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High-temperature ferrons in magnetic semiconductors and colossal magnetoresistance materials

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A type of bound magnetic polaron (ferron) is proposed in which the electron energy lowering occurs due to the electron interaction with the random magnetization fluctuations. These states can explain why some doped magnetic semiconductors are highly conductive at $T=0$ and insulating at $T\to\infty$. [S0163-1829(99)50534-1]

A specific property of magnetic semiconductors (to which the colossal magnetoresistance materials belong, too) consists in the fact that the charge-carrier energy is minimal for the ferromagnetic ordering. For this reason, the mobile electrons tend to establish the ferromagnetic ordering in nonferromagnetic materials or in ferromagnetic semiconductors at finite temperatures when the ferromagnetic ordering is partially destroyed. The manifestation of this tendency is the appearance of the ferromagnetic polarons (ferrons) in antiferromagnetic semiconductors when a charge carrier produces a ferromagnetic microregion inside the antiferromagnetic crystal and becomes self-trapped by it (the magnetic polaron, or ferron).[1]

A magnetized region can also arise in the vicinity of an unionized donor, being produced by its electron (the bound ferron). Similar phenomena can take place in the ferromagnetic semiconductors at elevated temperatures (see Refs. 2 and 3). The electron localization region is overmagnetized in this case, which means that inside it the binary spin correlation functions are positive and enhanced as compared with their values outside the localization region.

At high temperatures, one believes that the ferrons should disappear as the ferromagnetic ordering becomes destroyed even in the region of the electron localization. Mathematically, the disappearance of the correlations means that the binary spin correlation functions become zero if the atoms entering them do not coincide. The aim of this paper is to prove that the self-trapped states for the free charge carriers disappear at $T\to\infty$ (this means temperatures considerably exceeding the Curie point but at which the donors remain unionized). But interaction with uncorrelated magnetic fluctuations lowers the energy of a bound electron and diminishes its radius considerably. Thus, one can talk about a type of bound magnetic polaron not related to the ferromagnetic ordering.

Physically, the scenarios for the fluctuation lowering of the donor (acceptor) energy are different for the cases of a relatively weak *s-d* exchange energy (wide electron bands) and the opposite case known as the double exchange (narrow electron bands). In the former case the point is that the absolute value of a magnetic moment for any finite-size region is nonzero, being of order of the square-rooted number of the magnetic atoms inside it. The absence of the local ferromagnetic ordering is a consequence of the fact that the direction of this moment fluctuates randomly. But these fluctuations do not influence the exchange energy between the electron and the magnetic atom as the electron spin fluctuates jointly with the total moment of the region adjusting to it, i.e., being always parallel (or antiparallel to it). For this reason the total *s-d* exchange energy remains nonzero and lowers the localized electron energy more the smaller the region size. Meanwhile, the fluctuations do not influence the conduction band bottom.

In the case of the double exchange, the conduction bandwidth diminishes, and its bottom is boosted with increasing temperature. Meanwhile, the donor level rises considerably less, being pinned by the impurity potential. Hence, at $T\to\infty$, the donor level depth is larger and the radius smaller than at $T=0$.

In both cases, a reduced high-temperature value of the orbital radius as compared with that at $T=0$ can explain the fact often observed in the ferromagnetic semiconductors, including the manganites: If the donor electrons are delocalized at $T=0$ they can be localized at $T\to\infty$, i.e., the temperature-induced Mott transition takes place.[2,3]

To analyze the magnetic properties of the unionized donors, it is advisable to begin with the construction of a non-Ruderman-Kittel-Kasuya-Yosida (non-RKKY) magnetic Hamiltonian describing the indirect exchange via the only electron of the donor. As usual, the *s-d* model is used with the Hamiltonian

$$H=H_s(\mathbf{r})+H_{sd}(\mathbf{r})+H_{dd},\quad H_s=-\frac{\Delta}{2m}-\frac{e^2}{\epsilon r},\qquad(1)$$

$$H_{sd}=-A\sum_{\mathbf{g}}(\mathbf{S_g}s)D(\mathbf{r}-\mathbf{g}),\quad H_{dd}=-\frac{I}{2}\sum_{\mathbf{g},\mathbf{\Delta}}(\mathbf{S_g}\mathbf{S_{g+\Delta}}),$$

where $\mathbf{S_g}$ is the *d* spin of the atom $\mathbf{g}$, $\mathbf{s}$ the conduction electron spin, $D(\mathbf{r}-\mathbf{g})$ is equal to 1 inside the unit cell $\mathbf{g}$ and 0 outside it, m is the electron effective mass, ϵ is the dielectric constant, and $\mathbf{\Delta}$ is the vector connecting the nearest neighbors, $\hbar=1$. The *s-d* exchange integral A is assumed to be positive.

