Role of Anisotropic Exchange Interactions in Determining the Properties of Spin-Glasses

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Recent measurements on *Cu*Mn spin-glass alloys have revealed that the anisotropy field maintaining the remanent magnetization in the direction of the initial applied field is strongly enhanced by the addition of nonmagnetic Au or Pt impurities. We show that these results can be accounted for by the existence of Dzyaloshinsky-Moriya–type interactions between the Mn spins arising from spin-orbit scattering of the conduction electrons by nonmagnetic impurities. The magnitude of these interactions is surprisingly large.

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Recent experiments by Préjean, Joliclerc, and Monod[1] on *Cu*Mn doped with nonmagnetic impurities shine new light on the crucial role played by anisotropic couplings between local moments in stabilizing the remanent magnetization of spin-glasses. Préjean, Joliclerc, and Monod have shown that the addition of a few hundred ppm of Au or Pt nonmagnetic impurities in CuMn alloys considerably widens the hysteresis loop in the low-temperature spin-glass state. For example, the width of the hysteresis loop amounts to 170 Oe in "pure" *Cu*Mn (1-at.% Mn) but is increased by the addition of Au impurities at a linear rate of 6.2×10^3 Oe/at.% Au. Pt impurities are even more effective and increase the width at a rate of 34×10^3 Oe/at.% Pt. By contrast the addition of Al has practically no effect. Thus Préjean, Joliclerc, and Monod concluded that *the addition of nonmagnetic impurities with strong spin-orbit coupling (Au, Pt) sharply increases the anisotropy field which maintains the remanent magnetization in the direction of the initial applied field.*

Additional evidence for the selective effect of nonmagnetic impurities on the anisotropy field of spin-glasses is provided by EPR measurements on *Cu*Mn (2-at.% Mn) containing Al, Zn, Ti, Ni, Fe, Co, or Pd impurities. Okuda and Date[2] found that, in the spin-glass state, the spin resonance of these ternary alloys is shifted with respect to *Cu*Mn by an amount which varies linearly with the concentration of the added elements. The rate of increase of the shift varies from zero for Al to 6.6×10^3 G/at.% for Co impurities. As the resonance shift in the spin-glass state can be interpreted[3] as due to the anisotropy field of the alloy, these results provide further evidence for the enhancement of the anisotropy field by nonmagnetic impurities (Ni or Co impurities in Cu do not have a magnetic moment). As in the results of Préjean, Joliclerc, and Monod,[1] the impurities with strong spin-orbit scattering give the most marked effects.

In this Letter we show how the enhancement of the anisotropy field can arise from an additional term in the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction[4] which is of the Dzyaloshinsky-Moriya[5] (DM) type and is due to spin-orbit scattering of the conduction electrons by the nonmagnetic impurities. Smith[6] has already predicted the existence of such a term. Our aim is to calculate the coefficient of the DM interaction for nonmagnetic *transition-metal* impurities and to relate our calculation to the experimental results described above.

The RKKY interaction is based on the calculation of the shift in the ground-state energy of a gas of conduction electrons interacting with two localized spins. Here we add a spin-orbit interaction on the site of a nonmagnetic impurity at $\vec{R} = 0$ and therefore consider the following perturbing potential of the electron gas:

$$V = -\Gamma \delta(\vec{r} - \vec{R}_A)\vec{s} \cdot \vec{S}_A - \Gamma \delta(\vec{r} - \vec{R}_B)\vec{s} \cdot \vec{S}_B + \lambda(r)\vec{l} \cdot \vec{s}. \quad (1)$$

On the site of a nonmagnetic transition-metal impurity, the spin-orbit coupling of a conduction electron is considerably enhanced because the admixture of the impurity d states into the conduction band allows the conduction electrons to experience the strong spin-orbit forces of the d states.[7] In the virtual-

bound-state model,[8] the admixture of the atomic d states ψ_{2m} with plane waves is written as

$$\varphi_{\vec{k}} = \exp(i\vec{k}\cdot\vec{r}) + \exp(i\eta_2)\sin\eta_2 \frac{\langle d|V_0|k\rangle}{\Delta} \sum_{m=-2}^{2} Y_{2m}^*(\hat{k})\psi_{2m}(\vec{r}) + \ldots, \tag{2a}$$

