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Ferromagnetic transition in ordered double perovskites and related alloys

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Abstract. We study the electronic and magnetic properties of ordered perovskites Sr_2FeMO_6 (where M is a transition metal), among which some compounds, like Sr_2FeMoO_6 are half-metallic with high Curie temperature while Sr_2FeWO_6 is an antiferromagnetic insulator. Using a double exchange type model with an interaction between localized spins and conduction electrons together with a tight-binding Hamiltonian and the renormalized perturbation expansion method, we study the behavior of T_c as a function of the number of conduction electrons and also as a function of the Fe-M energy difference. We also consider the $Sr_2FeMo_xW_{1-x}O_6$ compounds which present a magnetic and metal-insulator transition as a function of doping.

PACS. 75.47.Gk Colossal magnetoresistance – 75.10.-b General theory and models of magnetic ordering – 71.30.+h Metal-insulator transitions and other electronic transitions

1 Introduction

Recently, the physics of half-metallic systems has become very attractive in view of the potential magnetoelectronic applications [1]. In this respect, a low-field magnetoresistance at room temperature is highly desirable. This magnetoresistance (MR) can be obtained in polycrystalline materials resulting from intergrain tunneling (TMR) and it is attributed to spin-dependent carrier scattering of spin-polarized electrons in a half-metallic ground state. This view is in agreement with the absence of strong MR effect in single crystals [2] and is verified by the observation of MR across an artificial bicrystal boundary [3]. It is therefore of fundamental interest to understand which parameters are controlling the half-metallic character as well as the Curie temperature T_c in order to optimize the electronic properties. 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 and appears to be very interesting to access to the role of electronic parameters because different members present a variety of electronic and magnetic properties. Among them, Sr_2FeMoO_6 and Sr_2FeReO_6 have shown low-field magnetoresistance remaining significant up to room temperature with half-metallic ferromagnetic character below T_c [4–6]. The fairly high T_c (≈450 K) compared to manganese perovskites makes them very attractive. On the other hand, Sr_2FeWO_6 is known as an antiferromagnetic (AF) insulator with $T_N \sim 37$ K [7]. As expected, a metal-insulator and magnetic transition has been reported in the substituted compounds $Sr_2FeMo_xW_{1-x}O_6$ [8–10].

In Sr_2FeMoO_6 the low-field MR is strongly affected by the long range ordering of Fe and Mo atoms [6,11], disordered samples do not exhibit the low-field sharp magnetoresistive response, though the MR remains very similar to that of the ordered sample in the high-field regime. One may think that disordering may modify the half-metallic character of the system. In addition, in general, the saturation magnetization (≈$3.2\mu_B$ per formula unit) is significantly lower than the saturation moment $4\mu_B$ ($S_{total} = 5/2 - 1/2$) expected from the polarized bands, a discrepancy which has been attributed to some degree of disorder between Fe and Mo atoms. Decrease of the saturation magnetization with increasing disorder is expected as a result of antiferromagnetic superexchange interaction between nearest-neighbors Fe [12]. Recently, with the same approach as used here, it has been shown how a small amount of positional disorder could affect the electronic structure and the Curie temperature [13]. In the present paper we will consider only fully ordered compounds.

2 Electronic scheme and model

In the following we will consider only Sr_2FeMO_6 double perovskites. In the fully ordered perovskite structure, Fe

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and M occupy two interpenetrating sublattices, respectively α and β, in a rock-salt structure. Oxygen atoms bridge the Fe and M ions to form alternating FeO_6 and MO_6 octahedra.

Let us first describe the electronic scheme of Sr_2FeMoO_6. The electronic structure of ordered ferromagnetic Sr_2FeMoO_6 investigated by optical spectroscopy [2] and photoemission spectroscopy [14,16] is in good agreement with band structure calculations [4,14,15]. 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 although slightly hybridized with Mo-d. The partly occupied minority 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 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. Inclusion of on-site correlations within the local-density approximation $+\,U$ $(LDA+U)$ scheme or the local-spin-density approximation $+\,U$ $(LSDA+U)$ do not modify qualitatively the electronic structure [16–18], it merely enhance the exchange splitting of Fe and brings the Fe up-spin occupied band further below the down-spin conduction band therefore reinforcing the localized character of the Fe up-spin states.

We consider here a strongly correlated picture of Fe with the stable configuration d^5, in agreement with the fact that there is no evidence for the presence of d^4 configuration in the ground state [16], implying that the energy $\Delta' = E(\text{Fe } d^4, \text{M } d^1) - E(\text{Fe } d^5, \text{M}d^0)$ to transfer an electron from Fe in the d^5 state to Mo is positive and large. Due to strong Hund's coupling on Fe sites parallel spins occupy the t_{2g} and e_g orbitals giving the high spin configuration $S = 5/2$ of the $3d^5$ configuration and we take these orbitals as frozen, depicted by a localized spin $\overrightarrow{S}_i$. 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 $3d^6$ $(S = 2)$ (Fe^{2+}) configuration on the Fe sites. The corresponding e_g orbitals split by the crystal-field are not occupied and will not be included. On a given Fe site all the five d-orbitals being occupied with the same spin direction, an itinerant electron is inevitably coupled antiferromagnetically to the Fe localized spins: this is indeed just the exclusion principle. Therefore itinerant electrons with spin σ can hop only to Fe sites with *antiparallel* localized spins. On the other hand Mo is not a strongly correlated metal and usually non magnetic, the intra-atomic exchange within d states being small compared to the $3d$ transition metals [20], therefore there is no constraint for electrons to hop on Mo sites. The Mo sites would have either $4d^1$ (Mo^{5+}) or $4d^0$ (Mo^{6+}) configuration. This electronic scheme is consistent with the ab initio calculations and with the current informations on electronic states emerging from photoemission spectroscopes [16] and a recent X-ray magnetic circular dichroism (XMCD) experiment [19] for the "ferrimagnetic" ground state of Sr_2FeMoO_6. It has been shown that the majority-spin states are well localized and behave as a spin 5/2 which is built essentially from the Fe states, no appreciable Mo weight being observed in photoemission [16]. We will consider this picture to be basically valid for other Fe double perovskites with different metals M as well. The model followed here for Fe double-perovskites Sr_2FeMO_6 does not differ in any essential way from that considered in recent works [21,22]. The method we used is however much simpler and transparent, and allows for a straightforward extension to consider substituted compounds like $Sr_2FeMo_xW_{1-x}O_6$.

