



# Effect of disorder on the electronic structure of the double perovskite $\text{Sr}_2\text{FeMoO}_6$

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## Abstract

Recently,  $\text{Sr}_2\text{FeMoO}_6$  has been established as a new colossal magnetoresistance material with substantial low-field magnetoresistance at room temperature and has attracted much attention in the double perovskite family. This material always appears with a certain degree of miss-site disorder where Fe and Mo interchange their positions. Using renormalized perturbation expansion, we calculate the density of states and determine the variation of the critical temperature in the low disorder regime. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Double perovskites  $\text{A}_2\text{MM}'\text{O}_6$  (A being an alkaline earth and M, M' two different transition-metal elements) have attracted recently much attention, in particular because ordered  $\text{Sr}_2\text{FeMoO}_6$  has shown low-field colossal magnetoresistance (CMR) remaining significant up to room temperature [1]. The origin of the magnetoresistance (MR) is attributed to the half-metallic ferromagnetic character below  $T_c$  [1] via intergrain carrier scattering. The low-field MR is strongly affected by the long-range ordering of Fe and Mo atoms [2,3]. Ordered and strongly disordered samples are distinguished by the existence of the larger change of the MR at low field for the

ordered samples. However, the way disorder is affecting the MR is not yet clear. Before considering such issue, it is therefore essential to address the question of the effect of positional disorder at Fe and Mo sites on the electronic structure of  $\text{Sr}_2\text{FeMoO}_6$ .

Decrease of the saturation magnetization with increasing disorder is expected as a result of antiferromagnetic super-exchange interaction between nearest-neighbors Fe [4].

## 2. Model and results

In the fully ordered perovskite structure, Fe and Mo occupy two interpenetrating sub-lattices.

Because the relevant states near the Fermi energy are derived from Fe and Mo d-orbitals we will use a simple tight-binding Hamiltonian

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based on the calculated band structure [1,5] 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. Due to strong Hund’s coupling on Fe sites parallel spins occupy  $t_{2g}$  and  $e_g$  orbitals giving the high-spin configuration  $S = \frac{5}{2}$  of the  $3d^5$  configuration. We will consider these orbitals frozen, depicted by a localized spin  $\vec{S}_i$ . To reduce the mathematical complexity we represent the localized spin as a spin  $\frac{1}{2}$  so that it can be parallel or antiparallel to the quantization direction, restricting our approach to ordered or disordered Ising magnetic structures.

In addition to this localized spin one itinerant electron can be added with opposite spin in the exchange split  $t_{2g}$  orbitals to give  $3d^6$  ( $Fe^{2+}$ ) configuration in the Fe sites. The corresponding  $e_g$  orbitals split by the crystal field are not occupied and will not be included. 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 [6]. The Mo sites would have either  $4d^1(Mo^{5+})$  or  $4d^0(Mo^{6+})$  configuration and the number of conduction electrons  $n$  correspond to one electron per Mo atom. This electronic scheme is consistent with the band structure calculations for the ferromagnetic ground state. 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. According to the above considerations we write the following model Hamiltonian for the ordered compound:

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

where  $a_{i\sigma}^+, a_{i\sigma}$  ( $b_{i\sigma}^+, b_{i\sigma}$ ) creates and destroys an itinerant electron with spin  $\sigma$  at site  $i$  occupied by Fe (Mo), respectively.  $\varepsilon_{Fe}$  and  $\varepsilon_{Mo}$  are the site diagonal energies at the Fe and Mo sites,

respectively. Finally, the hopping term  $t_{\mu,\sigma_j}$  is  $t$  when the localized spin  $\mu$  (+ for up and – for down) at site  $i$  is opposite to the itinerant spin  $\sigma$  ( $\uparrow$  or  $\downarrow$ ) and the hopping is zero when  $\mu$  and  $\sigma$  are parallel, this mechanism precludes the possibility to put an itinerant electron in the Fe site with the same spin as the localized spin. The hopping integral Fe–Mo can be chosen for best agreement with ab initio results [7], and we ignore Mo–Mo hopping which is not important to the density of states near the Fermi level. The hopping term gives rise to the band width in the minority spin channel as seen in the band structure [5] and favors a ferromagnetic background of the Fe spins with antiparallel polarized itinerant electrons, thus producing the “ferrimagnetic” ground state in the ordered case.

