

Effective exchange interaction and Curie temperature in magnetic semiconductors

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Based on a previously reported double-resonance mechanism, we present an analytical expression of the effective exchange interaction between impurity moments of transition-metal elements introduced in semiconductors. It is shown that the exchange interaction is enhanced by several orders of magnitude as compared with the ordinary RKKY interaction when the Fermi level and impurity states are close to the top of the valence band. Although the interaction is found to decay exponentially, the magnitude is large even when the distance between two impurities is several times as long as the lattice constant. The concentration dependence of the Curie temperature is calculated by using a percolation theory, and the calculated results are compared with the experimental findings.

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An important system for spin electronics is likely to be ferromagnetic semiconductors (FMSC's).¹⁻⁴ Thus far, it has been confirmed that Mn-doped III-V compounds, (Ga-Mn)As compounds,² and Ge-Mn compounds⁴ all show a high Curie temperatures (T_C). However, the Curie temperature of these compounds, remains below 110 K, and therefore FMSC's with higher T_C are needed for technological applications. In order to achieve this goal, the origin of ferromagnetism in this context should be clarified.

Several mechanisms have been proposed to explain the origin of the ferromagnetism of these FMSC's. Analyzing the magnetoresistance and the concentration dependence of T_C , Matsukura *et al.*⁵ showed that (Ga-Mn)As, with a higher Mn concentration, is a metallic ferromagnet, and they proposed that the RKKY interaction is the origin of such ferromagnetism. However, Beschoten *et al.*⁶ measured the magnetic circular dichroism spectrum of (Ga-Mn)As to show that the ferromagnetic state occurs even in the insulating phase, consistent with the variable-range hopping observed in the low-concentration regime.⁷ Furthermore, the estimated value of p - d exchange coupling⁵ was rather large, when compared with the value obtained in other experiments.^{8,9} In first-principles calculations, Akai¹⁰ performed Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA) calculations and showed that the ground state of (Ga-Mn)As is half-metallic. Thereby, a double-exchange mechanism was proposed for the ferromagnetism of these systems. The energy difference between the ferromagnetic ground state and the disordered spin state calculated in the KKR-CPA formalism may account for the observed T_C . Dietl *et al.*¹¹ have studied the material dependence of T_C in terms of the Zener model, and they predicted a higher T_C for GaN- or ZnO-based FMSC's. On the other hand, Inoue *et al.*¹² noted the characteristic features of the electronic state in FMSC and proposed a double-resonance mechanism¹³ in which impurity states caused by Mn ions play essential roles. The resonant character of the electronic states of the magnetic impurities has been shown to enhance the RKKY interaction, and this character accounts for the rather large p - d exchange interaction used in the experimental analysis.⁵ In order to describe the impurity states, Inoue and Maekawa and proposed an effective Hamiltonian, which is quite similar to the Zener or

double-exchange Hamiltonian.¹⁴ In addition to these theories, a modified spin-wave theory¹⁵ and a dynamical mean-field study¹⁶ have been reported to improve the conventional mean-field approximation. Furthermore, in order to take into account the diluteness of the magnetic impurities, a percolation theory¹⁷ has been applied to explain the concentration dependence of T_C .

In this paper, we present an analytical expression of the effective exchange interaction between magnetic impurities using the model which we proposed previously.¹² The concentration dependence of T_C will be estimated by using the percolation theory, and the calculated results will be compared with the experimental findings.

In the previous study, we proposed a simple Hamiltonian by taking into account the essence of the electronic structure of semiconductors doped with Mn impurities. An important feature of the density of states calculated is that the impurity states have one nonbonding (localized) state and two delocalized (resonant) states, one of which is close to the top of the valence band. The localized state, which is of e_g character and exchange splits due to the Coulomb interaction, couples ferromagnetically with the spin of the resonant state. The valence band is simplified as a single band with s symmetry which hybridizes the impurity level to produce a resonant state. The resulting Hamiltonian has been given as

$$H = -t \sum_{ij\sigma} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i\sigma} v_0 c_{i\sigma}^\dagger c_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - K \sum_i \mathbf{S}_i \cdot \mathbf{s}_i, \quad (1)$$

where t is the hopping integral which characterizes the valence band and the mixing between the valence band and impurity level v_0 , U is the Coulomb repulsion within the impurity state, and $K(>0)$ is the ferromagnetic exchange coupling between the itinerant spin \mathbf{s} and the localized spin \mathbf{S} . The summations in the latter three terms run only over the impurity sites. The Hamiltonian is actually the same as that of the double-exchange model for the manganites,¹⁴ except that the numbers of localized spins and carrier holes are much lower than those of manganites.

