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Self-Polarization Contribution to Magnetic Ordering in Systems with Singlet Ground State

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Self-polarization effects on the *f*-electron magnetization is found to contribute significantly to the susceptibility and critical value of the exchange for ordering of the rare-earth group-V intermetallic compounds where the ground state of the rare-earth ion is a crystal-field singlet. For PrBi, a typical example of such a system, the contribution from the self-polarization effect is found to be of the same order as the Ruderman-Kittel-Kasuya-Yosida contribution.

I. INTRODUCTION

The ground state of some rare-earth and group-V intermetallic compounds is a singlet[1] owing to crystal-field effects. The splitting between the ground state and the magnetic states is, however, small, leading to an appreciable Van Vleck susceptibility. Magnetic ordering in such materials is believed to take place[2–5] because of an exchange interaction with the conduction electrons leading to a Ruderman-Kittel-Kasuya-Yosida[6] (RKKY) interaction between the ions, the magnetic moment at each site being produced by mixing of the crystal-field states. Even at $T=0$, the exchange should exceed a certain critical value[2–5] for ordering to take place. Short-range correlation corrections[4] to the critical exchange calculated by considering the RKKY interaction in the molecular-field approximation have been calculated and found to be about 15%.

The purpose of this paper is to point out that the self-energy contribution of the *s*-*f* exchange to the *f*-electron magnetization is as important as the RKKY interaction for the rare-earth intermetallic compounds with singlet ground state. This contribution, which we refer to as self-polarization,[7] may physically be understood as follows: In the presence of an infinitesimal magnetic field, the magnetic moment at each site polarizes the conduction electrons via the exchange interaction. This in turn acts as an effective molecular field leading to a large mixing of the excited state at the same site, and hence a larger magnetic moment. Self-polarization would lead to an important modification of the critical exchange constant required for ordering.

II. CALCULATION OF SUSCEPTIBILITY

We derive here an expression for the total *f*-electron susceptibility χ_f, including the effects of the crystal field, the Pauli polarization of the conduction electrons, the RKKY polarization, and the self-polarization. All polarization effects are treated in the molecular-field approximation. The origin of both RKKY and self-polarization is the *s*-*f* exchange interaction between the localized *f* electrons and the conduction electrons.

In order to calculate χ_f, it is convenient to express the RKKY interaction between two *f* ions in terms of a spin Hamiltonian. This is achieved by starting from the *s*-*f* exchange Hamiltonian[8] given by

$$\mathcal{H}_{sf} = -\sum_{\vec{k}\vec{k}'} J(\vec{k},\vec{k}')[S_z(a^\dagger_{\vec{k}'+}a_{\vec{k}+} - a^\dagger_{\vec{k}'-}a_{\vec{k}-}) + S^-(a^\dagger_{\vec{k}'+}a_{\vec{k}-}) + S^+(a^\dagger_{\vec{k}'-}a_{\vec{k}+})] , \tag{1}$$

where $\vec{S}$ is the spin operator for the rare-earth ion, $a^\dagger_{\vec{k}\pm}$ and $a_{\vec{k}\pm}$ are the creation and anhilation operators for the conduction electrons with wave vector $\vec{k}$ and spins pointing either up (+) or down (−). The exchange integral $J(\vec{k},\vec{k}')$ in (1) is given by

$$J(\vec{k},\vec{k}') = -\int \psi^*_{\vec{k}}(\vec{r}_1)\psi^*_f(\vec{r}_2)(1/r_{12})\psi_f(\vec{r}_1)\psi_{\vec{k}}(\vec{r}_2)\,d\vec{r}_1\,d\vec{r}_2 , \tag{2}$$

where $\psi_{\vec{k}}$ and ψ_f are the wave functions of conduction electron in state $\vec{k}$ and rare-earth *f* electrons, respectively. We have assumed $\psi_{\vec{k}}$ to be normalized over a Wigner-Seitz cell. The *s*-*f* exchange Hamiltonian $\mathcal{H}_{sf}$ leads to the RKKY interaction between two rare-earth spins $\vec{S}_1$ and $\vec{S}_2$ which is represented by a spin Hamiltonian

$$\mathcal{H}_{\mathrm{RKKY}} = A\,\vec{S}_1\cdot\vec{S}_2 , \tag{3}$$

where

$$A = (3n/4\epsilon_F)\sum_{\vec{q}} |J(\vec{q})|^2 F(\vec{q})\, e^{i\vec{q}\cdot\vec{R}_{12}} . \tag{4}$$

