

Spin polarization in ordered and disordered double-perovskites

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Abstract

Recently, the double perovskites family $A_2MM'O_6$ (A being a divalent or trivalent cation and M, M' two transition metals) has attracted considerable interest with the view of using these materials in spin electronics. This has been triggered but the fact that some members, in particular $SrFe_2MoO_6$, present a Curie temperature T_C above room temperature and complete spin polarization. In view of improving the performances of these materials, 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. Fe–Mo double perovskites usually present some degree of Fe/Mo disorder which generally increases with the doping. We present a model considering a correlated electron picture with localized Fe-spins and conduction electron originating from the metals M and M' interacting with the local spins via a double-exchange type mechanism. This succeeds in stabilizing a ferromagnetic ground state in the absence of disorder. We will examine how electron disorder affect the ground state properties with a particular emphasis on the spin polarization.

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Half-metallic materials, in which only one-spin direction is present at the Fermi level, are extensively searched for in view of spintronics applications based on magnetoresistance (MR) effects. A lot of attention has focused on the double-perovskite Sr_2FeMoO_6 because of its high Curie temperature $T_C \sim 400$ K and substantial MR at room temperature as compared to manganites [1]. The low-field MR in granular materials is dominated by the intergrain spin-dependent tunneling magnetoresistance (TMR) through insulating grain boundaries, reflecting the spin polarization of the ferromagnetic grains. Of course TMR is favoured by the alignment of the magnetization of the neighbouring grains under application of the magnetic field. According to Inoue and Maekawa [2], the MR (defined as $MR = \Delta\rho/\rho_0 = (\rho(H) - \rho(0))/\rho(0)$, $\rho(H)$ being the field-dependent resistance as function of the applied field H) is given by

$$MR = -\frac{P^2 m^2}{1 + P^2 m^2}, \quad (1)$$

where $P = (N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$ represents the spin-polarization of the grains, N_\uparrow and N_\downarrow are the up and down electron densities of states at the Fermi level; $m = M(H)/M_S$ is the reduced magnetization, M_S being the saturation magnetization.

A high degree of spin polarization P is of great importance to reach large MR which can be at most -50% for $P = 1$, when the saturation magnetization is reached. The half-metallic fully polarized character of ordered Sr_2FeMoO_6 has been predicted by band-structure calculations [1]. However, to our knowledge, there are very few direct experimental measures of the spin polarization. $P \approx 0.85$ has been determined in a $SrFeMoO_6$ -based tunnel junction device [3] and in $(BaSr)_2FeMoO_6$ granular samples [4] from expression (1). Such a value can be attributed to *mis-site disorder* in which some Fe and Mo interchange their positions and is consistent both with a lower T_C and a saturation magnetization lower than the expected value of $4\mu_B$ in the ordered system. All samples present different degrees of disorder. The effect of disorder on the magnetization has been investigated in off-stoichiometric $Sr_2Fe_{1+x}Mo_{1-x}O_6$ ($-1 < x < 0.25$) showing the depolarization of the conduction band [5]. The TMR is

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strongly reduced by the disorder and suppressed in highly disordered samples [6,7]. It can be inferred that disorder is detrimental to the half-metallic character, giving rise to up-spin states at the Fermi energy thus depolarizing the conduction band. In the fully ordered case, half-metallicity can be understood on the basis of a simple picture with Fe-3d⁵ forming high-spin $S = \frac{5}{2}$ localized spins and one itinerant electron hopping between Fe and Mo [8]. All five Fe d-orbitals of one spin channel being occupied, itinerant electrons can hop to Fe sites only if its spin is antiparallel to the local spin; thus the hopping stabilizes a ferromagnetic arrangement of the local spins and also leads to a complete opposite spin polarization. The robustness of the ferromagnetic state is determined by the Fe–Mo charge transfer energy Δ and the hopping t [8,9]. It has been shown that small charge transfer is realized in Sr₂FeMoO₆ [8]. In the disordered case, the presence of mis-site disorder opens up Mo–Mo hopping channel for both spins up and down thereby depolarizing the conduction band. This occurs through *new bonding states* essentially Mo appearing at the Fermi energy. In this paper we clarify the evolution of the density of states and the resulting spin polarization as function of the disorder.