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) [8]. 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  $G_{\sigma\mu}^{Fe}$  and  $G_{\sigma}^{Mo}$  for Fe and Mo which include the probabilities  $v_{\pm} = (1 \pm m)/2$  that a Fe ion has its localized spin + or –. In accordance with the model Hamiltonian, on the Fe sites we have  $G_{\uparrow+}^{Fe} = G_{\downarrow-}^{Fe} = 0$  and only  $G_{\downarrow+}^{Fe}$  (or  $G_{\uparrow-}^{Fe}$ ) are given by

$$G_{\downarrow+}^{Fe} = \frac{v_+}{[\omega - \varepsilon_{Fe} - zt^2 g_{\downarrow}^{Mo}]}, \quad (2)$$

where we assume that the sum over neighbors can be replaced by the number of nearest-neighbors  $z$  times their average Green functions  $g_{\downarrow}^{\text{Mo}}$  given by

$$g_{\downarrow}^{\text{Mo}} = \frac{1}{[\omega - \varepsilon_{\text{Mo}} - (z-1)t^2 g_{\downarrow+}^{\text{Fe}}]} \quad (3)$$

with

$$g_{\downarrow+}^{\text{Fe}} = \frac{v_+}{[\omega - \varepsilon_{\text{Fe}} - (z-1)t^2 g_{\downarrow+}^{\text{Mo}}]} \quad (4)$$

Similarly, we can write

$$G_{\downarrow}^{\text{Mo}} = \frac{1}{[\omega - \varepsilon_{\text{Fe}} - zt^2 g_{\downarrow+}^{\text{Fe}}]} \quad (5)$$

The Green's functions for up electrons are obtained by replacing  $v_+$  by  $v_-$ .

Let us mention that, when the coordination number  $z \rightarrow \infty$ , the functions  $g \rightarrow G$  and the above equations reduce to those used in a dynamical mean-field approach. In that case  $zt^2$  scales as  $W^2/4$ ,  $W$  being half the band width. We take here  $z = 4$  to take into account that  $t_{2g}$  orbitals are connected only within its own plane.

Solving these equations we can calculate the partial densities of states for itinerant electrons on Fe and Mo sites. The density of states per Fe site can be written as  $\rho_{\uparrow}^{\text{Fe}}(m, \omega) = -1/\pi \text{Im}(G_{\uparrow-}^{\text{Fe}})$ . Similarly,  $\rho_{\downarrow+}^{\text{Fe}}(m, \omega)$  is obtained by changing  $v_-$  in  $v_+$ . For the Mo atoms we simply have  $\rho_{\sigma}^{\text{Mo}}(m, \omega) = -1/\pi \text{Im}(G_{\sigma}^{\text{Mo}})$ . The densities of states are shown in Fig. 1.

The total density of states  $\rho(m, \omega) = \sum_{\sigma} [\rho_{\sigma}^{\text{Fe}}(m, \omega) + \rho_{\sigma}^{\text{Mo}}(m, \omega)]$  allows us to write  $n = 3 \int_{-\infty}^{\varepsilon_{\text{F}}} \rho(m, \omega) d\omega$  and we take  $n = 1$  to determine the Fermi energy  $\varepsilon_{\text{F}}$  (indicated in Fig. 1 by thin lines), where the factor 3 is included to take into account the orbital degeneracy of  $t_{2g}$  levels. At this point we can calculate the kinetic energy of the conduction electrons  $E_{\text{kin}}(m) = 3 \int_{-\infty}^{\varepsilon_{\text{F}}} \rho(m, \omega) \omega d\omega$ . In order to obtain the thermodynamical value of  $m$  we need to calculate the minimum of the free energy  $F = E_{\text{kin}}(m) - TS(m)$ . We write the entropy of the system as  $S(m) = \ln(2) - v_+ \ln(2v_+) - v_- \ln(2v_-)$ , where we take the simplest possible form compatible with our earlier approximations.

