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# Ferromagnetic–antiferromagnetic transition in double perovskites

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## Abstract

We study the ordered double perovskite of the type $Sr_2FeMO_6$ using a tight-binding model with the renormalized perturbation expansion technique. In the ferromagnetic phase (F), we determine the behavior of the critical temperature as a function of the band filling and the Fe–M charge transfer energy. In the antiferromagnetic phase (AF) as in $Sr_2FeWO_6$ the bands reduce to three one-dimensional bands. The electronic energy remains larger than in the F state but the difference decreases with increasing charge transfer energy. Therefore, with increasing Fe–M charge transfer energy, the transition to the AF state can be easily driven by the superexchange interaction. We find that the transition occurs for values of the charge transfer energy such that the Fe and M valences obtained are compatible with the values 2+ and 6+ usually considered for $Sr_2FeWO_6$. Our approach thus provides a sensible scheme for the transition. We also discuss the F–AF transition in $Sr_2FeMo_xW_{1-x}O_6$ as a function of doping.
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The double perovskites $Sr_2FeMO_6$ (where M is a transition metal) are very good candidates for magneto-electronic applications, since some compounds, like $Sr_2FeMoO_6$ and $Sr_2FeReO_6$ may combine half-metallic ferromagnetic (F) character with a high Curie temperature $T_c$ ($\approx 450\,K$). A low-field magnetoresistance (MR) can be obtained in polycrystalline materials resulting from inter-grain tunneling 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 [1] and is verified by the observation of MR across an artificial bicrystal boundary [2]. It is therefore of fundamental interest to understand which parameters are controlling the half-metallic character as well as the $T_c$ in order to optimize the electronic properties.

From the fundamental point of view it is interesting that $Sr_2FeWO_6$ has completely different electronic and magnetic properties, it is known as an antiferromagnetic (AF)

insulator with $T_N \approx 37\,K$. One reason why $Sr_2FeWO_6$ is so different from $Sr_2FeMoO_6$ and $Sr_2FeReO_6$ has been suggested by band-structure analysis [3]. In this picture, the antibonding W(5d) states are pushed higher in energy by the stronger hybridization with oxygen p orbitals [3,4]. Because of this, 5d electrons prefer to move away from the W site, leaving it in a $W^{6+}(5d^0)$ configuration, and stay on the Fe 3d level even at the cost of paying extra Coulomb energy. Therefore, as expected, $Sr_2FeMo_xW_{1-x}O_6$ compounds exhibit a metal–insulator transition as a function of doping $x$ [5–7]. The results show that the physical properties of $Sr_2FeMo_xW_{1-x}O_6$ change from those of ferrimagnetic metal to those of AF insulator with increasing W doping. The critical composition, $x_c$, is found to be between 0.2 and 0.3.

In this work, we consider a fully ordered perovskite structure in which Fe and the other metal M(Mo,W) occupy two interpenetrating sublattices in a rock-salt structure. Although most of the FeM samples present Fe–M disorder [8,9] indicated by a saturation magnetization lower than the ideal value $4\mu_B$ expected in a fully polarized ground state, it has been shown that the ordering increases with the W concentration [6]. To picture these

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systems we follow the electronic scheme used recently [7,10]. Due to strong Hund's coupling Fe–3d$^5$ configuration is considered as a localized $S = \frac{5}{2}$ maximum spin. Beside these local spins one has $n$ itinerant electrons coming from M that can hop between Fe and M in the exchange split $t_{2g}$ orbitals. Electrons can hop onto an Fe site only if its spin is antiparallel to the local spin, all five d-orbitals being occupied. On the other hand Mo and W are not strongly correlated metal so that there is no constraint for the electrons to hop on M sites. As in the double-exchange mechanism the kinetic energy term favors a ferromagnetic ordering of the local moments. This scheme is consistent with the "ferrimagnetic" ground state of Sr$_2$FeMoO$_6$ in which the conduction electrons couple antiferromagnetically to the local ferromagnetic spins. We will study the competition of this ferromagnetic tendency with AF superexchange (SE) interactions resulting from virtual hopping among the Fe–3d$^5$ configurations. Here, we consider only the case $n = 1$ corresponding to Mo and W. Due to the symmetry of the intermediate oxygen orbitals, hoppings are nonzero only between orbitals with the same symmetry lying in the corresponding plane, thus giving three degenerate bands. According to the above considerations we write the model Hamiltonian for the ordered compound as Ref. [7]

$$H = E_{Fe} \sum_{i\{Fe\},\sigma} a_{i\sigma}^+ a_{i\sigma} + E_M \sum_{i\{M\},\sigma} b_{i\sigma}^+ b_{i\sigma}$$
$$- \sum_{\langle ij \rangle,\sigma} t_{\mu_i \sigma_j} (a_{i\sigma}^+ b_{j\sigma} + h.c.), \tag{1}$$

