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Magnetic transition in double perovskite systems

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ABSTRACT

The search for materials having complete spin polarization and high Curie temperature have received a lot of attention in view of spintronics applications, especially the ferromagnetic (F) Sr_2FeMoO_6, because of its fairly high Curie temperature ($T_C = 450$ K), half-metallic character, large magnetoresistance and potential applications. On the other hand, Sr_2FeWO_6 is insulating and antiferromagnetic (AF) with $T_N = 37$ K. With a double exchange type model it has been shown that F−AF transition can be driven by super-exchange interactions with increasing Fe−M (M = Mo, W) charge transfer energy. So, the charge transfer energy is expected to be larger in FeW than in FeMo compounds. Using a tight-binding model with the renormalized perturbation expansion technique, we determine the density of states for the AF phase and the electronic energy difference for the F- and AF-phases as a function of the Fe−M charge transfer energy. The F−AF transition in the ordered system $Sr_2FeMo_xW_{1-x}O_6$ occurs for $x \sim 0.3$, in good agreement with the experimental value. We also studied the effect of the diagonal disorder in the variation of the number of conduction electrons on Fe and M sites. Finally, the behavior of the Curie temperature as a function of the Mo/W concentration is determined.

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1. Introduction

The physics of double perovskite has been recently very attractive in view of their magnetoelectronic applications. In this report, we will consider only double perovskite structure of the type Sr_2FeMO_6 (M = Mo, W), where in the ordered case the Fe and M occupy two interpenetrating sublattices, α and β, respectively, in a rock-salt structure. Oxygen atoms bridge the Fe and M ions to form alternating FeO_6 and MO_6 octahedra. For M = Mo the compound has a ferromagnetic (F) behavior [1] and for M = W the system is insulating and antiferromagnetic (AF) [2]. As expected, $Sr_2FeMo_xW_{1-x}O_6$ compounds exhibit a F–AF transition as a function of doping x [3]. In the $Sr_2FeMo_xW_{1-x}O_6$ system, Mo and W occupy the same sublattice (say β) while Fe remains on the other one (α). Therefore one has a disordered alloy on one sublattice only, a situation quite different from ordinary alloys.

Our basic electronic picture is to consider the Fe-3d^5 configuration as a localized $S = \frac{5}{2}$ high-spin $\vec{S_i}$. This view is consistent with the informations on electronic states arising from photoemission [4] and X-ray magnetic circular dichroism [5] experiments for Sr_2FeMoO_6. In addition to these local spins one also has itinerant electrons coming from Mo and W that can hop between Mo/W and Fe in the exchange split t_{2g} orbitals. Both Mo and W would have d^0 (6+) core state providing one electron per atom so

that the number of itinerant electrons remains constant $n = 1$ over the series. In the Fe-3d^5 configuration all orbitals being occupied in one spin channel, itinerant electrons can hop to an Fe site only if its spin is antiparallel to the local spin $\vec{S_i}$. On the other hand, Mo and W are not correlated metals so that there is no constraint for electrons to hop on M sites. This coupling between conduction electrons and local spins is equivalent to the double exchange in manganites but with an effective AF and infinite exchange integral. The hopping of the itinerant electrons favors an F background of the Fe spins and also leads to its AF spin polarization with respect to this background corresponding to the so-called "ferrimagnetic" ground state of Sr_2FeMoO_6.

The conduction band is built from the three t_{2g} orbitals. We consider only nearest-neighbor Fe–M hopping. We assumed that the hopping is the same for Fe–Mo and Fe–W. Due to the symmetry of the bridging oxygen orbitals, hopping integrals are non-zero only between orbitals of the same symmetry and only between orbitals lying in the corresponding plane, i.e., xy-orbitals in the xy plane, etc., thus giving three degenerate two-dimensional bands.

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

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

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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. M being either Mo or W on the β sublattice; ε_{Fe} and $\varepsilon_{M} = \varepsilon_{Mo}$ or ε_{W} are the site diagonal energies for the itinerant electrons at Fe, Mo and W sites. These energies are defined from the charge transfer energies $\varepsilon_{M} - \varepsilon_{Fe} = E(\text{Fe}\,d^{5}, S = \frac{5}{2}; \text{M}\,d^{1}) - E(\text{Fe}\,d^{6}, S = 2; \text{M}\,d^{0})$, and are different quantities for Mo and W. We will take these parameters defining the alloy problem to be Δ and Δ' for Mo and W, respectively, but, of course our approach is applicable to other compounds with different transition metals M and M' as well. For the sake of simplicity we consider that the localized spins can be either parallel or antiparallel to a given quantization direction, $\mu_{i} = +$ for up or $-$ for down. So, the hopping term $t_{\mu_{i}\sigma}$ is t when the itinerant electron spin σ ($\uparrow$ or $\downarrow$) is opposite to μ_{i} and the hopping is zero when σ and μ_{i} are parallel.

