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Increase of Curie temperature with La doping in the double perovskite $\mathbf{Sr_{2-y}La_yFeMoO_6}$ within an electronic correlation approach

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The double perovskite compound Sr_2FeMoO_6 has a half-metallic ferromagnetic character and a high Curie temperature (420 K). Fe-Mo usually present some degree of disorder in either Fe or Mo ions, it is therefore fundamental to understand the role of electronic and structural parameters controlling the half-metallic character together with a Curie temperature as high as possible. We replaced divalent Sr^{2+} by trivalent La^{3+} ions in Sr_2FeMoO_6 system to observe the Curie temperature behavior. We present an electronic approach using the Green's functions and the renormalization perturbation expansion method, with localized Fe-spins and conduction Mo-electrons interacting with the local spins via a double-exchange-type mechanism. We also include the electronic correlations among the conduction electrons within a mean-field approximation. Our results show the density of states and the Curie temperature behavior when La concentration increases for the $Sr_{2-y}La_yFeMoO_6$ system.

Keywords: Double perovskites; Half-metallicity; Curie temperature.

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1. Introduction

The double perovskites $A_2BB'O_6$ systems (where A is an alkaline-earth, B and B' are two different transition-metal elements), have become very attractive in view of their potential spintronic applications [1, 2]. In particular, the double perovskite Sr_2FeMoO_6 (SFMO) has a substantial low-field magnetoresistance and combines half-metallic ferromagnetic character together with a high Curie temperature $T_C \sim 420$ K [3], thus giving the possibility of designing spintronics material operating at room temperature.

In the fully ordered double perovskite SFMO, FeO_6 and MoO_6 octahedron are alternating along the three crystallographic axes of the perovskite structure and Sr lies in the dodecahedral sites. Here, ferromagnetism and half-metallicity have been explained [4] from a strongly correlated picture, within this scheme Fe^{3+} ($3d^5$) localized ions are in a high-spin $S = 5/2$ configuration, the Mo^{5+} cores have $S = 1/2$ and there is one itinerant electron per formula unit (f.u.) which can hop to Fe sites only with an antiparallel orientation to the localized spin, stabilizing a ferromagnetic arrangement of local spins and fully opposite spin-polarized itinerant electrons. This formalism is consistent with ab initio calculations [3, 5, 6]. The saturation magnetization is significantly lower than 4 μ_B per f.u. ($S_{\text{total}} = 5/2 - 1/2$) expected from the polarized bands [3, 7], a discrepancy has been attributed to some degree of disorder between Fe and Mo atoms which interchange their crystallographic positions, creating the anti-sites.

Increasing the number of conduction electrons in SFMO by substitution of divalent Sr^{2+} by trivalent La^{3+} ions in $Sr_{2-y}La_yFeMoO_6$ (SLFMO) seems to be a good mechanism to increases the Curie temperature (T_C) [8, 9] because the increased number of electrons reinforces the ferromagnetic interactions between the Fe ions. However, this increase of T_C cannot be accounted for by just increasing the carrier density, it has been suggested [4] that correlations within the conduction band could play a crucial role, giving rise by itself to a ferromagnetic instability.

Experimental results [9] have obtained an important increment of the Curie temperature, reaching 490 K for SrLaFeMoO$_6$ ($y = 1$). The number of electrons per f.u. in SLFMO doped system is $1 + y$ while for the undoped SFMO compound is 1 electron per f.u. The substitution of Sr by La is associated with an increase of disorder in Fe and Mo ions, leading to a reduction of the magnetization, this fact is mainly for the increases of the magnetic moment on the Mo ions. The added electron occupies the minority spin band so that the total magnetic moment in the cell decreases by 1 μ_B. In this work, we present the Curie temperature behavior for the $Sr_{2-y}La_yFeMoO_6$ ($0 \leq y \leq 1$) doped system taking into account electronic correlation in Fe and Mo sites without disorder.

