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Theoretical calculations of valence states in Fe-Mo compounds

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Abstract. The half-metallic ferromagnetic double perovskite compound $\text{Sr}_2\text{FeMoO}_6$ is considered as an important material for spintronic applications. It appears to be fundamental to understand the role of electronic parameters controlling the half-metallic ground state. Fe-Mo double perovskites usually present some degree of Fe/Mo disorder which generally increases with doping. In this work, we study the valence states of Fe-Mo cations in the off-stoichiometric system $\text{Sr}_2\text{Fe}_{1+x}\text{Mo}_{1-x}\text{O}_6$ ($-1 \leq x \leq 1/3$) with disorder. Our results for Fe and Mo valence states are obtained using the Green functions and the renormalization perturbation expansion method. The model is based on a correlated electron picture with localized Fe-spins and conduction Mo-electrons interacting with the local spins via a double-exchange-type mechanism.

1. Introduction

Half-metallic materials, in which only one-spin direction is present at the Fermi level, have been investigated in view of their attractive properties for potential spintronic applications [1] and as potential candidates for memory devices by virtue of their large magnetoresistance (MR). The double perovskite $\text{Sr}_2\text{FeMoO}_6$ (SFMO) combines half-metallic ferromagnetic character with a high Curie temperature $T_c = 400\text{K}$ and substantial low-field MR [2]. The enhanced T_c , complete spin polarization and substantial low-field magnetoresistance (LFMR) at room temperature are compared to those of manganites and generate a great interest for magnetoelectronic applications [3].

In the fully ordered double perovskite structure, Fe and Mo occupy two interpenetrating sublattices, respectively α and β , in a rock-salt structure. Oxygen atoms bridge the Fe and Mo ions to form alternating FeO_6 and MoO_6 octahedra. The ferromagnetism and half-metallicity in ordered SFMO have been understood [4] on the basis of a strongly correlated picture, with Fe^{3+} ($3d^5$) localized high-spin $S = 5/2$ and Mo^{6+} cores together with one conduction electron (per formula unit) which can hop between Mo and Fe sites (S) only with an



antiparallel orientation to the localized spins (Hund's coupling). The Fe-Mo hopping stabilizes a ferromagnetic arrangement of the local spins and also leads to the opposite spin polarization of the conduction electrons, in agreement with *ab initio* calculations [2, 5, 6]. The energy Δ needed to transfer an electron from Fe to Mo (charge transfer energy in unit of the bandwidth w) is the key parameter determining the Curie temperature T_c . Therefore ordered SFMO is expected to have a full polarization of the conduction electrons ($P = 1$) (half-metallic) and a saturation magnetization of $4\mu_B$, however, experimental measurements give $P \approx 0.85$ in a SFMO-based tunnel junction device [7] and a saturation magnetization usually lower than the expected value in the ordered system [2, 8, 9]. These deviations can be attributed to antisite disorder in which some Fe and Mo atoms interchange their positions and is consistent with a lowering of T_c . To understand how the presence of AS affects the magnetic properties, the off-stoichiometric system $\text{Sr}_2\text{Fe}_{1+x}\text{Mo}_{1-x}\text{O}_6$ ($-1 \leq x \leq 0.25$) has been investigated [10] based on the simple idea that off-stoichiometry generates Fe(S)-O-Fe(AS) (Fe-rich regime $x > 0$) or Mo(S)-O-Mo(AS) (Mo-rich regime $x < 0$) nearest neighbors (n.n.) pairs even in the absence of disorder. Disorder produces both Fe(S)-O-Fe(AS) and Mo(S)-O-Mo(AS) pairs, the Mo(S)-O-Mo(AS) pairs play a fundamental role as they open new hopping channels available to both spin directions, thereby depolarizing the conduction band [11, 12]. The saturation magnetization shows the remarkable behavior of first increasing with x for $x < 0$ up to $x = 0$ and then decreasing for $x > 0$ [10], which can be qualitatively understood in terms of Fe local spins. The decrease for $x > 0$ has a very strong implication as it can be explained unambiguously considering that n.n. Fe(S) and Fe(AS) local spins are coupled antiferromagnetically. The electronic structure of the system $\text{Sr}_2\text{Fe}_{1+x}\text{Mo}_{1-x}\text{O}_6$ has been studied [13] using first-principles density functional theory DFT+U, with an effective on-site correlation energy only on Fe sites, though it has been shown [12] that electronic interaction in Mo sites is also important when disorder is included. In this work, we focus on the calculation of Fe and Mo valence states resulting from disorder in the above off-stoichiometric system $\text{Sr}_2\text{Fe}_{1+x}\text{Mo}_{1-x}\text{O}_6$ ($-1 \leq x \leq 1/3$) following the correlated picture of Carvajal et al.[4] for SFMO. We calculate the number of conduction electrons on Fe and Mo sites, n_α^{Fe} , n_β^{Mo} , the valence being defined as the core charge minus the local electronic charge.

