Double Resonance Mechanism of Ferromagnetism and Magnetotransport in (Ga-Mn)As

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We calculate the electronic states of the Mn-doped semiconductors and show that resonant states are formed at the top of the down spin valence band due to magnetic impurities and that they give rise to a strong and long-ranged ferromagnetic coupling between Mn moments. We propose that the coupling of the resonant states, in addition to the intra-atomic exchange interaction between the resonant and nonbonding states, is the origin of the ferromagnetism of (Ga-Mn)As. The mechanism is thus called "double resonance." The resonant states bring about the spin-dependent resistivity to produce magnetoresistive properties in (Ga-Mn)As and their junctions.

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Diluted magnetic semiconductors (DMSC's) of III-V elements, (In-Mn)As [1] and (Ga-Mn)As [2], attract much attention due to the ferromagnetism with high Curie temperatures (T_C). A success of spin injection through epitaxial ferromagnetic (Ga-Mn)As/semiconductor (SC) junctions indicates a large potential of these SC's for spin-electronic devices [3]. T_C of (Ga-Mn)As, however, is still below 120 K, and therefore ferromagnetic SC's with higher T_C are needed for technical applications. In order to achieve the purpose, the origin of the ferromagnetism should be clarified.

The electronic state of the Mn impurity in (Ga-Mn)As in the dilute limit has been shown to be $3d^5$ + hole with antiferromagnetic p-d coupling [4,5]. Analyzing the magnetoresistance and the concentration dependence of T_C, Matsukura *et al.* [6] showed that (Ga-Mn)As with higher Mn concentration is a metallic ferromagnet, and proposed that the RKKY interaction is the origin of the ferromagnetism. Beschoten *et al.* [7], however, have recently measured the magnetic circular dichroism spectrum of (Ga-Mn)As to show that the ferromagnetic state occurs even in the insulating phase, being consistent with a variable range hopping observed in the low concentration regime [8]. Furthermore, the value of p-d exchange coupling estimated is rather large as compared to that obtained in the other experiments [5]. An analysis of the current-bias relation of the resonant tunnel diode (RTD) also gives a smaller p-d exchange coupling by several factors [9]. From the theoretical point of view, on the other hand, Akai [10] has performed CPA (coherent potential approximation) combined with the *ab initio* Korringa-Kohn-Rostoker method and has shown that the ground state of (In-Mn)As is half-metallic, and thereby proposed a double exchange mechanism [11] for the ferromagnetism of these systems.

More detailed study is thus highly desirable to clarify the mechanism for the ferromagnetic coupling between Mn moments in these DMSC's. In this Letter, we show, by calculating the electronic states of Mn-doped SC's, that there appears a sharp resonant state at the top of the down spin valence band (VB), and demonstrate, by using a simpler model, that the resonant states give rise to a strong and long-range ferromagnetic coupling between Mn moments. The mechanism for the ferromagnetism is thus called double resonance. We further study the relevance of the electronic state to the spin-dependent transport properties of (Ga-Mn)As and to the p-d exchange coupling estimated in the RTD experiment.

We first perform realistic LCAO (tight-binding) calculations for a transition metal impurity in the SC, the band parameters of which are taken from the textbooks [12,13]. Here we use the band parameters of Ge instead of GaAs in order to avoid an additional complexity due to a larger unit cell of GaAs. The difference between the band structures of Ge and GaAs is actually small for the present purpose [12]. A geometrical approximation is adopted for the Ge-Mn bonds as the atomic distance of Ge is almost the same as that of bulk Mn. We neglect the spin-orbit coupling, which will be important for more quantitative studies. In order to describe the magnetic state of Mn ions, we adopt the simplest form of the exchange interaction of a Hubbard type and apply the Hartree-Fock approximation, which gives rise to the spin dependent atomic level of the Mn ion, $\upsilon_\sigma = \epsilon_d + Un_{-\sigma}$, where ϵ_d and U are the bare atomic level of the Mn ion and the Coulomb interaction, respectively, and n_σ is the number of $\sigma(\uparrow, \downarrow)$ spin electrons on a Mn impurity.

