PHYSICAL REVIEW B VOLUME 53, NUMBER 19 15 MAY 1996-I

Superexchange and spin-glass formation in semimagnetic semiconductors

Tomasz M. Rusin
Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46 02-668 Warsaw, Poland

(Received 21 March 1995; revised manuscript received 20 February 1996)

The Mn-Mn superexchange interaction in semimagnetic semiconductors $A_{1-x}\mathrm{Mn}_xB$ (where $A=\mathrm{Zn}$, Cd and $B=\mathrm{S}$, Se, Te) is studied within the three-level model of the band structure. We focus on the dependence of the interaction on the interion distance $J^{dd}(r)=J_0f(r)$. In the present work, the function $f(r)$ is obtained analytically. This, only weakly material-dependent function is found to decrease with Mn-Mn distance much slower than its Gaussian approximation derived previously. The exact form of the decay of the superexchange can be approximated by a power law $J_0r^{-8.5}$. This is close to an experimental result, $J_0r^{-6.8}$, determined on the basis of the spin-glass transition temperature on the composition. [S0163-1829(96)03720-4]

I. INTRODUCTION

The most widely accepted theory of a predominant interaction between localized magnetic moments in wide gap semimagnetic semiconductors (SMS)—a typical example being $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$—was proposed by Larson *et al.*[1,2] According to this theory, the interaction between two Mn magnetic moments results from virtual processes between Mn *d* electrons and the conduction band electrons or the valence band holes of a semiconductor matrix in the fourth order of perturbation in the hybridization parameter V_{kd}. The virtual processes in question may be divided in three distinct classes: two-hole processes, hole-electron processes, and two-electron processes. The first class, involving two holes, represents the superexchange interaction and contributes 95% of the value of the exchange coupling constant J^{dd} between magnetic moments localized in the nearest neighbors (NN), as well as second nearest neighbor (2NN), positions. Two remaining processes were shown to be negligible, leaving the superexchange as the most important mechanism of magnetic interactions in this class of SMS.[1,3]

The theoretical formulation of Larson *et al.*[1,2] predicts a fast decrease of the superexchange interaction strength with the distance r between Mn atoms: $J^{dd}(r)=J_0f(r)$, where $f(r)$ is argued to be only weakly dependent on a material constituting the semiconductor host. The function $f(r)$ was approximated in Refs. 1 and 2 by a Gaussian form $f(r)=\exp(-4.9r^2)$ for $r<1.5$ (r measured in the fcc lattice constant units). With this fast exponential dependence, the superexchange is, obviously, of importance only for the first or second nearest neighbors. Other coupling mechanisms (Blombergen Rowland or dipole interaction), possibly, become more important for more distant neighbors.

On the experimental side, there are accurate determinations of J_{NN} in several SMS materials and J_{2NN} in some of them.[3] The values of these quantities are in an overall agreement with theoretical calculations of Larson *et al.*[1,2] Unfortunately, for more distant Mn magnetic moments, the experimental determination is much more difficult and, therefore, inaccurate.

An indirect way of estimation of the long-range part of the exchange interaction was proposed by Escorne *et al.*[4] It consists of a measurement of the dependence of the spin-glass transition temperature T_F on the molar fraction x of Mn in SMS. Using rough estimates $S(S+1)J(R)=k_BT_F(x)$ and $R\propto x^{-1/3}$ (where R is the average distance between Mn ions for given x), one can find $J(r)$ knowing $T_F(x)$ for a range of x. Escorne *et al.*[4] predicted that the spin-glass transition should be observed in SMS not only for large Mn concentrations, where the short-range interactions dominate, but also for small x values, where the contributions due to interactions across longer distances can be expected. This is, in fact, found in experiments. To explain these results, Escorne *et al.*[4] assumed an exponential form of the decay of the interaction $J(r)=J_0\exp(-br)$. More accurate measurements performed by Twardowski *et al.*[5] and by Galazka *et al.*[6] indicated that, possibly, a power dependence of the exchange coupling constant gives a more accurate description of experimental data. For the wide gap, SMS Twardowski *et al.*[5] formed $J(r)=J_0r^{-6.8}$, while for narrow gap materials Galazka *et al.*[6] proposed $J(r)=J_0r^{-5.0}$. These scaling laws were verified for various compounds sometimes in a very wide range of concentration $(0.02<x<0.5)$.[3,5,6]