2. Model details

We assume the simple uncorrelated distribution of AS defects (no short range order) and define the order parameter a as the probability for Fe and Mo to occupy their correct positions, respectively sites α and β in the ordered structure. For $x \geq 0$, we have the occupation probabilities, $p_{Mo}^\beta = a(1-x)$, $p_{Fe}^\beta = 1 - a(1-x)$, $p_{Fe}^\alpha = x + a(1-x)$ and $p_{Mo}^\alpha = (1-a)(1-x)$. Similarly for $x \leq 0$, we have $p_{Fe}^\alpha = a(1+x)$, $p_{Mo}^\alpha = 1 - a(1+x)$, $p_{Mo}^\beta = a(1+x) - x$ and $p_{Fe}^\beta = (1-a)(1+x)$. Of course a is irrelevant for $x = -1$. As in SFMO we consider that Fe remains in the Fe^{3+} ($3d^5$) $S = 5/2$ localized spins state and Mo as Mo^{6+} ($4d^0$) cores. In addition, $n = 1 - 3x$ electrons ensure charge neutrality, these electrons are itinerant providing the metallic behavior of the system. This explains the limit $x = 1/3$ above which Fe can no longer retain its 3+ valency as Mo cannot take a valency larger than 6+. We incorporate intra-atomic correlations both for Fe and Mo itinerant electronic states[12, 14]. For Mo both intra and inter-orbitals correlations $U^{Mo} + 2J^{Mo}$, U^{Mo} , $U_{eff}^{Mo} = U^{Mo} - J^{Mo}$ are present while for Fe intervene only interactions between the same spin direction on different orbitals U_{eff}^{Fe} since only one spin direction is possible on Fe sites. In mean-field the correlations renormalize self-consistently the Fe and Mo site energies E_{Fe} , E_{Mo} as \tilde{E}_{Fe} , \tilde{E}_{Mo} and consequently the charge transfer energy $\Delta \rightarrow \tilde{\Delta}$. All the values of parameters are taken as a previous work[14]. In particular, the charge transfer energy Δ is taken in order to reproduce the mixed-valence character 2.5+ for Fe and 5.5+ for Mo in the ordered SFMO ($x = 0$, $a = 1$) as suggested experimentally[15, 16], therefore we choose $\tilde{\Delta} = 0$.

In order to obtain the density of states (DOS) per orbital for itinerant electrons on Fe and Mo sites, we calculate the local Green's functions within the renormalized perturbation expansion method [17]. In an alternating Bethe lattice in the limit $z \rightarrow \infty$ and zt^2 scaled as $w^2/4$, the local average Green's functions take the dynamical mean-field (DMF) form $G_{ii,\sigma}^{-1} = \omega - \varepsilon_i - \sum_{l \neq i} t^2 G_{ll,\sigma}$, where ε_i is the corresponding on-site energy and the summation is over all nearest neighbors sites. In the presence of disorder this requires to take an average over the different n.n. atomic configurations, thus simply considering the probabilities p_{Fe}^α , p_{Mo}^α , etc. defined above. This averaging procedure is an extension similar to the usual coherent potential approximation in the case of random alloys [18]. It includes both the disorder of the site energies and the difference in hopping parameters.

