

On the indirect exchange between localized moments of ions of rare-earth metals

A. M. Tsvetik

Institute of High Pressure Physics, Academy of Sciences of the USSR
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It is shown that, for systems containing ions of the rare-earth elements (REM) with an f -electron level $\epsilon_f \ll D$ (D is the conduction-band width and the energy is measured with respect to the chemical potential), the interaction between the REM-ion moments at distances $r \lesssim Da/|\epsilon_f|$ (a is the lattice constant) decreases like $\sin(2p_F r)/r^2$ (p_F is the Fermi momentum). The cause of the difference between the form of this interaction and the form of the conventional RKKY exchange is the strong energy dependence of the exchange interaction between a localized moment and the free electrons. The possible influence of the new type of exchange on the behavior of spin glasses containing REM atoms is also analyzed in the paper.

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1. As is well known, the presence in metals of magnetic impurities leads to a number of interesting effects connected with the intense scattering of the conduction electrons by the localized magnetic moments (LMM) of the impurities. Acting between a LMM and the conduction electrons are exchange forces that perturb the electron cloud surrounding the LMM. The LMM interact directly with the electron gas surrounding them and indirectly—via the polarization of this gas—among themselves. The indirect interaction—the RKKY exchange—may have a great influence on the low-temperature properties of the system.

Of greatest interest is the case of antiferromagnetic exchange between the LMM and the free electrons. In this case a competition arises between the screening of the LMM by the free electrons (the Kondo effect) and the striving of the impurity system to go over into a magnetically ordered phase or into a phase of the spin-glass type. Thus, for example, in AgMn and AuFe, the Kondo effect has been observed at magnetic-atom concentrations $c \sim 10^{-4}$, and the transition into the spin-glass phase, at $c \geq 0.2\%$.¹ The compounds of cerium are another typical example: β -Ce (Ref. 2) and CeAl₂ (Ref. 3) undergo a transition into a magnetically ordered phase, while the ground state of CeAl₃ is a Kondo singlet.⁴ The CeAl₃ example is all the more interesting, since each crystal unit cell in this case has a magnetic moment located in it, a situation which corresponds to $c = 1$.

It is clear from the foregoing that the study of the properties of the indirect exchange is of paramount importance for the understanding of the behavior of systems with magnetic impurities. In the case of transition-metal impurities, the form and properties of the RKKY exchange have been well studied: it is known that, at large distances, it behaves like $r^{-3} \cos 2p_F r$.⁵

In the present paper we demonstrate the possibility of the existence of a nonstandard type of exchange, which, apparently, occurs between rare-earth metal (REM) impurities, the level of whose localized f electrons lie near the Fermi surface. It will be shown that in this case $V(r) \sim \sin 2p_F r/r^2$. We shall in discussing the obtained results analyze the conditions most favorable for

the experimental observation of the new type of exchange, as well as its possible effect on the low-temperature properties of the system.

2. As is well known, the exchange between LMM and free electrons can be both direct and indirect in nature. The direct-exchange integral has the following form

$$A = \int \psi_f^*(r-n) \psi_k^*(r) V(r-r') \psi_f(r'-n) \psi_k(r') d^3r d^3r'. \quad (1)$$

Here $\psi_f(r-n)$ is the wave function of an electron localized at the n th lattice site, $\psi_k(r)$ is the wave function of a free electron with quasimomentum k , and $V(r-r')$ is the potential of the electron-electron interaction.

The matrix element of the indirect exchange, whose existence was pointed out by Schrieffer and Wolf,⁶ has the following form:

$$I = \frac{g_k^2}{\omega - \epsilon_f}, \quad (2)$$

where $g_k = \int \psi_f^*(r-n) U(r) \psi_k(r) d^3r$ is the hybridization constant, ϵ_f is the level of the localized d or f electrons, ω is the energy of the incoming free electron, and $U(r)$ is the crystal potential. Comparing the expressions (1) and (2), we obtain $A \sim g^2/D$ (D is the free-electron band width). In the transition metals $\epsilon_f, g \sim D$ and, hence, $A \sim I$; therefore, I can be considered to be energy independent.