Moreover, the magnetic susceptibility and the magnetic contribution to the specific heat calculated theoretically assuming the power dependence of the exchange integral on r are in a better agreement with experimental data than those calculated assuming the exponential form of $J(r)$.[5,7,8]

Here, we investigate if the Larson *et al.*[1,2] formulation of the superexchange can be reconciled with the observed long-range nature of the interaction in wide gap SMS. In particular, we trace the origin of the Gaussian form of $f(r)$ and found it to be a simple consequence of approximations used in Refs. 1 and 2. We find that the Gaussian form is suitable only for $r\leqslant 1$ i.e., for NN ($r=\sqrt{2}/2$) and 2NN ($r=1$) in the fcc lattice. The alternative function $f(r)$ obtained in this paper has an oscillatory character with a relatively slow decrease of the amplitude that can be approximated by $r^{-8.5}$.

II. DEPENDENCE OF SUPEREXCHANGE COUPLING ON INTER-MN DISTANCE

In the first part of this section, we follow closely Larson *et al.*[1,2] to introduce the notation. Let us consider the multisite Anderson Hamiltonian with a linearized Hubbard term

$H=H_b+H_d+H_{pd}$, where $H_b=\Sigma_{n,k,\sigma}\epsilon(n,k)\hat{c}^{\dagger}_{nk\sigma}\hat{c}_{nk\sigma}$ describes the one-electron conduction or valence band Hamiltonian and $H_d=\Sigma_{i,m,\sigma}(\epsilon_d+U_{\rm eff}\langle n_{im-\sigma}\rangle)\hat{d}^{\dagger}_{im\sigma}\hat{d}_{im\sigma}$ describes the electrons localized on the d shell of Mn atoms. The operator $\hat{c}^{\dagger}_{nk\sigma}$ creates an electron in the nth band, with the wave vector $\vec{k}$ and a spin σ, while $\hat{d}^{\dagger}_{im\sigma}$ creates mth electron with a spin σ on the ith atom. The meaning and numerical values of the parameters $V_{pd}(n,k)$, $U_{\rm eff}$, ϵ_d and $\epsilon(k,n)$ are thoroughly discussed in Larson *et al.*[1] The sum H_b+H_d represents the unperturbed Hamiltonian H_0, while H_{pd} describes the p-d hybridization which, in standard notation, reads $H_{pd}=\Sigma_{i,m,\sigma}\Sigma_{n,k}V_{pd}(n,k)\exp(\vec{k}\vec{R}_i)d^{\dagger}_{im\sigma}c_{nk\sigma}+\text{H.c.}$

In the fourth order of the perturbation in terms of H_{pd}, one obtains the effective interaction between localized Mn magnetic moments: $H_H=-\Sigma'_{i\neq j}J^{dd}(r)\vec{S}_i\vec{S}_j+H_{\rm aniz}$, where $J^{dd}(r)$ is the exchange integral between two Mn atoms separated by $r=|\vec{R}_i-\vec{R}_j|$ and $H_{\rm aniz}$ is the anizotropic part of the interaction. Larson and Ehrenreich[10] calculated the latter term and showed it to be much weaker than the isotropic part. Consequently, we shall neglect it in the further discussion.

