Exchange interaction in magnetic semiconductors

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A simple model is proposed for magnetic semiconductors based on rare earth metals with localized f electrons hybridized with an empty conduction band. The intraatomic exchange between f and sd electrons is also considered. Perturbation theory is used to derive an effective exchange interaction which can be written as the sum of antiferromagnetic and ferromagnetic parts. The total interaction can be either ferromagnetic or antiferromagnetic. The calculated dependences of the exchange integrals $\mathcal{J}_1$ and $\mathcal{J}_2$ on the interatomic distance are in agreement with the measured results for europium chalcogenides.

Magnetic semiconductors containing transition or rare earth ions, in particular, europium chalcogenides, are currently attracting considerable attention. Such materials can be either ferromagnetic (EuO, EuS) or antiferromagnetic (EuTe). Although the exchange interaction in standard magnetic insulators is now well understood (it is assumed that the principal mechanism is the Kramers superexchange[1]), there are several different models of the exchange in magnetic semiconductors. Sometimes, it is explained by the direct exchange or by the indirect exchange via anions or by the Bloembergen–Rowland polarization mechanism. There are also other, frequently complicated, models.[2] We propose a simple model, which explains well all the main features of the exchange interaction in magnetic semiconductors, particularly those based on rare earth metals. Our treatment is similar to the model of ref. 3, which applies to rare earth metals themselves.

The most important feature of the band structure of the materials under study is the existence of a conduction band (usually empty) which is derived from s or d states of the metal (or by their hybridization) and the existence of narrow f levels in the forbidden band, which can be assumed to be localized. For simplicity, we shall neglect the orbital moment and consider the case of a single f electron per center having spin s = 1/2. We shall also assume that the f electrons are localized and that there is at most one f electron per center because of a strong Coulomb repulsion. The corresponding Hamiltonian is given by

$$\hat{H} = \sum_{\mathbf{k},\sigma} \varepsilon_k a^+_{k\sigma} a_{k\sigma} + (-\Delta) \sum_{j,\sigma} b^+_{j\sigma} b_{j\sigma} + \frac{1}{\sqrt{N}} \sum_{j,\mathbf{k},\sigma} V_{j\mathbf{k}} a^+_{k\sigma} b_{j\sigma} + \text{H.c.} - \frac{\mathcal{J}}{2} \sum_{j,\sigma,\sigma'} a^+_{j\sigma} a_{j\sigma'} b^+_{j\sigma'} b_{j\sigma} = \hat{H}_0 + \hat{V} + \hat{f}. \tag{1}$$

Here, the first term is the kinetic energy of the conduction electrons (we shall call them sd electrons); the second term is the energy of the localized f electrons in the site representation (the f level is separated by a gap Δ from the bottom of the conduction band). The third term describes the hybridization and the fourth term the local intraatomic exchange [which can be written in the form $(-1/2)\mathcal{J}\sum_j (1/2 + 2\sigma_j \mathbf{s}_j)$, where σ_j is the conduction-electron spin and $\mathbf{s}_j$ is the spin of an f electron at a site j]. Since the f electron wave functions are strongly localized, we shall assume that the hybridization is local,[3] i.e., we shall set $V_{j\mathbf{k}} = V \exp(i\mathbf{k}\mathbf{R}_j)$. The hybridization and exchange in the materials under study are weak (V, $\mathcal{J} \ll \Delta$, B, where $B \approx 1/m^*$ is the width of the conduction band).

Our exchange mechanism represents a direct generalization of the Kramers–Anderson superexchange.[1] If the hybridization and intraatomic exchange terms are omitted the system reduces to a set of isolated localized f electrons; the ground state is 2^N-times degenerate with respect to spin. Because of the hybridization with the conduction band, virtual transitions of the f electrons to the conduction band can occur and, as a result, they can interact with one another (the hybridization and the kinetic energy of the sd electrons play the role analogous to electron transitions via oxygen ions in magnetic oxides). This effect lifts the spin degeneracy in the fourth order of the perturbation theory with respect to $\hat{V}$, which usually gives rise to an antiferromagnetic exchange interaction of localized spins.[3] However, the intraatomic exchange was not considered in ref. 3 [the last term in Eq. (1)]; when this term is included, the f electrons belonging to a given center can be excited to the conduction band where their interaction with other f electrons is of the exchange type and then they return to the original centers. This mechanism leads to a ferromagnetic exchange interaction. These two effects can explain all different properties of magnetic semiconductors.

The effective exchange Hamiltonian can be obtained by a perturbation expansion of Eq. (1):

$$H_{\text{eff}} = \left\langle \hat{V} \frac{1}{E_0 - H_0} \hat{V} \frac{1}{E_0 - H_0} \hat{V} \frac{1}{E_0 - H_0} \hat{V} + \hat{V} \frac{1}{E_0 - H_0} \mathcal{J} \frac{1}{E_0 - H_0} \hat{V} \right\rangle. \tag{2}$$

The averaging in Eq. (2) is over the 2^N-times degenerate subspace of the localized f-electron wave functions in the presence of an empty conduction band.