As will be discussed below, we treat the impurity state in such a way that a singular behavior in the expression of the effective interaction between impurity moments may be avoided. In other words, the impurity states treated in this formula are below the Fermi level. This means that $n_{i\uparrow}$ and $n_{i\downarrow}$ are close to 1 and that the U term in the Hamiltonian may be neglected. By applying a mean-field approximation, we obtain a spin-dependent potential $v_{i\sigma} = v_0 - \sigma KS/2 \equiv v_\sigma$ at zero temperature.

The expression of the free energy in the one-electron picture is given as

$$F = -\frac{1}{\pi} \text{Im} \int d\varepsilon f(\varepsilon) \text{Tr} \ln \mathbf{G}(\varepsilon), \quad (2)$$

using the Green's function $\mathbf{G}(\varepsilon) = (\varepsilon + i0 - H)^{-1}$, where $f(\varepsilon)$ is the Fermi distribution function. The Hamiltonian may be divided into two terms, an unperturbed term H_0 and a site-diagonal random potential V , i.e., $H = H_0 + V$. Instead of direct calculation of the excess energy, $\Delta F = \pi^{-1} \sum_\sigma \int_{-\infty}^E \text{Arg det}[1 - \mathbf{V}\mathbf{g}] d\varepsilon$, due to impurities, where $\mathbf{g} = (\varepsilon + i0 - H_0)^{-1}$ is the unperturbed Green's function, we expand $\ln \mathbf{G}(\varepsilon)$ in terms of the off-diagonal (in the site-representation) Green's function \mathbf{g}^{od} :

$$\ln \mathbf{G} = \ln \mathbf{g} - \ln(1 - \mathbf{g}^d \mathbf{V}) + \sum_{n=1}^{\infty} \frac{1}{n} [\mathbf{g}^{od} \mathbf{T}]^n, \quad (3)$$

where \mathbf{g}^d is the site-diagonal part of the Green's function and \mathbf{T} is the site-diagonal T matrix.¹⁸ By taking into account the spin indices, the T matrix of site i may be written as follows:

$$T_{i\sigma} = \frac{v_{i\sigma}}{1 - v_{i\sigma} g_{ii}^d}. \quad (4)$$

By keeping the terms up to the second order of \mathbf{g}^{od} and adopting the local spin axis for the impurity moments, we obtain the following equation:

$$\begin{aligned} F = F_0 &+ \frac{1}{\pi} \sum_{\sigma i} \text{Im} \int d\varepsilon f(\varepsilon) \ln(1 - g^d V_\sigma) \\ &- \frac{1}{2\pi} \text{Im} \sum_{ij} \int f(\varepsilon) g_{ij} g_{ji} \{ (T_{i\uparrow} + T_{i\downarrow})(T_{j\uparrow} + T_{j\downarrow}) \\ &+ \mathbf{e}_i \cdot \mathbf{e}_j (T_{i\uparrow} - T_{i\downarrow})(T_{j\uparrow} - T_{j\downarrow}) \}, \end{aligned} \quad (5)$$

where \mathbf{e}_i is the directional unit vector parallel to the impurity moment on site i and $g_{ij} \equiv g_{ij}^{od}$. In Eq. (5), the first term is the free energy of the host material, the second term is the contribution from the local part of the impurities, and the third term is related to the contribution from the coupling of impurities. The first part, in the parentheses of the third term, is independent of the direction of the local moments of the impurities and therefore is irrelevant to the exchange coupling. The second part in the parentheses denotes the exchange-type coupling between the moments of two impurities. Therefore, we may write down the free energy for the exchange interaction as

