Size-dependent indirect exchange, magnetoelectric effect, and superconductivity in small particles and thin films

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The indirect-exchange integral in small magnetic particles and magnetic thin films depends on the size of these objects. While indirect exchange gives rise to a ferromagnetic order in bulk samples, small particles may become antiferromagnetic and superconducting. The type of order can be varied by means of an electric field or adsorption.

In this letter we examine indirect exchange in magnetic samples with small dimensions. We find that there are two reasons for the size dependence of the indirect exchange: the appearance of a surface-related term in the effective exchange integral and a change in the bulk term due to the size dependence of the Fermi momentum. Each of these factors depends strongly on the boundary conditions for electrons at the surface of the sample. These factors can be altered by adsorption or an external electric field. Correspondingly, the type of magnetic order or the quantitative characteristics of this order will change, and we can speak in terms of a new magnetoelectric effect: a surface magnetoelectric effect.

A size dependence of the indirect exchange can also be linked with an exceedingly interesting effect:[1] While Gd clusters of certain sizes behave normally, i.e., as superparamagnetic particles, the behavior of Gd clusters of other sizes is anomalous. Specifically, in a Stern–Gerlach apparatus they are deflected in the weak-field direction. Comparing this fact with the circumstance that clusters of the weak magnets V, Pd, and Al and even clusters of the strong magnet Cr are not deflected at all in such an apparatus,[2] we naturally conclude that the anomalous Gd clusters are highly diamagnetic, possibly because they are in a superconducting state.

At first glance, this suggestion would seem to contradict the fact that Gd is a ferromagnetic metal, so a superconductivity would be forbidden. However, because of the size dependence of the indirect exchange, small Gd clusters would not necessarily be ferromagnetic, so the prohibition against superconductivity in them might be lifted.

We assume here that the test sample is a crystal platelet with a simple cubic unit cell. It is described by the Hamiltonian of the s–f model, in which the deviation of the surface potential Bv from the bulk potential (defined as zero) is taken into account:

$$H = Bv \sum a^*_{m\sigma} a_{m\sigma} + B \sum a^*_{g\sigma} a_{g+\vec{\Delta},\sigma} - A \sum (\mathbf{S}_g \mathbf{s})_{\sigma\sigma'} a^*_{g\sigma} a_{g\sigma'} . \quad (1)$$

Here g specifies the particular atom, m specifies the particular surface atom, the vector

Δ connects nearest neighbors, $a^*_{g\sigma}$ and $a_{g\sigma}$ are s-electron operators, the operators $\mathbf{S}_g$ and $\mathbf{s}$ represent the spin of the f-atom and of the s-electron, σ is the projection of the electron spin, B is the Bloch integral, A is the s–f exchange integral, and the parameter v specifies the surface potential. The thickness of the platelet along the z axis is $L=(2l+1)a$, where a is the lattice constant.

The indirect-exchange Hamiltonian is found from (1) in the second order of a perturbation theory in AS/W, where S is the magnitude of the f-spin, and $W = 12|B|$. This Hamiltonian is of the ordinary Heisenberg form, with an effective indirect-exchange integral

$$J(\mathbf{g},\mathbf{g}')=-\frac{A^2}{4(\pi a)^4}\sum_{t,t'}\sum_{k_t,k'_t}\int d^2p d^2p' \exp[i(\mathbf{p}-\mathbf{p}')(\mathbf{r}-\mathbf{r}')]\varphi_t(k_t,z)$$
$$\times\varphi_{t'}(k'_{t'},z')\varphi_{t'}(k'_{t'},z)\varphi_t(k_t,z')(n_{\mathbf{p}'},k'_{t'}-n_{\mathbf{p}},k_t)(E_{\mathbf{p}',k'_t}-E_{\mathbf{p},k_t})^{-1}, \quad (2)$$

where $\mathbf{r}=(x, y)$, and $n_{\mathbf{p},k}$ is the Fermi distribution for an electron with an energy $E_{\mathbf{p},k}$ in the state with wave function $\varphi_t(t = s, c)$, where

$$E_{\mathbf{p},k}=2B(\cos p_x a+\cos p_y a+\cos kz), \quad (3)$$

$$\varphi_s(k_s,z)=\left[\frac{L}{2a}(1-\chi_{k_s})\right]^{1/2}\sin k_s z, \quad \varphi_c(k_c,z)$$
$$=\left[\frac{L}{2a}(1+\chi_{k_c})\right]^{1/2}\cos k_c z, \quad \chi_k=\frac{a\sin Lk}{L\sin ak}. \quad (4)$$

