Molecular-Orbital Model of Heat-Induced Effective Exchange Coupling in Magnetic Multilayers

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Heat-induced effective exchange coupling between two ferromagnets across a semiconductor spacer layer is described by the interaction of localized, weakly bound electron states which are situated at the two interfaces. These states overlap across the spacer layer and form large molecular orbitals. The energies of these orbitals depend on the spin configuration of the electrons and therefore determine the exchange coupling. Thermal repopulation of the levels yields a positive temperature coefficient of the coupling. The results are found to well reproduce the experimental observations.

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Two ferromagnetic Fe layers separated by a nonmagnetic, amorphous semiconductor spacer layer are exchange coupled. An outstanding property of this effective exchange interaction is that its temperature coefficient can be positive. The coupling strength reversibly increases with rising temperature until it saturates. This property, which we label "heat-induced exchange," is of basic interest. It is the aim of this Letter to model heat-induced exchange coupling in magnetic multilayers with semiconductors. The present approach relies on weakly bound impurity states which are situated at the interfaces between the ferromagnets and the spacer and interact across the spacer layer. It is entirely different from earlier approaches by other authors which have used k-dependent tunneling [1], direct tunneling [2], or excitons in a direct band gap [3].

First, we briefly summarize the experimental findings which shall be modeled. Thin Fe layers separated by a semiconducting spacer layer have been studied. At spacer thicknesses of about 15 to 25 Å heat-induced antiferromagnetic coupling between the two ferromagnets exists for different spacer materials, namely a-Si [4,5], a-Ge [6], and a-ZnSe [7]. The thickness range of the spacer layer where antiferromagnetic coupling occurs is about the same for all spacer materials; it does not depend on the size of the energy gap. As depicted in Fig. 1, upper panel, for the case of a-ZnSe, this range is narrow at 40 K and broadens towards larger spacer thicknesses at 150 K. We note that in this particular experiment the negative sign of the polarization always means antiferromagnetic coupling, whereas positive polarization is ambiguous. Measurements of the compensation field show that here the positive polarization at low thicknesses corresponds to ferromagnetic coupling, while at large thicknesses it reflects very weak or zero coupling. Most remarkable indeed is the temperature dependence of the effective coupling strength J. J is defined by the exchange energy per unit area E_{ex} as

$$E_{\text{ex}} = -J \frac{\mathbf{M_1} \cdot \mathbf{M_2}}{|\mathbf{M_1}||\mathbf{M_2}|}, \quad (1)$$

where $\mathbf{M_1}$ and $\mathbf{M_2}$ denote the magnetizations of the two ferromagnetic layers. The size of J is experimentally found to increase upon heating until it saturates at a certain temperature, as depicted in Fig. 1, lower panel, again for the case of a-ZnSe. Depending on the spacer thickness an offset of the coupling strength is observed, which decreases with increasing spacer thickness. We emphasize that the magnitude of the coupling strength is very small. For a-ZnSe as spacer material it is around 10^{-6} J m^{-2} at thermal saturation. We note that it is of the same order of