The density of states (DOS) of SC atoms and local DOS of the impurity are calculated by using the recursion method [14,15] where the Green's function $\mathbf{G}$ of the Hamiltonian is expressed by a continued fraction. We prepare a system with more than 8000 atoms and calculate the continued fraction coefficients up to, at least, the 30th level. We found the convergence of the results is satisfactory. (We have shifted the p level of Ge from 8.04 to 10.0 eV to get a narrower band gap of $\sim$0.12 Ry.) The

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electronic state of the nearest neighbor (n.n.) SC sites of the impurity is calculated by solving $(1 - \mathbf{gV})\mathbf{G} = \mathbf{g}$ for a cluster which includes four SC atoms and one impurity. Here, $\mathbf{g}$ and $\mathbf{V}$ denote the Green's function of the pure SC and the perturbative potential due to the impurity, respectively.

We first examined the feature of the local DOS of the transition metal impurity in the paramagnetic state by shifting the position of ϵ_d, and confirmed that the results are consistent with those obtained in the Green function method by Zunger [16]; the local DOS of the impurity has two delocalized states of t_{2g} character and one nonbonding peak of e_g character. The bandwidth of the local DOS of the impurity is, however, a little narrower than that obtained in the Green function method. This may be due to the neglect of the longer range s-d and p-d mixing between SC atoms and the impurity. We have also calculated the local DOS of an impurity on the interstitial site, the features of which are also consistent with those in Ref. [16].

Self-consistent calculations for the magnetic state of Mn impurity have been done by choosing $U \sim 0.075$ Ry ($= 1.0$ eV), which is reasonable for metallic transition metals, and $\epsilon_d = 0.42$ Ry. The position of the Fermi level E_F is assumed to be the top of the VB, $\sim$0.52 Ry. These parameter values give $n = n_\uparrow + n_\downarrow = 4.8$ and $m = n_\uparrow - n_\downarrow = 3.1$ per Mn. The calculated DOS's of the magnetic Mn impurity and n.n. SC atoms are shown in Fig. 1, together with the DOS of the host SC. As a small damping factor is included in the energy, the band gap of SC is slightly smeared out. Several peaks of the DOS can be seen in Fig. 1, which can be interpreted as follows. The peaks A and C are the delocalized states of t_{2g} character (peak C in the $\downarrow$ spin state is not well resolved with peak B), and peak B is the nonbonding one of e_g character. The peak D in the DOS of n.n. SC sites is independent of spin and then identified to be a gap state produced by dangling bonds of SC. We see that peak A of $\downarrow$ spin state resonates strongly with the DOS of n.n. SC atoms while the peak B does not. The strong resonance of peak A is due to the fact that the position of this peak is close to the top of the VB. Note that the resonant peak A remains to be close to the top of the VB even if $v_\downarrow$ becomes higher [16].

Existence of the resonant peak of the DOS near E_F produces pronounced features in the photoemission spectrum and the optical conductivity $\sigma(\omega)$ [17,18]. The inset of Fig. 1(b) is a crude estimate of the change in $\sigma(\omega)$ due to the magnetic impurity. We see a broad peak appears near $\omega \sim 0.03$ Ry which agrees qualitatively with the experimental results [18]. The change in the number of $\downarrow$ spin electrons on the n.n. SC atoms is calculated to be $-0.1 - -0.2$ per atom, which is also consistent with the negative p-d coupling [4,5].

The formation of the resonant state near the top of the $\downarrow$ spin VB has a strong influence on the coupling between Mn moments and the transport properties. In order to capture the essence of these phenomena, we adopt a simpler model which can reproduce the results described above

