Double exchange and superexchange in a ferrimagnetic half-metal

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The mean field theory proposed originally by Kubo and Ohata for manganites is generalized for a ferrimagnetic half-metal and applied to the magnetite. The relevance of both the double exchange interaction and the superexchange one for the spin ordering in the conducting *B* sublattice of magnetite is shown. The shortcomings of the mean-field approximation are discussed.

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Spin-dependent electron transfer was intensively studied in the last years. Especially, the materials of the perovskite family $R_{1-x}A_xMnO_3$ (R=La,Pr,Nd; A=Sr,Ca, e.g.) are in the focus of interest[1,2] owing to the anomalously large magnetoresistance effects in the vicinity of the metal-insulator transition. On the other hand, these doped manganese oxides attracted nowadays a revived attention in connection with the development of the spin-electronic devices,[3] as they exhibit the ''half-metallic'' behavior in the ferromagnetic phase.[4] Indeed, in the ferromagnetic conducting phase of the doped manganites, the itinerant charge carriers are spin polarized owing to the strong Hund's rule coupling to the localized spins and, consequently, they appear to be a possible source of a highly spin-polarized current.

Another candidate for the spin electronics is the ferrimagnetic magnetite that, especially because of the high Curie temperature ($T_c \approx 870$ K), has promising application at room and higher temperatures. In the temperature range above the Verwey transition, the *B* sublattice of octahedral sites in magnetite may be represented by the system of N_B localized spins $S=5/2$ and of $N_B/2$ itinerant electrons.[5] Owing to the Hund's coupling, the spins of the itinerant electrons are antiferromagnetically coupled to the localized spins, forming thus $S'=2$ spins which are at each time randomly distributed over the sites of the *B* sublattice. Consequently, the *B* sublattice of magnetite represents a system resembling the hole-doped manganites and the question about the role of the double exchange (DE) interaction in magnetite naturally arises. Indeed, the magnetization of the *B* sublatice was deduced using the Kubo-Ohata DE mean field (MF) theory[6] in Ref. 7. However, the latter treatment did not take into account the antiferromagnetic exchange coupling between the *A* (tetrahedral) and *B* sublattice. No checking of the correctness of such approximation was made. Moreover, the itinerant spins were added to (instead of subtracted from) the localized spins; in particular an unphysical value $S'=2.9$ for the effective spin in the *B* sublattice was used when fitting the theory to the experimental results.

Motivated by the above facts, the MF theory of the two sublattice ferrimagnet, which takes into account both the superexchange (SE) and the DE interactions, is developed in the present paper. In particular, the existence of itinerant spin-polarized charge carriers in one of the sublattices (designated as *B* in the magnetite) will be assumed and the ferromagnetic ordering in this sublattice will be characterized by the MF parameter λ introduced by Kubo and Ohata.[6] The inter- and intrasublattice SE interactions will be represented by means of the effective fields. The model will be applied to magnetite and corresponding numerical results will be discussed.

The MF decoupling of the ferrimagnetic sublattices *A* and *B* will be carried out replacing the intersublattice SE interaction by the effective SE fields. These effective fields, proportional to the equilibrium values of the spin *z* components of the sublattices, $m_A(\mathrm{eq}) \equiv \langle S_A^z \rangle_{\mathrm{eq}}$ and $m_B(\mathrm{eq}) \equiv \langle S_B^z \rangle_{\mathrm{eq}}$, will act as ''external fields'' in the sublattices *B* and *A*, respectively. The equation for the equilibrium value of m_A at fixed (but unknown) value of $m_B(\mathrm{eq})$ is given by the well-known equation of the MF theory,

$$m_A = SB_S[\lambda_{AB} m_B(\mathrm{eq}) + \lambda_{AA} m_A]. \tag{1}$$

Here, B_S denotes the Brillouin function and the coefficients $\lambda_{\alpha,\gamma}$ (with α, γ equal to A, B) are defined as

$$\lambda_{\alpha\gamma} = \beta S J_{\alpha\gamma} z_\gamma(\alpha), \tag{2}$$

where the SE constants $J_{\alpha\gamma}$ are symmetrical in α, γ, the number of nearest-neighbor γ ions to the α ion is denoted by $z_\gamma(\alpha)$, and $\beta = 1/k_B T$.