2. Results and discussion

The density of states for itinerant electrons is calculated from the local Green's functions considering the limit of infinite coordination z in a two-sublattice Bethe approximation [6], i.e. $4t^{2}$ scales as $w^{2}/4$, $z = 4$ being the Fe–M coordination number inside each plane. In this case, the Green's functions reduce to those used in the dynamical mean field approach [7]:

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

and

$$G_{\downarrow}^{M} = \frac{1}{\omega - \Delta - \frac{w^{2}}{4}v_{+}G_{\downarrow+}^{Fe}}, \tag{3}$$

$$G_{\downarrow}^{M'} = \frac{1}{\omega - \Delta' - \frac{w^{2}}{4}v_{+}G_{\downarrow+}^{Fe}}, \tag{4}$$

where the configuration of the Fe spins is specified by the probabilities $v_{\pm} = (1 \pm m)/2$ that an Fe site has its spin $+$ or $-$, m being the magnetization parameter of the local spins. We took $\varepsilon_{Fe} = 0$ as the reference energy.

Similarly the Green's functions for up electrons $G_{\uparrow-}^{Fe}$ and $G_{\uparrow}^{M(M')}$ are obtained by replacing v_{+} by v_{-}.

Defining the Green's function on the β sites

$$\mathcal{G}_{\sigma} = xG_{\sigma}^{M} + (1-x)G_{\sigma}^{M'} \tag{5}$$

one obtains that $\mathcal{G}_{\sigma}$ obeys the usual coherent potential approximation (CPA) [8]:

$$\frac{x}{1 - (\Delta - \Sigma_{\sigma})\mathcal{G}_{\sigma}} + \frac{1-x}{1 - (\Delta' - \Sigma_{\sigma})\mathcal{G}_{\sigma}} = 1, \tag{6}$$

where the self-energy Σ_{σ} is defined by

$$\mathcal{G}_{\downarrow(\uparrow)} = \frac{1}{\omega - \Sigma_{\downarrow(\uparrow)} - \frac{w^{2}}{4}v_{+(-)}G_{\downarrow+(\uparrow-)}^{Fe}}. \tag{7}$$

This generalizes the usual CPA equations to the present two-sublattice case where only one sublattice is disordered. $\mathcal{G}_{\downarrow(\uparrow)}$ and $G_{\downarrow+(\uparrow-)}^{Fe}$ are solutions of a third degree equation from which the partial and total densities of states are obtained. One can calculate the energy of the F and paramagnetic (P) states, and the Curie temperature T_{C} following Ref. [6].

In the following we present results for the case $\Delta = 0$ and we vary Δ'. We think that this situation is pertinent for Mo in Fe−Mo/M' systems. Nevertheless our results can be easily extended to the case $\Delta \neq 0$. An estimate of the charge transfer

energy can be obtained from the Fe and M valence in $Sr_{2}FeMO_{6}$ compounds. In the case of $Sr_{2}FeMoO_{6}$ recent experimental estimations of the valence [9,10] seem to converge towards values close to 2.5+ for Fe indicating that ε_{Fe} and ε_{Mo} should be quite close. The value of the Mo moment obtained by Besse et al. [5] also indicates that Δ is quite small; from the theoretical determination of the valence in the F ground state [11] we get a value as small as $\Delta/w \simeq 0.05$, w being half the bandwidth. For $Sr_{2}FeWO_{6}$ the charge transfer energy has been estimated from the stability of the AF ground state to be $\Delta'/w \gtrsim 4$ [12,13]. For such large value of charge transfer the calculated Fe valence is nearly 2+ in agreement with experimental evidences [2,15].