To consider the effect of antisites (AS) in the dilute limit we note first that Fe AS will be

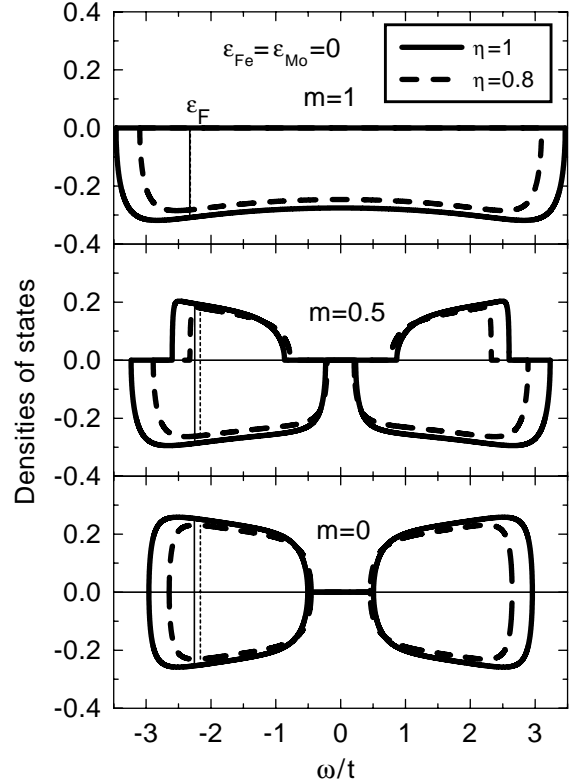


Fig. 1. Densities of states ( $\rho_{\uparrow}$  and  $\rho_{\downarrow}$ ) vs. energies ( $\omega/t$ ) for different values of the magnetization in the ordered case  $\eta = 1$  (full line), and disordered case  $\eta = 0.8$  (dashed line). Positive Y-axis correspond to  $\rho_{\uparrow}$  and negative for  $\rho_{\downarrow}$ . The Fermi level  $\varepsilon_{\text{F}}$  is indicated with vertical thin lines.

surrounded by  $\text{Fe}^{3+}$  ions instead of  $\text{Mo}^{5+}$  ions. In consequence their  $t_{2g}$  orbitals site energies will be shifted up in a magnitude much larger than the hopping between its neighbors. Similarly, the Mo diagonal energy at the AS will be strongly reduced. In consequence we neglect all hopping terms from sites to AS. Thus, AS Fe ions correspond to  $\text{Fe}^{2+}$  (empty orbital) while AS Mo correspond to  $\text{Mo}^{4+}$ . We define an order parameter  $\eta$  as the probability of finding a Fe (Mo) ion in its corresponding sublattice, so that the probability of finding an AS is  $1 - \eta$ .

To take in account that AS are not connected to its neighbors, Eqs. (2)–(5) have to be modified by multiplying the Green's functions  $g$  in the

denominators by  $\eta$  on one side and also multiplying  $G$  in Eqs. (2) and (5) by  $\eta$ . For comparison the modified densities of states are shown in Fig. 1.

Besides the contribution from the itinerant electrons to the kinetic energy of the system in the presence of AS one should also consider the super-exchange interaction among the localized spins  $\vec{S}_i$  which occurs when two Fe atoms are nearest-neighbors. The super-exchange Hamiltonian is  $H_M = J\vec{S}_i \cdot \vec{S}_j$ . As we neglect the hopping between Fe sites and antisites, AF superexchange coupling prevails and the Fe AS are AF (with magnetization  $-m$ ) relative to the Fe sites, which, in the mean-field approximation contributes to the ground state energy as  $E_M = Jz(1 - \eta)\eta m^2$ . Having included these changes in the Green's functions and in the free energy we can calculate again the free energy and the thermodynamical properties.

Recently, Linden et al. [9] have interpreted their recent Mössbauer data as indicating an intermediate valence state close to  $\text{Fe}^{2.5+}$ , literally meaning that  $\varepsilon_{\text{Fe}} \approx \varepsilon_{\text{Mo}}$ . Qualitatively, this is, in fact, what the band structure results tell us clearly showing that the minority spin bands up to Fermi level  $\varepsilon_F$  are almost equally populated from Fe and Mo contributions [1,5]. Therefore, we will assume that  $\varepsilon_{\text{Fe}} = \varepsilon_{\text{Mo}} = 0$ .