So we describe the conduction band arising from the three degenerate t_{2g} (d_{xy}, d_{yz}, d_{zx}) orbital states by a tight-binding model taking into account the constraints on the hopping we just mentioned. To reduce the mathematical complexity we consider that the localized spins can be either parallel or antiparallel to the quantization direction; this precludes the possibility of canted or spiral phases and restricts our approach to simple magnetic structures (ferro, antiferro). So the hopping $t_{\mu_i\sigma}$ of an electron with spin σ between a site M and a local spin μ_i (+ for up and − for down) at an Fe site i is t when the itinerant electron spin σ (↑ or ↓) is opposite to the localized spin and the hopping is zero when μ_i and σ are parallel. In the cubic symmetry, due to the symmetry of the intermediate O orbitals, the first and second neighbor hoppings are nonzero only between orbitals of the same symmetry $\gamma = xy, yz, zx$ and only between orbitals lying in the corresponding plane γ; it is the same for the three orbitals, thus giving three degenerate two-dimensional bands. In order to give a simple theoretical picture we neglect intra-atomic correlation among the three possible t_{2g} Fe/M orbitals. As we mentioned above this interaction is quite small for Mo and other metals with extended $4d/5d$ states; for Fe it is certainly stronger, values $U_{\text{Fe}} \sim 2{-}4$ eV have been reported [16–18], but since the three orbitals are occupied by the same spin direction it has to be reduced by the exchange interaction J: $U_{eff} = U - J$. Strong Coulomb repulsion among these orbitals at Fe sites has been taken into account to study the possibility of a metal-insulator transition within the ferrimagnetic phase using a slave-boson approach [23]. Here we will consider only the metallic regime and we may think of the electronic parameters of our Hamiltonian, in particular the hopping, as renormalized by the correlations in the spirit of the slave-boson approach. This will not change qualitatively our results.

According to the above considerations we write the following model Hamiltonian for each t_{2g} orbital:

$$H = \varepsilon_{\mathrm{Fe}} \sum_{i\{\mathrm{Fe}\},\sigma} a^{+}_{i\sigma} a_{i\sigma} + \varepsilon_{\mathrm{M}} \sum_{i\{\mathrm{M}\},\sigma} b^{+}_{i\sigma} b_{i\sigma} - \sum_{\langle i,j\rangle,\sigma} t_{\mu_i \sigma} \left(a^{+}_{i\sigma} b_{j\sigma} + \mathrm{h.c.} \right) \quad (1)$$

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. $\varepsilon_{\mathrm{Fe}}$ and ε_{M} are the site diagonal energies at the Fe and M sites respectively, $\varepsilon_{\mathrm{M}} - \varepsilon_{\mathrm{Fe}}$ being the charge transfer energy $\Delta = E(\mathrm{Fe}\ d^5, S = 5/2; \mathrm{M}\ d^1) - E(\mathrm{Fe}\ d^6, S = 2; \mathrm{M}\ d^0)$. The hopping $t_{\mu_i \sigma}$ has been defined above. We consider only nearest-neighbors (n.n) Fe-M hopping and ignore M-M hopping. The number of carriers per unit cell is respectively $n = 1$ and $n = 2$ for Mo/W and Re compounds; it can also be varied by substitution of the divalent Sr by trivalent ions as, for example, in $\mathrm{Sr}_{2-y}\mathrm{La}_y\mathrm{FeMoO}_6$ [24,25] in which case $n = 1 + y$.

A ferromagnetic ordering of the local spins favors a larger mobility (wider band) for the antiparallel (down) itinerant electrons and forbids parallel (up) electrons to move. This lowers the kinetic energy of the conduction electrons and stabilizes the "ferrimagnetic" phase. Although the physical origin is different, this mechanism is similar and acts in the same way as the double-exchange for manganites in which the Hund's rule couples ferromagnetically the itinerant electrons and the localized spins: in both cases, ferromagnetic ordering of the local moments occurs because of the kinetic energy gain. It is clear that here the robustness of the ferrimagnetic state is governed by the hopping t and the charge transfer energy $\Delta = \varepsilon_{\mathrm{M}} - \varepsilon_{\mathrm{Fe}}$. One understand easily that a large 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 ferrimagnetic state.

However this is not the only interaction which determines the magnetic structure of the double perovskites. The majority spin occupied t_{2g} and e_g bands gives rise to an AF superexchange interaction (SE) $J_{ij} \overrightarrow{S}_i \overrightarrow{S}_j$ between the Fe localized spins mediated by Fe-O-M-O-Fe paths with 90° and 180° Fe-M-Fe bonds. This SE is typically $J \sim \frac{t^2_{\mathit{eff}}}{U'}$, where $U' = E(\mathrm{Fe}\ d^6) + E(\mathrm{Fe}\ d^4) - 2E(\mathrm{Fe}\ d^5)$ and the effective Fe-Fe hopping $t_{\mathit{eff}} \sim \frac{t^2}{\Delta'}$ so that $J \sim t^4/(\Delta')^2 U'$. The contribution from the e_g orbitals is the strongest because the hopping t' between the e_g orbitals is larger than t between t_{2g} orbitals, $t'/t = 3$ [26]. The competition between these two tendencies, which determines whether the system will be ferrimagnetic or antiferromagnetic, is quite subtle. This requires much care in the determination of the SE interaction parameters, including the degeneracy of the orbitals and all the different virtual processes involved. In this paper we consider only the ferrimagnetic state, a detailed study of the ferrimagnetic-antiferromagnetic transition will be published elsewhere [27]. Anyhow, we have to keep in mind that the Curie temperature T_c is reduced by the SE interactions, the value that we calculate represents the contribution from the itinerant electrons only.