The condition for the equilibrium value of the spin *z* component per ion in the *B* sublattice, at fixed value of $m_A(\mathrm{eq})$, will be deduced by means of a generalized treatment of Kubo and Ohata.[6] At first, the MF parameter $\lambda = \beta S g \mu_B H_{\mathrm{eff}}^z$ will be introduced, where the effective field H_{eff}^z determines the probabilties of the orientations of the spin in the *B* sublattice. Consequently, the mean value of the spin *z* component per ion in the *B* sublattice, with the concentration *x* of the itinerant carriers, is equal to

$$m_B(\lambda) = \langle S_B^z(\lambda) \rangle = (1-x) S B_S(\lambda) + x S' B_{S'}\left(\frac{S'}{S}\lambda\right), \tag{3}$$

where S' is the spin composed of spins S and $s=1/2$ according to the Hund's rule ($S=5/2$ and $S'=2$ for the magnetite). The condition for the equilibrium MF parameter λ [or, equivalently, $m_B(\mathrm{eq})$] is deduced from the extremum free energy of the *B*-sublattice system, i.e., of the itinerant electrons and localized spins, subjected to the effective SE field proportional to $m_A(\mathrm{eq})$. Accordingly, we shall consider

$$f_B = F/N_B = x\mu + \Omega + \langle \mathcal{H}_{SE} \rangle - T\mathcal{S}^{(S)} \tag{4}$$

as the MF approximation of the *B*-sublattice free energy per ion, which is to be minimized at fixed $m_A(\mathrm{eq})$.[8] Here μ means the chemical potential, Ω is the grand-canonical potential of the itinerant carriers having the density of states (DOS) $g_\lambda(\varepsilon)$,

$$\Omega = -\frac{1}{\beta}\int d\varepsilon g_\lambda(\varepsilon)\ln(1+e^{\beta(\mu-\varepsilon)}), \tag{5}$$

and the contribution to the energy arising from the effective SE field from the sublattice *A*, as well as from the SE interaction inside the sublattice *B*, is

$$\langle \mathcal{H}_{\mathrm{SE}}\rangle = -\frac{1}{\beta S}[m_B\lambda_{BA}m_A(\mathrm{eq}) + \tfrac{1}{2}\lambda_{BB}m_B^2]. \tag{6}$$

The MF entropy of the ion spins S,S' randomly distributed in the *B* sublattice is

$$\mathcal{S}^S(\lambda) = k_B\left\{[(1-x)\ln\nu_S(\lambda) + x\ln\nu_{S'}(\lambda)] - \frac{1}{S}\lambda m_B\right\} \tag{7}$$

with

$$\nu_S(\lambda) = \sum_{|m|\leqslant\frac{5}{2}} \exp\left(\lambda\frac{m}{S}\right), \quad \nu_{S'}(\lambda) = \sum_{|m|\leqslant 2} \exp\left(\lambda\frac{m}{S'}\right). \tag{8}$$

The DOS implies the effect of the spin order on the bandwidth; accordingly, the chemical potential determined by the equation

$$x = \int d\varepsilon g_\lambda(\varepsilon)\frac{1}{e^{\beta(\varepsilon-\mu)}+1} \tag{9}$$

is λ dependent, too. Consequently, the extremum of Eq. (4) with respect to the parameter λ at fixed temperature is to be determined on the curve $\mu(\lambda,\beta)$ defined by Eq. (9). The extremum conditions with respect to the variable λ (or m_B) obtained in this way, together with Eq. (1), represent the system of coupled equations determining self-consistently the equilibrium sublattice spin *z* components.