2. Model

In the ordered Sr_2FeMoO_6 system, Fe and Mo ions are contained in two interpenetrating sublattices α and β respectively, where the oxygen atoms bridge the Fe and Mo ions to form alternating FeO_6 and MoO_6 octahedra. The minority spin-down band of this half-metallic double perovskite consist of a strongly mixed Fe and Mo t_{2g} states crossing the Fermi level, while majority spin-up band, formed of t_{2g} and e_g states of Fe-d and Mo-d, shows a gap $\sim 0.5 - 0.8$ eV. In our model we will use a tight-binding Hamiltonian considering only Fe and Mo sites, mainly because of the states near the Fermi energy come from Fe and Mo d-orbitals. We will also consider a strongly correlated picture of Fe^{3+} (d^5) and Mo^{6+} (d^0) states. In the ordered case, each electron on Fe^{3+} (α) site is surrounded by Mo^{6+} (β) ions and viceversa. Since the Fe ions have a strong Hund's coupling, we take these orbitals as frozen with localized spin $\mathbf{S}_i$. Itinerant electrons from Mo move between Fe t_{2g} and Mo t_{2g} orbitals via O-p states with the same symmetry, giving three degenerate two-dimensional bands with coordination $z = 4$ and a mixed valence configuration of $Fe^{2.5+}$ and $Mo^{5.5+}$. These itinerant electrons are coupled anti-ferromagnetically to the Fe localized spins, because all the five d-orbitals are occupied by an Fe electron with the same spin direction, it means, itinerant electron with spin σ can hop only to Fe sites with antiparallel localized spins (Pauli's exclusion principle).

In Fig. 1 we show a scheme of Fe and Mo ions without disorder and considering only nearest-neighbors hopping. Fig. 1(a) shows the localized Fe (in squares) and itinerant Mo (in circles) spin configuration, while the Fig. 1(b) presents the itinerant electron that comes from the substitution of divalent Sr by trivalent La (pentagons) which goes to Mo sites. In both cases, itinerants electrons can hop to α lattice, it means, to Fe sites with spin down orientation.

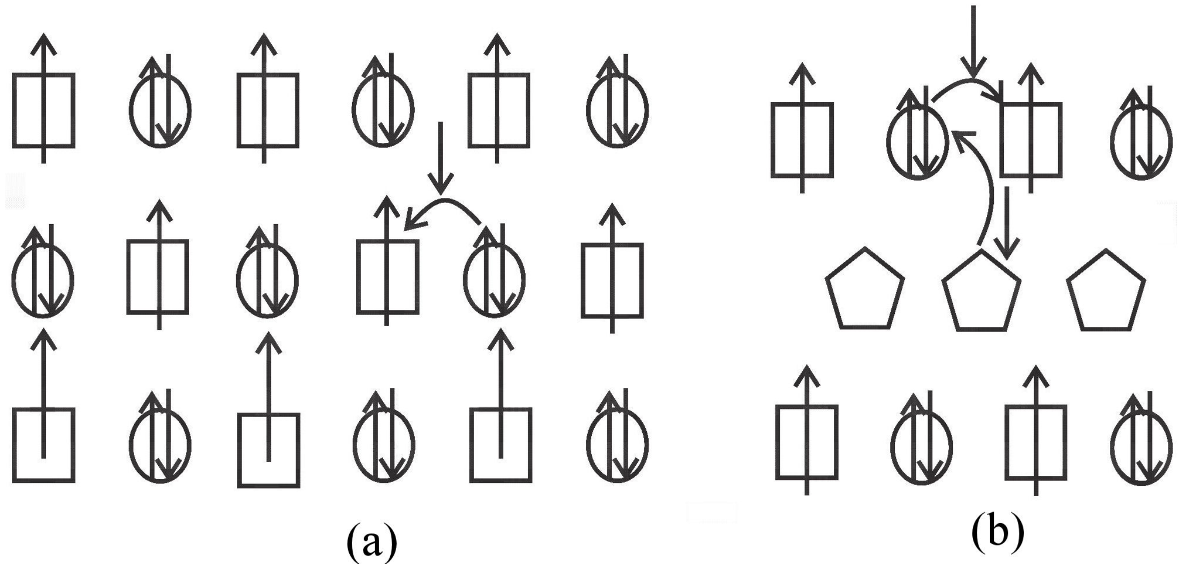

FIGURE 1. (a) Spin configuration for Fe (squares) and Mo (circles) ions in a perfect lattice, itinerant electron from Mo is shown too. (b) La (pentagons) ion provides an extra itinerant electron.