The stability of the F state decreases with respect to the pure systems $Sr_{2}FeMoO_{6}$ and $Sr_{2}FeWO_{6}$. This is clearly reflected on the behavior of T_{C}/w represented in Fig. 1. T_{C}/w decreases on both sides and eventually becomes zero at low $x \lesssim 0.2$ for $\Delta'/w \gtrsim 1.75$. This shows that the F state becomes unstable with respect to the P state. When $\Delta'/w \gtrsim 1.75$, T_{C}/w vs. x becomes almost independent of Δ'/w. This, therefore, justifies our approximation taking $\Delta'/w \to \infty$ and neglecting Fe–W hopping as in our previous
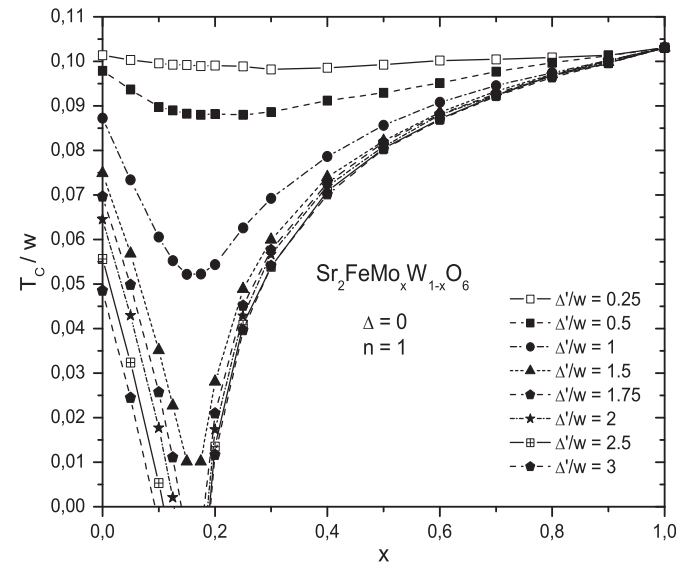

Fig. 1. Variation of the Curie temperature as a function of the concentration x for different values of the disorder parameter Δ'/w, $\Delta = 0$ and the band filling $n = 1$.
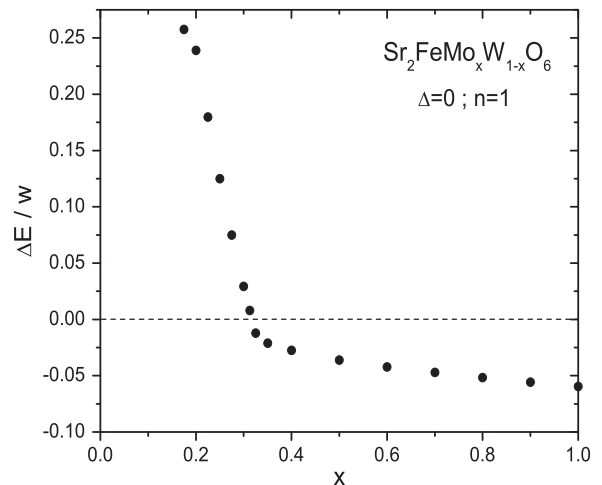

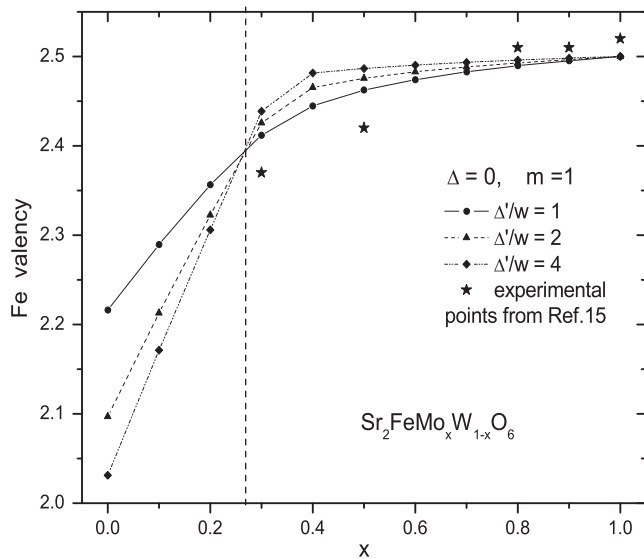**Fig. 2.** Energy difference for the F- and the AF-phases as a function of the concentration x.

Fig. 3. Fe valency as a function of the concentration x.

To make our view more precise, it is worthwhile to determine the evolution of Fe valence state upon Mo/W alloying. In Fig. 3, we show Fe valence calculated in the F state as a function of the concentration x for different values of $\Delta'/w = 1, 2, 4$ together with the experimental values obtained by Linden et al. [15]. For $\Delta'/w = 4$ our results reproduce correctly the decrease of Fe valence towards 2+ when the W concentration is increasing.

Acknowledgments

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studies [6,11,13,14]. Of course, when x is small and Δ' large the AF ground state should be considered. For the AF phase with [1 1 1] F planes coupled antiferromagnetically, as observed in Sr_2FeWO_6, we get F chains alternating antiferromagnetically. Therefore, due to the AF structure, one obtains now three degenerate one-dimensional 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. The difference of electronic energy between the F- and AF-phases is shown in Fig. 2 as function of x for $\Delta = 0$. We see that an F–AF transition occurs for $x \sim 0.3$ in remarkably good agreement with the experimental value [3]. This indicate that this transition is essentially of electronic origin, resulting from the double-exchange type of interaction which is the basis of our approach.