In obtaining (3) and (4), we have assumed that the conduction electrons can be treated in a free-electron approximation, and the exchange integral $J(\vec{k},\vec{k}')$ in Eq. (2) depends only on the magnitude of momentum transfer[9,10] $|\vec{k}'-\vec{k}|=\vec{q}$. In Eq. (4), n is the number density of conduction electrons, ϵ_F is the Fermi energy, and R_{12} is the distance between two spins S_1 and S_2. The function $F(\vec{q})$ is the linear dielectric-response function which, in the free-electron approximation, is given by

$$F(q)=1+\frac{q^2-4k_F^2}{4qk_F}\ \ln\left|\frac{q-2k_F}{q+2k_F}\right| \quad . \tag{5}$$

We shall now derive an expression for the total f-electron susceptibility χ_f in a molecular-field approximation. In the presence of an external field H_{ex} applied in the Z direction, the conduction electrons develop a uniform Pauli spin polarization which is proportional to χ_P, the Pauli susceptibility of conduction electrons and H_{ex}. The f electrons interact with both the external magnetic field, and the exchange field H_P produced by the uniformly polarized conduction electrons. This induces magnetic moments in the f shells which can then polarize the conduction electrons further by s-f exchange interaction. This additional polarization of the conduction electrons, by the same s-f exchange interaction, induces additional magnetic moments in the f shells; one therefore has to calculate the magnetic moment induced in the f shells self-consistently. In the molecular-field approximation, the f electrons see two types of fields in addition to H_{ex} and H_P. One of these, to be denoted as H_{RKKY}, is due to $\mathcal{H}_{\mathrm{RKKY}}$ of Eq. (3), and the other H_{sp} is due to the self-polarization effect mentioned earlier. Thus the Hamiltonian for a rare-earth ion (besides $\mathcal{H}_{\mathrm{cf}}$, the crystal-field Hamiltonian) in the presence of all four fields is given by

$$\mathcal{H}=-g_J\mu_B J_Z(H_{\mathrm{ex}}+H_P+H_{\mathrm{RKKY}}+H_{\mathrm{sp}}) \quad , \tag{6}$$

where

$$H_{\mathrm{RKKY}}=(g_J-1)^2/(g_J\mu_\beta)\langle J_Z\rangle a_{\mathrm{RKKY}} \quad , \tag{7}$$

$$H_{\mathrm{sp}}=(g_J-1)^2/(g_J\mu_\beta)\langle J_Z\rangle a_{\mathrm{sp}} \tag{8}$$

$$H_p=\alpha H_{\mathrm{ex}} \quad . \tag{9}$$

The quantities a_{RKKY} and a_{sp} and α depend upon the exchange integral $J(\vec{q})$ and are given by

$$a_{\mathrm{RKKY}}=Z(3n/4\epsilon_F)\sum_{\vec{q}}|J(\vec{q})^2|F(\vec{q})e^{i\vec{q}\cdot\vec{R}_{12}} \quad , \tag{10}$$

$$a_{\mathrm{sp}}=(3n/4\epsilon_F)\sum_{\vec{q}}|J(\vec{q})|^2F(\vec{q}) \quad , \tag{11}$$

and

$$\alpha=J(0)(g_J-1/g_J)\chi_P/\mu_\beta^2 \ . \tag{12}$$

In the above equations, g_J is the Lande g factor for the f electrons. In obtaining the RKKY molecular field, we have considered the contributions from nearest neighbors only, Z being the number of nearest neighbors.

To calculate χ_f, let us denote the crystal-field states in the absence of perturbator $\mathcal{H}$ [Eq. (6)] as $|J,n\rangle$, where $n=1$ refers to the singlet ground state. The energies corresponding to these states are E_n. The ground state is singlet and nonmagnetic, i.e.,

$$\langle J,1|J_Z|J,1\rangle=0 \quad . \tag{13}$$

In the presence of $\mathcal{H}$, the perturbed ground state, which we shall denote as $|J,1\rangle\rangle$, is given by

$$|J,1\rangle\rangle=|J,1\rangle+\sum_{n\neq1}\frac{\langle J,n|\mathcal{H}|J,1\rangle}{E_1-E_n}|J,n\rangle \ . \tag{14}$$