As we mentioned in the previous section, in view of studying T_C, it is essential to take into account correlations both on Fe and Mo ions. Contrary to the assertion of Brey *et al*. [10], on Fe sites the inter-band is the only interaction intervening, it means, only one spin direction being possible on sites with $+$ or $-$ local spins. The intra-atomic correlations among itinerant electrons are given by

$$\begin{aligned} H_c^{Mo} &= (U^{Mo} + 2J^{Mo}) \sum_{i,\nu} n_{i\nu\uparrow} n_{i\nu\downarrow} \\ &\quad + U^{Mo} \sum_{i,\nu,\nu'\neq\nu,\sigma} n_{i\nu\uparrow} n_{i\nu'\downarrow} \\ &\quad + (U^{Mo} - J^{Mo}) \sum_{i,\nu,\nu'\neq\nu,\sigma} n_{i\nu\sigma} n_{i\nu'\sigma}, \end{aligned} \tag{1}$$

$$H_c^{Fe} = (U^{Fe} - J^{Fe}) \sum_{j,\nu,\nu'\neq\nu,\sigma} n_{j\nu\sigma} n_{j\nu'\sigma}, \tag{2}$$

ν and ν' label the three t_{2g} orbitals and i, j correspond to sites occupied by Mo and Fe. Site energies are calculated using mean-field approximation to obtain the renormalized energies $\tilde{E}_{Fe,\sigma}$ and $\tilde{E}_{Mo,\sigma}$, it means,

$$\tilde{E}_{Fe,\sigma} = E_{Fe} + \frac{2}{3} U_{eff}^{Fe} \langle n_{\alpha,\sigma}^{Fe} \rangle, \tag{3}$$

$$\begin{aligned} \tilde{E}_{Mo,\sigma} &= E_{Mo} + \left(U^{Mo} + \frac{2}{3} J^{Mo} \right) \langle n_{\beta,-\sigma}^{Mo} \rangle \\ &\quad + \frac{2}{3} U_{eff}^{Mo} \langle n_{\beta,\sigma}^{Mo} \rangle, \end{aligned} \tag{4}$$

where $\tilde{E}_{Fe,\uparrow}$ ($\tilde{E}_{Fe,\downarrow}$) refers to Fe sites with localized spin $-(+)$. $\langle n^{Fe}_{\alpha,\sigma}\rangle$, $\langle n^{Mo}_{\beta,\sigma}\rangle$ are the occupation numbers of electrons σ on Fe and Mo sites;

$$U^{Mo}_{eff} = U^{Mo} - J^{Mo},$$

$$U^{Fe}_{eff} = U^{Fe} - J^{Fe}$$

and we used $\langle n_{i\nu\sigma}\rangle = \langle n_{i\sigma}\rangle/3$ due to the degeneracy of the three t$_{2g}$ orbitals. We shall take

$$U^{Fe}_{eff} = 3w, \quad U^{Mo}_{eff} = w, \quad J^{Mo} = 0.1w$$

since these values have been shown to provide good results in disordered compound [11, 12].

From the local Green's functions within the renormalized perturbation expansion method [4, 13], we calculate the density of states per orbital on Fe and Mo sites for itinerant electrons. In an alternating Bethe lattice in the limit of infinity coordination number, $z \to \infty$, where zt^2 scales as $w^2/4$, w being half the bandwidth. The local average Green's functions take the dynamical mean-field form

$$G^{-1}_{ii,\sigma} = \omega - \varepsilon_i - \sum_{l\neq i} t^2 G_{ll,\sigma},$$

where ε_i is the corresponding on-site energy and the summation is over all nearest neighbors sites.

Expressions for the Green's functions with an itinerant electron are given as: for spin $\downarrow$

$$G^{\alpha Fe}_{\downarrow +} = \frac{1}{\omega - \tilde{E}_{Fe,\downarrow} - \frac{w^2}{4} G^{\beta Mo}_{\downarrow}}, \tag{5}$$

$$G^{\beta Mo}_{\downarrow} = \frac{1}{\omega - \tilde{E}_{Mo,\downarrow} - \frac{w^2}{4}\nu_+ G^{\alpha Fe}_{\downarrow +}}, \tag{6}$$

and for spin $\uparrow$

$$G^{\alpha Fe}_{\uparrow -} = \frac{1}{\omega - \tilde{E}_{Fe,\uparrow} - \frac{w^2}{4} G^{\beta Mo}_{\uparrow}}, \tag{7}$$

$$G^{\beta Mo}_{\uparrow} = \frac{1}{\omega - \tilde{E}_{Mo,\uparrow} - \frac{w^2}{4}\nu_- G^{\alpha Fe}_{\uparrow -}}, \tag{8}$$

where $\tilde{E}_{Fe,\sigma}$ and $\tilde{E}_{Mo,\sigma}$ denote the effective Fe and Mo site energies respectively including electronic correlation, we also introduce the probability $\nu_\pm = (1 \pm m)/2$ that an Fe ion has its localized spin $+$ or $-$.