The perfectly ordered lattice of SrFeMoO₆ consists of alternating Fe and Mo along the three cubic axis of the perovskite structure. So, we define the order parameter a ($\frac{1}{2} < a < 1$) as the probability to find Fe and Mo in its correct position, respectively, sublattice α and β of the ordered structure i.e. $n_{\text{Fe}}^{\alpha} = n_{\text{Mo}}^{\beta} = a$ while the proportion of Fe and Mo in the wrong position or antisites (AS) are $n_{\text{Fe}}^{\beta} = n_{\text{Mo}}^{\alpha} = 1 - a$. In a disordered state, both Fe(AS)–O–Fe and Mo(AS)–O–Mo bonds are generated. Fe–Fe bonds are antiferromagnetically coupled [5], so we consider all Fe ^{α} to be \uparrow (+) and all Fe ^{β} \downarrow (–).

We treat the Green's functions within the dynamical mean field approach corresponding to the limit of infinite coordination and $4t^2$ scaled as $w^2/4$ [8]:

$$G_{\downarrow+}^{\alpha\text{Fe}} = \frac{1}{\omega - E_{\text{Fe}} - (w^2/4)aG_{\downarrow}^{\beta\text{Mo}}}, \quad (2)$$

$$G_{\downarrow}^{\beta\text{Mo}} = \frac{1}{\omega - E_{\text{Mo}} - (w^2/4)aG_{\downarrow+}^{\alpha\text{Fe}} - (w^2/4)(1-a)G_{\downarrow}^{\alpha\text{Mo}}}, \quad (3)$$

$$G_{\downarrow}^{\alpha\text{Mo}} = \frac{1}{\omega - E'_{\text{Mo}} - (w^2/4)aG_{\downarrow}^{\beta\text{Mo}}}, \quad (4)$$

and

$$G_{\uparrow-}^{\beta\text{Fe}} = \frac{1}{\omega - E'_{\text{Fe}} - (w^2/4)(1-a)G_{\uparrow-}^{\alpha\text{Mo}}}, \quad (5)$$

$$G_{\uparrow}^{\alpha\text{Mo}} = \frac{1}{\omega - E'_{\text{Mo}} - (w^2/4)(1-a)G_{\uparrow-}^{\beta\text{Fe}} - (w^2/4)aG_{\uparrow}^{\beta\text{Mo}}}, \quad (6)$$

$$G_{\uparrow}^{\beta\text{Mo}} = \frac{1}{\omega - E_{\text{Mo}} - (w^2/4)(1-a)G_{\uparrow}^{\alpha\text{Mo}}}. \quad (7)$$

E_{Fe} , E_{Mo} are Fe and Mo site energies on the right sublattice, $E_{\text{Mo}} - E_{\text{Fe}} = \Delta$ represents the charge transfer energy in the ordered lattice. Due to different environment, it has been pointed out [10] that AS energies E'_{Fe} and E'_{Mo} might be different. A view supported by the estimate of the diagonal energies from ab initio calculations [11], AS Fe is found to have an energy that is about 1 eV higher than the energy of the Fe at the regular site, but the effect of the environment seems however much weaker for Mo [12], so we will take $E'_{\text{Mo}} = E_{\text{Mo}}$. Considering a Madelung-like contribution from the nearest charges we can write, $E'_{\text{Fe}} = E_{\text{Fe}} + \delta(2a - 1)$, $E_{\text{Mo}} = E_{\text{Fe}} + \Delta - \delta(1 - a)$; so we take $\Delta = 0$ [8] and $\delta = w$, since $w = 1$ eV is a good estimation from band structure calculations. $E_{\text{Fe}} = 0$ will be our reference energy.