In order to obtain the density of states for itinerant electrons, we calculate local Green's functions in an interpenetrating Bethe lattice using the Renormalized Perturbation Expansion (RPE) [28]. The RPE connects the propagator at site i to propagators at the nearest neighbor sites $i + \delta$ which exclude visiting site i again and which we will denote by small g's. These new propagators are in turn connected to propagators of the same type at sites $i + \delta + \delta'$, etc., so that Green's function at each site depends, through this chain, on the local spin configuration of the Fe sites. This procedure leads to different Green's functions for different sites, according to the local spin configuration around the site. We are interested in the configurational average of Green's functions over all possible spin configurations. This configurational average over local spin directions is assumed to be the same at every site of the same sublattice, to restore translational invariance in the spirit of the mean-field theories as ATA, CPA, etc. To this end we introduce the local average Green's functions $G^{\mathrm{Fe}}_{\sigma\mu}$ and G^{M}_{σ} for Fe and M. In accordance with the model Hamiltonian, on the Fe sites we have $G^{\mathrm{Fe}}_{\uparrow+} = G^{\mathrm{Fe}}_{\downarrow-} = 0$ and only $G^{\mathrm{Fe}}_{\downarrow+}$ (or $G^{\mathrm{Fe}}_{\uparrow-}$) are given by

$$G^{\mathrm{Fe}}_{\downarrow+} = \frac{1}{\left[\omega - \varepsilon_{\mathrm{Fe}} - zt^2 g^{\mathrm{M}}_{\downarrow}\right]}, \quad (2)$$

where we assume that the sum over neighbors can be replaced by the number of n.n z times their average Green functions. Here $z = 4$. At this point we introduce the probabilities $\nu_{\pm} = (1 \pm m)/2$ that an Fe ion has its localized spin + or −, the magnetization due to the localized spins being then $M = 5m\mu_B$, and we can write

$$g^{\mathrm{M}}_{\downarrow} = \frac{1}{\left[\omega - \varepsilon_{\mathrm{M}} - (z-1)\, t^2 \nu_{+} g^{\mathrm{Fe}}_{\downarrow+}\right]}, \quad (3)$$

and

$$g^{\mathrm{Fe}}_{\downarrow+} = \frac{1}{\left[\omega - \varepsilon_{\mathrm{Fe}} - (z-1)\, t^2 g^{\mathrm{M}}_{\downarrow}\right]}. \quad (4)$$

Similarly for M ions we can write

$$G^{\mathrm{M}}_{\downarrow} = \frac{1}{\left[\omega - \varepsilon_{\mathrm{M}} - zt^2 \nu_{+} g^{\mathrm{Fe}}_{\downarrow+}\right]}. \quad (5)$$

The Green's functions for up electrons are obtained by replacing ν_{+} by ν_{-}.

Let us mention that, in our calculation we consider the limit of infinite coordination number ($z \to \infty$), in this case zt^2 scales as $w^2/4$, w being half the bandwidth. In our numerical calculations we take $t = 1$ i.e. $w = 4$. Then the functions $g \to G$ and the Green's functions reduce to those used in a dynamical mean field approach (DMF):

$$G^{\mathrm{Fe}}_{\downarrow +} = \frac{1}{\left[\omega - \varepsilon_{\mathrm{Fe}} - \frac{w^2}{4} G^{\mathrm{M}}_{\downarrow}\right]} \tag{6}$$

$$G^{\mathrm{M}}_{\downarrow} = \frac{1}{\left[\omega - \varepsilon_{\mathrm{M}} - \frac{w^2}{4}\nu_+ G^{\mathrm{Fe}}_{\downarrow +}\right]}. \tag{7}$$

The charge transfer energy Δ between M and Fe itinerant states is the key parameter in determining the M and Fe valence as well as the magnetic moment on Fe and on M. However this parameter is not well known from experiments. For example, even if we look at the case of the most studied system $\mathrm{Sr_2FeMoO_6}$ we find contradictory results concerning the valence of Fe and Mo. It is worth mentioning that assigning a specific valence to ions having a contribution from conduction electrons is always somewhat ambiguous. Early Mössbauer experiments by Nakagawa [29] were interpreted as reflecting the ionic configuration "Fe^{3+}" and consequently Mo should be "Mo^{5+}", which would mean Δ negative and large. On the other hand, different neutron diffraction studies have been reported, one [30] claiming that the Fe magnetic moment is $4\mu_B$ and the absence of any moment at the Mo sites, thus pointing towards the possibility of "Fe^{2+}" and "Mo^{6+}" i.e. Δ large and positive, whereas other studies by the same group proposed either $\mu_{\mathrm{Mo}} \sim -1\mu_B$ [31] or $\sim -0.5\mu_B$ [25]. Other Mössbauer and neutron experiments [32,33] seems to converge towards an intermediate valence state close to $\mathrm{Fe}^{2.5+}$, literally meaning that $\varepsilon_{\mathrm{Fe}}$ and $\varepsilon_{\mathrm{Mo}}$ should be quite close. The value of the Mo moment $\mu_{\mathrm{Mo}} = -0.35\mu_B$ claimed by Besse et al. [19] is also compatible with this view. Qualitatively this is in fact what the band structure results tell us, clearly showing that the minority-spin bands up to $\varepsilon_{\mathrm{Fe}}$ are almost equally populated from Fe and Mo contributions [4,14]. Therefore it seems to be quite reasonable to assume that Δ is small for $\mathrm{Sr_2FeMoO_6}$. To keep the model applicable to a large variety of compounds we will consider Δ as a parameter, taking $\varepsilon_{\mathrm{Fe}} = 0$ and $\varepsilon_{\mathrm{M}} = \Delta$.