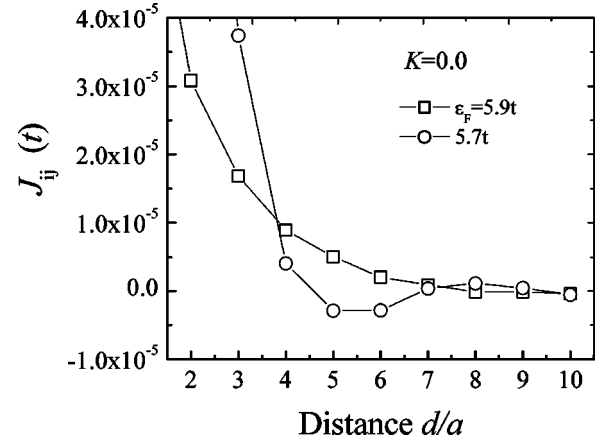


FIG. 1. Calculated results of the effective interaction for $v_\sigma = 0$ and $K = 1.2t$ as functions of the distance d between impurities.

$$F_{ex} = -2 \sum_{\langle ij \rangle} \tilde{J}_{ij} S^2 \cos \theta_{ij}, \quad (6)$$

with

$$\tilde{J}_{ij} = \frac{1}{\pi} \text{Im} \int f(\varepsilon) \frac{K^2 g_{ij} g_{ji}}{(1 - v_\uparrow g_{ii})^2 (1 - v_\downarrow g_{ii})^2} d\varepsilon. \quad (7)$$

We calculate the effective exchange interaction \tilde{J}_{ij} between localized moments of the impurities as a function of the distance $i-j$ for given values of the impurity potential v_0 , local exchange interaction K , the spin magnitude of the impurity $S (= 3/2)$, and Fermi level ε_F . The nonlocal Green's function g_{ij} may be easily calculated for the (100) direction of the simple cubic lattice.¹⁹ We calculate up to $i-j = d = 10$ in units of the lattice constant a for the (100) direction. Because we are dealing with an isotropic system with the simple cubic lattice, the qualitative features of g_{ij} may be independent of the crystal direction. The calculation is performed at zero temperature by neglecting the Fermi distribution function $f(\varepsilon)$. This simplification will be justified as we choose the position of the Fermi level about $0.1t$ below the top of the valence band. This value of $0.1t \approx 1000$ K, when $t \approx 1$ eV, may be sufficiently higher than the observed T_C .

Figure 1 shows the calculated results of \tilde{J}_{ij} as a function of distance for $v_\sigma = 0$. We have set $K = 1.2t$, taking into consideration the experimental results.⁸ In this case, there is almost no enhancement for \tilde{J}_{ij} . A clear oscillation can be seen when the Fermi level is far below the top of the band, i.e., $\varepsilon_F = 5.7t$ (band top = $6.0t$). This is a tight-binding version of the RKKY oscillation. When the Fermi level approaches to the top of the band, e.g., $\varepsilon_F = 5.9t$, the oscillatory behavior diminishes as expected. The magnitude of \tilde{J}_{ij} at a distance of $d = 4a$ is on the order of $10^{-5}t$, which corresponds to about 0.2 K when we assume that $t \approx 1$ eV. Thus, we may conclude that this kind of RKKY interaction is completely ineffective for long-range ferromagnetism.

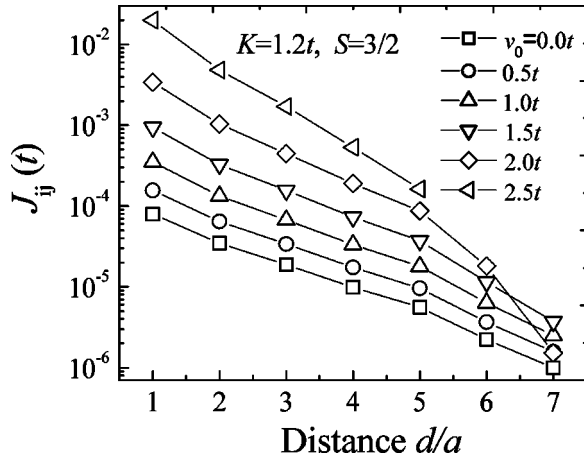


FIG. 2. Calculated results of the effective interaction with $K = 1.2t$ for various values of the impurity potential v_0 as a function of the impurity distance d .