Substituting in Eq. (2) the explicit expressions for the appropriate operators and carrying out the necessary commutations of the operators $a_{\mathbf{k}\sigma}$ and $a^+_{\mathbf{k}\sigma}$, we obtain

$$H_{\text{eff}} = \sum_{i \neq j} (J^a_{ij} - J^f_{ij}) \mathbf{s}_i \mathbf{s}_j, \tag{3}$$

where

$$J^a_{ij} = \frac{2}{N^2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \frac{V^2 e^{i(\mathbf{k}_1 - \mathbf{k}_2)(\mathbf{R}_i - \mathbf{R}_j)}}{(\Delta + \varepsilon_{k_1})^2 (\Delta + \varepsilon_{k_2})}, \tag{4}$$

$$J^f_{ij} = \frac{2}{N^2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \frac{\mathcal{J}}{2} \frac{V^2 e^{i(\mathbf{k}_1 - \mathbf{k}_2)(\mathbf{R}_i - \mathbf{R}_j)}}{(\Delta + \varepsilon_{k_1})(\Delta + \varepsilon_{k_2})}; \tag{5}$$

we have used the standard transformation from the electron to the spin operators $b^+_{i\pm} b_{i\pm} = 1/2 \pm s^z_i$, $b^+_{i\pm} b_{i\mp} = s^{\pm}_i$.

* The actual form of the exchange integrals (4) and (5) depends on the spectrum of ε_k although the qualitative behavior of the exchange integrals is practically independent of the spectrum. For the simplest spectrum $\varepsilon_k = k^2/2m^*$, the exchange interaction has the form

$$J^a_{ij} = \frac{V^4\Omega^2 m^{*3}}{2\pi^3\sqrt{2m^*\Delta}}\frac{e^{-2\sqrt{2m^*\Delta}R}}{R}, \quad J^f_{ij} = \frac{2V^4\Omega^2 m^{*2}}{4\pi^3}\frac{e^{-2\sqrt{2m^*\Delta}R}}{R^2}; \tag{6}$$

here, $\Omega = V/N$ is the volume of a unit cell which appears as a result of the transformation

$$\frac{1}{N}\sum_k \to \frac{V}{N}\frac{1}{(2\pi)^3}\int dk$$

(V is the volume of a crystal).

Our expression for J^a_{ij} is identical with that obtained in ref. 3 (however, the equation obtained in ref. 3 contains an erroneous additional power of R in the denominator); the ferromagnetic part of the exchange J^f_{ij} has the same dependence on R.

Equations (3) and (6) can be applied to magnetic semiconductors. It follows from these equations that the resulting interaction can be either ferromagnetic or antiferromagnetic, depending on the relative magnitude of the parameters of the system. The ferromagnetic part of the interaction [Eq. (6)] decreases faster as a function of the distance, which implies that the resulting interaction is mainly antiferromagnetic at large distances.

Measurements on europium chalcogenides yield the exchange integrals J_1 and J_2 governing the interaction with the nearest and second-nearest neighbors. Denoting the distance between nearest neighbors by d, we find that the distance between second-nearest neighbors is $d\sqrt{2}$ for the EuO lattice, which is similar to NaCl. The total interaction calculated from Eq. (6), given by $J_1 = J^a(d) + J^f(d)$ and

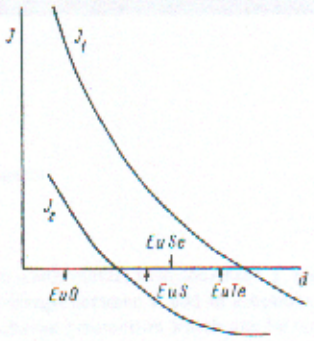

Fig. 1. Dependences of the exchange integrals J_1 and J_2 on the interatomic distance for europium chalcogenides.

$J_2 = J^a(d\sqrt{2}) + J^f(d\sqrt{2})$, is shown schematically in Fig. 1. The measured values of J_1 and J_2 for europium chalcogenides have the same dependences on the interatomic distance (see Fig. 3 in ref. 2); a comparison with different materials is also shown in Fig. 1.

It follows from Eq. (6) that J_1 has a zero at $R_1 = \sqrt{2m^*\Delta}/2m^*V^2$ and J_2 at $R_2 = R_1\sqrt{2}$; using Fig. 3 of ref. 2, we can estimate the experimental ratio $R_1/R_2 \approx 1.3$, which is in good agreement with the calculated value $R_1/R_2 = \sqrt{2}$.

We made several simplifying assumptions (the hybridization was assumed to be constant and the spectrum ε_k had the simplest form); furthermore, in our comparison with the experimental results, we assumed that the parameters V and m^* had the same values for all europium chalcogenides and only the interatomic distance d was variable. Nevertheless, in spite of these simplifications, our model provides a good qualitative description of the exchange interaction in magnetic semiconductors based on rare earth metals.

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