In the ordered state, the effective charge transfer energy in the ferromagnetic state for $\downarrow$ spin electrons is defined by Δ,

$$\begin{aligned}\Delta &= \tilde{E}_{Mo,\downarrow} - \tilde{E}_{Fe,\sigma} \\ &= E_{Mo} - E_{Fe} + \frac{2}{3}U^{Mo}_{eff}\langle n^{Mo}_{\beta,\downarrow}\rangle - \frac{2}{3}U^{Fe}_{eff}\langle n^{Fe}_{\alpha,\downarrow}\rangle. \end{aligned} \tag{9}$$

Here, $E_{Mo} - E_{Fe} = \Delta_0$, where Δ_0 is the bare charge transfer energy for the non correlated case.

The charge transfer energy in SFMO is quite small [4], therefore in this paper we consider $\Delta = 0$ in order to reproduce the mixed-valence character in Fe$^{2.5+}$ and Mo$^{5.5+}$ observed experimentally [14, 15]. For $\Delta = 0$ in Eq. (9) and considering the values of the correlations parameters mentioned above, we obtain $\Delta_0 = 2nw/3$ for any concentration n. In particular, for $n = 1$ we have the SFMO compound and $\Delta_0 = 2w/3$.

The total density of states

$$\rho(m, \omega, \Delta_0) = \sum_\sigma [\rho^{Fe}_\sigma(m, \omega, \Delta_0) + \rho^{Mo}_\sigma(m, \omega, \Delta_0)], \tag{10}$$

where ρ^{Fe}_σ and ρ^{Mo}_σ denote the partial density of states for Fe and Mo sites respectively, allows us to determine the Fermi energy (E_F) using the expression for the number of particles

$$n = 3\int_{-\infty}^{E_F} \rho(m, \omega, \Delta_0)\, d\omega,$$

where the number 3 is due to the degeneracy of the three t$_{2g}$ orbitals. The kinetic energy of the conduction electrons is determined by

$$E_{kin}(m, \Delta_0) = 3\int_{-\infty}^{E_F} \rho(m, \omega, \Delta_0)\,\omega\, d\omega.$$

To obtain the thermodynamical values of $m(T)$ we need to calculate the minimum of the free energy

$$F = E_{kin}(m, \Delta_0) - TS(m),$$

where $S(m)$ is the entropy term of the local spins,

$$S(m) = \ln(2) - \nu_+ \ln(2\nu_+) - \nu_- \ln(2\nu_-),$$

which is consistent with our approximation that these are either up or down. Finally, Curie temperature T_C is calculated from $m(T_C) = 0$ [4].

3. Results and discussion

In Fig. 2 we show the density of states for the doping Sr$_{2-y}$La$_y$FeMoO$_6$ system, here the number of carriers increases by replacing divalent Sr^{2+} by trivalent La^{3+} as $n = 1 + y$ [9]. We keep $\Delta_0 = 2w/3$ as in pure Sr$_2$FeMO$_6$ and vary only $n(y)$. Figure 2 also shows a Fermi energy represented by dashed line and the results of the density of states for $y = 0, 0.5, 1.0$. In the ferromagnetic case ($m = 1$) the system has a half-metallic character because electron adds occupies the minority spin band as we can see in Fig. 2(a), and also presents a gap in the middle of the band which reflects the fact that $\Delta \neq 0$ due to the correlations although $\Delta = 0$ for $y = 0$ ($n = 1$). In Fig. 2(b) we observe how the density of states for the paramagnetic state ($m = 0$) goes to higher energies. In both cases, ferromagnetic and paramagnetic states, Fermi energy goes toward the gap.