3. Results and discussion

In Figure 1 we show the density of states over the whole range of disorder for $x = 0.1$ and $x = -0.1$. In Figure 1(a), for the Fe-rich regime ($x = 0.1$) and in the order case, $a = 1$, we observed that spin up electrons cannot move because all α -sites are occupied by Fe ions (localized spin up), so the ground state remains half-metallic. However, when disorder increases, $1 < a \leq 0.5$, states appear with spin up resulting from Mo(AS)-Fe(AS) hoppings and the system losing its half-metallic character. In Fe-deficient regime ($x = -0.1$), Figure 1(b) shows a quite different behavior, states with spin up appear as a result of Mo-Mo hoppings, the system losing its half-metallic character.

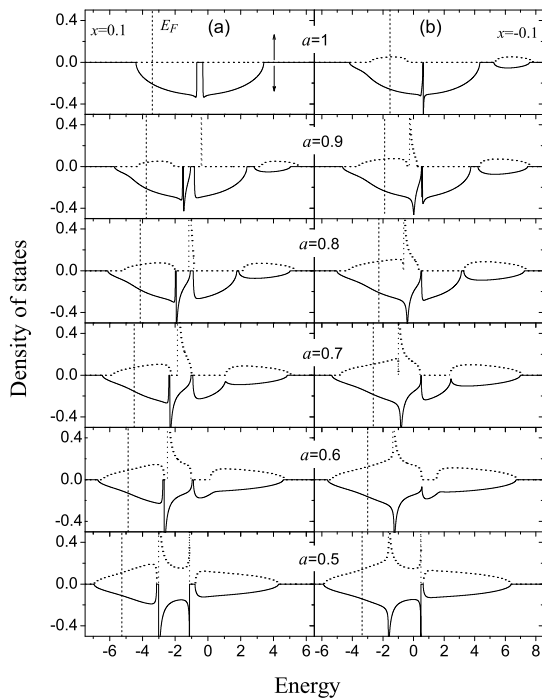


Figure 1. Evolution of the density of states as a function of disorder, a : (a) in the Fe-rich regime, $x = 0.1$; (b) in the Fe-deficient regime, $x = -0.1$. Dashed lines indicate the Fermi energy, E_F . Parameters of electronic correlation are defined by $U_{eff}^{Mo} = w$, $U_{eff}^{Fe} = 3w$ and $U^{Mo} = U_{eff}^{Mo} + \frac{w}{6}$.

We calculate the numbers of conduction electrons, n_α^{Fe} , n_β^{Mo} , through expressions n_α^{Fe} , $n_\beta^{Mo} = 3 \int_{-\infty}^{E_F} \rho(\omega) d\omega$, where a factor of 3 takes into account the orbital degeneracy of t_{2g} states, $\rho(\omega)$ is the local density of state (Fe or Mo) and E_F is the Fermi energy of the system.

Figure 2 shows the number of conduction electrons in Fe^α sites as a function of disorder. In Figure 2(a), Fe-rich regime ($x \geq 0$), the number of Fe ions increases in the system while the number of Mo ions decreases, we observe that the number of electrons decreases when disorder

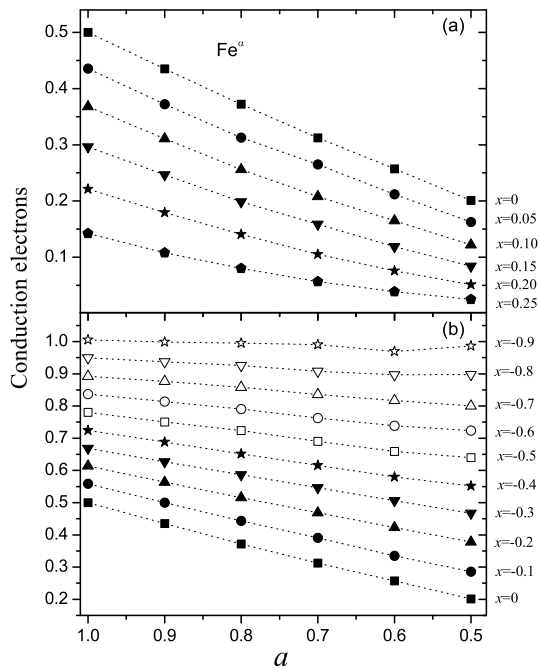


Figure 2. Conduction electrons in Fe sites (Fe^α) as a function of disorder: (a) in the Fe-rich regime ($x \geq 0$); (b) in the Fe-deficient regime ($x \leq 0$).