Figure 2 shows the calculated results of \tilde{J}_{ij} for various values of v_0 with $K = 1.2t$ and $\varepsilon_F = 5.9t$. We first notice that the d dependence of \tilde{J}_{ij} below $d \leq 5a$ changes to that of an exponential type, which is consistent with the well-known result of the disorder-mediated RKKY interaction.²⁰ A rapid decay of \tilde{J}_{ij} for $d \geq 6a$ when $v_0 = 2.0t$ and $2.5t$ (not shown) is due to the oscillatory behavior of the RKKY interaction. More importantly, the values of \tilde{J}_{ij} are enhanced by several orders of magnitude when the impurity level increases. This effect is due to the enhancement factors in Eq. (7). Now the value of \tilde{J}_{ij} at $d = 3$ for $v_0 = 2.5t$ is several 10 K when $t \approx 1$ eV. \tilde{J}_{ij} is still large at $d = 5$ as compared with J_{ij} in the RKKY interaction.

Next, the Curie temperature T_C is estimated. Because the quantity K of the largest energy scale has been transformed into a smaller energy scale interaction \tilde{J}_{ij} , a mean-field approximation might be applied. However, additional care must be taken as regards the effects of disorder due to the low concentration of magnetic impurities. Therefore, we adopt percolation theory¹⁷ to estimate T_C . In the percolation theory, T_C is given as $k_B T_C = S(S+1)\tilde{J}(d_{\text{perc}})$, with $d_{\text{perc}} = \bar{R}B_c^{1/3}$. \bar{R} is an average distance between magnetic impurities at concentration x and is given as $\bar{R}/a = (3/4\pi x)^{1/3}$ for a simple cubic lattice with a lattice constant of a . The value of B_c is 2.4. The distance dependence of \tilde{J}_{ij} has been fitted to an exponential type, such that $\tilde{J}_{ij} = J_0 \exp(-\alpha d)$. We can safely neglect the oscillatory part of \tilde{J}_{ij} , except for the extremely low concentrations of the magnetic impurities, because \tilde{J}_{ij} decays exponentially up to $d = 5a$.

Figure 3 shows the calculated results of $k_B T_C$ as a function of concentration x of the magnetic impurities. The Curie temperature increases nearly linearly with increasing x and is enhanced as the impurity levels increases. When $t \sim 1$ eV, the results of $k_B T_C$ for $v_0 = 2.5t$ ($v_\uparrow = 1.4, v_\downarrow = 3.4$) agree qualitatively with the experimental observation of the Curie temperatures.

In spite of a simple model to calculate the Curie tempera-

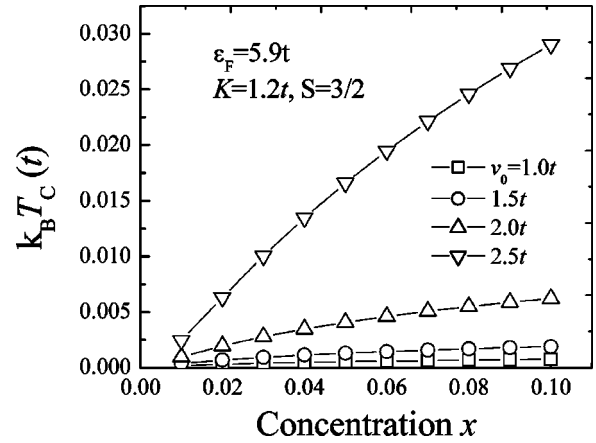


FIG. 3. Concentration dependence of the Curie temperature for various values of v_0 .

ture, it remains constructive to compare the theoretical results of T_C with the experimental findings. In order to accomplish this, we take into account the antiferromagnetic exchange interaction J_{AF} between the nearest-neighbor impurity moments. This interaction may be a superexchange-type interaction, given as $J_{AF} = 4t_d^2/K$, where t_d is the direct hopping integral between impurity d states. Because t_d is proportional to d^{-5} , we assume $J_{AF} = J_{AF}^0 d^{-10}$, by letting J_{AF}^0 be an adjustable parameter. Figure 4 shows the calculated results together with the experimental findings^{4,5} regarding the Curie temperature as a function of the concentration. The agreement in this case is satisfactory.