In the case of $\mathrm{Sr_2FeWO_6}$, the valence of Fe (Fe^{2+}) and W (W^{6+}) [7] implies that Δ is much larger than the hopping between Fe-W neighbors as just mentioned. As a consequence, the conduction electrons cannot hop from Fe to W.

In the compounds $\mathrm{Sr_2FeMo}_x\mathrm{W}_{1-x}\mathrm{O}_6$ where W is substituted for Mo on the same sublattice, Fe is connected to xz Mo nearest-neighbors only. The Green's function for Fe is then modified accordingly giving:

$$G^{\mathrm{Fe}}_{\downarrow +} = \frac{1}{\left[\omega - \varepsilon_{\mathrm{Fe}} - x\frac{w^2}{4} G^{\mathrm{M}}_{\downarrow}\right]} \tag{8}$$

while the Mo Green's function is not changed.

Solving these equations we can calculate the partial densities of states per orbital for itinerant electrons on Fe and Mo sites. In the following we always consider densities of states per orbital and we include a factor 3 whenever necessary to take into account the orbital degeneracy of t_{2g} states. The total density of states $\rho(m,\omega,\Delta) = \sum_\sigma \left[\rho^{\mathrm{Fe}}_\sigma(m,\omega,\Delta) + \rho^{\mathrm{Mo}}_\sigma(m,\omega,\Delta)\right]$, where $\rho^{\mathrm{Fe}}_\sigma(m,\omega,\Delta) = \nu_\mu \rho^{\mathrm{Fe}}_{\sigma\mu}(m,\omega,\Delta) = -\frac{\nu_\mu}{\pi}\,\mathrm{Im}(G^{\mathrm{Fe}}_{\sigma\mu})$ and $\rho^{\mathrm{Mo}}_\sigma(m,\omega,\Delta) = -\frac{x}{\pi}\,\mathrm{Im}(G^{\mathrm{Mo}}_\sigma)$ allows us to write $n = 3\int_{-\infty}^{\varepsilon_F} \rho(m,\omega,\Delta)\, d\omega$ to determine the Fermi energy ε_F. We can calculate the kinetic energy of the conduction electrons $E_{kin}(m,\Delta) = 3\int_{-\infty}^{\varepsilon_F} \rho(m,\omega,\Delta)\,\omega\, d\omega$. In order to obtain the thermodynamical values of $m(T)$ we need to calculate the minimum of the free energy $F = E_{kin}(m,\Delta) - TS(m)$, where $S(m) = \ln(2) - \nu_+\ln(2\nu_+) - \nu_-\ln(2\nu_-)$ is the entropy term of the local spins consistent with our approximation that these are either up or down. The Curie temperature T_c is easily determined from $m(T_c) = 0$.

3 Results and discussion

Let us first consider some general properties of the density of states in the general case of $\mathrm{Sr_2FeMo}_x\mathrm{W}_{1-x}\mathrm{O}_6$ systems. We have two alternating lattices with different site diagonal energies given by the parameter Δ which should open a gap in the density of states. In addition the two lattices also have in general different connectivities which are $z\nu_+$ ($z\nu_-$) for the Mo sublattice depending on the spin of the itinerant electron, and zx for the Fe sublattice. This also gives a gap as in chains with alternating hopping. Therefore, in general, the density of states for spin σ has two bands with a gap E^σ_g which depends simultaneously on Δ, m and x as $E^\sigma_g = \sqrt{\Delta^2 + w^2\left(\sqrt{x} - \sqrt{\frac{1-\sigma m}{2}}\right)^2}$. Besides these bands the spectrum also shows δ-peaks arising from the poles of the Green's functions. Depending on the relative values of x and m, these peaks have Fe or Mo character. The total spectral weight is of course $1 + 2x$, since there is only one state available per Fe, 2 per Mo and W but the W states are projected out.

In the general case when $\Delta \neq 0$, the partial densities of states are different for Fe and Mo. However they obey to the following symmetry properties when $\Delta \to -\Delta$:

$$\rho^{\mathrm{Mo}}_\sigma(m,\omega-\Delta,-\Delta) = \rho^{\mathrm{Fe}}_\sigma(m,\omega,\Delta)$$

$$\rho^{\mathrm{Fe}}_\sigma(m,\omega-\Delta,-\Delta) = \rho^{\mathrm{Mo}}_\sigma(m,\omega,\Delta).$$

A typical example of the density of states in the paramagnetic state ($m = 0$) for different values of Δ is given in Figure 1 for the two cases $x = 1$ (a) and $x = 0.6$ (b). This shows the narrowing of the two bands and how the gap increases with increasing Δ in the two cases. For a given Δ, this shows that the gap is maximum for $x = 1$ and decreases for $x = 0.6$ according to the above formula. The behavior of the density of states is further illustrated in Figure 2 where we show the evolution of the density of states with x in the ferromagnetic ($m = 1$) (Fig. 2a) and the paramagnetic ($m = 0$) (Fig. 2b) states, taking $\Delta = 0$ and $w = 4$. As discussed above, it consists of two identical bands separated by a gap and the partial density of states are the same for Fe and Mo. In the ferromagnetic case, for

