}\downarrow_y \mathrm{As})\mathrm{As}$ for $(x, y, z) = (0.06, 0, 0)$ and $(0.03, 0.03, 0)$. The Mn d-DOS is obtained by integrating the local d-DOS within the Mn muffin-tin sphere. The total energies of these systems relative to the energy of the nonmagnetic system of the same composition are -3.278 mRy and -3.096 mRy for the ferromagnetic (i.e., $x = 0.06$ and $y = 0$) and local-moment disordered (LMD, i.e., $x = y = 0.03$) states, respectively, showing that the ground state is ferromagnetic and that the nonmagnetic state has the highest total energy among the three. The local magnetic moment of Mn is $4.208\mu_B$ and $4.218\mu_B$ for ferromagnetic and LMD states, respectively.

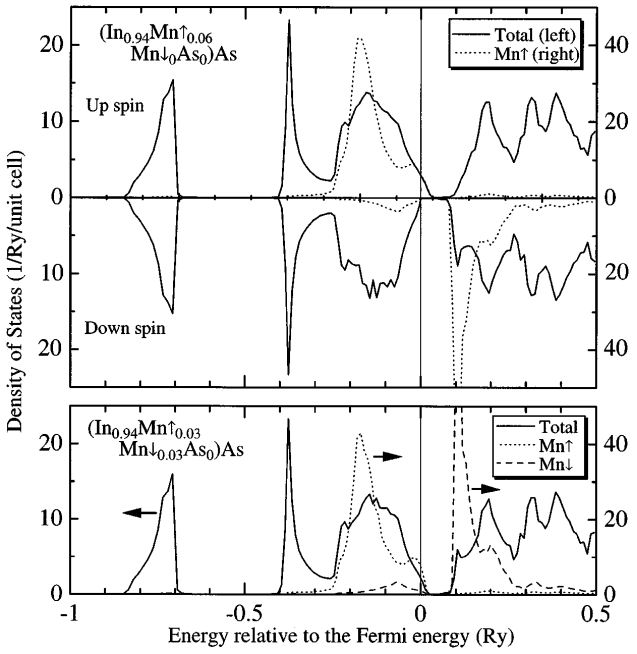

FIG. 1. The total DOS and the Mn d-DOS of $(\mathrm{In}_{1-x-y-z} \times \mathrm{Mn}\uparrow_x \mathrm{Mn}\downarrow_y \mathrm{As})\mathrm{As}$ for $(x, y, z) = (0.06, 0, 0)$ (ferromagnetic state, upper panel) and $(0.03, 0.03, 0)$ (LMD state, lower panel).

An important fact seen in Fig. 1 is that the ferromagnetic state is half metallic, namely, the Fermi surfaces exist only in the majority spin bands. Moreover, the larger part of the carriers consists of the Mn d states. In this respect, the argument that the usual RKKY interaction mediated by unpolarized nearly free electrons might not be a good starting point for the discussion of the magnetism of these systems seems to be rather reasonable. The above situation is in some ways similar to that realized in $\mathrm{La}_{1-x}A_x\mathrm{MnO}_3$, which exhibits the so called colossal magnetoresistance, where A = Ca, Sr, or Ba is an alkaline-earth element, in their ferromagnetic phase [16,17]. It is well known that the mechanism that stabilizes the ferromagnetism of LaMnO_3 under doping is the double exchange proposed by Zener [18]. In the framework of band structure, double exchange essentially means the following: Near the half filling, and when the exchange splitting is bigger than the bandwidth, the band energy of the ferromagnetic state is lower than that of the antiferromagnetic state if a sufficient (usually rather small) number of holes (or electrons) exist. In the present case of (In, Mn)As, the exchange splitting is much bigger than the valence d band, and it also has a considerable number of holes. Thereby, the conditions mentioned above are fulfilled, and it is quite natural to suppose that the same mechanism also works in the present system. A closer look at the d-DOS reveals that the valence band edge of the majority (up spin) DOS of the ferromagnetic state is located at a slightly higher position (by $\sim$10 mRy) than in the LMD state. This is a general feature observed in systems with rather large local magnetic moments, and originates from the fact that there exists extra scattering in the LMD state (or antiferromagnetic state) caused by the difference in the atomic potentials reflecting the orientation of the magnetic moment. This tiny difference in the DOS makes the total energy of the ferromagnetic state lower than that of the LMD state; introducing the holes to the valence bands lowers the band energy more in the ferromagnetic state than the LMD state. It should be noticed that the ferromagnetism in this case has some similarities with Nagaoka's ferromagnetism [19]. However, for a strong but finite intra-atomic exchange interaction with multiorbital bands, it might be more suitable to call this mechanism "double exchange."

With increasing As concentration at the antisite, the holes at the conduction bands are gradually compensated.