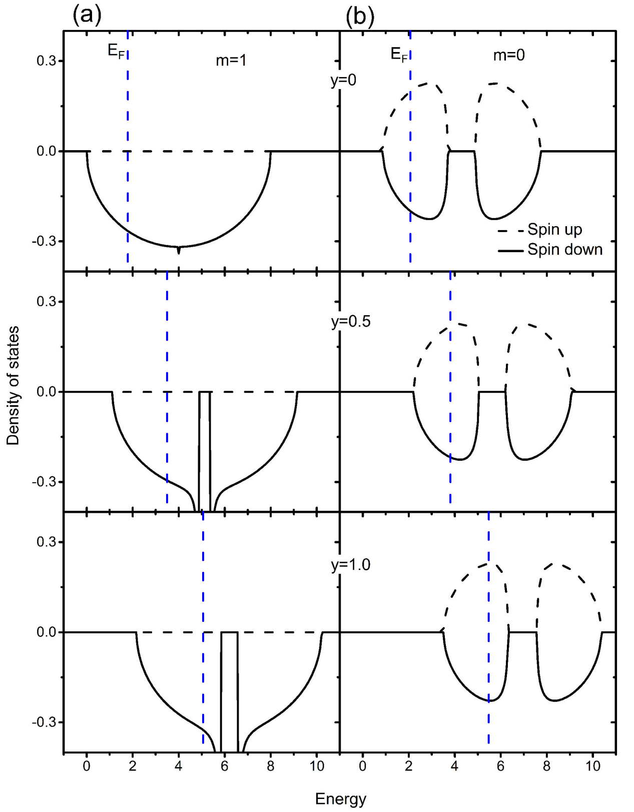

FIGURE 2. Density of states versus energy for (a) ferromagnetic ($m = 1$) and (b) paramagnetic ($m = 0$) states as function of La concentration (y). Dashed lines indicate the Fermi energy (E_F). Electronic correlation parameters are $U_{eff}^{Fe} = 3w$, $U_{eff}^{Mo} = w$ and $J^{Mo} = 0.1w$.

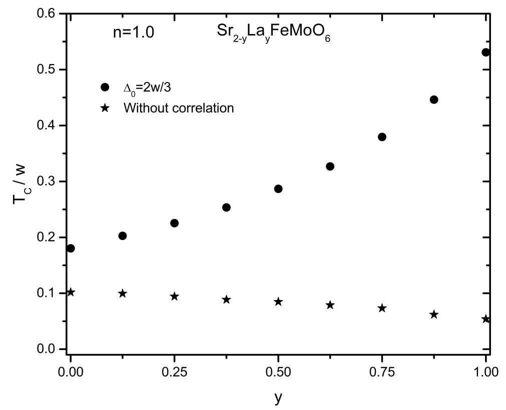

FIGURE 3. Curie temperature as function of La concentration (y) for $Sr_{2-y}La_yFeMoO_6$. The electronic correlation parameters are the same as those in Fig. 2.

In Fig. 3 we present the behavior of Curie temperature as function of La doping y for ($0 \leq y \leq 1$) as in the experimental results [9]. Curie temperature increases as increasing La concentration reaching its highest value for $y = 1$, this values for $\Delta_0 = 2w/3$ (Δ_0 associated with Sr_2FeMoO_6) is by far too large as compared with experimental results. However, we have to remember that La doping induces disorder between Fe and Mo sites [9] which is detrimental to T_C. This disorder is because the Fe atoms migrate to the Mo sites in order to balance the charge introduced by La doping into the cell, the number of oxygens atoms should be constant to keep the crystalline structure [16]. Considering disorder, the variation of T_C as function of y will certainly be slower than obtaining here. In our model, it is posible to introduce disorder [12] which will be very relevant on the calculation of the Curie temperature, unfortunately it is not yet known with certainty how disorder varies with La doping in these systems. Regarding the correlated ($\Delta_0 = 2w/3$) and non-correlated ($\Delta_0 = 0$) results we observe a substantial increase of T_C due to the correlations effects on Fe and Mo sites.

In summary, substitution of Sr^{2+} by La^{3+} increases itinerant electrons in the $Sr_{2-y}La_yFeMoO_6$ compound which reinforces the ferromagnetic state and increases the T_C. We have presented an electronic correlation study of this double perovskite compound within the dynamical mean-field approach. We obtained that our calculation of T_C in $Sr_{2-y}La_yFeMoO_6$ for small La concentration, where disorder is not dominant and using $\Delta_0 = 2w/3$, is in qualitative agreement with experimental results.

Acknowledgments

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