First, the inequality $AS\ll W$ is assumed to be met where S is the *d*-spin magnitude, and W the conduction bandwidth. As usual in the theory of the indirect exchange, the adiabatic approximation is used when, in dealing with the *s* electron, the *d* spins are considered as the classical vectors. In the first approximation in AS/W the wave function of the system can be separated into the orbital and spin parts:

$$\Psi(\mathbf{r},\{S^z\},\sigma)=\psi(\mathbf{r})\,\eta(\{S^z\},\sigma),\qquad(2)$$

$$\eta(\{S^z\},\sigma)=\phi(\{S^z\})\,\delta(\sigma,1/2)+\chi(\{S^z\})\,\delta(\sigma,-1/2),$$

where η is a function of the set of the d-spin variables $\{S^z\}$ and the s-electron spin variable $\sigma[\,\delta(x,y)=1$ for $x=y$ and 0 otherwise]. It should be an eigenfunction of the Hamiltonian (1), averaged over the orbital wave function $\mathbf{r}$:

$$H_{av}\eta=(E-E_I)\,\eta,\quad E_I=\int d^3r\,\psi H_s\psi, \tag{3}$$

$$H_{av}=-A\sum\, w(\mathbf{g})(\mathbf{S_g s}),\quad w(\mathbf{g})=\psi^2(\mathbf{g})a^3,$$

where E_I is the energy of the s electron bound to the impurity, and a the lattice constant.

Making use of Eqs. (1)–(3), one can represent the wave equation in the form (E_I is omitted):

$$\frac{AL^+}{2}\phi+\left(E-\frac{AL^z}{2}\right)\chi=0,$$

$$\frac{AL^-}{2}\chi+\left(E+\frac{AL^z}{2}\right)\phi=0, \tag{4}$$

$$\mathbf{L}=\sum\, w(\mathbf{g})\mathbf{S_g},\quad L^{\pm}=L^x\pm iL^y.$$

The following relations are used which are valid for any function $f(S^z)$ of S^z:

$$S^-f(S^z)=f(S^z+1)S^-,\quad L^-L^+=L^2-L^z(L^z+1).$$

For an arbitrary $w(\mathbf{g})$, the set of Eq. (4) can be solved with accuracy of $1/2SN_l$, where N_l is the number of magnetic atoms over which the localized electron is spread. This solution makes it possible to introduce an effective indirect exchange Hamiltonian H_{ml} whose eigenvalues represent the s-d exchange energy of the bound electron:

$$H_{ml}=\pm\frac{A}{2}\sqrt{\sum_{\mathbf{g},\mathbf{f}}\, w(\mathbf{g})w(\mathbf{f})(\mathbf{S_gS_f})}. \tag{5}$$

Two signs in Eq. (5) correspond to two s electron spin projections. Below, under assumption of $A>0$, only the lower sign will be used.

As is seen from Eq. (5), in the limit $T\to\infty$, though the correlations between the d spins are absent, the s-d exchange energy remains nonzero in the first order in AS/W, being of order $AS/\sqrt{N_l}$. Hence, the interaction with random magnetization fluctuations tends to diminish the orbital radius.

The problem of the localized electron state at $T\to\infty$ will be solved using a variational procedure for the free energy of the system:

$$F^{Pl}=E_l-\frac{A}{2}\sqrt{P}-NT\ln(2S+1), \tag{6}$$

$$P=S(S+1)\sum\, w^2(\mathbf{g}).$$

The second term in Eq. (6) is obtained from Eq. (5) using the condition of the weak correlations between spins:

$$\sqrt{\sum_{\mathbf{g},\mathbf{f}}\, w(\mathbf{g})w(\mathbf{f})(\mathbf{S_gS_f})}$$

$$=\sqrt{S(S+1)\sum_{\mathbf{g}}\, w^2(\mathbf{2})+\sum_{\mathbf{g}\neq\mathbf{f}}\, w(\mathbf{g})w(\mathbf{f})(\mathbf{S_gS_f})}$$

$$\approx\sqrt{P}\left[1+\frac{\sum_{\mathbf{g}\neq\mathbf{f}}\, w(\mathbf{g})w(\mathbf{f})(\mathbf{S_gS_f})}{2P}\right]. \tag{6a}$$

The last term in Eq. (6a) with the Heisenberg-like structure omitted here will be taken into account in a special publication.

