Increase of Curie temperature with La doping in the double perovskite 
$\text{Sr}_{2-y}\text{La}_{y}\text{FeMoO}_6$ within an electronic correlation approach

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The double perovskite compound $\text{Sr}_2\text{FeMoO}_6$ 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 $\text{Sr}_2\text{FeMoO}_6$ 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 $\text{Sr}_{2-y}\text{La}_y\text{FeMoO}_6$ system.

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

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1. Introduction

The double perovskites $\text{A}_2\text{BB’O}_6$ 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 $\text{Sr}_2\text{FeMoO}_6$ (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, $\text{FeO}_6$ and $\text{MoO}_6$ 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 $\mu_B$ 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 $\text{Sr}_{2-y}\text{La}_y\text{FeMoO}_6$ (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 Sr$\text{LaFeMoO}_6$ ($y = 1$). 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 $\mu_B$.

In this work, we present the Curie temperature behavior for the $\text{Sr}_{2-y}\text{La}_y\text{FeMoO}_6$ ($0 \leq y \leq 1$) doped system taking into
account electronic correlation in Fe and Mo sites without disorder.

2. Model

In the ordered Sr$_2$FeMoO$_6$ system, Fe and Mo ions are contained in two interpenetrating sublattices $\alpha$ and $\beta$ 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$^{3+}$ ($\alpha$) site is surrounded by Mo$^{6+}$ ($\beta$) ions and vice versa. Since the Fe ions have a strong Hund’s coupling, we take these orbitals as frozen with localized spin $S_i$. 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 $\sigma$ 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, itinerant electrons can hop to $\alpha$ lattice, it means, to Fe sites with spin down orientation.

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

$$H_{Mo}^c = (U_{Mo}^c + 2J_{Mo}^c) \sum_{i,\nu} n_{i\nu \uparrow} n_{i\nu \downarrow}$$

$$+ U_{Mo}^c \sum_{i,\nu,\nu' \neq \nu,\sigma} n_{i\nu \uparrow} n_{i\nu' \downarrow}$$

$$+ (U_{Mo}^c - J_{Mo}^c) \sum_{i,\nu,\nu' \neq \nu,\sigma} n_{i\sigma \nu} n_{i\nu' \sigma},$$

(1)

$$H_{Fe}^c = (U_{Fe}^c - J_{Fe}^c) \sum_{j,\nu,\nu' \neq \nu,\sigma} n_{j\nu \sigma} n_{j\nu' \sigma},$$

(2)

$\nu$ and $\nu'$ 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,

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

(3)

$$\tilde{E}_{Mo,\sigma} = E_{Mo} + \left( U_{Mo}^c + \frac{2}{3} J_{Mo}^c \right) \langle n_{\beta,-\sigma} \rangle + \frac{2}{3} U_{eff}^{Mo} \langle n_{\beta,\sigma} \rangle,$$

(4)

![Figure 1](image.png)

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

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

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

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

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

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 $x^{z}$ scales as $w^{2}/4$, $w$ being half the bandwidth. The local average Green’s functions take the dynamical mean-field form

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

where $\varepsilon_i$ 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 $\downarrow$

$$G_{\downarrow}^{Fe} = \frac{1}{\omega - \tilde{E}_{Fe,\downarrow} - \frac{w^2}{4} G_{\downarrow}^{Mo}},$$

$$G_{\downarrow}^{Mo} = \frac{1}{\omega - \tilde{E}_{Mo,\downarrow} - \frac{w^2}{4} \nu \nu_{\downarrow} G_{\downarrow}^{Fe}},$$

and for spin $\uparrow$

$$G_{\uparrow}^{Fe} = \frac{1}{\omega - \tilde{E}_{Fe,\uparrow} - \frac{w^2}{4} G_{\uparrow}^{Mo}},$$

$$G_{\uparrow}^{Mo} = \frac{1}{\omega - \tilde{E}_{Mo,\uparrow} - \frac{w^2}{4} \nu \nu_{\uparrow} G_{\uparrow}^{Fe}},$$

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 $+\sigma$ or $-\sigma$.

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

$$\Delta = \tilde{E}_{Mo,\downarrow} - \tilde{E}_{Fe,\sigma} = E_{Mo} - E_{Fe} + \frac{2}{3} U_{eff}^{Mo} \langle n_{\beta,\downarrow} \rangle - \frac{2}{3} U_{eff}^{Fe} \langle n_{\alpha,\downarrow} \rangle. \quad (9)$$

Here, $E_{Mo} - E_{Fe} = \Delta_0$, where $\Delta_0$ 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

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

where $\rho^{Fe}_{\sigma}$ and $\rho^{Mo}_{\sigma}$ 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$_2$FeMoO$_6$ 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 $U_{\text{eff}} = 3w$, $V_{\text{eff}} = w$ and $J^{\text{Mo}} = 0.1w$.

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 $\Delta_0 = 2w/3$ ($\Delta_0$ associated with Sr$_2$FeMoO$_6$) 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 possible 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$_y$FeMoO$_6$ 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$_y$FeMoO$_6$ for small La concentration, where disorder is not dominant and using $\Delta_0 = 2w/3$, is in qualitative agreement with experimental results.

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