Theoretical study of the double perovskite Sr$_2$FeMO$_6$ (M = Mo, W)

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Abstract

We study the double perovskite Sr$_2$FeMO$_6$ using a tight-binding model with the renormalized perturbation expansion technique. An analysis of the antiferromagnetic (AF) phase shows that the electronic energy remains larger than in the ferromagnetic (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. The F–AF transition in the system Sr$_2$FeMo$_x$W$_{1-x}$O$_6$ vs. doping is also presented.

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The double perovskite Sr$_2$FeMO$_6$ have received a lot of attention, in particular ferromagnetic Sr$_2$FeMoO$_6$ because of its high Curie temperature $T_c \approx 450$ K, half-metallic character and large magnetoresistance [1]. On the other hand, Sr$_2$FeWO$_6$ is insulating and antiferromagnetic with $T_N \approx 37$ K [2]. As expected, Sr$_2$FeMo$_x$W$_{1-x}$O$_6$ compounds exhibit a ferromagnetic metal–antiferromagnetic insulator transition for a critical composition $x_c \sim 0.3$ [3]. From band structure it has been suggested that the different behavior between Mo and W systems originates from W(5d) antibonding states pushed higher in energy by a stronger hybridization with oxygen p states [4]. To elucidate the origin of this difference, we analyze the importance of the Fe–M charge transfer energy in a strongly correlated picture. Although most of the samples present Fe/M disorder, we consider a fully ordered perovskite structure Sr$_2$FeMO$_6$ in which Fe and the other metal M(Mo,W) occupy two interpenetrating sublattices in a rock-salt structure. 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, W are uncorrelated metals 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. The hopping stabilization of the itinerant electrons also leads to its spin polarization, antiferromagnetic with respect to the local spins ferromagnetic background consistent with the "ferrimagnetic" ground state of Sr$_2$FeMoO$_6$. This ferromagnetic tendency competes with antiferromagnetic superexchange interactions (SE) resulting from virtual hopping among the Fe-3d^5 configurations. Although we will focus here mostly on the case of Mo and W corresponding to $n = 1$, we consider the general case of band filling n. 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 2D bands. According to the above considerations we write the model Hamiltonian for the ordered compound as [5]

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

$\Delta = E(\text{Fed}^5,\ S = \frac{5}{2};\ \text{Md}^1) - E(\text{Fed}^6,\ S = 2;\ \text{Md}^0)$. The operators $a_{i\sigma}^+$, $a_{i\sigma}$ ($b_{i\sigma}^+$, $b_{i\sigma}$) create and destroy an itinerant electron with spin σ at site i occupied by Fe (M), respectively. The hopping term $t_{\mu_i \sigma_j}$ is t when the localized spin μ (+ for up and − for down) at site i is opposite to the itinerant spin σ (↑ or ↓) and the hopping is zero when μ and σ 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.

For the ferromagnetic phase the density of states are calculated [5] considering the limit of infinite coordination in the Bethe lattice approximation $z \to \infty$ i.e. $4t^2$ scales as $w^2/4$, w being the half band width and the Green's functions reduce to those obtained in the dynamical mean field approach:

$$G_\downarrow^M = \frac{1}{\omega - \Delta - (w^2/4)G_{\downarrow+}^{Fe}}, \qquad G_{\downarrow+}^{Fe} = \frac{1}{\omega - (w^2/4)G_\downarrow^M}$$

taking E_{Fe} as the reference energy.

It is clear that large Δ tends to localize the electrons either on Fe or on M thus weakening the polarization of Fe spins and reducing the stability of the ferromagnetic state [5]. Then one understands that SE may stabilize an AF state.

For the AF phase as observed in Sr_2FeWO_6 which corresponds to [1 1 1] ferromagnetic planes coupled anti-ferromagnetically one can see that, within the xy-(yz, zx) planes, one has ferromagnetic chains alternating antiferro-magnetically [6]. Therefore, due to the AF structure, one obtains now three degenerate 1D bands along [1 1 0] ([0 1 1] and [1 0 1]) Fe chains. Along each kind of chains, Fe spins are either up or down, so only one spin direction is allowed for the itinerant electrons. However, each M site is connected to two Fe chains with opposite spins; as a result $n_\uparrow^M = n_\downarrow^M$ giving non-magnetic M sites. These Fe chains are decorated with M sites to which electrons can hop, each Fe is connected to four M sites while M sites are connected to
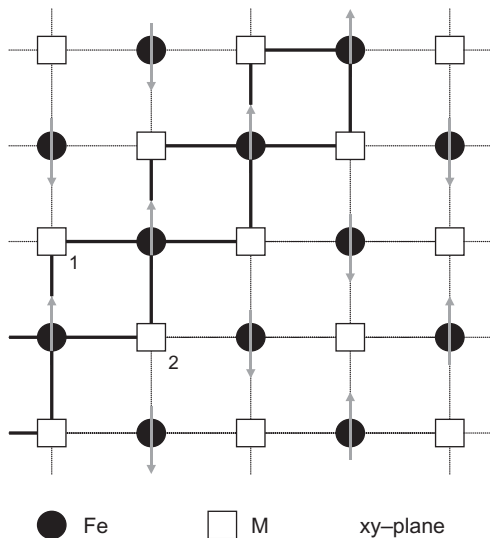
two Fe (see Fig. 1). The unit cell contains one Fe and two M sites labelled 1 and 2. One can easily show that Fe can hybridize only with the combination $\frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$ of the t_{2g}-states at sites 1 and 2, giving chains with alternating Fe and M sites and effective hopping $\sqrt{2}t$. The unhybridized orthogonal combination has energy $\omega = \Delta$. The Green functions as well as the Fe and M densities of states are directly calculated for the 1D system with alternating energies $\omega = 0$ and Δ and effective hopping $t_e = \sqrt{2}t$.