Under the condition $|v| \leqslant 1$, the allowed values of the transverse components of the momentum $k\in[0, \pi/a]$ are found from the relations (n_c and n_s are integers)

$$lk_s a=\pi n_s+\operatorname{arccot}\{(v\text{-}\cos k_s a)/\sin k_s a\},$$
$$lk_c a=\pi n_c\text{-}\arctan\{(v\text{-}\cos k_c a)/\sin k_c a\}. \quad (5)$$

Below we discuss the most important case, "weak" spatial quantization, in which all quantities can be decomposed into bulk and surface parts. In the simplest case, this is done by using the Euler-Maclaurin summation formula in first order [3] in $1/(k_F L)$. We restrict the discussion to the cases $v = 0, \pm 1$, in which Eqs. (5) can be solved exactly. In the first of these equations, there is no surface correction to $J(g, g')$ for a given Fermi energy μ (but this is not true for a given s-electron density n!), while in other cases this correction is

$$J_s(g,g')=-\frac{A^4a^6}{8(2\pi)^5L}\int d^2pd^2p'dk\exp\{i(\mathbf{p}-\mathbf{p}')(\mathbf{r}-\mathbf{r}')\}$$
$$\times\cos k(z-z')(n_{\mathbf{p}'q}-n_{\mathbf{p}k})(E_{\mathbf{p}'q}-E_{\mathbf{p}k})^{-1}, \quad (6)$$

where $q=0$ for $v=1$ and $q=\pi/a$ for $v=-1$.

At small values of na^3, the integral in (6) with $r = r'$, $v = 1$ can be evaluated analytically by using a quadratic approximation for dispersion relation (3) ($B<0$):

$$J_s(\zeta)=\frac{A^2ma^6}{64\pi^2L\zeta}\left\{k_F^2\frac{k_F\sin k_F\zeta}{\zeta}-\frac{\cos k_F\zeta}{\zeta^2}+\frac{1}{\zeta^2}\right\},$$

$$\zeta=|z-z'|\geqslant a,\quad 1/m=|B|a^2\quad(\hbar=1). \tag{7}$$

The Fermi momentum k_F in (7) can be assumed to be the same as for a bulk sample. In this case, for both small and large values of ζ, the integral J_s is proportional to k_F^2, *i.e.*, to the quantity $n^{2/3}$, which represents the surface density of electrons. This result stems from the circumstance that J_s is due to electrons in virtual surface levels (the value $v=1$ is a limiting value at which virtual surface levels convert into real levels). The dependence of J_s on the distance between spins is completely different from that described by the familiar expression for the bulk part of the indirect-exchange integral (see Ref. 4, for example). If $B<0$, then in the case $v=-1$ the virtual levels lie near the top of band (3), and there are no electrons in them. For this reason, J_s is vastly smaller in this case.

A second source of a size dependence of the exchange interaction is a size dependence of the electron-Fermi energy at a fixed electron density. If $v=0$, the size-dependent part k_{FS} of the Fermi momentum for a sample of volume V and surface area S is[3] $\pi S/8V$ at small values of n. According to numerical calculations,[4] the paramagnetic Curie temperature in the case of indirect exchange is an oscillatory, variable-sign function of k_Fa. In the model which we are using here, the ferromagnetic order becomes unstable at $k_Fa\approx 2$; as this parameter is increased by 0.1, a ferromagnet with a fairly high Curie point converts into an antiferromagnet with a fairly high Néel temperature. However, a change in k_Fa of precisely this order of magnitude follows from the estimate above for the size-dependent shift of the Fermi momentum in small particles with a radius not exceeding $10a$. If the bulk metal is ferromagnetic, a small particle made of this metal may thus be an antiferromagnet if its dimensions lie in a certain interval.

Adsorption on the surface of the sample or the presence of an external electric field will alter the surface potential vB in (1). Corresponding changes will occur in both J_s and k_F and thus in the magnetic characteristics of the sample, to the point that there is a change in the type of magnetic order. The behavior of k_F as a function of v in samples of finite dimensions is described in Ref. 3.

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[4] D. Mattis, *The Theory of Magnetism* (Harper and Rowe, New York, 1965).

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