Using Eqs. (6)–(14), one can calculate the total induced angular momentum $\langle J_Z\rangle$ in the f shell,

$$\langle J_Z\rangle=\frac{pg_J\mu_BH_{\mathrm{ex}}(1+\alpha)}{1-pg_J\mu_B\beta(a_{\mathrm{RKKY}}+a_{\mathrm{sp}})} \quad , \tag{15}$$

where

$$\beta=(g_J-1)/g_J \tag{16}$$

and

$$p=2\sum_{n\neq1}\frac{\langle J,n|J_Z|J,1\rangle}{E_n-E_1} \quad . \tag{17}$$

The factor P depends only on the crystal-field parameters and can be calculated from a knowledge of the symmetry and strength of the crystal field. In the absence of conduction electrons, a_{RKKY}, a_{sp}, and α vanish and one has the susceptibility in the presence of crystal field only. This is given by

$$\chi_{\mathrm{cf}}=(g_J\mu_B)^2p \quad . \tag{18}$$

Using Eq. (15) for $\langle J_Z\rangle$ and noting that

$$\chi_f=g_J\mu_B\langle J_Z\rangle/H_{\mathrm{ex}} \quad ,$$

one obtains the total f-electron susceptibility on

$$\chi_f=\chi_{\mathrm{cf}}(1+\alpha)\Big/\left[1-\beta^2\left(\frac{\chi_{\mathrm{cf}}}{\mu_B^2}\right)(a_{\mathrm{RKKY}}+a_{\mathrm{sp}})\right]. \tag{19}$$

Thus, it is seen that the additional contribution to χ_f coming from the self-polarization effect, as would have been anticipated, occurs in the same manner as the RKKY contribution. We define a ratio R

$$R=a_{\mathrm{sp}}/a_{\mathrm{RKKY}} \quad , \tag{20}$$

which measures the relative strength of the self-polarization and RKKY contributions to the susceptibility and to the critical value of exchange necessary for ordering. The calculation of this ratio, using relevant parameters for PrBi, is presented in Sec. III.

III. CALCULATION FOR R FOR PrBi

The rare-earth group-V compounds have NaCl structure, and the crystal field at the site of the rare-earth ion (Pr^{3+}) has octahedral symmetry. The energy difference between the singlet ground state and the triplet first excited state is found[11] to be of the order of 60 °K. Although the first excited state is triply degenerate, only one of the three states mixes with the ground state by the J_z operator. Thus if we disregard the admixture of higher excited states, the two relevant states that occur in the calculation of p are

$$|J,1\rangle = (\tfrac{5}{24})^{1/2}[\,|4\rangle + |-4\rangle\,] + (\tfrac{7}{12})^{1/2}\,|0\rangle \tag{21}$$

and

$$|J,2\rangle = (\tfrac{1}{2})^{1/2}[\,|4\rangle - |-4\rangle\,], \tag{22}$$

where the state $|M_J\rangle$ is denoted by the quantum number M_J, $(-J\cdots+J)$. Considering this two-level system, one has

$$p = \tfrac{40}{3}(\Delta E)^{-1}. \tag{23}$$

One can now calculate the various contributions to χ_f^{-1} by using Eqs. (18), (19), (23) and knowing a_{RKKY} and a_{sp}. However, our main interest in this paper is to point out the significance of the self-polarization term, particularly in relation to the RKKY term. For this purpose, it is sufficient to calculate R which has been defined in Eq. (20). This partly avoids the necessity of a precise knowledge of n, ϵ_F, and the actual magnitude of $J(q)$. However, the calculation of R does require a detailed knowledge of the band structure through the function $F(q)$. No such calculations are available for PrBi at the present time. For an estimation of R, we shall assume that the conduction electrons can be treated like free electrons. The value of k_F can then be calculated by knowing the electron density n from the observed electronic specific-heat[11] coefficient γ and assuming that $m^* = m_e$.

In a free-electron approximation,

$$R = \int_0^\infty q^2|J(q)|^2F(q)\,dq \bigg/ Z\int_0^\infty q^2\,\frac{\sin qR_{12}}{qR_{12}}\,|J(q)|^2F(q)\,dq\ , \tag{24}$$

where $F(q)$ has been defined earlier in Eq. (5).

The relevant parameters[12] for PrBi are (in atomic units) $R_{12} = 8.58a_0$, $k_F = 0.20a_0^{-1}$, and $Z = 8$.

In most of the calculations of s-f coupling, the exchange integral $J(q)$ is assumed to be independent of q. If one makes this approximation, the numerator in Eq. (24) goes to infinity. In reality, however, $J(q)$ should fall off with q. Watson and Freeman[10] have evaluated $J(\vec{k}, \vec{k}')$ for different values of $\vec{k}$ and $\vec{k}'$ and have come to the conclusion that there is no reason to believe that $J(\vec{k}, \vec{k}')$ should only depend upon $|\vec{k} - \vec{k}'| = q$. For the present we are only interested in the ratio of two contributions rather than their absolute values, and it is sufficient to use some approximate forms for the q dependence of $J(q)$. We shall utilize two rather physically different approaches for estimating $J(q)$.