The approximations of the above equations, corresponding to the theory of Ref. 6, consist in replacing the temperature-dependent carrier free energy by the temperature-independent mean energy. Using the notation of Ref. 6, the latter quantity is equal to $\gamma_S(\lambda)\overline{\varepsilon}$, where $\overline{\varepsilon}$ is the mean "bare" band energy at $T=0$ and the DE band-narrowing factor $\gamma_S(\lambda)$ equals

$$\gamma_S(\lambda) = \frac{1}{2} + \frac{S}{2S+1}\coth\left(\frac{2S+1}{2S}\lambda\right) \times\left[\coth(\lambda) - \frac{1}{2S}\coth\left(\frac{\lambda}{2S}\right)\right]. \tag{10}$$

Replacing in Eq. (4) the term $x\mu+\Omega$ by $\gamma_S(\lambda)\overline{\varepsilon}$, the condition for the minimum of f_B reads

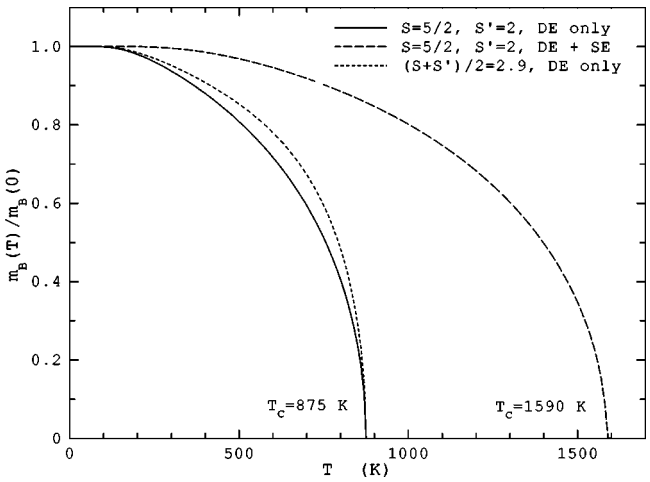

FIG. 1. Comparison of reduced magnetization of the sublattice *B* calculated with DE only, $(S+S')/2=2.9$ as in Fig. 8 of Ref. 7; DE only, $S=5/2$, $S'=2$; and with both DE and SE (exchange parameters of Ref. 7, $\overline{\varepsilon}=-0.32$ eV).

$$\beta S\overline{\varepsilon}\frac{\partial\gamma_S}{\partial m_B} - (\lambda_{BA}m_A + \lambda_{BB}m_B) + \lambda = 0, \tag{11}$$

which is to be solved together with Eqs. (1) and (3).

For the special case of zero SE, the Kubo-Ohata result[6] is obtained, namely,

$$\lambda = -\beta S\overline{\varepsilon}\frac{\partial\gamma_S/\partial\lambda}{\partial m_B/\partial\lambda}. \tag{12}$$

The opposite limitting case, $\overline{\varepsilon}=0$, gives the following relation between the equilibrium values of λ, m_B, m_A:

$$\lambda = \lambda_{BA}m_A + \lambda_{BB}m_B, \tag{13}$$

which leads to the standard MF equations for the two-sublattice ferrimagnet, if Eqs. (1) and (3) are used.

At first, we reconsider the possible application of the Kubo-Ohata theory[6] to the *B* sublattice of magnetite, as it has been attempted in Ref. 7. In the latter paper, the temperature dependence of the MF parameter λ has been calculated according to Ref. 6 using the above equations [Eqs. (10) and (12)] and $m_B(\lambda)/S = B_S(\lambda)$; the *A*-sublattice magnetization has been consecutively determined by Eq. (1) using $J_{AB} = -46$ K, $J_{AA} = -22$ K for the Heisenberg exchange constants. Very good fit of the experimental temperature dependence of the *B*-sublattice magnetization was achieved in Ref. 7 taking $T_C = 875$ K for the Curie temperature and $S'=2.9$ for the effective spin of the *B*-sublattice ions. However, this choice of the effective spin is wrong, as the spins of Fe^{3+} and Fe^{2+} ions are equal to $S=5/2$ and $S'=2$, respectively. The *B*-sublattice magnetization calculated according to Eqs. (3), (10), and (12) of the present paper is compared with that of Ref. 7 in Fig. 1. The comparison shows that the temperature dependence of m_B, calculated according to the Kubo-Ohata theory,[6] differs appreciably from that presented in Ref. 7, if the correct value $S'=2$ is used.