We consider only the nearest-neighbour hoppings between the two different sublattices. w and w' being the bandwidths corresponding to Fe–Mo and Mo–Mo hopping, respectively, $w' = qw > w$ due to the larger extension of the Mo 5d states; $q \sim 2-2.5$ appears reasonable and compatible with some ab initio calculations, we will take $q = 2$. The evolution of the density of states with the

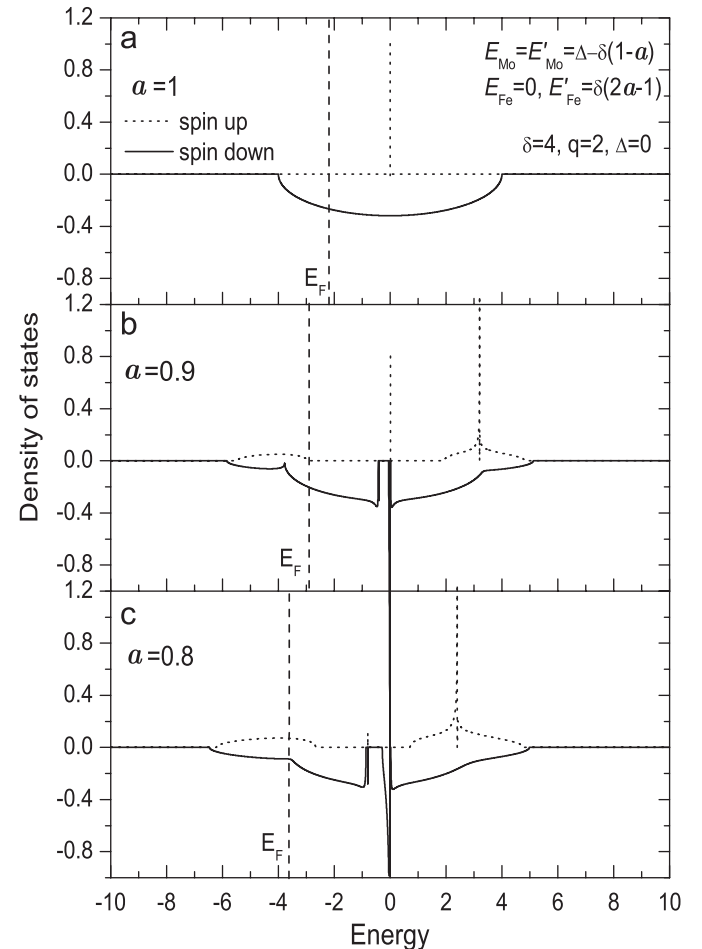


Fig. 1. Evolution of the density of states with the disorder.

amount of disorder is shown in Fig. 1 (energies are in units of t , $w = 4$). Fig. 1a represents the density of states for the ordered half-metallic state ($a = 1$), corresponding to the partially filled minority Fe–Mo spin- \downarrow band. One has also a δ -peak Mo spin- \uparrow above the Fermi energy at $\omega = \Delta$ corresponding to the unoccupied narrow band seen in the band structure calculations, the finite bandwidth being due to the Mo–Mo hopping within the sublattice β not included in our calculation. Fig. 1b–c illustrates the behaviour with disorder $a = 0.9$ and $a = 0.8$. This shows the appearance of bonding and antibonding states around energies $\omega = \pm w'/2$, resulting from $\text{Mo}^\beta\text{--Mo}^\alpha$ hopping. These *new* small bands are particularly well defined in the spin- \uparrow channel, they are only weakly mixed with the Fe^β states at E'_{Fe} and have a spectral weight $(1 - a)$. These states are also present in the spin- \downarrow channel at the bottom and the top of the main Fe–Mo band but there is a stronger admixture with $\text{Fe}^\alpha\text{--Mo}^\beta$ states. *The bonding states are partially filled giving rise to the spin depolarization of the conduction band.* It is important to mention that this is quite different from the rigid band shift recently proposed [13]. More complete and quantitative results will be presented elsewhere [14]. We see that the degree of spin depolarization depends on the position of the Mo states which is not precisely known; the electronic occupation on the AS Mo is large, so that the intra-atomic correlations U even moderate $\sim 1\text{--}2\text{ eV}$ may play an important role in shifting E'_{Mo} towards higher energies. However, the present

results illustrate how mis-sites disorder inevitably reduces the spin polarization.

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