Now several points are ready to discuss. The impurity state in the semiconductors may be quite different from those in simple metals. In the latter case, the interaction may not be long range because the Fermi level occurs near the middle of the band and the Fermi wavelength is quite short. When the Fermi level is located near the bottom of the band of a simple metal, the Fermi wavelength might be sufficiently

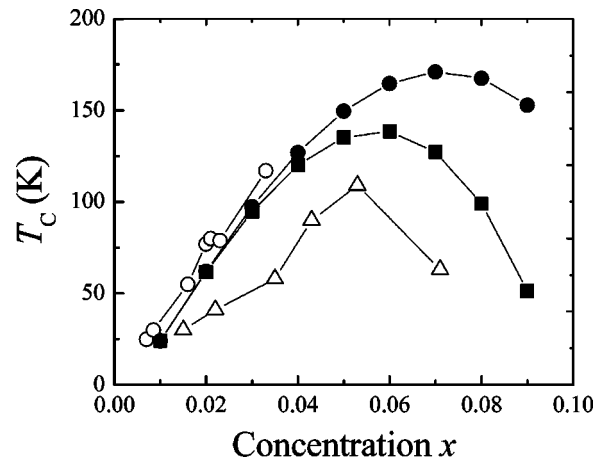


FIG. 4. Calculated results (solid squares, $J_{AF}^0 = -1.5t$, and solid circles, $J_{AF}^0 = -0.8t$) of Curie temperature with a near-neighbor anti ferromagnetic interaction between localized moments and experimental results for Ge-Mn (open circles) and (Ga-Mn)As (open triangles).

long, but on the other hand, there may not be a sufficient number of electrons on the impurities to sustain the local moments.

The approximation to expand the free energy up to the second order of the T matrix in Eq. (5) breaks down as the resonant states are formed. Although the range of parameter values which guarantee the expansion has not been checked, the values of v_0 used in our numerical calculations are restricted in order to avoid the singular behavior in Eq. (7) and therefore do not violate the expansion. When the resonant states are formed, we must directly calculate the energy difference ΔF caused by impurities, as has already been reported in our previous work. The magnetic part of ΔF , calculated previously, is $-0.02t$ to $-0.01t$ for the second- and third-nearest-neighboring pairs of magnetic impurities.^{12,21} Therefore, the effective exchange interaction \tilde{J}_{ij} may saturate within a reasonable value even though v_0 is increased more than those used in this work.

The spin-orbit interaction, neglected in the present model, makes the valence band split into heavy-hole and light-hole bands. Because the number of carriers is small, ϵ_F may reside at or near the heavy-hole band in real systems. As the spin states of $S_z = \pm 1/2$ are mixed in the band, the spin-orbit interaction may hinder the valence holes from mediating the interaction between magnetic impurities. In the ferromagnetic state, however, the asymmetry in the spin states of $S_z = \pm 1/2$ may be realized in the heavy-hole band due to an effective field caused by the magnetic impurities. Therefore the heavy-hole band could mediate the interaction between impurity spins.²² In order to take the effective field into con-

sideration a self-consistent treatment should be carried out. The enhancement of the effective interaction treated in the present work may survive even in the self-consistent treatment. One should note, however, that the spin-orbit interaction may result in an anisotropic exchange interaction between impurity moments as proposed recently.²³ They²³ showed that the ground state is still ferromagnetic even though the interaction is frustrated.

In conclusion, we have shown that as the impurity states approach the Fermi level located near the top of the valence band, the effective RKKY-type exchange interaction is enhanced, showing exponential dependence on the distance between impurities. The enhancement of the effective interaction may sufficiently explain the high Curie temperature observed in ferromagnetic semiconductors. We believe that the existence of an energy band gap near the Fermi level in semiconductors and the appearance of impurity states near the band gap are both essential to elucidate the origin of the ferromagnetism of (Ga-Mn)As-type magnetic semiconductors. It should be noted that the electronic structures calculated in the first-principles method also show impurity states near the energy band gap.^{24,25} The states of double resonance introduced by the magnetic impurities may thus be a possible origin of the ferromagnetism of these magnetic semiconductors.

