

Electronic properties of double perovskite compounds

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The double perovskites family $A_2MM'O_6$ (A being an alkaline-earth and M, M' two different transition-metal elements) is considered as a serious candidate for magnetoelectronic applications. It appears to be fundamental to understand the role of electronic parameters controlling the half-metallic ground state and high Curie temperature T_c . In this respect it is very interesting that different members of the family present a variety of electronic and magnetic properties. Among them, Sr_2FeMoO_6 and Sr_2FeReO_6 are half-metallic ferromagnets with fairly large T_c (≈ 450 K) while Sr_2FeWO_6 is known as an antiferromagnetic insulator with $T_N \approx 37$ K. As expected, a metal–insulator and magnetic transition has been reported in these substituted compounds $Sr_2FeMo_xW_{1-x}O_6$. To elucidate the origin of such different behavior in these Sr_2FeMO_6 double perovskites we consider a correlated electron picture with localized Fe-spins (d^5 configuration) and conduction electrons originating from M (M = Mo, Re or W) together with the double-exchange type interaction taking place in the hybridized Fe–M t_{2g} band and competing with the antiferromagnetic superexchange interactions between the Fe-spins. We consider here only the ordered structure in which Fe and M constitute two interpenetrating sublattices. Using a tight-binding model and the renormalized perturbation expansion technique, we calculate the density of states and determine the behaviour of the critical temperature as a function of the band filling and the Fe–M charge transfer energy. This allows us to discuss the stability of the half-metallic ferromagnetic state with increasing charge transfer energy. We will also discuss the electronic properties and the ferro-antiferromagnetic transition in the substituted compounds like $Sr_2FeMo_xW_{1-x}O_6$, when disorder among Mo/W takes place in the M-sublattice.

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1 Introduction

The double perovskite Sr_2FeMoO_6 is a very good candidate for magnetic devices, since it combines a high Curie temperature and a half-metallic conduction band [1]. In this work, we will consider double perovskites structures of the type Sr_2FeMO_6 , where in the fully ordered perovskite, Fe and M occupy two interpenetrating sublattices. Oxygen atoms bridge the Fe and M ions to form alternating FeO_6 and MO_6 octahedra.

The electronic structure of ordered ferromagnetic Sr_2FeMoO_6 investigated by optical spectroscopy [2] and photoemission spectroscopy [3, 4] is in good agreement with band structure calculations [1, 3]. The majority spin-up bands exhibit a bandgap (~ 0.5 – 0.8 eV) while minority spin-down bands cross the Fermi level giving rise to the half-metallic character in the ground state. In the majority channel, the occupied part of the bands near the Fermi level comes from filled t_{2g} and e_g bands with mainly Fe-d character, no appreciable Mo weight being observed in photoemission [4]. The partly occupied minority

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spin-down band comes from strongly mixed Fe and Mo t_{2g} states. All bands present an important mixing with oxygen p-states. Because the relevant states near the Fermi energy are derived from Fe and Mo d-orbitals we will use a simple tight-binding Hamiltonian based on the calculated band structure [1, 3] and containing only Fe and Mo sites. The nominal configurations are $3d^5$ for Fe and $4d^1$ for Mo. Of course these states are hybridized with the oxygen lying in between them as indicated by band structure calculations. However these O degrees of freedom can be eliminated to produce Mo–Mo, Mo–Fe and Fe–Fe effective hoppings as well as effective site diagonal energies at Fe and Mo sites. We should think of these states as nominally Mo $4d - O 2p$ and Fe $3d - O 2p$ derived states. Due to strong Hund's coupling on Fe sites parallel spins occupy t_{2g} and e_g orbitals giving the high spin configuration $S = 5/2$ of the $3d^5$ configuration. We will consider these orbitals frozen, depicted by a localized spin S_i . To reduce the mathematical complexity we represent the localized spin as a spin $1/2$ so that it can be parallel or antiparallel to the quantization direction, restricting our approach to simple magnetic structures (ferro, antiferro). In addition to these localized Fe spins, itinerant electrons coming from Mo can move around between Fe and Mo ions in the exchange split t_{2g} orbitals to give $3d^6$ (Fe^{2+}) configuration in the Fe sites. The corresponding crystal-field split e_g orbitals are not occupied and will not be included. These itinerant electrons are inevitably coupled antiferromagnetically to the Fe localized spins. Mo is not a strongly correlated metal and usually non magnetic, and would have either $4d^1$ (Mo^{5+}) or $4d^0$ (Mo^{6+}) configuration. This electronic scheme is consistent with the band structure calculations and various spectroscopies for the ferromagnetic ground state of Sr_2FeMoO_6 [4, 5] and will be considered to be basically valid for other Fe double perovskites Sr_2FeMO_6 with different metals as well.