As mentioned, the matrix elements of H_H between states $|i\rangle$ and $|f\rangle$ are equal to the matrix elements of the fourth order term in perturbation series between the same states $|i\rangle$ and $|f\rangle$. In this way, we may find directly the exchange integral $J^{dd}(r)$ (Ref. 9) as

$$-2\left(\frac{5}{2}\right)J^{dd}(r) = \sum_{a,b,c}\frac{\langle f|H_{pd}|a\rangle\langle a|H_{pd}|b\rangle\langle b|H_{pd}|c\rangle\langle c|H_{pd}|i\rangle}{(E_0-E_a)(E_0-E_b)(E_0-E_c)}. \tag{1}$$

In the equation above $|f\rangle$ and $|i\rangle$ are the final and the initial eigenstate of H_0+H_d, with the energy E_0, the states $|a\rangle,|b\rangle,|c\rangle$ are intermediate states with energies E_a, E_b, and E_c, respectively. As shown in Refs. 1, 2, and 9, the sum in (1) over all intermediate states may be divided into three classes of processes mentioned in the Introduction: two-hole processes (superexchange), hole-electron processes (Blombergen Rowland mechanism) and two-electron processes. Thus, the exchange coupling constant can be expressed as a sum of the three factors $J^{dd}=J^{dd}_{hh}+J^{dd}_{he}+J^{dd}_{ee}$. It was shown by Larson *et al.*[1,2] that J^{dd}_{hh} contributes 95% of the total value of J^{dd}, with 5% contributed by J^{dd}_{he} and practically no contribution from J^{dd}_{ee}. This allows us to simplify the model by considering the superexchange retaining only the most upper valence band in the sum in (1). More specifically, a three-level model was used[1,2] with a single, filled valence band characterized by an energy edge E_v, an occupied d level with the energy ϵ_d, and unoccupied d level with the energy $\epsilon_d+U_{\rm eff}$. A single hybridization parameter V_{pd} was assumed.

Calculating the coupling constant in the three-level model, we obtain

$$\begin{aligned}J^{dd}(r)&=-2V^4_{pd}[U^{-1}_{\rm eff}(E_v-\epsilon_d-U_{\rm eff})^{-2}\\&\quad-(E_v-\epsilon_d-U_{\rm eff})^{-3}]f(r)=J_0f(r).\end{aligned} \tag{2}$$

Comparing (2) with (1) and averaging the energy denominators over a spherical Brillouin zone, Larson *et al.*[1,2] found $f(r)$ to be $f(r)=g^2(r)$ with

$$g(r)=\frac{1}{2\pi^3}\int d^3k\cos(\vec{k}\vec{r})\cos^2(\tfrac{1}{4}k), \tag{3}$$

where $\vec{r}$ is measured in the fcc lattice constant a, $\vec{k}$ in reciprocal of a.

The integral in Eq. (3) is performed over the Brillouin zone, which is approximated by a sphere with the radius 2π. Larson *et al.*[1,2] calculate the integral in (3) to be

$$\begin{aligned}g(r)&=\frac{1}{\pi^2}\int_0^{2\pi}k^2dk\int_{-1}^{1}dx\ \cos(krx)\cos^2(\tfrac{1}{4}k)\\&=\frac{-2}{\pi r}\frac{\partial}{\partial r}[\Gamma(2+2r)\Gamma(2-2r)]^{-1}.\end{aligned} \tag{4}$$

A product of Γ functions in (4) was further approximated by Larson *et al.*[1,2] for $r<1.5$ by an exponential form $1/[\Gamma(2+2r)\Gamma(2-2r)]\simeq 3.3\exp(-2.58r^2)$. However, this approximation is not necessary because applying the identities $\Gamma(x+1)=x\Gamma(x)$ and $\Gamma(x)\Gamma(1-x)=\pi/\sin(\pi x)$ to Eq. (4) we find

$$\frac{1}{\Gamma(2+2r)\Gamma(2-2r)}=\frac{\sin(2\pi r)}{\pi(2r-8r^3)}, \tag{5}$$

and, then

$$\begin{aligned}f(r)&=g(r)^2\\&=\frac{4}{\pi^4}\left[\frac{-\pi}{r^2(1-4r^2)}\cos(2\pi r)+\frac{1-12r^2}{2r^3(1-4r^2)^2}\sin(2\pi r)\right]^2.\end{aligned} \tag{6}$$