Figure 2 shows the total DOS and the Mn d-DOS at $(x, y, z) = (0.06, 0, 0.04)$ and $(0.03, 0.03, 0.04)$. The states at the Fermi energy are primarily impurity bands composed of As at the antisite, and, except in the majority spin band of the ferromagnetic state, are split off from the valence bands. In this respect, the d holes are mostly compensated in this composition. The total energies of these systems relative to the energy of the nonmagnetic system are -5.331 mRy and -5.343 mRy for the ferromagnetic and LMD states, respectively. The local magnetic moments of Mn atoms are slightly bigger than the undoped cases: $4.310\mu_B$ in the ferromagnetic state and $4.306\mu_B$ in the LMD state. The ground state is now the LMD state. It is the superexchange mechanism that stabilizes the LMD state (or antiferromagnetic state) at the half filling. Again in the language of band structure, the superexchange originates from the downward shift of the center of gravity of the lower subband of the split d bands. This lowers the band energy. The effect is expected only for the LMD (or antiferromagnetic) configuration, and the gain in the band energy obviously is biggest when the lower subband is completely filled.

Figure 3 shows the total energy of the LMD state relative to that of the ferromagnetic state as a function of the concentration of antisite As (circle) or Sn (triangle). At around 3 at.% (6%) As (Sn), with increasing As (Sn) concentration, the ferromagnetic state becomes unstable and the LMD state becomes the ground state. The difference in the concentration dependence between the As and Sn cases arises from the fact that in InAs an As atom on antisite acts as a double donor, while a Sn atom is a single donor. The transition takes place because the holes in the valence bands are compensated by electrons provided by As or Sn atoms on the antisite, which makes the double exchange less effective and finally impossible. The transition is of first order.

The crossover region where the superexchange mechanism prevails over the double-exchange mechanism is rather narrow; the double-exchange mechanism is so strong that it is taken over only just before it becomes entirely impossible. The superexchange is rather weak when the intra-atomic exchange (or Coulomb) interaction is strong as in the present case. The energy gain due to the local-moment disorder, therefore, is small compared to the energy that stabilizes the ferromagnetic state.

Figure 4 summarizes the above discussion schematically. Here we assume that the intra-atomic exchange coupling (Hund's coupling), $\sim J_H$, is bigger than the bandwidth. In the ferromagnetic state (upper panel), each spin band shows a splitting which is typically of the order of the nearest neighbor hopping t, leaving the center of gravity of both the majority (up) and minority (down) spin bands, separated by $\sim J_H$, unchanged. On the other hand, in the antiferromagnetic state (lower panel), the splitting originating from the nearest neighbor hopping pushes down (up) the occupied (unoccupied) bands by an amount of order of $\sim t^2/J_H$ [20]. If the bands are half filled, a gain in the band energy is expected only for the antiferromagnetic state, which is identified as the superexchange mechanism. If the electron filling deviates from the above case, a gain in band energy is also expected for the ferromagnetic state. The gain in this case is proportional to $\sim tn$, where n is the number of holes

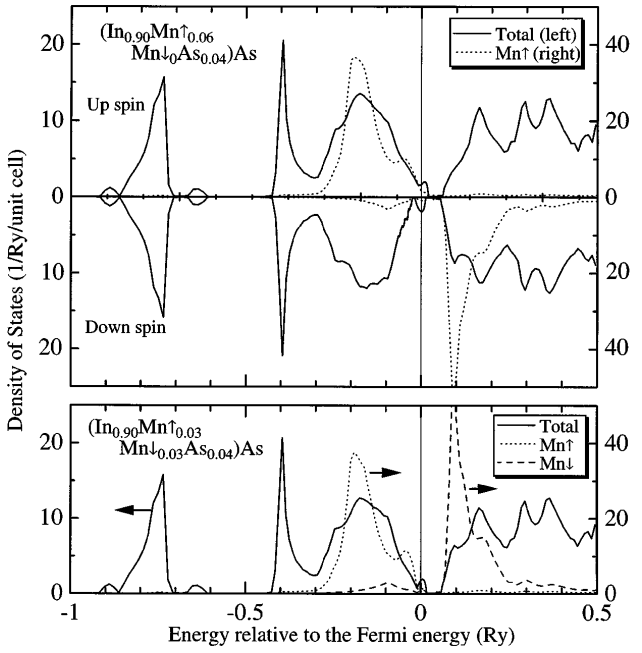

FIG. 2. The total DOS and the Mn d-DOS of $(In_{1-x-y-z} \times Mn\uparrow_x Mn\downarrow_y As_z)As$ for $(x, y, z) = (0.06, 0, 0.04)$ (ferromagnetic state, upper panel) and $(0.03, 0.03, 0.04)$ (LMD state, lower panel).