So, for chains with Fe spins − (+)

$$G_{\uparrow-(\downarrow+)}^{Fe} = \frac{1}{\omega - 2t_e^2 g_{\uparrow(\downarrow)}^M}, \tag{2}$$

$$G_{\uparrow(\downarrow)}^M = \frac{1}{\omega - \Delta - 2t_e^2 g_{\uparrow-(\downarrow+)}^{Fe}}, \tag{3}$$

while

$$g_{\uparrow(\downarrow)}^M = \frac{1}{\omega - \Delta - t_e^2 g_{\uparrow-(\downarrow+)}^{Fe}}, \tag{4}$$

$$g_{\uparrow-(\downarrow+)}^{Fe} = \frac{1}{\omega - t_e^2 g_{\uparrow(\downarrow)}^M}. \tag{5}$$

Due to the ↑, ↓ symmetry for Fe −,+ sites and remembering that each Mo sites belong to two Fe chains with +,− spins, one gets $G_{\uparrow-}^{Fe} = G_{\downarrow+}^{Fe}$ and $g_\uparrow^M = g_\downarrow^M$. Then,

$$\rho_{\uparrow-(\downarrow+)}^{Fe} = \rho^{Fe} = \frac{1}{\pi}\sqrt{\frac{\omega - \Delta}{\omega[8t^2 - \omega(\omega - \Delta)]}}, \tag{6}$$

$$\rho_{\uparrow(\downarrow)}^M = \rho^M = \frac{1}{\pi}\sqrt{\frac{\omega}{(\omega - \Delta)[8t^2 - \omega(\omega - \Delta)]}}. \tag{7}$$

The difference of the electronic energy between the F and AF phases as function of the band filling n and different values of Δ is shown in Fig. 2. The F state has lower kinetic energy for $n \lesssim 1.7 - 2$ depending on Δ. For $n = 1$ the electronic energy of the AF state remains larger than in the

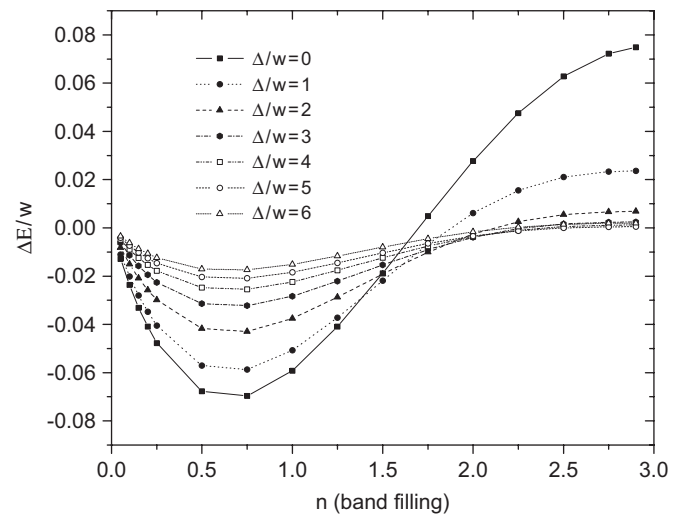Fig. 1. Magnetic structure of the AF Sr_2FeWO_6 system.

Fig. 2. Energy difference between the ferro-antiferromagnetic phases vs. the band filling for different values of Δ.

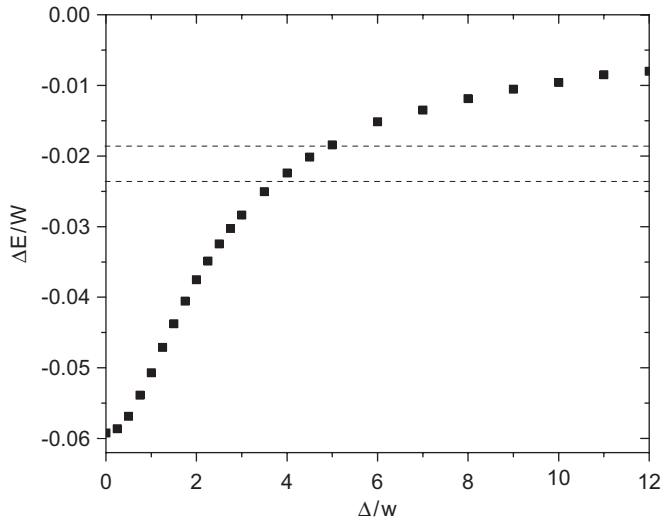Fig. 3. Energy difference for the ferro-antiferromagnetic phases vs. Δ for $n = 1$.