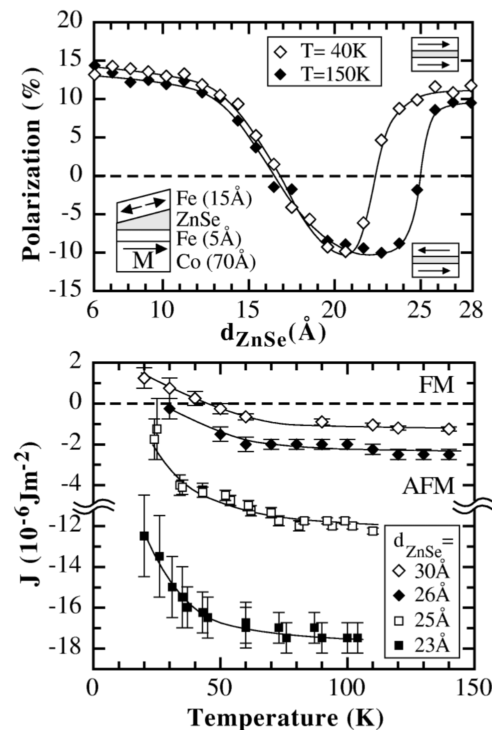

FIG. 1. Upper panel: Measured magnetization at remanence (which is proportional to the observed spin polarization) of the top Fe layer of an Fe/a-ZnSe(wedge)/Fe sample vs ZnSe spacer thickness at 40 and 150 K. The negative sign always means antiferromagnetic coupling. The positive sign at low thicknesses corresponds to ferromagnetic coupling. At large thicknesses the positive sign indicates weak or no coupling. Lower panel: Measured coupling strength J vs temperature for various Fe/a-ZnSe/Fe trilayers with different spacer thicknesses. J by definition is negative for antiferromagnetic coupling. (Experiments from Ref. [7].)

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magnitude also for a-Si and for a-Ge, again irrespective of the size of the energy gap.

Another important common feature of the experimental observations is the occurrence of an irreversible transition upon heating to around room temperature under which the heat-induced behavior disappears. This led to the early conclusion that defects in the semiconductors are responsible for the heat-induced coupling [8]. Therefore, in order to model the exchange coupling, we assume localized, weakly bound electron states to be present *at or near the interfaces*. These states may belong to impurities in the semiconducting material. The role of the nearby metal might be decisive to form shallow donors. Preliminary results of conductivity measurements along Fe/ZnSe bilayers corroborate the assumption of the existence of such localized electron states near or at the interfaces.

For the model let us consider an amorphous semiconductor layer of thickness d embedded between two ferromagnetic metal layers of thicknesses much larger than d. The semiconductor material is characterized by a dielectric constant ε and an effective mass m^*. Most importantly, as mentioned, localized, weakly bound electron states shall be present in the semiconducting material near the interfaces. These shallow donor states are described as ground states of hydrogenlike impurities, the central charge of which is screened by the dielectricity ε of the semiconductor. Furthermore, the weakly bound electrons are magnetically coupled to the nearby ferromagnet at the corresponding interface. This coupling is described in mean-field approximation by a strong exchange field, the Weiss field, to which these electrons are exposed. Finally, the impurity states interfere across the spacer layer and in this way mediate the effective exchange coupling between the ferromagnets. The density of the impurity states per interface area, however, shall be low enough so that the localized electrons do not interact along the interfaces. A possible charge transfer between the metal layers and the semiconductor gives rise to electrical dipoles across the interfaces. Since d is small the effect of these dipoles can be approximated by a shift in energy between the band structures of the metal layers and the semiconductor.

In order to calculate the electronic states of the impurities we first neglect the exchange field. The familiar ground state then is a $1s$-like orbital,

$$\phi(\varepsilon, m^*) \sim \left(\frac{m^*}{m\varepsilon a_0}\right)^{3/2} \exp\left\{-\frac{m^* r}{m\varepsilon a_0}\right\}, \tag{2}$$

where a_0 is the Bohr radius. The corresponding energy is

$$E_S = \frac{m^*}{m}\frac{1}{\varepsilon^2}E_0, \tag{3}$$

where E_0 is the Rydberg energy.

The introduction of a screening $\varepsilon > 1$ and a reduced mass $m^* < m$ obviously enlarges the spatial extension of the impurity states, which is of decisive importance. We note that the variation of both parameters qualitatively has the same effect. Therefore, for the sake of simplicity, we choose $m^* = m$ for the remainder of the calculations and only retain ε as a free parameter.