for electrons in the immediate region about the transition-metal impurity ($\vec{R}=0$). In the region of large R the wave function is written as

$$\varphi_{\vec{k}} = \exp(i\vec{k}\cdot\vec{r}) + 4\pi\exp(i\eta_2)\sin\eta_2(e^{ikr}/kr)\sum_{m=-2}^{2} Y_{2m}^*(\hat{k})Y_{2m}(\hat{r}), \tag{2b}$$

where Δ is the half-width of the virtual bound state and η_2 is the phase shift of the $l=2$ partial waves. The phase shift at the Fermi level is related to the number Z_d of d electrons by the Friedel rule

$$\eta_2(E_F) = (\pi/10)Z_d \tag{3}$$

and the matrix element $\langle d|V_0|k\rangle$ is related to the density of states for one spin direction at the Fermi level $N(E_F)$ by the relation[8]

$$|\langle k|V_0|d\rangle|^2 = 4\Delta/N(E_F).$$

The lowest-order correction term to the ground-state energy due to the perturbation Eq. (1) in which all three scattering centers appear is[9]

$$E^{(3)} = \left(\frac{1}{8\pi^3}\right)^3 \mathrm{P}\int_{k_1\le k_F} d^3k_1 \int d^3k_2 \int d^3k_3 \left[\frac{1}{(E_1-E_2)(E_1-E_3)} - \frac{\pi^2}{3}\delta(E_2-E_1)\delta(E_3-E_2)\right] \mathrm{Tr}_\sigma V_{\vec{k}_1\vec{k}_2} V_{\vec{k}_2\vec{k}_3} V_{\vec{k}_3\vec{k}_1}, \tag{4}$$

where P denotes the principal part of the integral. In the systems to which we apply Eq. (4), the magnetic ions at $\vec{R}_A$ and $\vec{R}_B$ are far from the nonmagnetic impurity ($R_\alpha \sim 10$ Å). Therefore to calculate the matrix elements of the exchange terms Γ in the perturbation Eq. (1) we use the form of the wave function at large r, Eq. (2b), while for the spin-orbit coupling term we use the form appropriate for small r, Eq. (2a). The trace over the conduction-electron spin states that enters Eq. (4) is

$$\mathrm{Tr}_\sigma(\vec{S}_A\cdot\vec{s})(\vec{s})(\vec{S}_B\cdot\vec{s}) = -(i/4)(\vec{S}_A\times\vec{S}_B).$$

After performing the integrations in Eq. (4) we finally obtain the leading term (in $1/R$) to the energy that is trilinear in the three parts of the perturbation V,[10]

$$H_{\mathrm{DM}} = -V_1 \frac{\sin[k_F(R_A+R_B+R_{AB}) + (\pi/10)Z_d]\hat{R}_A\cdot\hat{R}_B}{R_A R_B R_{AB}} (\hat{R}_A\times\hat{R}_B)\cdot(\vec{S}_A\times\vec{S}_B) \tag{5}$$

with

$$V_1 = (135\pi/32)(\lambda_d\,\Gamma^2/E_F^2 k_F^3)\sin[(\pi/10)Z_d]. \tag{6}$$

Here R_A, R_B, and R_{AB} are the lengths of the three sides of the triangle formed by the ions at A, B, and the spin-orbit center, λ_d is the spin-orbit coupling constant for a d electron and we have assumed one conduction electron per atom of the metal. Other anisotropic terms appear in higher-order perturbation terms but they are proportional to $(\lambda_d/E_F)^n$ with $n \ge 2$ and we can neglect them.

The energy term H_{DM}, Eq. (5), corresponds to an interaction of the DM type between the localized spins. While the standard RKKY interaction is invariant under rotations of the spin system, this DM interaction depends on the orientation of $\vec{S}_A\times\vec{S}_B$ with respect to the local axis $\hat{R}_A\times\hat{R}_B$; therefore this interaction gives rise to anisotropy effects. The crucial role of the nonmagnetic impurities in giving rise to such interactions is twofold. (a) They introduce a spin-orbit scattering and thus couple the spin and space coordinates. (b) They break the inversion symmetry with respect to the midpoint between the two spin sites, which is a necessary condition for the existence of a DM type of interaction.