However, it is easy to see that in the rare earths, in which $g/D \sim 0.05$, when the level is located near the Fermi surface (i.e., when $-\epsilon_f \ll D$), the direct exchange will be negligible as compared to $I(\omega)$ for all $|\omega| \lesssim D$, and $I(\omega)$ will depend strongly on energy. It is precisely this fact that will make the indirect exchange different from the conventional RKKY exchange.

We shall describe the system with the aid of the Anderson model, assuming that only the states with the same angular-momentum components, γ , hybridize. The f -electron level lies sufficiently deep below the Fermi surface ($-\epsilon_f \gg \rho g^2$), the multiplicity of the term $M = 2J + 1 \gg 1$, and the temperature T is higher than the Kondo temperature:

$$T \gg T_K = |\epsilon_f| \exp(-|\epsilon_f|/\alpha), \quad \alpha = M\rho g^2.$$

It will subsequently turn out that the condition $M \gg 1$

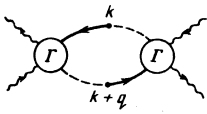


FIG. 1.

does not play a fundamental role in so far as the spatial dependence $V(r)$ is concerned.

It is not difficult to see that the exchange matrix element will, when allowance is made for all the powers of α/ϵ_f , be represented by the diagram shown in Fig. 1. Let us recall that the wavy lines represent the Green functions of pseudo-Fermions of energy λ ; the dashed and continuous lines, the Green functions of the s and f electrons respectively. The vertex Γ is represented by the conventional "ladder" (Fig. 2):

$$\Gamma^s(\omega-\lambda) = \frac{\omega - \epsilon_f}{\omega - \epsilon_f(\omega) + i\pi\alpha n(\omega)}; \quad (3)$$

$$\epsilon_f(\omega) = \epsilon_f + \frac{\alpha}{2} \int_{-\infty}^{+\infty} \text{th} \frac{x}{2T} \left(\frac{1}{x-\omega} - \frac{1}{x-\epsilon_f} \right) dx,$$

$$n(\omega) = (e^{\omega/T} + 1)^{-1}.$$

The scale of the energies determining the frequency dependence of the quantities entering into the exchange matrix element V_q is of the order of α . The energies that are typically required for the description of the correlations in a LMM system are of the order of the matrix element itself, which, as will be shown below, $\ll \alpha$. Therefore, we can disregard the dependence of V_q on the external frequency and set $i\omega = \lambda$ in $\Gamma(i\omega' + \lambda - i\omega)$. Thus, the matrix element of the interaction has, in our approximation, the following form:

$$V_q = g^4 T \sum_{n,k} I^s(\omega_n)(i\omega_n - \epsilon_{k+q/2} - g^2 \Sigma(\omega_n))^{-1} \times (i\omega_n - \epsilon_{k-q/2} - g^2 \Sigma(\omega_n))^{-1},$$

$$I(\omega) = \Gamma(\omega)/(\omega - \epsilon_f), \quad (4)$$

where $\Sigma(\omega)$ is the self-energy part of the s electrons.

The expression (4) can be rewritten in the form of an integral along a contour that encloses all the poles of the function $n(-z) = (e^{-z/T} + 1)^{-1}$:

$$V_q = 2g^4 \sum_k \frac{1}{\epsilon_{k-q} - \epsilon_k} \left(\frac{1}{2\pi i} \oint_C \frac{I^s(z)n(-z)}{z - \epsilon_k - g^2 \Sigma(z)} dz \right). \quad (5)$$

Further, we shall, for simplicity, assume that the spectrum of the free electrons is a square-law spectrum, i.e., that $\epsilon_k = k^2/2m - \mu$. This assumption makes the integration of (5) over the angles possible:

$$\frac{1}{2} \int d \cos \theta \frac{1}{\epsilon_{k-q} - \epsilon_k} = \frac{m}{2kq} \ln \left| \frac{2k+q}{2k-q} \right|. \quad (6)$$

Deforming the contour C in the manner shown in Fig. 3, we obtain

$$U_q = \frac{m^2 g^4 \Omega}{4\pi^2 q} \int d\epsilon_k \ln \left| \frac{2p_F + 2\epsilon_k/v_0 + q}{2p_F + 2\epsilon_k/v_0 - q} \right| \frac{1}{\pi} \int_{-\infty}^{+\infty} n(-x) \text{Im} \left\{ \frac{I_R^s(x)}{x - \epsilon_k - g^2 \Sigma_R(x)} \right\} dx, \quad (7)$$

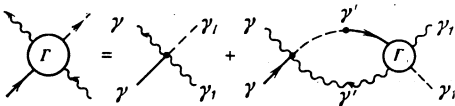


FIG. 2.