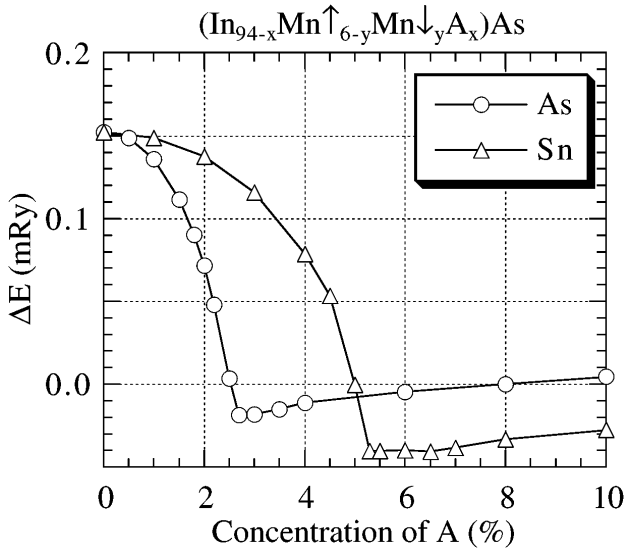

FIG. 3. The difference $\Delta E = E_{LMD} - E_{ferro}$ in the total energy between $(In_{0.94-x}Mn\uparrow_{0.03}Mn\downarrow_{0.03}A_x)As$ and $(In_{0.94-x} \times Mn\uparrow_{0.06}Mn\downarrow_0 A_x)As$ as a function of the concentration x of $A =$ As or Sn at the antisite.

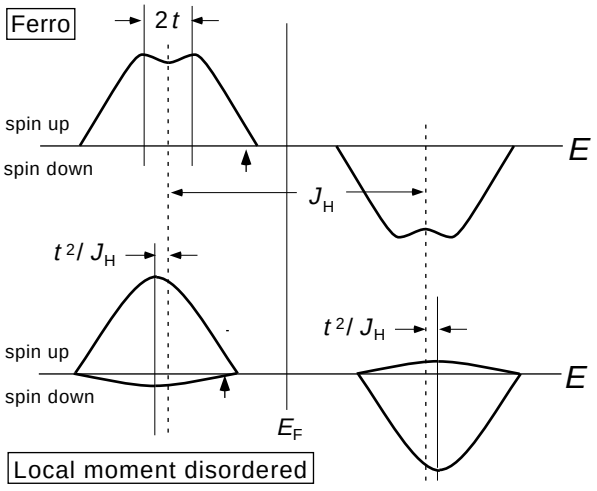

FIG. 4. A conceptual view of the competition between the double-exchange and superexchange mechanisms in diluted magnetic semiconductors. The positions of the Fermi energy in the uncompensated cases are indicated by the arrows.

(or electrons). Such a stabilization of the ferromagnetism can be regarded as the double-exchange mechanism (or Nagaoka's ferromagnetism in the limit of $J_H \to \infty$ and $n \to 0$). Since the energy gain for the antiferromagnetic state, $\sim t^2/J_H$, is nearly constant for low hole (or electron) concentrations, an increase in the hole density will eventually stabilize the ferromagnetic state. The same argument also applies to the case of the LMD state as far as its magnetic stability is concerned.

It is very likely that a similar situation is also realized in (Ga, Mn)As systems. The band structure calculation by Shirai *et al.* predicted a ferromagnetic state for ordered alloys [11] and also that those alloys would be half metallic in the ferromagnetic state. Those observations strongly support the idea that the above mechanism is common to all the diluted magnetic III-V semiconductors.

Our discussion does not necessarily mean that the spin-glass-like behavior should be observed in the low carrier concentration region of diluted magnetic semiconductors. It should be noted that our discussion has been restricted to the ground state properties. It is rather likely that the system is paramagnetic down to a very low temperature; the ordering temperature T_g could be low because of the weak superexchange coupling (i.e., large J_H). On the other hand, the calculation predicts that the ferromagnetic Curie temperature could be rather high. A reasonable measure of the transition temperature is the energy difference between the ferromagnetic and the LMD states; this obviously is large (see Fig. 3) in the region where the ferromagnetic state is sufficiently stable.

In summary, we have performed KKR-CPA-LDA calculations on the multicomponent partially disordered systems $(In_{1-x-y-z}Mn\uparrow_x Mn\downarrow_y A_z)As$ in order to make clear the mechanism of the carrier induced ferromagnetism. We have found that the transition from the LMD state to the ferromagnetic state takes place as a result of the competition between the double-exchange and superexchange mechanisms. This seems to explain the observed ferromagnetism of (In, Mn)As and (Ga, Mn)As diluted magnetic semiconductors very well.

This work is supported in part by Grant-in-Aid for Scientific Research on Priority Areas, The Japanese Ministry of Education, Science, Sports and Culture.

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