Because of their large spatial extensions the impurity orbitals from the "right" and the "left" interface may overlap across the semiconductor to form giant molecular orbitals. The Pauli principle requires that the molecular-orbital wave function with parallel spins has a lower probability amplitude within the spacer layer than the one with antiparallel spins. This causes a difference between the energies of the two spin configurations which eventually drives the effective exchange coupling. Therefore, in order to obtain the coupling strength, we have to determine these energies. As an approximation we combine via a Slater determinant a "left" and a "right" unperturbed impurity wave function to form a molecular orbital. We use this particular approximation because in the presence of the Weiss field the spin of the impurity must always remain antiparallel to the magnetization of the respective neighboring ferromagnet. For the first step of the calculation we neglect the magnetic energies of the Weiss fields. The Hamiltonian then consists of the single electron energies $H_{S,L}$ and $H_{S,R}$, where L and R denote "left" and "right," and the Coulomb interactions across the spacer layer. The electrons are labeled 1 and 2, and $r_{j,i}$ stands for the distance $|r_j - r_i|$ with $j = R, L$ and $i = 1, 2$:

$$H = H_{S,L} + H_{S,R} + \frac{e^2}{\varepsilon}\left(-\frac{1}{r_{L,2}} - \frac{1}{r_{R,1}} + \frac{1}{r_{1,2}} + \frac{1}{d}\right). \tag{4}$$

The wave functions are Slater determinants as mentioned, where ϕ denotes the orbital and χ the spin functions:

$$\Psi_{\uparrow\downarrow}(1,2) = \frac{1}{\sqrt{2}}[\phi_L(1)\chi_\uparrow(1)\phi_R(2)\chi_\downarrow(2) - \phi_L(2)\chi_\uparrow(2)\phi_R(1)\chi_\downarrow(1)], \tag{5}$$

$$\Psi_{\uparrow\uparrow}(1,2) = \frac{1}{\sqrt{2(1-S^2)}}\chi_\uparrow(1)\chi_\uparrow(2) \times [\phi_L(1)\phi_R(2) - \phi_L(2)\phi_R(1)]. \tag{6}$$

S is the overlap integral $\int \phi_L(r)\phi_R(r)\,d^3r$. If we assume the single electron energies to be the same at both sites, the average energies per electron become

$$E_{\uparrow\downarrow} = E_S(\varepsilon) + \frac{1}{2}\left[\frac{e^2}{\varepsilon d} + V_c(d,\varepsilon)\right], \tag{7}$$

$$E_{\uparrow\uparrow} = E_S(\varepsilon) + \frac{1}{2}\left[\frac{e^2}{\varepsilon d} + \frac{V_c(d,\varepsilon) - V_{\rm ex}(d,\varepsilon)}{1 - S^2(d,\varepsilon)}\right]. \tag{8}$$

V_c and $V_{\rm ex}$ are the Coulomb and exchange energies, respectively:

$$V_c = \int\int \phi_L^2(r_1)\phi_R^2(r_2)\frac{e^2}{\varepsilon}\left(-\frac{1}{r_{L,2}} - \frac{1}{r_{R,1}} + \frac{1}{r_{1,2}}\right) \times d^3r_1\,d^3r_2, \tag{9}$$

$$V_{\text{ex}} = \int \int \phi_L(r_1)\phi_R(r_2)\frac{e^2}{\varepsilon}\left(-\frac{1}{r_{L,2}} - \frac{1}{r_{R,1}} + \frac{1}{r_{1,2}}\right) \times \phi_L(r_2)\phi_R(r_1)\, d^3r_1\, d^3r_2 \,. \quad (10)$$

The orbitals $\phi_{L(R)}$ are inserted from Eq. (2).

Next, we briefly discuss the coupling between the donors and the nearby ferromagnet. This coupling is approximated by a Weiss field $\mathbf{H_w}$. The magnetic energy of an electron with magnetic moment $\mathbf{m}$ in this field is given by $E_m = -\mathbf{m}\mathbf{H_w}$. In the ground state $\mathbf{m}$ is parallel to the field. A magnetic moment standing antiparallel to $\mathbf{H_w}$ thus gains an energy of $2mH_w$ relative to the ground state. A Weiss field is approximately $H_w \sim 10^7$ Oe which yields $2mH_w$ to be of the order of 1 eV. At ambient temperatures this energy is huge compared to kT. Therefore the levels with one or both moments antiparallel to the corresponding Weiss field can be ignored for thermodynamical considerations. It is sufficient to retain the ground states, i.e., the states with $\mathbf{m}$ parallel to $\mathbf{H_w}$. Thus, for antiparallel and parallel alignment of the magnetizations of the two ferromagnets, the energies of the interfering electrons are described by Eqs. (7) and (8), respectively. Using the integrals by Sugiura [9] we numerically evaluate these two equations with the free parameter $\varepsilon = 10$, which roughly corresponds to the value of ZnSe. The results are shown in Fig. 2.