Besides, applying the original equations of Ref. 6 to magnetite one assumes that the Curie temperature is mainly de-

termined by the mean band energy $\bar{\varepsilon}$, characterizing the strength of the DE interaction. Assuming this point of view, the following relation between the experimental Curie temperature and the mean band energy

$$k_B T_C = -\frac{1}{45}\frac{(2S-1)(4S+1)(S+1)}{c_B S(2S+1)}\bar{\varepsilon} \tag{14}$$

is obtained from Eqs. (3) and (12) if $\lambda \to 0+$, where

$$c_B = (1-x)\frac{S+1}{3} + x\frac{S'(S'+1)}{3S}. \tag{15}$$

Substituting $x=1/2$, $S=5/2$, $S'=2$, and the value $T_C = 870$ K, $(-\bar{\varepsilon}) = 0.32$ eV is obtained. To test the (in)consistency of such a procedure, we look for the change of T_C if the SE interactions are taken into account. Using Eqs. (1) and (3), the following relation between $\bar{\varepsilon}$ and T_C results from Eq. (11):

$$1 = -\frac{\bar{\varepsilon}}{k_B T_C}\frac{1}{45}\frac{(2S-1)(4S+1)(S+1)}{c_B S(2S+1)} + \bar{\lambda}_{BA}\frac{c_A \bar{\lambda}_{AB} c_B}{1-c_A\bar{\lambda}_{AA}} + \bar{\lambda}_{BB} c_B, \tag{16}$$

where $\bar{\lambda}_{\alpha\gamma}$ are equal to the coefficients $\lambda_{\alpha,\gamma}$ for $T=T_C$ and $c_A=(S+1)/3$. Substituting the above determined $-\bar{\varepsilon}$, as well as $J_{AB}=-46$ K, $J_{AA}=-22$ K, and $J_{BB}=0$, used in Ref. 7, the Curie temperature $T_C=1590$ K results from Eq. (16); the corresponding temperature dependence of the reduced B-sublattice magnetization m_B is shown in Fig. 1. Consequently, the results based on the DE theory[6] only are changed entirely if the SE interactions are taken into account and, therefore, the latter interactions cannot be disregarded.

Accordingly, the generalized MF equations [Eqs. (1), (3), (11)] with the relevant parameters $\bar{\varepsilon}$ and $J_{\alpha\beta}$ will be considered. The estimate of the mean carrier kinetic energy in the B sublattice per ion, $\bar{\varepsilon}$, cannot be based on the known band calculation of the magnetite (e.g., Ref. 9 and the references therein), as these calculations do not take into account the electron correlations and, especially, the electron-phonon interaction that reduces strongly the electron transport in the B sublattice. In fact, the measured temperature dependence of the dc conductivity in magnetite was satisfactorily interpreted by means of the small polaron model;[10] the analysis of the optical conductivity $\sigma(\omega)$ made in this paper shows the small polaron maximum for the contribution to $\sigma(\omega)$ from the transport of the d electrons. Taking the ω dependence of the latter contribution at the room temperature from Ref. 10, the mean kinetic energy $\langle T\rangle$ of the d electrons in the B sublattice may be estimated by means of the sum rule for the real part of the optical conductivity $\sigma_1(\omega)$,[11]

$$\frac{2}{\pi}\int_0^\infty \sigma_1(\omega)\,d\omega = -\sigma_0\langle T\rangle. \tag{17}$$

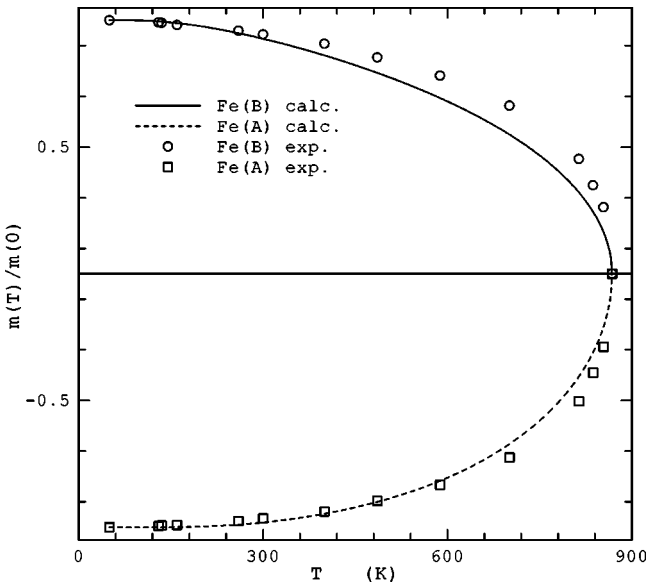

FIG. 2. Comparison of the calculated and experimental reduced magnetizations in magnetite. Parameters in units of K are $J_{AA}=-22$, $J_{AB}=-46$, $J_{BB}=-11$, $\bar{\varepsilon}=-272$.