Let us first compare the strength of the DM interaction with the leading term in $1/R$ of the RKKY interaction[4] which, for one electron per atom, is given by

$$H_{\mathrm{RKKY}} = V_0 \frac{\cos(2k_F R_{AB})}{R_{AB}^3} \vec{S}_A\cdot\vec{S}_B, \tag{7}$$

with

$$V_0 = 9\pi\Gamma^2/32E_F k_F^3. \tag{8}$$

The ratio of V_1, Eq. (6), to V_0 is a simple function of the reliably known parameters λ_d, E_F, and Z_d,

$$V_1/V_0 = 15(\lambda_d/E_F)\sin[(\pi/10)Z_d]. \quad (9)$$

For Pt impurities ($\lambda_d = 0.51$ eV, $Z_d \simeq 9.4$) and Co ($\lambda_d = 0.065$ eV, $Z_d \simeq 7$) in CuMn ($E_F = 7$ eV) and we obtain $V_1/V_0 = 0.2$ and $V_1/V_0 = 0.11$, respectively. Thus, the DM interactions are quite significant.

To evaluate the anisotropy energy arising from the DM interactions, we assume that the average of H_{DM} vanishes when taken over spin configurations determined by RKKY interactions. Therefore, to obtain a finite anisotropy energy, we must determine the reorientation of the spins due to the DM interaction. The mean distortion angle $d\theta$ is of the order of magnitude of the ratio of the characteristic energies of the DM and RKKY interactions, E_{DM}/E_{RKKY}. Thus we expect the anisotropy energy per Mn ion to be of the order of magnitude of $E_{DM}d\theta$ or E_{DM}^2/E_{RKKY}. As a numerical illustration we consider $CuMn_xT_x$ alloys in which the mean distance between nearest-neighbor impurities is the same for Mn-Mn pairs and Mn-T pairs ($R_A \sim R_B \sim R_{AB} \sim r_0$) so that we can predict the following anisotropy energy per Mn,

$$E_a^{cal} = \frac{E_{DM}^2}{E_{RKKY}} = \left(\frac{V_1 S^2}{r_0^3}\right)^2 \left(\frac{V_0 S^2}{r_0^3}\right)^{-1} = \left(\frac{V_1}{V_0}\right)^2 \frac{V_0 S^2}{r_0^3}. \quad (10)$$

On Fig. 1, we compare the anisotropy energies for Mn evaluated from experimental data[1,2] to the calculated values E_a^{cal} for several types of nonmagnetic impurities in CuMn. It can be seen that, with the exception of Ni, the calculation reproduces very well over two decades the variation of the anisotropy energy with the type of nonmagnetic impurity. This firmly supports our interpretation that E_a is proportional to $(E_{DM})^2/E_{RKKY}$.[13] While the experimental values of E_a are about six times smaller than the calculated ones (Ni is the only exception), such a reduction for disordered systems is not surprising as our estimates [Eq. (10)] are the maximum values possible.

Finally, we briefly discuss the origin of the anisotropy fields in *binary* spin-glass alloys. In "pure" CuMn the anisotropy is very small (corresponding to $E_a \sim 0.06\times10^{-18}$ erg per Mn for 1 at.% concentration, see Ref. 1) and could be due either to DM interactions arising from (weak) spin-orbit scattering off neighboring Mn atoms