V_c is always larger than V_{ex} and therefore the energy of the antiparallel spin configuration is always lower than the one of the parallel spins. If only these states are occupied, antiferromagnetic coupling exists but no temperature dependence is found.

The temperature dependence of the effective coupling strength J is a consequence of thermal repopulation of the states depicted in Fig. 2. In order to maintain overall charge neutrality we must allow for transfer of electrons from or to the metals, which serve as particle reservoirs with chemical potential μ. We then need to consider the thermodynamic potential $\Omega = \sum_i n_i E_i - \mu \sum_i n_i$, where

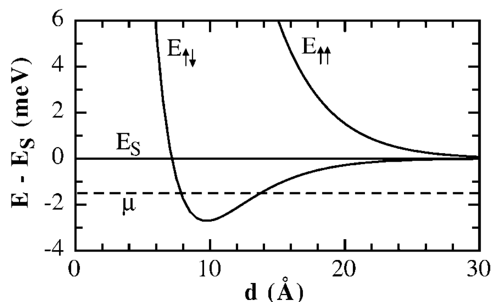

FIG. 2. Calculated electron energies vs spacer thickness d for $\varepsilon = 10$. E_S is the energy of a noninteracting impurity state, set to zero. $E_{\uparrow\uparrow}$ and $E_{\uparrow\downarrow}$ are the energies of interacting impurity states for the magnetizations of the ferromagnets parallel and antiparallel to each other, respectively. μ is the chemical potential, treated as a free parameter.

E_i are the one particle energies and n_i their respective occupations. The energy position of μ within the semiconductor is determined by the details of the electronic structures of the semiconductor and of the metal layers. As an approximation we set the energy difference $E_S - \mu =$ const throughout the semiconductor layer. μ is shown in Fig. 2 as a dashed line, and we treat the quantity $E_S - \mu$ as the second free parameter of the calculation. The occupations are governed by the Fermi distribution $f(E_i) = [1 + \exp\{(E_i - \mu)/kT\}]^{-1}$ since the interfering electrons still are fermions. Considering that the molecular levels $E_{\uparrow\downarrow}$ and $E_{\uparrow\uparrow}$ are doubly occupied and the levels E_S are the same impurity orbitals but singly occupied, we obtain the thermodynamical potentials $\Omega_{\uparrow\downarrow}$ and $\Omega_{\uparrow\uparrow}$ for antiparallel and parallel alignment of the ferromagnetic layers, respectively,

$$\Omega_{\uparrow\downarrow(\uparrow\uparrow)} = AN\{2f(E_{\uparrow\downarrow(\uparrow\uparrow)})[E_{\uparrow\downarrow(\uparrow\uparrow)} - \mu] + [1 - f(E_{\uparrow\downarrow(\uparrow\uparrow)})]f(E_S)[E_S - \mu]\}, \quad (11)$$

where N is the number of impurities at one interface per interface area A. N is treated as the third free parameter of the calculation.

The effective coupling strength J as defined in Eq. (1) is identified with the difference of the thermodynamic potentials per unit area $J = (\Omega_{\uparrow\downarrow} - \Omega_{\uparrow\uparrow})/A$ [10]. This yields

$$J = N\{2f(E_{\uparrow\downarrow})[E_{\uparrow\downarrow} - \mu] - 2f(E_{\uparrow\uparrow})[E_{\uparrow\uparrow} - \mu] + [f(E_{\uparrow\uparrow}) - f(E_{\uparrow\downarrow})]f(E_S)[E_S - \mu]\}. \quad (12)$$

Numerical results of J are presented in Fig. 3 with appropriate choices of the free parameters, namely $\varepsilon = 10$, $E_S - \mu = 2$ meV, and $N = 1 \times 10^{12}$ cm^{-2}. We find that the results well reproduce the experimental observations shown in Fig. 1.