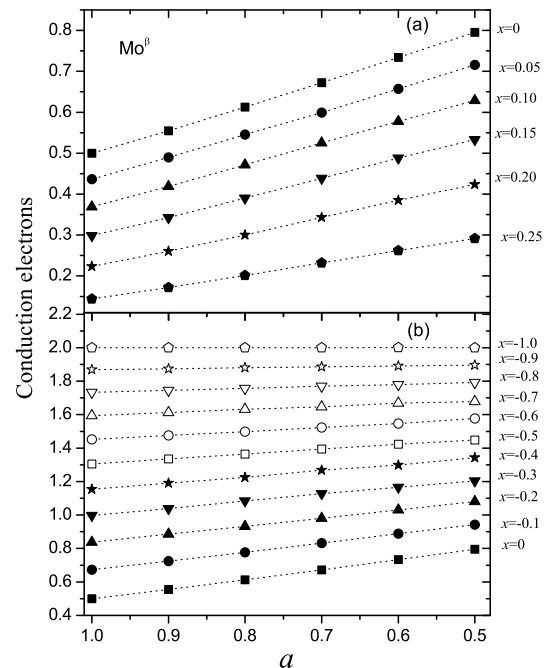


Figure 3. Conduction electrons in Mo sites (Mo^β) as a function of disorder: (a) in the Fe-rich regime ($x \geq 0$); (b) in the Fe-deficient regime ($x \leq 0$).

and x increase. As x approaches $1/3$ and disorder increases, the number of conduction electrons becomes 0, therefore the valence state in Fe sites goes from $2.5+$ to $3+$. In case of Fe-deficient regime ($x \leq 0$), see Figure 2(b), we observe for $a = 1$ that the number of conduction electrons increases as x goes to -1 because the number of Mo ions increases in the system, therefore, the valence state in Fe sites goes from $2.5+$ ($x = 0$) to $2+$ ($x = -1$). Increasing of disorder generates both types of bonding Fe(S)-O-Fe(AS) and Mo(S)-O-Mo(AS) which allow spin up electrons itinerant, so there is an increases in the valence state in Fe sites from $2.8+$ ($a = 0.5$) to $2+$ ($a = 1$). Figure 3 shows the number of conduction electrons in Mo^β sites as a function of disorder. Figure 3(a) shows that the number of conduction electron increases with disorder, it also should be noted that n decreases in the Fe-rich regime. In this regime the number of itinerant electrons decreases since the Mo sites are occupied by Fe ions. For $x = 0$ and $a = 1$, the valence state of Mo sites is $5.5+$, which tends to $6+$ as x goes to $1/3$. When disorder increases and $x \rightarrow 0$ the Mo valence state goes to $5+$. The Fe-deficient regime is shows in Figure 3(b), where it is observed that in the ordered system the valence state in Mo changes from $5.5+$ ($x = 0$) to $4+$ ($x = -1$) and with disorder goes from $5.2+$ ($a = 0.5$) to $4+$ ($a = 1$). In the limit case $x = -1$ we obtain the $SrMoO_3$ structure, where the valence state for Mo is $4+$ as it should.

In summary, for Fe-rich regime the number of conduction electrons decreases so valence states in Fe sites go up from $2.5+$ to $3+$, whereas for Fe-deficient regime the number of conduction electrons increases so that valence states in Fe sites tend to $2+$. Regarding Mo sites, valence states go from $5.5+$ to $6+$ when the system is Fe-rich and from $5.2+$ to $4+$ in the Fe-deficient regime.

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