Fig. 4. Energy difference for the ferro-antiferromagnetic phases vs. the concentration x.

F state but the difference decreases with increasing charge transfer energy as seen in Fig. 3. Therefore, we expect that SE interactions can drive a transition to the AF ground state at large Δ. We believe that this is the case of Sr_2FeWO_6 and in Fig. 3 the dashed lines represent SE energies compatible with the value of the Néel temperature [7]. The charge transfer is large enough to strongly reduce the effective Fe–Fe hopping, as a result Fe becomes nearly 2+ in agreement with the experimental observation [7].

In the case of $Sr_2FeMo_xW_{1-x}O_6$, we consider that Fe–W charge transfer energy is sufficiently larger than for Fe–Mo to justify that the Fe–W hopping can be neglected as a first approximation. As a consequence Fe will be connected to Mo nearest-neighbors only, respectively $4x$ and $2x$ in the F and AF states. In the following Δ refers to Fe–Mo charge transfer energy. The Green's function for Fe is then modified accordingly

$$G_{\downarrow +}^{Fe} = \frac{1}{\omega - (w^2/4)xG_{\downarrow}^M}$$

in the F state. The evolution of the density of states has been presented in Ref. [5].

Similarly in the AF state, assuming that the AF Sr_2FeWO_6 structure is preserved for all x, one gets

$$G_{\uparrow - (\downarrow +)}^{Fe} = \frac{1}{\omega - 2xt_e^2 g_{\uparrow(\downarrow)}^M}, \tag{8}$$

$$g_{\uparrow - (\downarrow +)}^{Fe} = \frac{1}{\omega - xt_e^2 g_{\uparrow(\downarrow)}^M}. \tag{9}$$

One can drop the indices $\uparrow, \downarrow$ and $-, +$ to obtain

$$\rho^{Fe} = \frac{1}{\pi} \frac{\sqrt{8t^2\omega(\omega - \Delta) - [\omega(\omega - \Delta) + x']^2}}{|\omega|[2x' - \omega(\omega - \Delta)]}, \tag{10}$$
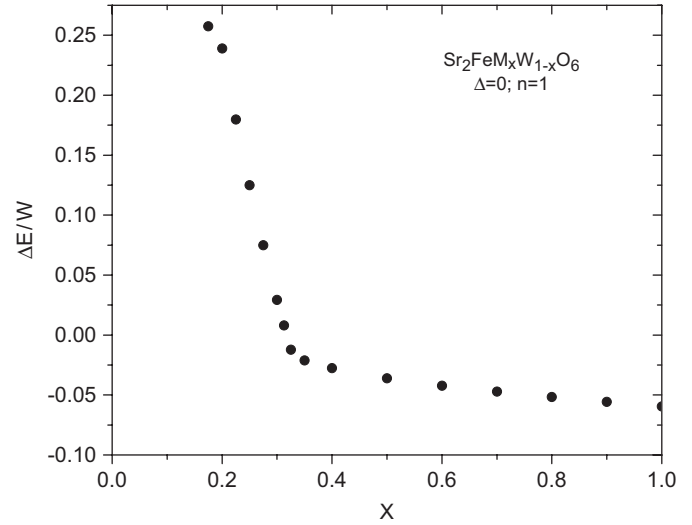
$$\rho^M = \frac{x}{\pi} \frac{\sqrt{8t^2\omega(\omega - \Delta) - [\omega(\omega - \Delta) + x']^2}}{|\omega - \Delta|[2x' - \omega(\omega - \Delta)]}, \tag{11}$$

where $x' = 2t^2(1 - x)$. For $x \neq 1$ the 1D density of states splits in two bands. Beside these bands we should not forget that the M density of states also shows a peak of weight x at $\omega = \Delta$ due to the unhybridized combination of the two M orbitals. In addition there are also peaks with weight $(1 - x)/(1 + x)$ at $\omega = 0$ and $\omega = \Delta$, respectively, in the partial Fe and M density of states, giving a total weight $(1 - x)$. For $\Delta = 0$ each subband has a spectral weight x.

The difference of electronic energy between the F and AF phases is shown in Fig. 4 as function of x for $\Delta = 0$. The F–AF transition occurs for $x \sim 0.3$ in good agreement with the experiment value [3]. The SE energy do not modify significantly this result.

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