In order to give a simple theoretical picture we neglect the correlations among the three possible t_{2g} orbitals and reduce the itinerant orbitals to one on each site. The t_{2g} orbital degeneracy is accounted for at the end. According to the above considerations we write the following model Hamiltonian:

$$H = \varepsilon_{Fe} \sum_{i \in \{Fe\}, \sigma} a_{i\sigma}^+ a_{i\sigma} + \varepsilon_M \sum_{i \in \{M\}, \sigma} b_{i\sigma}^+ b_{i\sigma} - \sum_{\langle i,j \rangle, \sigma} t_{\mu, \sigma} (a_{i\sigma}^+ b_{j\sigma} + \text{h.c.}), \quad (1)$$

where $a_{i\sigma}^+$, $a_{i\sigma}$ ($b_{i\sigma}^+$, $b_{i\sigma}$) creates and destroys an itinerant electron with spin σ at site i occupied by Fe (M) respectively. ε_{Fe} and ε_M are the site diagonal energies at the Fe and M sites respectively. Finally the hopping term $t_{\mu, \sigma}$ is t when the localized spin μ (+ for up and – for down) at site i is opposite to the itinerant spin σ (\uparrow or \downarrow) and the hopping is zero when μ and σ are parallel, this mechanism precludes the possibility to put an itinerant electron in the Fe site with the same spin as the localized spin. We ignore M–M hopping and consider only nearest-neighbors Fe–M hopping. The hopping term gives rise to the bandwidth in the minority spin channel as seen in the band structure [3] and favors a ferromagnetic background of the Fe-spins with antiparallel polarized itinerant electrons, thus producing what is often called the “ferrimagnetic” ground state in the ordered case.

2 Results and discussion

The density of states for itinerant electrons is obtained from the local Green's functions for different sites in an interpenetrating Bethe lattice, using the renormalization perturbation expansion (RPE) method. We take the limit of infinite coordination number in the Bethe lattice ($z \rightarrow \infty$). In this case zt^2 scales as $w^2/4$, w being half of the band width, and the Green's functions reduce to those used in a dynamical mean field approach:

$$G_{\uparrow}^M = \frac{1}{\omega - \varepsilon_M - \frac{w^2}{4} V_- G_{\uparrow-}^{Fe}}, \quad (2)$$

$$G_{\uparrow-}^{Fe} = \frac{1}{\omega - \varepsilon_{Fe} - \frac{w^2}{4} G_{\uparrow}^{Mo}}, \quad (3)$$

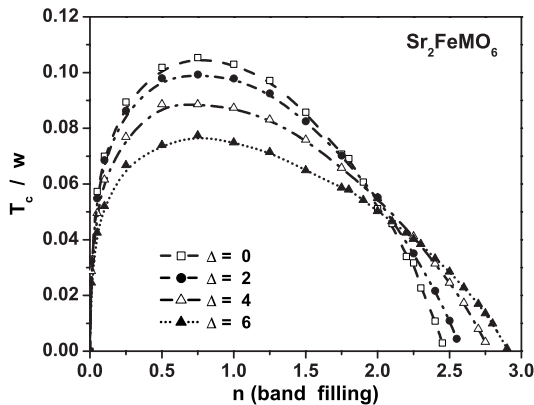


Fig. 1 Variation of the Curie temperature T_c vs. band filling (n) for different values of Δ .

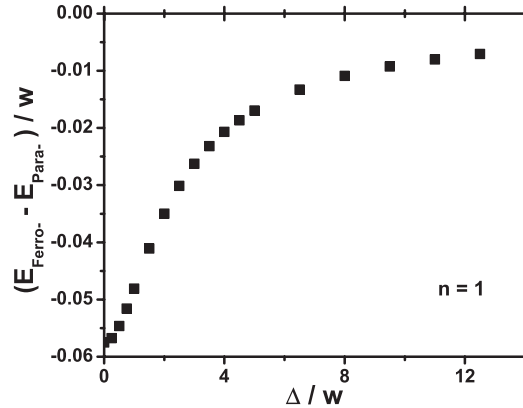


Fig. 2 Energy difference between the phases ferro and para vs. Δ for $n = 1$ in Sr_2FeMO_6 .

similarly for down spin electrons replacing ν_- by ν_+ , with $\nu_{\pm} = (1 \pm m)/2$, m being the magnetization. We take ε_{Fe} as the reference energy and $\varepsilon_M = \Delta$.

The relative position Δ of the metal M and Fe itinerant states is a key parameter determining the M and Fe valence and may be very different for various compounds. For example, in $\text{Sr}_2\text{FeMoO}_6$ recent experiments converge towards an intermediate valence state $\text{Fe}^{2.5+}$ [6, 7], meaning that Δ is certainly small while, in Sr_2FeWO_6 , the valences of $\text{Fe}(\text{Fe}^{2+})$ and $\text{W}(\text{W}^{6+})$ [8] implies that Δ is much larger than the bandwidth w .