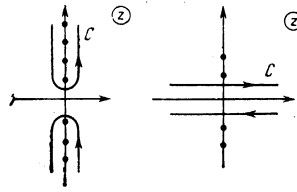


FIG. 3.

where Ω is the volume of the unit cell and p_F and v_0 are the momentum and velocity at the Fermi surface. In writing down the formula (7), we took into account the fact that $I^s(x)$ decrease rapidly when $|x| > |\epsilon_f|$, and, thus, the interaction is localized near the Fermi surface. Therefore, we can replace k by $p_F + \epsilon_k/v_0$ in the $d\epsilon_k$ integral. Further, it turns out to be convenient to go over to the coordinate representation $V(r)$, using the exact equality

$$\frac{1}{q} \ln \left| \frac{2p+q}{2p-q} \right| = 2 \int_0^{\infty} \frac{\sin 2px \sin qx}{qx} dx$$

(see, for example, White's book⁷). Neglecting the contribution from $\text{Im} I_R^s(x)$, we obtain

$$V(r) = -\frac{\pi}{4} (\rho g^2)^2 \frac{1}{(p_F r)^2} \int_{-\infty}^{+\infty} d\epsilon_k dx \frac{\gamma}{\pi} \frac{\text{Re} I_R^s(x) n(-x)}{(x - A(x) - \epsilon_k)^2 + \gamma^2} \times \sin \left[\left(2p_F + \frac{2\epsilon_k}{v_0} \right) r \right]; \quad (8)$$

$$A(x) = g^2 \text{Re} \Sigma(x), \quad \gamma(x) = -\text{Im} \Sigma_R(x) g^2.$$

The $d\epsilon_k$ integral can be evaluated with the aid of the method of residues. After its evaluation, we obtain from (8) the expression

$$V(r) = -\frac{\pi}{4} (\rho g^2)^2 \frac{1}{(p_F r)^2} \int_{-\infty}^{+\infty} \sin \left\{ r \left(2p_F + \frac{2}{v_0} (x - A(x)) \right) \right\} \times \exp \left(-\frac{r\gamma(x)}{v_0} \right) n(-x) \text{Re} I_R^s(x) dx. \quad (9)$$

The dx integral converges to $|x| \sim |\epsilon_f|$. If

$$r\gamma(\epsilon_f)/v_0 \ll 1, \quad (10a)$$

$$r(|\epsilon_f| + A(\epsilon_f))/v_0 \ll 1, \quad (10b)$$

then we can disregard the variation of the sine and take it out from under the integration sign. Then the remaining integral can be expressed in terms of the number, n_f , of f electrons:

$$\rho g^2 \int_{-\infty}^{+\infty} n(-x) \text{Re} I_R^s(x) dx \approx \frac{1}{M} \int_{-\infty}^{+\infty} \frac{n(-x) \alpha dx}{(x - \epsilon_f(x))^2 + (\pi \alpha n(x))^2} = 1 - n_f.$$

Here n_f is the number of f electrons at a site.

Thus, if the conditions (10) are fulfilled, then the interaction has the following form:

$$V(r) = -\frac{\pi}{4} \rho g^2 (1 - n_f) \frac{\sin 2p_F r}{(p_F r)^2}. \quad (11)$$

For $\alpha \ll |\epsilon_f|$, the quantity $1 - n_f \approx \rho g^2/|\epsilon_f|$ and $V(r)$ generally do not depend on M . This corresponds to $\Gamma = 1$ in (4). In such a form the formula (11) is applicable also for $M \sim 1$. As can be seen from (9), the violation of the condition (10a) entails an exponential cutoff of the interaction, while the effect of the violation of the condition (10b) is to make the interaction go over into the conventional RKKY exchange

$$V_{\text{RKKY}} \sim \left(\frac{\rho g^2}{\epsilon_f} \right)^2 \frac{\cos 2p_F r}{(p_F r)^2}. \quad (12)$$

This assertion becomes understandable when account is taken of the fact that, for $1 \sim r[|\epsilon_f| + A(\epsilon_f)]/v_0$, the sine in the integrand in (9) has time to oscillate many times over the convergence length $\int dx$, and so the exchange integral $I(x)$ for such distances becomes effectively a constant.