The function $f(r)$ in the form given by Eq. (6) represents the main result of this work. The exponential approximation of $\sin(2\pi r)/(2r-8r^3)$ proposed by Larson *et al.* is quite accurate for small r, but it fails for $r>1$, the reason being that sign of $\sin(2\pi r)/(2r-8r^3)$ alternates, while its Gaussian approximation remains always positive. The exact function $f(r)$ being proportional to the square of the derivative of $\sin(2\pi r)/(2r-8r^3)$ is a positive oscillating function. On the other hand, the Larson *et al.*[1] approximation of $f(r)$ decays monotonically with r, as shown in Fig. 1. From this figure, it follows that the approximation proposed by Larson is valid for $r\leqslant 1$, instead of for $r<1.5$, as suggested in Ref. 1, i.e., the approximation is suitable for the first and the second neighbors only (not up to the fourth neighbors). Then, the validity of the three-level model proposed by Larson *et al.* may be extended to interactions between Mn atoms placed on *arbitrary* distances. Moreover, the envelope of the exact form of $f(r)$ [see Eq. (6)] decays according to the power law which is "slower," in a better agreement with experimental findings.

To find the form of the decay let us note, that the strongest couplings appears for Mn atoms located close to local maxima of $f(r)$ and that for large r, the allowed distances

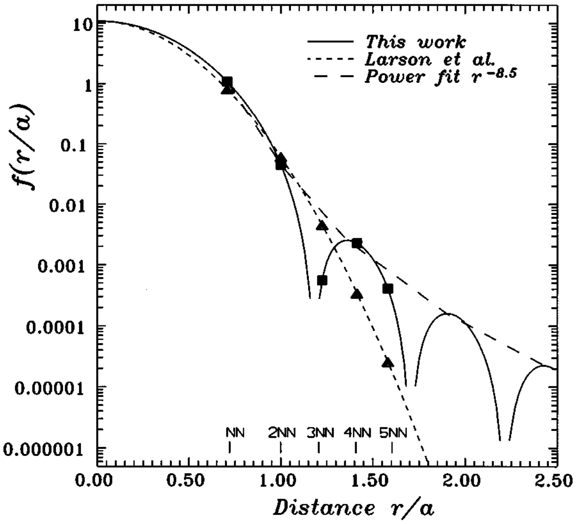

FIG. 1. The material parameter insensitive function $f(r)$ versus r (in lattice constant units). Solid line: the function $f(r)$ calculated from (6). Dashed line: the exponential approximation of $f(r)$ according to Larson *et al.* (Ref. 1) $f(r)=10.8\exp(-5.16r^2)$. Squares: the values of $f(r)$ calculated from Eq. (6) for the five nearest neighbors. Triangles: the same for the exponential approximation $f(r)=10.8\exp(-5.16r^2)$. "NN" denotes the nearest neighbors distance in the fcc lattice using the following notation: NN=0.71, 2NN=1.0, 3NN=1.22, 4NN=1.42, 5NN=1.58. The minima of the solid line are equal zero and they cannot be plotted on the logarithmic scale.

between lattice points become very close to each other, which makes the "occupation" the maxima of $f(r)$ by Mn atoms quite probable. Thus, we performed a power dependence $J^{dd}=J_0r^{-n}$ to values corresponding to the first and the second nearest neighbors, as well as to the first six maxima of $f(r)$. We found $n=8.5$, which is slightly larger than $n=6.8$ obtained experimentally by Twardowski *et al.*[5]

We plotted the values of the analytical function $f(r)$ at the discrete lattice points (squares) and the values of the Gaussian approximation of $f(r)$ at the same points (triangles). The exponential approximation is correct for NN and quite accurate for 2NN, but fails for 3NN, 4NN, and 5NN (cf. Fig. 1). The decay of the interaction is not found to be monotonic and, therefore, the influence of the distant neighbors on magnetic properties of the SMS materials may not be negligible.