Of particular interest is the role of the three free parameters of the calculation. The easiest to understand is the number of impurities per interface area N. The coupling strength J is proportional to N, and there is no qualitative change of J upon variation of N. The chosen value of $N = 1 \times 10^{12}$ cm^{-2} is realistic for this type of interface. It is supported by preliminary transport measurements. The dielectric constant ε and the position of the chemical potential μ, on the other hand, influence the thickness and temperature dependences of J. We wish to emphasize, however, that the gross features of J persist upon considerable variation of ε and μ. The chosen value of $\varepsilon = 10$ lies within the range of the dielectric constants of the semiconductors under investigation. The energetic position of the chemical potential in the semiconductor, on the other hand, is hard to estimate because it depends on particularities of the electronic structures of the materials. It is likely to be near the impurity levels and thus we choose $E_S - \mu = 2$ meV as a physically meaningful value.

In conclusion, we propose a molecular-orbital model of heat-induced exchange coupling between ferromagnetic

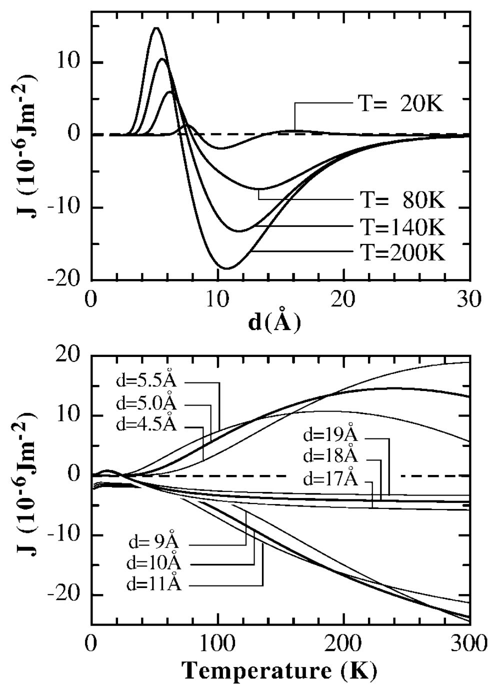

FIG. 3. Calculated effective coupling strength J vs spacer thickness d (upper panel), and vs temperature (lower panel). The free parameters are set $N = 1 \times 10^{12}$ cm^{-2}, $\varepsilon = 10$, and $E_S - \mu = 2$ meV.

layers separated by an amorphous semiconductor spacer layer. The mechanism is based on the assumption of localized, weakly bound electron states to exist at the semiconductor-metal interfaces. They are described as ground states of hydrogenlike impurities which are screened by the dielectricity of the semiconductor. They can form molecular orbitals across the spacer layer and thus mediate an exchange interaction. The present calculation, even with rough approximations, yields antiferromagnetic coupling across amorphous semiconductors with a positive temperature coefficient. With a physically meaningful choice of the three free parameters of the calculation we find that the antiferromagnetic coupling occurs in a range of spacer thicknesses which well corresponds to the experimental observations. At low temperatures this range is quite narrow and broadens towards larger spacer thicknesses with rising temperature. At very small spacer thicknesses the calculation yields no coupling, at variance with the experimental result. This may be explained by pinholes which are likely to occur at very small spacer thicknesses. The calculated temperature dependences exhibit a positive temperature coefficient or heat-induced behavior, which is the key feature of exchange coupling across amorphous semiconductors. In particular, one finds good agreement to the experimental data for larger spacer thicknesses. The magnitude of the coupling strength is well reproduced; the calculated and experimental results turn out to be within the same order of magnitude.

We are confident that the present molecular-orbital model for heat-induced effective exchange, which we have introduced in the simplest possible approximation, will stimulate further theoretical and experimental work on exchange coupling across semiconductors in magnetic multilayers. As a particular challenge we propose to study the effect of an applied voltage across the spacer on the exchange coupling. This is of interest since nondissipative steering of exchange interaction with an applied voltage has a great technological potential.

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