3. Let us proceed to discuss the obtained results. Let us first analyze the fulfillability of the condition (10a). In dilute systems $g^2\Sigma \leq cD$, and the long-range interaction remains. However, in dense media, such as the Ce compounds listed in Sec. 1, resonance scattering by the LMM located in each crystal unit cell leads to the relation $g^2\Sigma \sim D$, which implies a transition to short-range interaction. It is clear that the establishment of magnetic order in such systems becomes possible only because of such a cutoff of the RKKY interaction.

The properties of the exchange described in the present paper would be most fully manifested in a system of the spin-glass type. Using the method of virial expansion, we shall make a few estimates of the behavior of the thermal capacity of such a glass. Larkin and Khmel'nitskiĭ have shown⁸ that, for a system of spins interacting according to the law $V(R)$, the second-order term in the expansion of the free energy in powers of the concentration has the form

$$F^{(2)} = -Tc \frac{N}{2} \int d^3R \Phi \left(\frac{V(R)}{T} \right),$$

$$\Phi(y) = \ln \left\{ \sum_{n=0}^{2S} \frac{(2n+1) \exp(y(S(S+1) - 1/2n(n+1)))}{(2S+1)^2} \right\}$$

and N is the total number of impurities.

Averaging the interaction $V(R)$ over the half-period of the oscillations, we obtain

$$F^{(2)} = - \frac{Tc}{4\pi^{3/2}} \frac{V_0^{3/2}}{T^{3/2}} N \int_{-\infty}^{+\infty} dy \frac{\Phi(y)}{|y|^{3/2}}. \quad (13)$$

Apparently, the freezing temperature, T_f , of the glass will be significantly less than the crystal field acting in a REM. Therefore, we shall assume that the level ϵ_f is two fold degenerate. As can be seen from (13), the parameter of the virial expansion is the quantity $q = c(V_0/\pi T)^{3/2}$. It is natural to assume that the thermal capacity C_v has a maximum at $q \sim 1$, i.e., that

$$T \sim T_f = 4c^{2/3} (\rho g^2)^{2/3} / \pi^2 |\epsilon_f|.$$

Further, it may turn out that, for $T \ll T_f$, $F \sim -Tc q / (1+q)$ and, consequently, $C_v \propto T^{3/2}$, with a coefficient that does not depend on the impurity concentration. It is

intuitively clear that, in the presence of long-range interaction in the system at sufficiently low temperatures, the discrete structure of the system should have no effect on the behavior of the thermodynamic quantities, i.e., their dependence on the concentration should disappear. Therefore, the estimate $C_v \propto T^{3/2}$ seems to us to be reasonable.

Let us recall that in the case of the conventional RKKY exchange it has been found⁸ that $C_v \sim T$ and $T_f \sim c$. These results agree with the experimental data on glasses with the RKKY exchange.⁹

Let us make a few order-of-magnitude estimates. For the REM the realistic value $\rho g^2 / |\epsilon_f| \sim 0.04$, $\rho g^2 \sim 100-200$ K gives

$$T_f \sim c^{2/3} \text{ K}, \quad T_f = |\epsilon_f| \exp(-|\epsilon_f|/2\rho g^2) \sim 0.01 \text{ K}.$$

Thus, the spin-glass ground state should be realized at $c \gg 10^{-3}$.

The distance over which the interaction behaves like $1/r^2$ is $r_0 \sim aD/|\epsilon_f|$, which is of the order of 50 interatomic distances. At the remotest points, i.e., for $r \gg r_0$, the interaction law goes over into $1/r^3$, and, therefore, the thermodynamics of the glass will not be different from the conventional thermodynamics at $T < T_f (a/r_0 c^{1/3})^2$.

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