III. DISCUSSION

The analysis above suggests, that the superexchange with the exact form of $f(r)$ given (6) is, in fact, a good candidate for a mechanism that is responsible for the spin-glass formation. Let us consider here two other mechanisms of the coupling between magnetic moments that are negligible compared to the superexchange at short distances, but which are characterized by a long-range decay: the Blombergen-Rowland (the hole-electron processes) and the dipolar interaction. Because our discussion has an approximate character, we consider the superexchange in its asymptotic form of (6): $J^{dd}(r)=J_0r^{-8.5}$ obtained above and restrict the analysis to $Cd_{1-x}Mn_xTe$. Then we have $J_0=8$ K and $J^{dd}(r)=0.42r^{-8.5}$ (K) (for NN, the distance $r=0.71$).

The dipolar interaction in $Cd_{1-x}Mn_xTe$ for NN is 20 mK and decays as r^{-3}.[10] Comparing this value with $J^{dd}(r)$, one finds that the dipolar interaction is of the same order of the magnitude as superexchange for $r>2.7$. The absolute value of the dipolar interaction (and superexchange) for such r is below 0.3 mK, while x is of order of 1%. So, possibly, the dipolar interaction may dominate for strongly diluted samples ($x\ll 1\%$). However, for $x\ll$ 1%, the existence of the spin-glass state is uncertain. So the dipolelike decay of the coupling may not be observable anyway.

Since there is no analytical expression on the Blombergen Rowland (BR) coupling in terms of the Larson *et al.*[1,2] model, we shall consider its form taken from Ref. 11 $J_{\mathrm{BR}}=\mathrm{C}r^{-3}\exp(-\mathrm{A}r)$. According to Sokel and Harrison,[11] $A^2=(m_c+m_v)E_ga^2/\hbar^2$ in a standard notation. As an approximation let us assume $J_{\mathrm{BR}}(\mathrm{NN})=0.05J_0$, which follows from the finding of Larson *et al.*,[1,2] that the BR interaction in $Cd_{1-x}Mn_xTe$ is 5% of the total value of the exchange coupling. Taking values of electron and hole effective masses in $Cd_{1-x}Mn_xTe$, it is easy to verify that BR interaction remains considerably smaller than superexchange, even in the asymptotic regime.

To assess the possibility of confronting the above results with experiment, let us critically review possible methods of direct measurement of the long-range magnetic interaction in semimagnetic semiconductors.

(1) Magnetization steps. Let us denote by J_n the exchange integral between nth nearest neighbors. Using the next nearest neighbor cluster model proposed by Larson *et al.*,[12] it is possible to find J_1, J_2, and J_3 for $Cd_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xSe$ from the magnetization steps at low temperatures. For $Cd_{0.95}Mn_{0.05}Te$ they obtained[12]: $J_1=-6.3$ K±0.3 K, $J_2=-1.9$ K±1.1 K, and $J_3=-0.4$ K±0.3 K. Large relative errors of J_2 and J_3 stem from a fit of the steplike pattern to a multiparameter function $F(J_1..J_n)$, with different order of magnitudes of the parameters, necessarily leading to large relative errors of the small quantities. The simplest way to decrease the influence of the first (large) J_n is to measure the magnetization of strongly diluted samples at low temperatures. But for, say $x=0.01$, the largest fraction of Mn atoms belong to isolated entities (88.6%) and the only remaining 11.4% of them is grouped in all other kinds of clusters. This makes observation of the effects of the long-range interactions very difficult. Moreover, the experiments should be performed in temperatures comparable to the magnitude of expected coupling constants. Otherwise, the step pattern will be washed out by the thermal fluctuations of the magnetization. Nevertheless, this method seems to be the most promising method of direct measurement of J_n for larger n's.