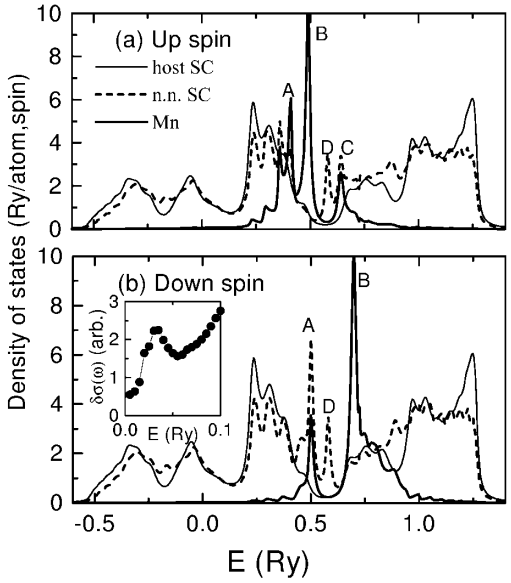

FIG. 1. Densities of states of the impurity (solid curves), n.n. SC (broken curves), and host SC atoms (thin solid curves) for (a) up and (b) down spin states. Inset shows the change in the optical conductivity $\delta\sigma(\omega)$ due to Mn dopant. See text for the meaning of peaks A, B, C, and D.

and makes detailed analyses possible. The important features of the DOS calculated are that the impurity states have one nonbonding (localized) state and two delocalized (resonant) states, one of which is close to the top of the VB. Because the localized state is of e_g character being exchange split due to the Coulomb interaction, we may treat it as a localized spin of $S = 1$ which is coupled ferromagnetically with the spin of the resonant state. The VB is simplified as a single band with s symmetry which hybridizes the impurity level and produces a resonant state at the top of the "VB" of this model. The resulting Hamiltonian may be given as

$$H = -t \sum_{ij\sigma} c^\dagger_{i\sigma} c_{j\sigma} + \sum_{i\sigma} \epsilon_d c^\dagger_{i\sigma} c_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - J \sum_i \mathbf{S}_i \cdot \mathbf{s}_i , \quad (1)$$

where t is the hopping integral which characterizes the VB and the mixing between the VB and impurity level and $J(>0)$ is the ferromagnetic coupling between the itinerant spin $\mathbf{s}$ and the localized one $\mathbf{S}$. The summations in the latter three terms run only over the impurity sites. The Hamiltonian is actually the same with that of the double exchange model for the manganites [19], except that the numbers of localized spins and carrier holes are very few as compared with those of manganites.

The qualitative features of the local DOS of the impurity can be reproduced by applying the Hartree-Fock approximation to the Hamiltonian (1) with parameter values, e.g., $U = J = 1.5t$, $\epsilon_d = 1.2t$. The resultant values of $v_\sigma \sim \epsilon_d + U\langle n_{-\sigma}\rangle - \sigma JS/2$ determined self-consistently are $v_\uparrow = 1.91t$ and $v_\downarrow = 3.45t$. The position of E_F is taken near the top of the band, at $5.9t$ in this

case, for a simple cubic lattice. The result is insensitive to the position of E_F as long as E_F is close to the top of the band. The DOS's of ↑ and ↓ spin states of the impurity are depicted in the inset of Fig. 2(a) together with the VB of the simple cubic lattice. We see the DOS of the ↓ spin impurity state forms a peaky structure near the top of the band.

The excess energy ΔF due to two impurities on sites $(0,0,0)$ and $(m,0,0)$ on the simple cubic lattice is calculated for the values of v_σ determined above by using the formula,

$$\Delta F = \pi^{-1} \sum_\sigma \int_{-\infty}^{E} \arg \det[1 - \mathbf{V}\mathbf{g}]\, d\epsilon\,, \qquad (2)$$

where $\mathbf{V}$ is a 2×2 site-diagonal matrix with matrix elements v_σ on site $(0,0,0)$ and $v_{\sigma'}$ on site $(m,0,0)$. The coupling energy of two magnetic impurities is given as $\Delta F_{\mathrm{mag}} = \Delta F(P) - \Delta F(AP)$ with $E = E_F$, where P and AP denote the parallel and antiparallel alignment of two magnetic moments. Figure 2(a) shows the calculated results of ΔF_{mag} as functions of energy E for $m = 1$–4. We see several characteristic features in Fig. 2(a). (i) The parallel alignment of the magnetic moments is stable for all m when the VB is almost occupied (long-range ferromagnetic coupling), whereas the coupling oscillates as a function of m when there are appreciable holes in the VB. (ii) The second feature, which is more striking, is that the coupling energy is strongly enhanced due to the presence of the resonant state near the top of the ↓ spin band. (iii) The value of ΔF_{mag} for n.n. impurities is negative even when the VB is completely occupied.