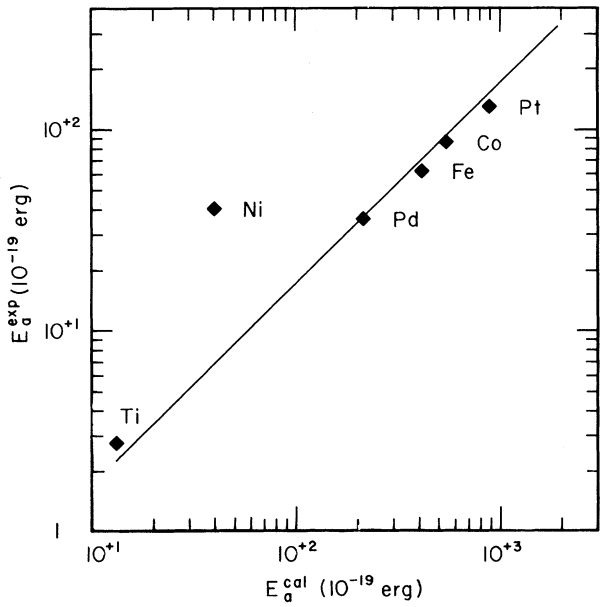

FIG. 1. A comparison of experimental and calculated anisotropy energies per Mn in $CuMn_xT_x$ alloys for several transition-metal impurities. The straight line corresponds to $E_a^{exp} = \frac{1}{6}E_a^{cal}$ and is a guide to the eye. The calculations were performed by using Eqs. (9) and (10) with atomic values for λ_d (see Ref. 12); $Z_d = 2$ for T = Ti, $Z_d = 6$ for T = Fe, $Z_d = 7$ for T = Co, $Z_d = 9.4$ for T = Ni, Pd, and Pt; $S = 1.88$; $V_0 = 7.5\times10^{-37}$ erg cm^3 (see Ref. 11); $E_F = 7$ eV; and $r_0 \simeq 10.8\times10^{-8}$ cm for $x = 1\%$ (Pt) or $r_0 \simeq 7.6\times10^{-8}$ cm for $x = 2\%$ (Ti, Fe, Co, Ni, and Pd). E_a^{exp} was evaluated from experimental data on the width of the hysteresis loop (see Ref. 1) and the resonance shift (see Ref. 2). For T = Pt, E_a^{exp} is given by the product of the rate of increase of the hysteresis width per at.% Pt in CuMn 1 at.% at 1.45 K and μ_r, where μ_r is the remanent magnetization, $\mu_r \simeq 0.04\mu_B$ for the experimental conditions of Ref. 1. For T = Ti, Fe, Co, Ni, and Pd, E_a^{exp} was evaluated from the resonance shift ΔH per at.% T at 4.2 K in CuMn 2 at.% (see Ref. 2), and from unpublished resonance and magnetization data on CuMn alloys communicated by P. Monod and H. Hurdequint, $E_a \simeq (2\Delta H)(0.07\mu_B)$.

of Mn pairs or to dipolar couplings. In AuFe spin-glass alloys the anisotropy is much larger, corresponding to $E_a \simeq 20\times10^{-18}$ erg per Fe in Au + 3-at.% Fe.[14] The difference with respect to CuMn is that Fe impurities in Au carry an orbital angular momentum. The experimental evidence for this is the skew-scattering contributions to the Hall effect.[15] While the DM interaction is not ruled out in those disordered alloys we are inclined to ascribe the strong anisotropy energy of AuFe to pseudodipolar interactions arising from

the orbital character of the Fe moments.

In summary, we have presented the calculation of the DM interaction between impurity spins arising from the spin-orbit scattering of conduction electrons by nonmagnetic transition-metal impurities. We have shown that this mechanism can account for the magnitude of the anisotropy fields measured in $CuMn_x T_x$ spin-glass alloys and for their dependence on the nonmagnetic element T. Experiments are in progress on these alloys to investigate whether the effects of DM interactions are limited to producing magnetic anisotropy or whether they play a more fundamental role in determining spin-glass behavior.[16] We emphasize that the DM interactions we have calculated can be remarkably large and should give important effects in many magnetic systems with low symmetry, e.g., alloys and metallic glasses. Similar DM-type interactions between nuclei may also be at the origin of the unexplained NMR line broadening in cold-worked metals.[17]

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Hierarchy of Exchange Interactions in a Disordered Magnetic System

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A simple and very physical model to explain the magnetic properties of heavily doped, n-type semiconductors below the metal-nonmetal transition is proposed. Based on the wide distribution of exchange interactions between donors, this model establishes a hierarchy of exchange interactions accounting for the existence of the low-lying energy levels which determine the magnetization of the donor system at low temperature, and explain the absence of a transition to an ordered antiferromagnetic state.

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Heavily doped, n-type semiconductors undergo a transition from insulating to metallic state, when the donor concentration N_D is increased above a critical value N_C.[1] On the insulating side of the transition, the electrons are localized on randomly distributed donors and the semiconduc-