The electron energy E_l is calculated with the aid of the Hamiltonian H_s (1) and the trial wave function

$$\psi(r)=\left(\frac{x^3}{\pi a_B^3}\right)^{1/2}\exp\left(-\frac{xr}{a_B}\right),\quad a_B=\frac{\epsilon}{me^2}, \tag{7}$$

where x is the variational parameter.

In the leading approximation in $1/T$ one can write down the x-dependent portion of the free energy (7) in the form

$$F^{Pl}(x)=(x^2-2x)E_B-Lx^{3/2},\quad E_B=\frac{e^2}{2\epsilon a_B}. \tag{8}$$

Minimizing the free energy (8) with respect to x, one obtains its optimal value and inverse orbital radius for $T\to\infty$ (in the E_B and $1/a_B$, units, respectively):

$$F_\infty=-\tfrac{8}{3}l^3[l+\sqrt{1+l^2}]-\tfrac{8}{3}l\sqrt{1+l^2}-4l^2-1, \tag{9}$$

$$x_\infty=[l+\sqrt{1+l^2}]^2;\quad l=\frac{3L}{8E_B}\sim\frac{AS}{(We^2/\epsilon a)^{1/2}}. \tag{10}$$

With $a_B=a$, for AS/E_B varying from 1 to 5, F_∞ varies from -1.104 to -1.659 and x_∞ from 1.077 to 1.1445, whereas both these quantities were equal to 1 at $T=0$ (in corresponding units). Hence, the electron interaction with random (uncorrelated) magnetization fluctuations leads to a marked decrease in the bound electron energy and in the orbital radius, and this is true for any type of magnetic ordering at $T=0$. The corresponding electron state can be called the bound paramagnetic fluctuation polaron (ferron).

Formally, based on Eqs. (9) and (10) one might arrive at the conclusion that random fluctuations could cause the trapping of a charge carrier in the absence of the impurity potential (the free paramagnetic ferron). But its energy turns out to be of order $(AS)^4/W^3$, which is far beyond the accuracy of the present calculation and, hence, can be put equal to zero.

Now the case of the double exchange in the ferromagnetic semiconductors will be discussed. In this limit in the zero approximation in W/AS, the s electron spin is parallel to the spin of the atom at which it is located at the moment. The opposite s electron spin projection is prohibited, so that the s electrons can be considered as spinless fermions, their operators being $c_{\mathbf{g}}^*, c_{\mathbf{g}}$. In the classical limit $S\to\infty$, introducing the polar angles $\theta_{\mathbf{g}}$ and $\phi_{\mathbf{g}}$ for the $\mathbf{S_g}$ spins, one arrives at the classical Hamiltonian:[4,2]

$$H_{ef}=\frac{AS}{2}\sum c_{\mathbf{g}}^{*}c_{\mathbf{g}}-t\sum \cos\frac{\theta_{\mathbf{g},\mathbf{g}+\Delta}}{2}\exp(-i\gamma_{\mathbf{g},\mathbf{g}+\Delta})c_{\mathbf{g}}^{*}c_{\mathbf{g}+\Delta}$$

$$-\frac{I}{2}\sum (\mathbf{S}_{\mathbf{g}}\mathbf{S}_{\mathbf{g}+\Delta}), \tag{11}$$

where $\theta_{\mathbf{g},\mathbf{g}+\Delta}$ is the angle between the spins of the $\mathbf{g}$ and $\mathbf{g}+\Delta$ atoms, and the expressions for the phases are

$$\gamma_{\mathbf{g},\mathbf{g}+\Delta}=\tan^{-1}\left[\frac{\cos\eta_{\mathbf{g},\mathbf{g}+\Delta}}{\cos\xi_{\mathbf{g},\mathbf{g}+\Delta}}\tan\zeta_{\mathbf{g},\mathbf{g}+\Delta}\right],$$

$$\zeta_{\mathbf{g},\mathbf{g}+\Delta}=\frac{\phi_{\mathbf{g}}-\phi_{\mathbf{g}+\Delta}}{2},\quad \nu_{\mathbf{g},\mathbf{g}+\Delta}=\frac{\theta_{\mathbf{g}}+\phi_{\mathbf{g}+\Delta}}{2},$$

$$\xi_{\mathbf{g},\mathbf{g}+\Delta}=\frac{\theta_{\mathbf{g}}-\phi_{\mathbf{g}+\Delta}}{2}.$$