In Fig. 1, the Curie temperature T_c/w is shown vs. the band filling n for different values of Δ . T_c scales as the bandwidth w due to Fe–M hopping and does not depend on the sign of Δ . The overall behavior is similar to the one obtained in Ref. [9]. In the range $n \sim 1$, corresponding to FeMo compounds, T_c/w reaches its maximum for $\Delta = 0$. From the point of view of energy levels, Fe–Mo seems to correspond to an optimal situation for high T_c . For $n > 1$, T_c/w decreases and is about a factor of two smaller for $n = 2$ corresponding to the case of $\text{Sr}_2\text{FeReO}_6$. The number of conduction electrons can be increased to $n > 1$ by substitution of the divalent Sr by trivalent ions as in $\text{Sr}_{2-y}\text{La}_y\text{FeMoO}_6$ [10, 11], giving $n = 1 + y$. It is clear that the observed increase of T_c cannot be a genuine effect of the increase of the carrier density. We may mention that T_c may be affected by the presence of antisites. An enhanced number of antisites [10] may increase T_c due to a superexchange interaction between the Fe–Fe nearest-neighbors [12].

For $n \sim 1$, T_c/w decreases with increasing Δ . It is clear that the robustness of the ferromagnetic state is governed by the hopping and the charge transfer energy $\Delta = \varepsilon_M - \varepsilon_{\text{Fe}}$. One understands easily that increasing Δ tends to localize the electrons either on Fe or on the metal M thus inhibiting the polarization of the Fe spins and reducing the stability of the ferromagnetic state (Fig. 2 and 3). Therefore an antiferromagnetic interaction between Fe localized spins may stabilize an antiferromagnetic phase for Δ larger than a critical value as in Sr_2FeWO_6 . A detailed analysis of the ferromagnetic-antiferromagnetic transition will be published elsewhere [13]. In Fig. 4, we present the variation of the number of conduction electrons on Fe and M sites as function of Δ/w for the ferromagnetic and paramagnetic phases. We see little difference in the two phases and that values of $\Delta/w \sim 2-3$ are compatible with the observed Fe and W valence $2+$ and $6+$ in Sr_2FeWO_6 .

Let us now consider the case of substituted compounds like $\text{Sr}_2\text{FeMo}_x\text{W}_{1-x}\text{O}_6$ with $n = 1$. As mentioned above, Δ is large for W, as a consequence, the hopping to W sites is inhibited therefore reducing the number of Fe nearest-neighbors to the xz Mo neighbors. The Green's function for Fe is then modified with the factor x as:

$$G_{\uparrow}^{\text{Fe}} = \frac{1}{\omega - \varepsilon_{\text{Fe}} - x \frac{w^2}{4} G_{\uparrow}^{\text{Mo}}}.$$

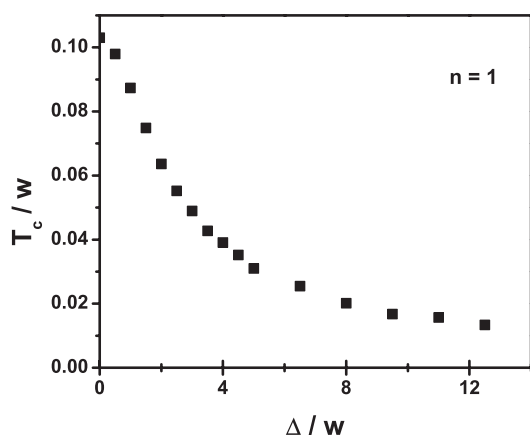


Fig. 3 Variation of the Curie temperature T_c vs. charge transfer energy Δ for $n = 1$ in Sr_2FeMO_6 .

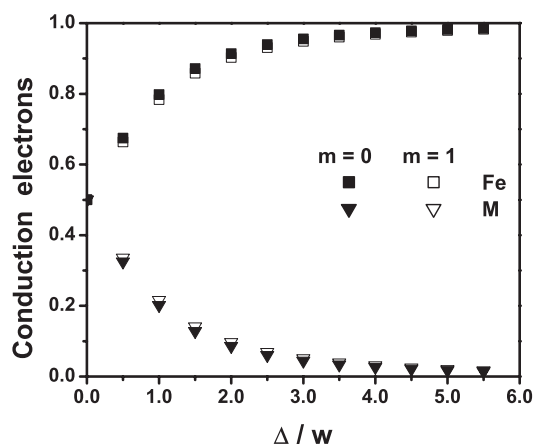


Fig. 4 Variation of the number of conduction electrons on Fe and M sites as a function of Δ .

Of course, in the general case, one should consider the disorder induced by the substitution of Mo by W, with two different site energies Δ and Δ' for Mo and W. The situation differs from the standard disordered alloys because here the disorder is taking place only on one of the two sublattices. Work along this line is in progress. When $\Delta' \gg w$ one recovers the above Fe-Green's function. We obtain that the Curie temperature T_c tends to zero for doping $x \sim 0.2$. This indicates the instability of the ferromagnetic phase and the possibility of a magnetic transition in these systems. Therefore an antiferromagnetic super-exchange interaction between the Fe localized spins will stabilize an antiferromagnetic phase as in pure Sr_2FeWO_6 , for a concentration $x < x_c \sim 0.25$. This critical value is almost independent of Δ in the range we considered [14]. We believe that this critical doping is related to the metal–insulator transition taking place in these systems, and it is interesting to note that it is remarkably close to the experimental critical concentration [15].

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