where $E_{Fe}$ and $E_M$ are the energies at the Fe and M sites, respectively, $E_M - E_{Fe}$ being the charge transfer energy $\Delta = E(Fe\, d^5,\ S = \frac{5}{2};\ M\, d^1) - E(Fe\, d^6,\ S = 2;\ M\, d^0)$. The operators $a_{i\sigma}^+$, $a_{i\sigma}$ ($b_{i\sigma}^+$, $b_{i\sigma}$) creates and destroys an itinerant electron with spin $\sigma$ at site $i$ occupied by Fe (M), respectively. The hopping term $t_{\mu_i \sigma_j}$ is $t$ when the localized spin $\mu$ (+ for up and − for down) at site $i$ is opposite to the itinerant spin $\sigma$ (↑ or ↓) and the hopping is zero when $\mu$ and $\sigma$ are parallel, this mechanism precludes the possibility to put an itinerant electron in the Fe sites with the same spin as the localized spin. The M–M hopping is ignored. 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 ($z \longrightarrow \infty$). 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:

$$G_\uparrow^M = \frac{1}{\omega - E_M - (w^2/4)v_- G_{\uparrow-}^{Fe}}, \tag{2}$$

$$G_{\uparrow-}^{Fe} = \frac{1}{\omega - E_{Fe} - (w^2/4)G_\uparrow^M}, \tag{3}$$

and similarly for down spin electrons replacing $v_-$ by $v_+$, where $v_\pm = (1 \pm m)/2$ and $m$ being the magnetization. We take $E_{Fe}$ as the reference energy and $E_M = \Delta$. In the ferromagnetic case one has two-dimensional bands and $z = 4$. Fig. 1 shows the Curie temperature $T_c/w$ vs. $\Delta$ for the band filling $n = 1$. $T_c$ scales as the bandwidth $w$ due to Fe–M hopping and does not depend on the sign of $\Delta$.

The magnetic structure of AF Sr$_2$FeWO$_6$ has been reported recently in Ref. [11] and consists of alternating ferromagnetic {1 1 1} planes coupled antiferromagnetically. Within $xy - (yz, zx)$ one gets ferromagnetic Fe-chains alternating antiferromagnetically as shown in Fig. 2. One
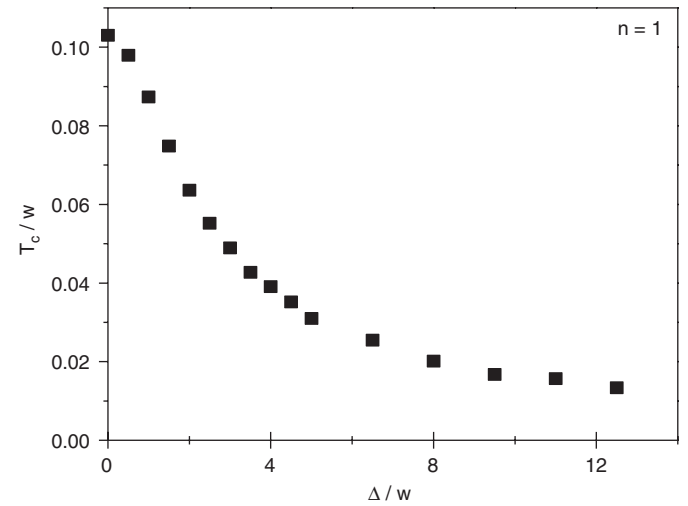


Fig. 1. Variation of the Curie temperature $T_c$ as a function of the transfer energy $\Delta$ for Sr$_2$FeMoO$_6$.
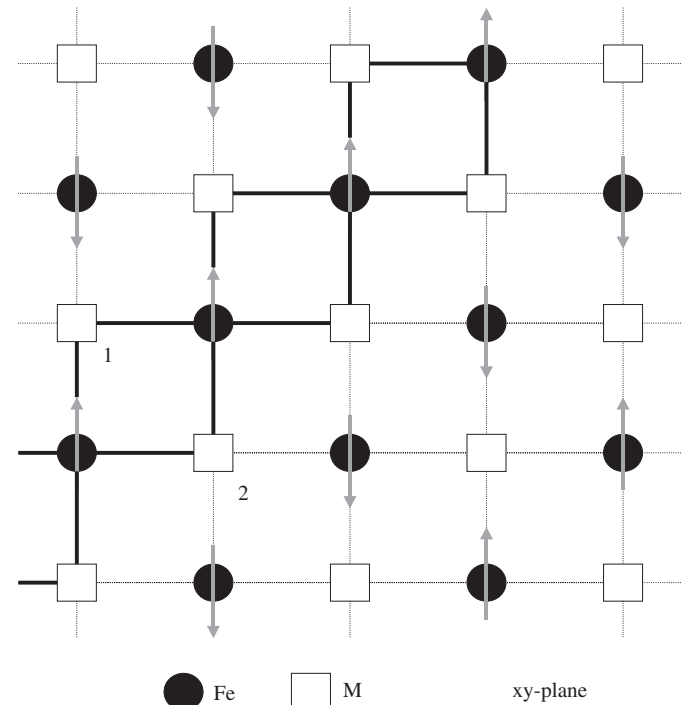