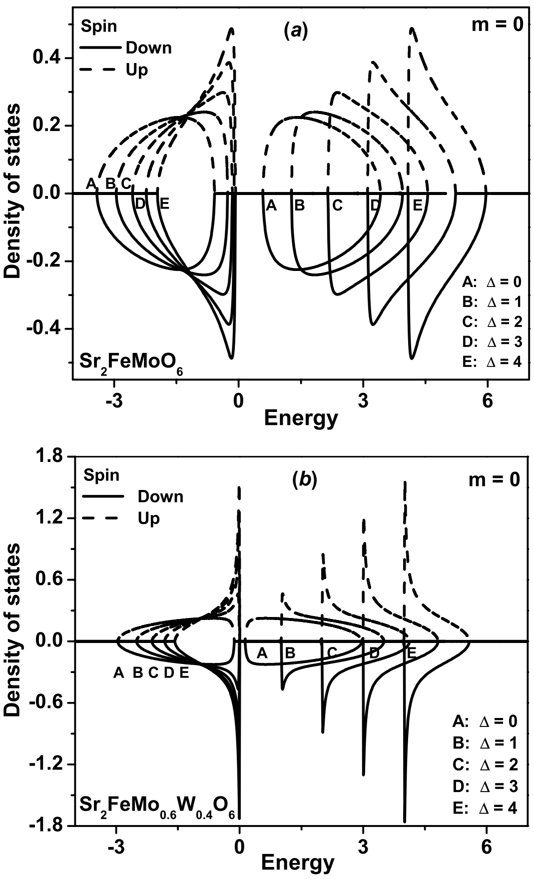

Fig. 1. Total density of states versus energies (ω) for different values of the charge transfer energy (Δ) between transition metals Fe and M (a) for the double perovskite Sr_2FeMoO_6 (b) $Sr_2FeMo_xW_{1-x}O_6$ compound for $x = 0.6$ in the paramagnetic phase taking $w = 4$.

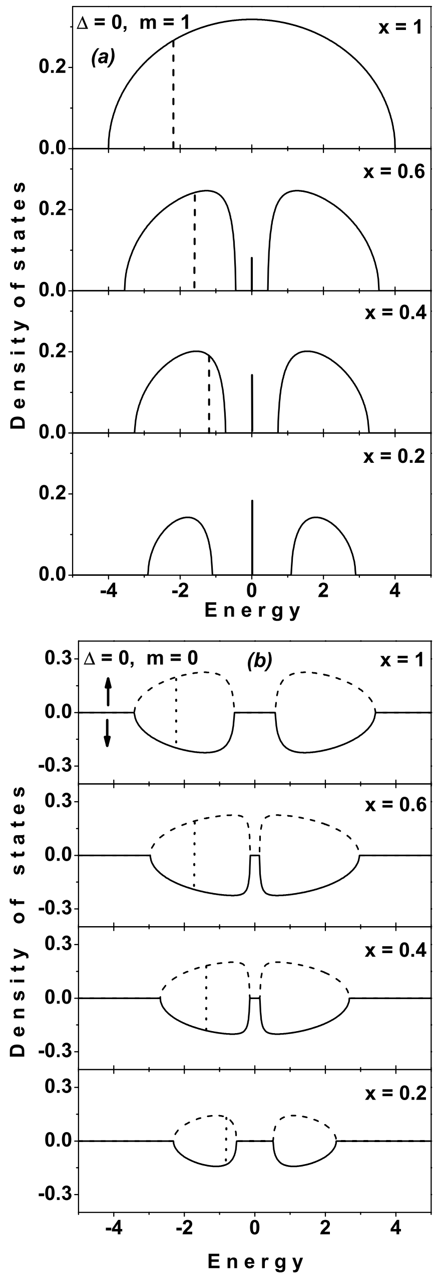

Fig. 2. Density of states ρ_σ vs. energy for $Sr_2FeMo_xW_{1-x}O_6$ with different values of the concentration x: (a) in the ferromagnetic state (b) in the paramagnetic state. In all cases $\Delta = 0$ and $w = 4$. The vertical full line at $\omega = 0$ represents the Fe-derived peak with weight $(1 - x)$. The Fermi energy indicated by a vertical short dashed line corresponds to $n = 1$. For $x < 1/3$ the Fermi energy coincides with the peak at $\omega = 0$.

$x = 1$ one recovers the semi-elliptic model density of states extending from $-w$ to $+w$. This represents the minority spin-down density of states, on the other hand one has also a δ-peak at $\omega = \Delta$ in the Mo up-spin density of states corresponding to the unoccupied narrow Mo-derived spin-up band seen in the band structure calculations. For $x \neq 1$ a gap $w\,(1 - \sqrt{x})$ develops and increases with decreasing x; the spectral weight of each band is equal to x. In addition there is a peak of weight $(1 - x)$ at $\omega = 0$ in the Fe partial density, shown by the full lines in Figure 2a. As x decreases the bands narrow and their spectral weight is diminished due to the reduction of Fe-M nearest-neighbors, therefore the gain in kinetic energy decreases. At finite temperature local spins disorder ($m \neq 0$) and electrons with spin up start to move giving rise to Fe-Mo bandwidth in the up channel. To see the effect of magnetization on the electronic spectrum let us look at the simpler case $x = 1$. Now the down-spin band splits in two bands separated by a band gap $w(1 - \sqrt{\frac{1+m}{2}})$, each band has a spectral weight $(\frac{1+m}{2})$; the spin-up density of states also shows two bands of weight $(\frac{1-m}{2})$ with a larger gap $w(1 - \sqrt{\frac{1-m}{2}})$, therefore evolving towards the paramagnetic case (upper case in Fig. 2b). In addition Mo-peaks are present at $\omega = 0$ (in general this peak appears at $\omega = \varepsilon_{\mathrm{M}} = \Delta$, but we have taken here $\Delta = 0$) with weight $(\frac{1-m}{2})$ and $(\frac{1+m}{2})$ for down and up-spins respectively (not shown); for $m = 1$ one recovers the up-spin peak only. For $x \neq 1$, the evolution with m is quite similar but, as we mentioned above, the spectral weight of each band as well as the gap depends on x and m. In the paramagnetic phase, the