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- ¹H. Munekata, H. Ohno, S. von Molnar, A. Segmuller, L.L. Chang, and L. Esaki, *Phys. Rev. Lett.* **63**, 1849 (1989).
- ²H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and H. Iye, *Appl. Phys. Lett.* **69**, 363 (1996).
- ³Y. Ohno, D.K. Young, B. Beschoten, F. Matsukura, H. Ohno, and D.D. Awschalom, *Nature (London)* **402**, 790 (1999).
- ⁴Y.D. Park, A.T. Hanbicki, S.C. Erwin, C.S. Hellberg, J.M. Sullivan, J.E. Mattson, T.F. Ambrose, A. Wilson, G. Spanos, and B.T. Jonker, *Science* **295**, 651 (2002).
- ⁵F. Matsukura, H. Ohno, A. Shen, and Y. Sugawara, *Phys. Rev. B* **57**, R2037 (1998).
- ⁶B. Beschoten, P.A. Crowell, I. Malajovich, and D.D. Awschalom, F. Matsukura, A. Shen, and H. Ohno, *Phys. Rev. Lett.* **83**, 3073 (1999).
- ⁷A. Van Esch, L. Van Bockstal, J. De Boeck, G. Verbanck, A.S. van Steenberghe, P.J. Wellmann, B. Grietens, R. Bogaerts, F. Herlach, and G. Borghs, *Phys. Rev. B* **56**, 13 103 (1997).
- ⁸J. Okabayashi, A. Kimura, T. Mizokawa, A. Fujimori, T. Hayashi, and M. Tanaka, *Phys. Rev. B* **58**, R4211 (1998).
- ⁹H. Ohno, H. Akiba, F. Matsukura, A. Shen, K. Ohtani, and Y. Ohno, *Appl. Phys. Lett.* **73**, 363 (1998).
- ¹⁰H. Akai, *Phys. Rev. Lett.* **81**, 3002 (1998).
- ¹¹T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* **287**, 1019 (2000).
- ¹²J. Inoue, S. Nonoyama, and H. Itoh, *Phys. Rev. Lett.* **85**, 4610 (2000).
- ¹³B. Caroli, *J. Phys. Chem. Solids* **28**, 1427 (1967).
- ¹⁴J. Inoue and S. Maekawa, *Phys. Rev. Lett.* **74**, 3407 (1995).
- ¹⁵J. König, H.-H. Lin, and A.H. MacDonald, *Phys. Rev. Lett.* **84**, 5628 (2000).
- ¹⁶A. Chattopadhyay, S.D. Sarma, and A.J. Millis, *Phys. Rev. Lett.* **87**, 227202 (2001).
- ¹⁷V.I. Litvinov and V.K. Dugaev, *Phys. Rev. Lett.* **86**, 5593 (2001).
- ¹⁸See, e.g., F. Gautier in *Magnetism of Metals and Alloys*, edited by M. Cyrot (North-Holland, Amsterdam, 1982).
- ¹⁹E. N. Economou, *Green's Functions in Quantum Physics* (Springer-Verlag, Berlin, 1983).
- ²⁰See, e.g., C. Kittel, *Solid State Phys.* **22**, 1 (1968).
- ²¹J. Kudrnovsky *et al.* (unpublished) and Sato *et al.* (unpublished) have recently reported similar results in the first-principles calculations.
- ²²P. M. Krstajic, V. A. Ivanov, F. M. Peeters, V. Fleurov, and K. Kikoin, *Europhys. Lett.* **61**, 235 (2003).
- ²³G. Zarand and B. Janko, *Phys. Rev. Lett.* **89**, 047201 (2002).
- ²⁴P. Mahadevan and A. Zunger, *Phys. Rev. Lett.* **88**, 047205 (2002).
- ²⁵P.A. Korzhavyi, I.A. Abrikosov, E.A. Smirnova, L. Bergquist, P. Mohn, R. Mathieu, P. Svedlindh, J. Sadowski, E.I. Isaev, Yu.Kh. Vekilov, and O. Eriksson, *Phys. Rev. Lett.* **88**, 187202 (2002).