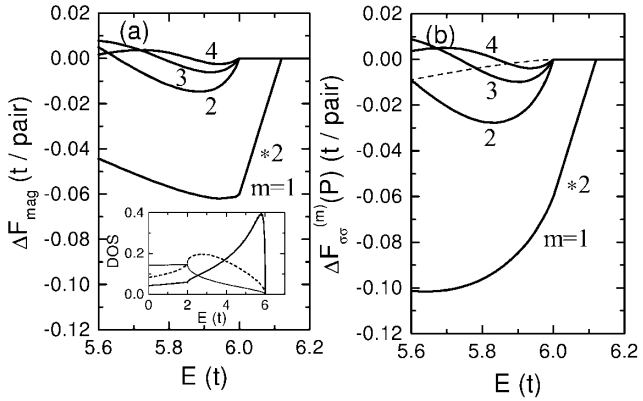

FIG. 2. (a) Magnetic coupling energy ΔF_{mag}, that is, the energy difference between parallel and antiparallel alignments of two impurity moments on site $(0,0,0)$ and $(m,0,0)$ with $m = 1$–4 (curves 1–4), calculated as functions of energy. Inset: Densities of states of up (broken curve) and down (solid curve) spin impurity states in a simple model (see text). Thin solid curve is the DOS for the simple cubic lattice. (b) Contribution to the coupling energy from the down spin state ($\sigma = \downarrow$) in the parallel alignment of the impurity moments calculated as functions of energy.

In order to analyze the results in more detail, we show in Fig. 2(b) the excess energy of down spin states in the parallel alignment, which can be expressed explicitly as

$$\Delta F_{\downarrow\downarrow}^{(m)}(P) = \pi^{-1} \int_{-\infty}^{E} \arg[1 - g_{0m} g_{m0} v_\downarrow^2/(1 - v_\downarrow g_{00})\,(1 - v_\downarrow g_{mm})]\, d\epsilon\,, \qquad (3)$$

where g_{nm} is the Green's function between sites $(n,0,0)$ and $(m,0,0)$. Comparing the results shown in Figs. 2(a) and 2(b), we see that the features in Fig. 2(a) are almost the same with those of $\Delta F_{\downarrow\downarrow}^{(m)}(P)$. The oscillation of ΔF_{mag} is governed by the factor of $g_{0m} g_{m0}$ which is related to the nonlocal susceptibility $\chi_{0m} = -\pi^{-1} \mathrm{Im} \int g_{0m} g_{m0}\, d\epsilon$. It is well known that the period of oscillation of χ_{0m} with respect to the distance m is long when E_F is close to the band edge. This is the tight-binding version of the RKKY oscillation. The enhancement comes from the factor $[(1 - v_\downarrow g_{00})\,(1 - v_\downarrow g_{mm})]^{-1}$, which is responsible to the resonant state. For comparison, we show a result of $\Delta F_{\downarrow\downarrow}^{(1)}(P)$ without this enhancement factor by a broken curve in Fig. 2(b). We see it is much smaller than the corresponding result shown by curve 1. The negative values of ΔF_{mag} and $\Delta F_{\downarrow\downarrow}^{(1)}(P)$ above the band edge ($6t$) are due to a bound state appeared above the top of the band in the case where two impurities are on the n.n. sites. The results may suggest that the coupling between two impurities is ferromagnetic even in the insulating phase. In this way, the ferromagnetic coupling between two magnetic impurities is governed by the resonant state on each impurity site near the top of the VB. This mechanism of the ferromagnetism may then be called "double resonance" mechanism [20]. It is worthwhile to note that the magnitude of ΔF_{mag} can be ~100 K for $m = 2$ and 3 when $t \sim 1$ eV.

Stable moments on the Mn ions are realized due to the intra-atomic ferromagnetic exchange interaction between spins in the resonant and localized (nonbonding) states. These Mn moments couple ferromagnetically via the ↓ spin resonant states. Because the local Green's function of the real system shows a similar energy dependence near the top of the VB with that of the simple model, the double resonance mechanism works also in (Ga-Mn)As [21]. The combination of the double resonance mechanism and the intra-atomic exchange interaction is the present scenario for the ferromagnetism of (Ga-Mn)As.