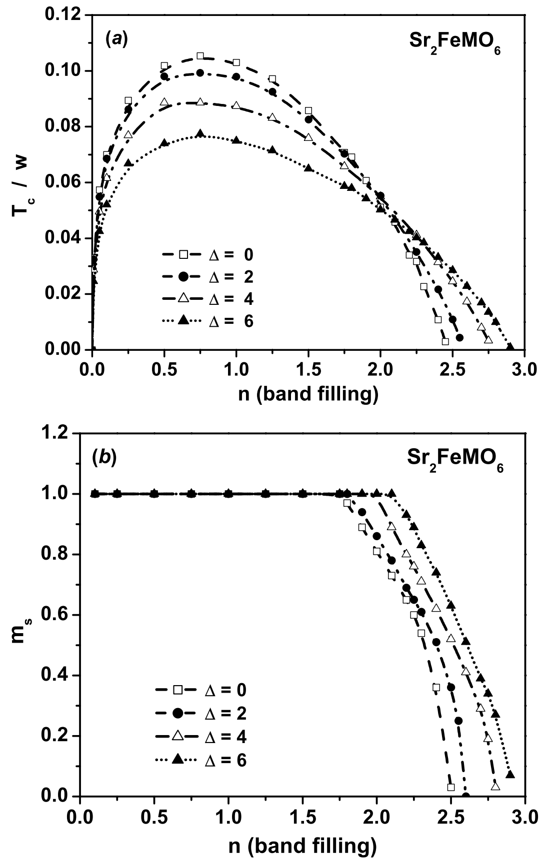

Fig. 3. (a) Variation of the Curie temperature T_c as function of the band filling for different Δ, (b) same for the saturation magnetization m_s.

bandwidth is reduced and the two bands are separated by a gap $E_g = w\left|\sqrt{x} - \frac{1}{\sqrt{2}}\right|$ which closes for $x = 1/2$. The spectral weight of each band for each spin direction depends on x, it is 1/2 when $x > 1/2$, and x for $x < 1/2$. The peaks have the same weight for each spin and different character depending on x: they are Mo states (weight $x - 1/2$) for $x > 1/2$ and Fe-states (weight $1/2 - x$) for $x < 1/2$.

Let us consider the Curie temperature T_c in pure Sr_2FeMoO_6 compounds ($x = 1$). T_c scales as the bandwidth w due to Fe-Mo hopping. In Figure 3a, the Curie temperature T_c/w is shown for different values of Δ as function of the band filling n. T_c does not depend on the sign of Δ, and the overall behavior is similar to the one obtained in reference [21] under the same conditions [34]; the differences comes from the different densities of states used, in particular from the fact that M-M hopping is included in reference [21]. In the range $n = 1$, corresponding to Fe-Mo 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. We also see that, for $n = 2$, T_c/w is about a factor of two smaller, depending very little on Δ. Note that the value of T_c for Sr_2FeReO_6 ($n = 2$) is in disagreement with this trend, Sr_2FeReO_6 having similar T_c and w as Sr_2FeMoO_6 [5]. This is an important point which requires further study. A possibility is that, in this case, with a larger number of itinerant electrons, the electronic correlations within the conduction band itself play a crucial role giving rise to a ferromagnetic instability of the band states. For illustration, in Figure 3b, we have shown the saturation magnetization in units of $5\mu_B$, formally $m_s = m(T = 0)$ as function of the band filling. The behavior of T_c in the region of large band filling ($n \sim 2$–3) corresponds to the rapid decrease of m_s from its maximum value. For n up to $n \sim 2$, we find that the local spins ground state is fully ferromagnetic ($m_s = 1$). In this range, the conduction electrons are fully polarized and the system is half-metallic. For higher filling of the band $n \gtrsim 2$ the system becomes partially disordered in order to accommodate more electrons and progressively looses its half-metallic and ferrimagnetic character. Above the critical carrier concentration corresponding to $T_c(n_c, \Delta) = 0$ the ferrimagnetic state becomes unstable in agreement with a spin-wave theory [22]. As we mentioned above, T_c is reduced by the SE interactions. Including only spins interactions J_1 between Fe in 90° Fe-M-Fe bonds, T_c becomes $T_c^* = T_c - 2S(S+1)z_1J_1/3$, $z_1 = 12$ is the number of n.n. Finally, let us mention that T_c may be affected by the presence of antisites. An enhanced number of antisites [24] may increase T_c due to a superexchange interaction between the Fe-Fe nearest-neighbors [13]. More complete work on the effect of disorder on T_c is in progress [35].

It has been considered that a possible strategy to enhance T_c could be to increase the number of conduction electrons in Sr_2FeMoO_6 by substitution of the divalent Sr by trivalent ions in $Sr_{2-y}La_yFeMoO_6$ [24,25]. A substantial increase of the Curie temperature has been obtained from $y = 0$ reaching $T_c \approx 490$ K for $y = 1$ ($n = 2$). However it is clear from Figure 3a that this cannot be a genuine effect of the increase of the carrier density and other factors have to be invoked to understand the origin of such an increase of T_c. The change in the number of electrons is not the only parameter that may change upon doping with trivalent ions like La. Among them the most direct one could be an increase of the bandwidth w with increasing y (n). Unfortunately, upon La doping the cell expands and the angle of the Fe-O-Mo bonds closes, as a consequence the hopping integral between Fe and Mo $t_{\text{Fe-Mo}}$ is reduced, resulting in a decrease of w and consequently of T_c: thus this cannot account for the observed behavior. One may also think that the direct Mo-Mo hopping that we have neglected may plays a role here. It has been shown that T_c/w decreases with increasing M-M hopping $t_{\text{M-M}}$, indeed with the ratio $t_{\text{M-M}}/t_{\text{Fe-M}}$ [21]. It is likely that $t_{\text{Mo-Mo}}$ also weakens under the deformation of the lattice with doping, however it is not clear how $t_{\text{Mo-Mo}}/t_{\text{Fe-Mo}}$ would vary and if it could decrease in a way to overbalance the diminution of w. A complete analysis of the lattice deformation effects on the overlap integrals is required to conclude on this point. Again the superexchange interactions due to the existence of antisites may affect T_c, however the combined effect of the disorder and the change in the number of carriers is not known. This question is currently under investigation [35].