For the magnetite the prefactor σ_0 equals to $\frac{2}{3}[(e/\hbar)a]^2$, where a is the distance between the B site and the nearest oxygen ion, $a=0.2059$ nm. Setting then $\bar{\varepsilon}=\langle T\rangle/N_B$, the estimate $\bar{\varepsilon}=-272$ K is obtained. This value of $\bar{\varepsilon}$ is two orders of magnitude smaller than the Hund's coupling constant J and, consequently, the assumption of infinite J of the DE theory[6] is justified (the discussion of the dependence of T_C on the ratio of J to the hopping constant in manganites may be found, e.g., in Ref. 12).

For the SE parameters J_{AA} and J_{AB} we take the same values as De Grave *et al.*,[7] $J_{AA}=-22$ K and $J_{AB}=-46$ K, as these values reproduce well the temperature dependence of m_A, provided that $m_B(T)$ is taken from the experiment. The remaining parameter J_{BB} is determined from Eq. (16). Using the above values of $\bar{\varepsilon}$, J_{AA}, and J_{AB} and the experimental $T_C=870$ K, it follows $J_{BB}=-11$ K. The magnetization curves calculated with this set of parameters according to Eqs. (1), (3), and (11) are compared with the experiment in Fig. 2. We also considered the fitting of the experimental curves by means of the SE parameters only. The curves calculated in this way are close to those in Fig. 2, but this fit with $\bar{\varepsilon}=0$ requires a ferromagnetic B-B interaction (positive J_{BB}), which contradicts the situation in the spinel ferrites.[13]

Relatively poor quantitative agreement between the calculated curves and the experimental ones in Fig. 2 shows that the inclusion of the DE interaction into the MF description of the ferrimagnet does not improve the calculated magnetization dependences, contrary to what was proposed in Ref. 7. To check this statement, we tried to vary the model parameters at fixed T_C to obtain better fit, but the discrepancy between the theory and the experiment remained. Most likely this discrepancy is to be attributed to the insufficiency of the MF approximation. Namely, it was shown[14] for the Heisen-

berg ferromagnet that a more rapid drop of the magnetization when approaching T_C (in comparison with the MF curves) is obtained if the short-range order effects are taken into account. We note that an inclusion of the exchange-striction term would lead to a similar effect.[15] The better agreement of the calculated $m_A(T)$ with experiment could be ascribed to the fact that the MF approximation gets better with increasing number of neighbors. The Fe^{3+} ion on the *A* site has 12 nearest magnetic neighbors, while the iron ions on the *B* sites have six nearest magnetic neighbors only.

In summary the generalization of the MF DE theory[6] by inclusion of the SE fields for a two-sublattice half-metallic ferrimagnet was presented. Applying this generalization to magnetite we found the following.

(1) The calculation of the *B*-sublattice magnetization without taking into account the SE interactions turns out to be inconsistent; the seemingly good agreement of the MF DE theory[6] with the experimental magnetization curve achieved in Ref. 7 appears only owing to the unphysically large *B*-sublattice effective spin $S=2.9$.

(2) On the other hand, the fit of the magnetization curves without the DE interaction requires the positive value of the SE interaction constant J_{BB}, in contradiction to the negative J_{BB} in similar ferrites.

The model parameters $\bar{\varepsilon}$, $J_{\alpha\beta}$ were determined on the basis of the experimental data for the optical conductivity, sublattice magnetizations, and the Curie temperature. Relatively poor quantitative agreement of the calculated and experimental magnetization curves is to be ascribed mainly to the deficiency of the MF description that does not take into account the short-range effects.

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