(2) Curie temperature Θ. In the mean field theory of antiferromagnetism $\Theta=x\Sigma_nZ_nJ_n$, where Z_n is a number of nth neighbors. Because of different magnitudes of J_n, the most important term in Θ is that involving Z_1. According to Larson *et al.*[12] in $Cd_{0.95}Mn_{0.05}Te$, this term contributes 78% of the total value of Θ with Z_2J_2 giving 12% and Z_3J_3-10%, respectively. Calculating in the same way a contribution to Θ due to jointly 3, 4, and 5 neighbors using Eq. (6), we find that it is about 50% of Z_3J_3 obtained in Ref. 12.

Because the experimental error of J_3 determination is 70%, we think that this method is not suitable for evidencing long-range coupling.

(3) Spin-glass freezing temperature. In this method information obtained does not refer to any particular coupling constant J_n, but rather to the total effect of all kinds of magnetic interactions at all distances. However, it is the method in which we can confirm the presence (or absence) of the long-range coupling between Mn atoms, estimate the range of the interaction, and even find its asymptotic form of decay.

The analysis above suggests that, within experimental errors, the exact function $f(r)$ given by Eq. (6) and its approximation proposed by Larson *et al.* in Refs. 1 and 2 are equally successful when compared to the results of experiment involving the magnetization steps measurements or for the Curie-Weiss temperature. But the form of $J^{dd}(r)$ from this work is closer to the form of $J^{dd}(r)$ obtained from the scaling law proposed by Twardowski *et al.*[5] Therefore, it is possible that the spin-glass transition in the wide gap diluted magnetic semiconductors is caused by the *superexchange*.

ACKNOWLEDGMENTS

The author acknowledges Professor R.R. Galazka and Professor J. Kossut for numerous discussions. The work was supported in part by KBN Grant No. 2P03B10308.

---

[1] B.E. Larson, K.C. Hass, H. Ehrenreich, and A.E. Carlsson, Phys. Rev. B **37**, 4137 (1988).

[2] B.E. Larson, K.C. Hass, H. Ehrenreich, and A.E. Carlsson, Solid State Commun. **56**, 347 (1985).

[3] W.J.M. de Jonge and H.J.M. Swagten, J. Magn. Magn. Mater. **100**, 322 (1991).

[4] M. Escorne, A. Mauger, R. Triboulet, and J.L. Tholence, Physica **107B**, 309 (1981).

[5] A. Twardowski, H.J. Swagten, W.J.M. de Jonge, and M. Demianiuk, Phys. Rev. B **36**, 7013 (1987).

[6] R.R. Galazka, W.J.M. de Jonge, A.T.A.M. de Waele, and J. Zeegers, Solid State Commun. **68**, 1047 (1988).

[7] C.J.M. Denissen and W.J.M de Jonge, Solid State Commun. **59**, 5013 (1986).

[8] W.J.M. de Jonge, A.Twardowski, and C.J.M. Denissen, in *Diluted Magnetic (Semimagnetic) Semiconductors*, edited by R.L. Aggarwal, J.K. Furdyna, and S. von Molnar, MRS Symposia Proceedings No. 89 (Materials Research Society, Pittsburgh, 1987), p. 153.

[9] C.E.T. Goncales da Silva and L.M. Falicov, J. Phys. C **5**, 63 (1972); B. Koiler and L.M. Falicov, *ibid.* **8**, 695 (1975).

[10] B.E. Larson and H. Ehrenreich, Phys. Rev. B **39**, 1747 (1989).

[11] R. Sokel and W.A. Harrison, Phys. Rev. Lett. **36**, 61 (1976).

[12] B.E. Larson, K.C. Hass, and R.L. Aggarwal, Phys. Rev. B **33**, 1789 (1986).