The phases γ appear when one takes into account the fact that the spin of the s electron is parallel to the spin of the atom at which it is located at the moment. When the s electron goes over to another atom, it changes its spin direction. Hence, when one calculates the effective hopping integral between two atoms, one should take the s electron spin rotation accompanying the electron transition. This means using the transformation rules for the spinors. As is well known, the coefficients of the corresponding linear relationships are complex numbers. This leads to the appearance of the phases in the expressions for the effective hopping integral. The results of Refs. 2 and 4 were reproduced by many authors (e.g., Ref. 5), and it is customary to term the γ phases as the Berry phases.

For the aim of the present paper it is sufficient to point out that both $\gamma_{\mathbf{g},\mathbf{g}+\Delta}$ and $\theta_{\mathbf{g},\mathbf{g}+\Delta}$ vanish at $T=0$ and are random at $T\to\infty$.

We shall analyze the temperature dependence of the charge-carrier spectrum in the paramagnetic region, when it is generally impossible to diagonalize the Hamiltonian (11) even approximately. For this reason, a very useful approach to the problem is the method of moments, which does not require the prior diagonalization of these Hamiltonians. The moments are determined by expressions

$$M_n=\frac{1}{N}\langle \mathrm{Tr}\, H_{ef}^{n}\rangle, \tag{12}$$

where trace is calculated for a fixed set of the spin projections, and $\langle\cdots\rangle$ denotes the temperature averaging over spins.[4,2] The constant term $-AS/2$ is omitted.

Only even central moments are nonzero for the Hamiltonian (11). One may infer from the ratio $r(T)=M_4^{1/4}/M_2^{1/2}$ whether the conduction band form is strongly temperature dependent. One obtains

$$M_2=zt_{ef}^{2},\quad t_{ef}^{2}=\frac{t^2}{2}\left[1+\frac{\langle \mathbf{S_0}\mathbf{S_1}\rangle}{S^2}\right]. \tag{13}$$

An explicit expression for M_4 is presented in Refs. 4 and 2. For our aims it is sufficient to present the r values for a simple cubic lattice found there: $r(0)=1.25$, and $r(\infty)=1.23$. (At $T\to\infty$ all the binary correlation functions are presumed zeroes.)

As is seen from these figures, the ratio r changes very little with temperature, which suggests that the shape of the density of states remains close to that for the simple cosine dispersion law when $W=12t$ at $T=0$. Hence, the density of states becomes essentially nonzero only for energies exceeding the effective band bottom $-6t_{ef}(T)$. As follows from Eq. (13), for the classical spins, the bandwidth at $T\to\infty$ is 29% less than at $T=0$.

It remains to demonstrate that the band narrowing enhances the depth of the donor or acceptor level. To make one sure of this, it is sufficient to consider a system with a point defect of the strength U described by the Hamiltonian

$$H_i=-Uc_0^{*}c_0+H_{ef}, \tag{14}$$

with H_{ef} given by Eq. (11). For U sufficiently large, the s electron is distributed between the impurity atom 0 and its nearest neighbors Δ. According to Eqs. (13) and (14), the temperature-dependent depth of the impurity level is

$$D(T)=-zt_{ef}(T)+\frac{U}{2}+\sqrt{\frac{U^2}{4}+zt_{ef}^{2}(T)}. \tag{15}$$

One sees from Eq. (15) that at $T=0$ the discrete level exists for $U/t>5$, and the difference $D(0)-D(\infty)$ is always negative, tending to $W(0)/2-W(\infty)/2$ with $U\to\infty$. Respectively, the radius R of the localized state diminishes with increasing temperature:

$$R=\frac{za}{z+(\nu+\sqrt{\nu^2+z^2})},\quad \nu=\frac{U}{t_{ef}^{2}(T)}. \tag{16}$$

As was already said above, an increase in the donor level depth and a decrease in the donor orbit radius stabilizes the insulating state and hinders the transition into the highly conductive state.

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