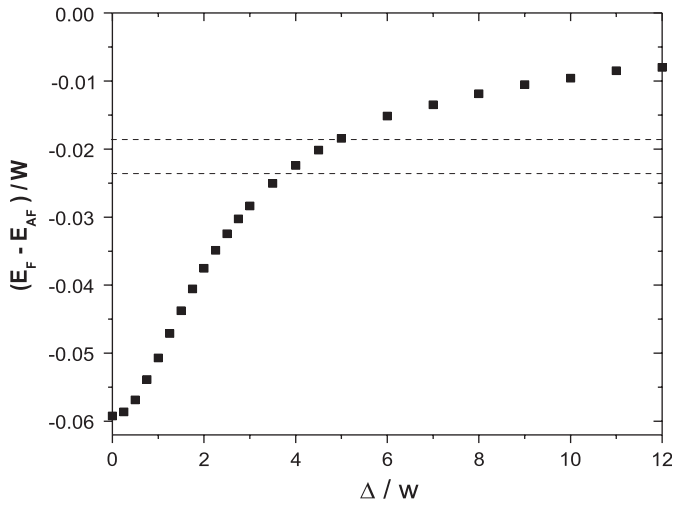Fig. 2. Magnetic structure of the AF Sr$_2$FeWO$_6$ system.

Fig. 3. Energy difference between the ferro- and antiferromagnetic phases vs. $\Delta$ for $n = 1$.



Fig. 4. Number of conduction electrons for Fe and M sites.

now has three one-dimensional bands and in this case the density of states reduces to

$$\rho^{Fe} = \frac{1}{\pi} \sqrt{\frac{\omega - \Delta}{\omega[8t^2 - \omega(\omega - \Delta)]}}$$

and

$$\rho^{M} = \frac{1}{\pi} \sqrt{\frac{\omega}{(\omega - \Delta)[8t^2 - \omega(\omega - \Delta)]}}.$$

The difference of the electronic energy between the F and AF phases is shown in Fig. 3 and the stability of the ferromagnetic state decreases with increasing $\Delta$. Therefore, we expect that SE interactions between Fe localized spins may stabilize the AF phase at large $\Delta$. Denoting $J_1$ and $J_2$ the n.n and n.n.n SE interactions one gets the contributions in the F and AF states as $E_M^F = S(S+1)(z_1 J_1 + z_2 J_2)/2$ ($z_1 = 12$, $z_2 = 6$) and $E_M^{AF} = -S(S+1)z_2 J_2/2$, $J_2$ can be related to the Néel temperature in $Sr_2FeWO_6$. Starting from the insulating state it has been suggested that $J_1 \approx J_2/2$ [12]; this includes the processes involving the fourth $t_{2g}$ electron with opposite spin present in the $Fe^{2+}$ ions (giving $S = 2$) which, is contained in Hamiltonian (1). However, 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, we take the ratio $J_1/J_2$ in the range 0.5–1. The Fe–Mo bandwidth can be obtained from Fig. 1, $T_c/w \approx 0.1$ for $\Delta = 0$ and $T_c = 450$ K, thus giving $(E_M^F - E_M^{AF})/w \approx 1.8 - 2.4 \times 10^{-2}$; these values are shown by the dashed lines in Fig. 3. Therefore, the AF state becomes stable for $\Delta/w \gtrsim$ 4–5. Calculating the number of conduction electrons in Fe and M sites as a function of $\Delta/w$ (Fig. 4) we see that Fe is
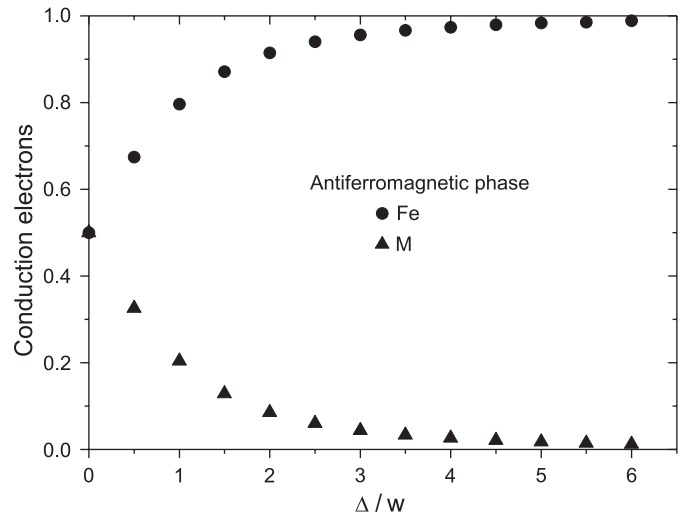
nearly 2+ in the AF state in agreement with experimental observation.

In the $Sr_2FeMo_xW_{1-x}O_6$ compound with $n = 1$, the hopping to W sites is inhibited since $\Delta$ should be quite large for W, so, the number of Fe n.n. is reduced to the $xz$ Mo neighbors. The Green's function for Fe is then modified with a factor $x$ as

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

In the ferromagnetic states it is found that the $T_c$ goes to zero for doping around $x \approx 0.2$ indicating the possibility of a magnetic transition. Taking into account the SE we find a critical concentration for the F–AF transition $x_c \approx 0.25 - 0.3$ in good agreement with the experimental value.

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