The first one was suggested by Overhauser.[13] In this case, the exchange integral $J(q)$ is approximated by the form factor

$$J_1(q) = \int e^{i\vec{q}\cdot\vec{r}}\,|\psi_f(r)|^2\,d\tau\ , \tag{25}$$

a result obtained by replacing $1/r_{12}$ by a δ function. This is physically equivalent to a strongly screened exchange between the localized f and itinerant s electrons. $J_1(q)$ is structurally quite simple and easy to evaluate numerically. The q dependence of $J_1(q)$ has been given in the paper by Watson and Freeman,[10] and the R calculated using this will be denoted as R_1.

The second approximation corresponds to ignoring the screening of the exchange altogether and treating the exchange in a Hartree-Fock approximation. In our calculation, we have utilized a typical q dependence of $J(q)$ obtained by Watson and Freeman,[10] and we shall denote the corresponding R as R_2.

Defining a dimensionless parameter $x = q/2k_F$, we have

$$R = \int_0^\infty x^2|J(x)|^2F(x)\,dx \bigg/ Z\int_0^\infty x^2|J(x)|^2\,\frac{\sin\alpha x}{\alpha x}\,F(x)\,dx\ , \tag{26}$$

where $\alpha = 2k_FR_{12}$. R is expected to depend quite sensitively on α. Furthermore, the x dependence of $J(x)$ does implicitly depend upon α for the Hartree-Fock exchange case. One has to, in principle, calculate $J(x)$ for different values of α. However, in our estimation of R_2, using Watson and Freeman's $J(x)$, only a typical value of α has been chosen. For a detailed quantitative evaluation of R_2, this is not adequate. The ratios R_1 and R_2 have been calculated for a series of α values and the results are given in the Table I.

The two interesting features of the result in Table I are the magnitude and α dependence of the ratios R_1 and R_2. For the case of perfectly screened exchange (R_1), the ratio of the self-polarization term to the RKKY term changes quite rapidly with α and changes sign. This implies that the two fields act in opposite directions. The reason for this strong α dependence is that the molecular field goes through zero at a certain value of α and becomes negative, an outcome of the usual oscillatory behavior of the RKKY polarization. On the other hand, the self-polarization field varies rather slowly with α. For PrBi, the appropriate value of α is equal to 3.4 and the corresponding value of

TABLE I. Ratio R of the self-polarization to RKKY field for perfectly screened (R_1) and unscreened (R_2) exchange, as a function of $\alpha = 2k_F R_{12}$.

$\alpha = 2k_F R_{12}$	$R_1(\alpha)$	$R_2(\alpha)$
0.4	0.1340	0.1326
0.8	0.1628	0.1543
1.2	0.2160	0.1846
1.6	0.2992	0.2174
2.0	0.4217	0.2564
2.4	0.6052	0.3102
2.8	0.8938	0.3768
3.2	1.3797	0.4388
3.6	2.2915	0.4848
4.0	4.3478	0.5240
4.4	11.2410	0.5716
4.8	−1000.0000	0.6412

R_1 is 1.75. Thus, we see that the self-polarization effect may be quite important and may have a larger contribution than the RKKY term itself.

For the case of Hartree-Fock unscreened exchange, the α dependence of the ratio R_2, is rather slow. For PrBi, the self-polarization field is nearly 46% of the RKKY molecular field. Although its magnitude is smaller than that obtained by using perfectly screened exchange, in both cases, the effect is more important than the short-range correlation effects pointed out by Cooper.[4] This latter correlation was estimated to be of the order of 15–20% of the molecular-field term.

The sensitive dependence of R on the choice of a particular form of exchange integral clearly indicates that one has to be quite careful in any detailed quantitative analysis of the susceptibility and critical-exchange parameter. In conclusion, we would like to emphasize that the self-polarization effect, neglected in calculations until now, is expected to play an important role in the magnetic properties of rare-earth group-V intermetallic compounds with singlet ground states.

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Electron States in Ferromagnetic Iron. I. Band Properties

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A new band-structure calculation is reported for the ferromagnetic state of iron, in which the exchange interaction is given particularly careful treatment. A variational procedure was used with the wave functions expanded in terms of tight-binding functions and orthogonalized plane waves. Hybridization and spin polarization of the wave functions were allowed. Correlation corrections were incorporated. The energy bands are somewhat wider than those previously published; comparison is made with photoemission and optical reflection and x-ray emission data. The calculation leads self-consistently to the observed magnetic moment. The roles of intra-atomic exchange and itinerancy in the origin of iron's ferromagnetism are discussed.

I. INTRODUCTION

It has long been clear from both experimental and theoretical points of view that in the transition metals the conduction electrons consist of semilocalized