In order to make a systematic study our approach can be extended to other double perovskite compounds lifting this constraint. These results will be published elsewhere.

Let us consider first the ordered case  $\eta = 1$ . In Fig. 1 we show the evolution of the density of states as function of energy for three different values of the magnetization  $m$ . The density of state of the fully ferromagnetic state is in qualitative agreement with band structure results, the Fermi energy  $\varepsilon_F$  lying below the minority spin “localized” level at  $\varepsilon = 0$ . As the magnetization decreases, the band width of the minority spin channel increases, the bottom of the band is pushed down and eventually crosses  $\varepsilon_F$ . One can see that the effect of spin disorder is a narrowing of the spin down band and the apparition of a spin up band.

The magnetization as function of temperature in units of  $t$  is shown in Fig. 2 indicating  $T_c/t \approx 0.53$ .

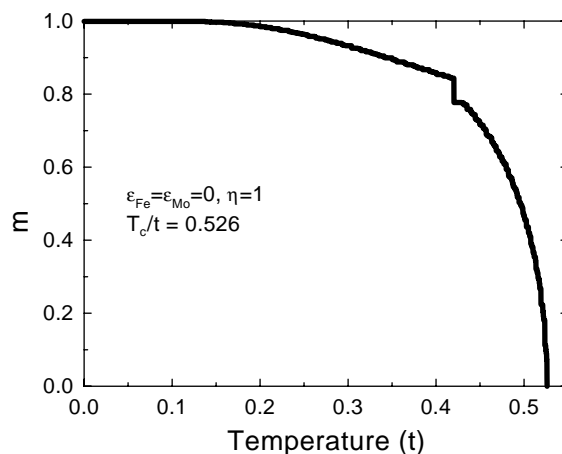


Fig. 2. Magnetization  $m$  vs. temperature  $T/t$  for the ordered system. For  $T/t \approx 0.42$ , the jump in  $m$  correspond to the transition half-metal to metal.

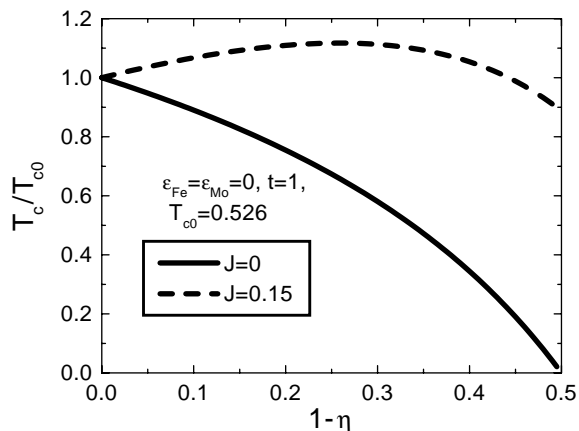


Fig. 3. The Curie temperature  $T_c$  vs.  $\eta$  for  $J/t = 0$  and  $0.15$ .

In our results the half-metallic character is lost for a fairly large value of the magnetization  $m \approx 0.85$ . This is a consequence of the Ising approach used in the RPE and is only indicative of a significant increase of the up spin density of states at the Fermi level for approximately this value of  $m$ .

Now let us turn to the effect of disorder. As seen in Fig. 1 the bands narrow and loose weight as  $\eta$  increases. Furthermore, the filling of the bands lowers because the AS Mo ions absorb electrons. This would cause a lowering of the Curie

temperature ( $T_c$ ), however, since the super-exchange interaction of AS Fe ions may be very large [10], it can rise  $T_c$ . So that, the competition between these two effects determines  $T_c$ . These results are seen in Fig. 3.

To resume, we have shown the electronic structure of  $\text{Sr}_2\text{FeMoO}_6$ , and from it calculated magnetization as function of temperature and the Curie temperature both for ordered and disordered systems.

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