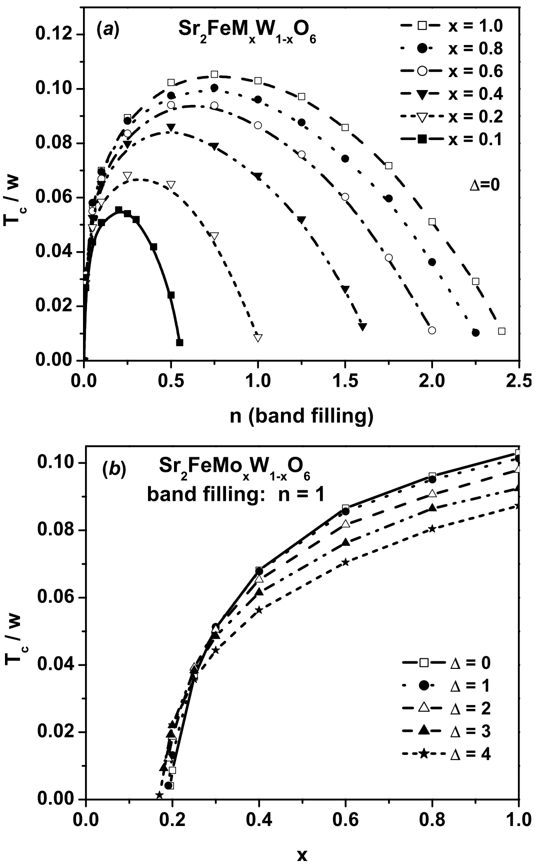

Fig. 4. Variation of the Curie temperature T_c (a) for $Sr_2FeM_xW_{1-x}O_6$ compounds as a function of the band filling n for different values of the concentration x and $\Delta = 0$ (b) for $Sr_2FeMo_xW_{1-x}O_6$ compounds, corresponding to $n = 1$, vs. concentration x for different values of Δ.

Let us now turn our attention to the case of Fe-(M,W) alloys. To keep our model as general as possible we calculated T_c for arbitrary band filling. Figure 4a shows T_c/w for different values of the concentration x as function of the filling n and $\Delta = 0$. We see how the ferromagnetic phase is suppressed by the weakening of the kinetic energy with decreasing M concentration as shown in the evolution of the density of states in Figure 2. In Figure 4b we plotted T_c/w vs. x for the particular case $n = 1$ corresponding to $Sr_2FeMo_xW_{1-x}O_6$. Overall, $T_c(x)$ gives a good description of the magnetic behavior in these compounds [9,10]. We obtain that the Curie temperature T_c drops to zero for concentration $x_c \sim 0.2$, indicating the possibility of a magnetic transition. Compounds with $1 \geq x > x_c$ are ferrimagnetic while, for $x \lesssim x_c$ the antiferromagnetic super-exchange interaction between the Fe localized spins may stabilize an antiferromagnetic ground state as in pure Sr_2FeWO_6. We will consider this in more detail below. We see that this critical value is almost independent of Δ, and note that it is in fairly good agreement with the critical concentration $x_c \sim 0.2{-}0.3$ reported by different groups [9,10]. However, the value reported in the earlier work [8] is significantly larger $x_c \sim 0.4{-}0.5$ probably due to grain boundary effects [10]. From our Figure 4b, taking $T_c \approx 450$ K for $x = 1$, we may estimate that T_c exceeds room temperature for $x \gtrsim 0.3{-}0.4$ (a value depending slightly on the value of Δ we take), again this is in good agreement with the experimental temperature dependence of the magnetization [9]. So, at 300 K, compounds should be paramagnetic for $x \lesssim 0.3{-}0.4$ (remember that the Néel temperature of the antiferromagnetic phase is much smaller than room temperature, $T_N \sim 37$ K for $x = 0$) and ferrimagnetic at higher concentration, in qualitative agreement with recent Mössbauer data [36]. It is worth to discuss the valence arising from our approach for two reasons, first because the Fe-valence has been estimated recently in this family of compounds [36], second because ideas of valence transition have been invoked to explain the observed results [8–10]. In our picture, in the saturated ferromagnetic state ($m = 1$), because $\Delta = 0$ the lower band has equal Fe and Mo character with spectral weight $x/2$ each, so Fe remains $Fe^{2.5+}$ (as we assumed in Sr_2FeMoO_6) as long as $x > 1/3$; below 1/3 Fe-localized states starts to be occupied pushing the valence towards 2+. This strongly suggests that there is a valence transition around the critical concentration x_c, in qualitative agreement with the estimates of the Fe valence reported in reference [36]. This valence transition scenario has some similarity with the ones proposed earlier [8–10] although it differs in the details. It differs in the sense that the models proposed by Nakagawa et al. [8], Kobayashi et al. [9] and Ray et al. [10] are all based on an "ionic picture", Fe being either in the 3+ or 2+ state and Mo in the 5+ or 6+ state, in contrast to the mixed-valence character in Sr_2FeMoO_6 which is explicit in our approach. We emphasized the role played by the itinerant electrons interacting with the background of localized spins.