Now we move to the magnetotransport properties. The spin-dependent conductance is easily calculated in a numerical simulation for a finite size system by using the Kubo formalism [22] for the simple model proposed above. We adopt a system which consists of a cluster of $20 \times 20 \times 20$ sites with 3% Mn impurities and lead wires. Figure 3(a) shows the calculated results of the conductance Γ_σ as functions of energy [23]. The values $v_\uparrow = 1.91t$ and $v_\downarrow = 3.45t$ determined already have been used. There is a large spin asymmetry $\Gamma_\uparrow/\Gamma_\downarrow \sim 3$ as expected, which suggests that large magnetoresistive

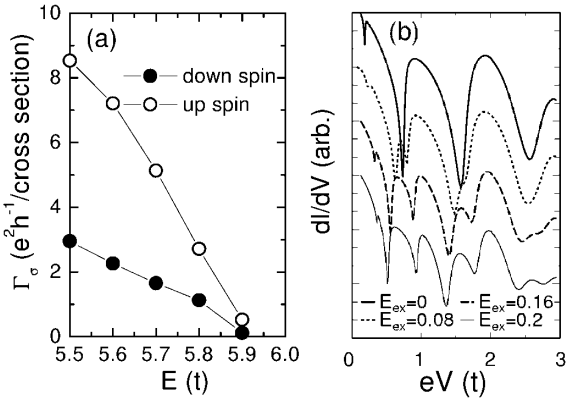

FIG. 3. (a) Spin-dependent conductance calculated for a finite size system as functions of energy. (b) Calculated results of dI/dV for a resonant tunnel diode using a model with an effective exchange splitting $E_{\rm ex}$. Here we took $E_{\rm F} = 5.8t$ and the lifetime broadening $0.2t$ at $E_{\rm F}$; see text.

effects can be realized in magnetic junctions using (Ga-Mn)As [24].

The results in Fig. 3(a) show no clear difference between the band edges of ↑ and ↓ spin conductance. In real systems, broadening of the resonant states and a finite number of holes may give rise to an effective exchange splitting $E_{\rm ex}$. Actually, $E_{\rm ex}$ has been estimated from the current-voltage (I-V) relation of RTD [9]. Here we adopt the Keldysh formalism [25] to calculate the dI/dV-V relation in RTD and estimate the value of $E_{\rm ex}$ in a simple lattice model with a uniform exchange splitting [26]. Figure 3(b) show the calculated results of the dI/dV-V relation for various values of $E_{\rm ex}$. The value of $E_{\rm ex}$ corresponds to the half of the energy separation between nearby dips in dI/dV. Comparing the calculated and experimental ones, we obtain $E_{\rm ex} \sim 0.1t \sim 0.2t$ with $t \sim 1$ eV. It should be stressed here that a lifetime broadening at $E_{\rm F}$ due to magnetic impurities is necessary to eliminate sharp peaks that usually appear in dI/dV of the resonant tunneling. In the present calculation, the lifetime broadening was replaced by a temperature broadening ($k_BT \sim 0.2t$) for simplicity. The magnitude of the broadening was estimated by calculating the self-energy of the model, Eq. (1), in the CPA [26].

The present mechanism for the ferromagnetism of (Ga-Mn)As resolves the controversies raised so far. The large values of the coupling constant estimated in the RKKY model can be interpreted by the enhancement due to the resonant state near $E_{\rm F}$. With decreasing concentration, the metallicity may be destroyed but the ferromagnetism can survive even in the insulating phase. As the model Hamiltonian is of the double exchange type, the double resonance mechanism proposed in this work may bridge over the interpretations of the RKKY and the double exchange models [6,10,27].

In conclusion, we have shown that resonant states are formed at the top of the ↓ spin valence band in the Mn-doped semiconductors and they give rise to a strong and long-ranged ferromagnetic coupling between Mn moments. The double resonance mechanism and the exchange interaction within Mn ions have been proposed to be the origin of the ferromagnetism of (Ga-Mn)As. The resonant states of the ↓ spin state make the resistance spin asymmetric and bring about strong magnetoresistive properties in junctions with (Ga-Mn)As. The present picture for the electronic state and mechanism for the ferromagnetism resolve several controversies existing so far.

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