Let us discuss the effect of the antiferromagnetic SE interaction between the Fe localized spins on x_c. As we mentioned above, it reduces T_c and will push the critical concentration x_c to a value larger than 0.2. We can get a reasonable estimate of the magnetic energy E_M^F resulting from the SE interactions in the ferrimagnetic ground-state. Denoting by J_1 and J_2 the n.n and next nearest neighbors (n.n.n) SE coupling constants between Fe spins, one gets $E_M^F = S(S+1)(z_1 J_1 + z_2 J_2)/2$ ($z_1 = 12$, $z_2 = 6$). J_2 can be related to the Néel temperature of the AF phase in Sr_2FeWO_6. The magnetic structure has been reported recently [37] and consists of alternating ferromagnetic {111} planes coupled antiferromagnetically. In this structure there is an equal number of n.n ferro- and antiferro-bonds, so only n.n.n interactions J_2 contribute to the AF ground-state. So, the Néel temperature is $T_N = 2S(S+1)z_2 J_2/3$, using this expression for T_N means that we neglect the lowering due to the ferromagnetic contribution of the kinetic energy, which is consistent with our assumption that $\Delta \gg w$ in the case of Sr_2FeWO_6. For $S = 5/2$ and $T_N = 37$ K in Sr_2FeWO_6 one obtains $J_2 \simeq 0.1$ meV. We are not aware of any estimate of J_1 for the spins $S = 5/2$. Taking Fe^{2+} ($S = 2$) ions as a starting point, a SE theory of Sr_2FeWO_6 has been derived [38] suggesting that, in this case, J_1 is around half of J_2; of course, this includes the processes involving the fourth t_{2g} electron with opposite spin present in the

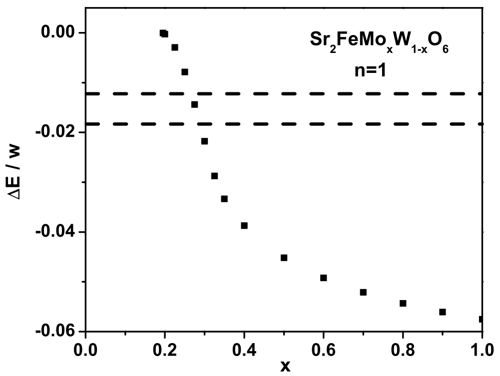

Fig. 5. The electronic energy difference $\Delta E/w$ between the ferrimagnetic and paramagnetic phases vs. concentration x for $\Delta = 0$ and $n = 1$. The dashed lines represents the SE contribution for $J_1/J_2 = 0.5$ (upper line) and 1 (lower line). This gives the concentration range ∼0.25−0.3 below which the ferrimagnetic phase becomes unstable.

Fe^{2+} ions (giving $S = 2$) which, in our approach, is contained in our Hamiltonian (1). However, remembering that the dominant SE contribution comes from the e_g electrons, we may think that this would be a reasonable order of magnitude in our case also. So, taking the ratio J_1/J_2 in the range 0.5−1, we get $E_M^F = 1.5\text{–}2.25\ T_N$. The Fe-Mo bandwidth can be obtained from Figure 3, $T_c/w \approx 0.1$ for $\Delta = 0$ and $T_c = 450$ K, thus giving $E_M^F/w \approx 1.2\text{–}1.8 \times 10^{-2}$; these values are shown by the dashed lines in Figure 5 together with the difference of electronic energy between the ferrimagnetic and the paramagnetic phases for $\Delta = 0$. We see that the critical concentration at which the ferrimagnetic instability occurs is now pushed towards $x_c \sim 0.25\text{–}0.3$, close to the experimental critical concentration. For $x \lesssim x_c$, the SE energy $E_M^{AF} = -S(S+1)z_2J_2/2$ will stabilize the AF structure.

The correlation between the metal-insulator transition and the ferrimagnetic-antiferromagnetic transition is not clearly established although the metal-insulator transition takes place around the same concentration x_c. We may emphasize that the metallic character of the ferrimagnetic compounds for $x > x_c$ follows from our densities of states. This is easily obtained for the saturated ferromagnetic state ($m = 1$), the lower band has a spectral weight x, so it remains partially filled for $x > 1/3$ ensuring the metallic character. It is more difficult to address the question of the insulating behavior since we have not studied the electronic properties of the antiferromagnetic phase. However, we think that the AF state is not a band insulator but, most probably, a disorder induced insulator. In the AF structure, electrons are confined along one-dimensional ferromagnetic paths corresponding to the intersection of the {111} ferromagnetic planes with the xy, yz, zx-planes. Then W ions introduce strong diagonal disorder giving rise to Anderson localization. We believe that this is the probable origin of the insulating behavior in the AF phase below x_c. We should also mention that previously the insulating character has not been interpreted as an intrinsic property of the antiferromagnetic phase but, instead has been attributed to the existence of inhomogeneneous phases in the systems and to a percolation process [9,10], a picture which is beyond the scope of our paper.

To summarize, we have presented a simple model for ordered perovskites based on Hund's rule coupling in which the $3d^5$ Fe majority-spins are localized and considered as local spins interacting antiferromagnetically with itinerant electrons. The ferromagnetic state is stabilized by the kinetic energy of the conduction electrons, similar to the double-exchange mechanism. We have shown the role of the charge transfer energy on the Curie temperature as well as the effect of the band filling. Maximum T_c is obtained in the range $n = 0.5\text{–}1$ and small charge transfer energy between the two metal ions. The half-metallic character is nevertheless preserved for band filling up to $n \sim 2$. For alloy compounds like Sr$_2$FeMo$_x$W$_{1-x}$O$_6$ we have been able to reproduce the general behavior of the magnetic transition observed experimentally. Our approach can be extended to the study of disorder between Fe and M atoms [13,35] and to the study of off-stoechiometric Sr$_2$Fe$_{1+x}$Mo$_{1-x}$O$_6$ [39].

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