

Theory of transition temperature of magnetic double perovskites

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We formulate a theory of double perovskite compounds such as $\text{Sr}_2\text{FeReO}_6$ and $\text{Sr}_2\text{FeMoO}_6$ which have attracted recent attention for their possible uses as spin valves and sources of spin-polarized electrons. We solve the theory in the dynamical mean-field approximation to find the magnetic transition temperature T_c . We find that T_c is determined by a subtle interplay between carrier density and the Fe-Mo/Re site energy difference, and that the non-Fe same-sublattice hopping acts to reduce T_c . Our results suggest that presently existing materials do not optimize T_c .

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Identification of a ferromagnet with high spin polarization at room temperature and stable surface properties is an important goal in the field of magnetic materials. Such a system would allow, for example the fabrication of ‘‘spin-valve’’ devices of greatly improved efficiency for magnetic field sensing,¹ the development of new magnetic recording media,² and perhaps the construction of improved sources of spin-polarized electrons for ‘‘spin-tronic’’ applications.³ One promising family of materials are the ‘‘double perovskites.’’^{4–6} These are compounds of chemical formula $AB'B'O_6$, with A an alkaline earth such as Sr, Ca or Ba, and B, B' two different transition metal ions. Double perovskites in which B is Fe and B' is Mo or Re are of particular recent interest because they seem⁵ to be metallic ferrimagnets with very high magnetic transition temperatures and highly spin-polarized conduction bands. However, neither the physics nor the materials science of these compounds is yet well understood. The magnetic transition temperature and whether the ground state is metallic or insulating vary as A is changed from Ba to Sr to Ca.⁷ Mis-site ($B-B'$) disorder has a pronounced effect.⁸

In this paper we take a step towards a theoretical understanding for these materials. We derive a many-body Hamiltonian, using band theory calculations⁵ to fix important parameters. We calculate the magnetic transition temperature T_c , and determine how different material parameters affect it. Our results should provide guidance in attempts to design double perovskite materials with improved properties, and an appropriate starting point for calculations of other properties.

Double perovskites have a crystal structure which generalizes the familiar ABO_3 perovskite structure by having two

B -site ions, which in the ideal structure alternate in a simple two sublattice pattern. The band theory has been determined.⁵ The conduction bands are derived from transition metal B -site t_{2g} d orbitals, in agreement with quantum chemical considerations.⁷ There are six conduction bands per spin direction per unit cell; roughly, one triplet arises mainly from the $d_{xy,xz,yz}$ orbitals on the Fe and the other from the same orbitals on Mo/Re. The occupied bands are fully polarized at $T=0$.

Because the near-fermi-surface bands are derived from transition metal d orbitals, we argue that a simple tight-binding parametrization of the band theory is adequate. We therefore model the ideal compound as a cubic lattice of transition metal sites, divided in the usual way into two interpenetrating fcc sublattices, which we denote as A (Mo/Re) and B (Fe). On each site we include 3 t_{2g} orbitals, d_{xy}, d_{xz}, d_{yz} . A good fit to the band structure requires both first and second neighbor hoppings, probably because the Mo/Re conduction electrons come from the $4d$ shell, which is spatially extended. If only first and second neighbor hoppings are considered, then the t_{2g} orbital symmetry implies that a given orbital can mix only with orbitals of the same symmetry and only with orbitals in the appropriate plane (d_{xy} couples only to d_{xy} orbitals in the xy plane).

The band theory is thus a sum of three two dimensional tight binding models, which we write as $H_{\text{band}} = H_{\text{on-site}} + H_{xy}^{\text{hop}} + H_{yz}^{\text{hop}} + H_{xz}^{\text{hop}}$. The on-site term $H_{\text{on-site}}$ consists of an $A-B$ site energy difference, which has a spin-independent term Δ_m (independent of orbital m in cubic symmetry) and a spin dependent term $J\sigma$,

$$H_{xy}^{\text{hop}} = \sum_{p,\sigma} \begin{pmatrix} a_{p(xy)\sigma}^\dagger & b_{p(xy)\sigma}^\dagger \end{pmatrix} \begin{pmatrix} -4t_{aa} \cos(p_x) \cos(p_y) & -t_{ab} [\cos(p_x) + \cos(p_y)] \\ -t_{ab} [\cos(p_x) + \cos(p_y)] & -4t_{bb} \cos(p_x) \cos(p_y) \end{pmatrix} \begin{pmatrix} a_{p(xy)\sigma} \\ b_{p(xy)\sigma} \end{pmatrix}, \quad (1)$$

where $a_{im\sigma}^\dagger$ creates an electron on site i of orbital state m and spin σ .

We now fix parameters by computing the density of states (shown in Fig. 1) and comparing to band calculations. The

calculated tight-binding band structure displays features that depend sensitively on parameters. The parameters which best fit Ref. 5 are shown in Fig. 1, with uncertainties of 10–15% on all quantities.

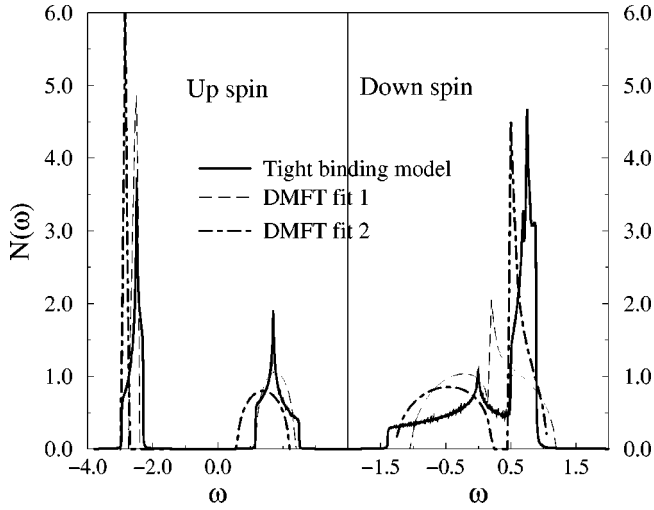


FIG. 1. Density of states from tight-binding model and dynamical mean-field theory. The solid line shows the tight-binding DOS ($t_{ab}=0.5$ eV, $t_{aa}=0.18$ eV, $t_{bb}=0.05$ eV, $\Delta=2.35$ eV, and $J=1.85$ eV); DMFT fit-1 is the local DOS from DMFT for essentially the same parameter values as the tight-binding model ($W_{AB}=0.5$ eV, $W_{AA}=0.22$ eV, $W_{BB}=0.05$ eV, $J=2.2$ eV, and $\Delta=2.0$ eV). DMFT fit-2 is another fit to the tight-binding model ($W_{AB}=0.4$ eV, $W_{AA}=0.4$ eV, $W_{BB}=0.02$ eV, and $J=2.5$ eV, and $\Delta=2.0$ eV). The first DMFT fit gives a T_c that is twice as much as the second one.

For the $|t_{aa}| < |t_{ab}|$ case of relevance here the band minima and maxima are at $\frac{1}{2}[(\Delta - J) - 4(t_{aa} + t_{bb})] \mp \frac{1}{2}\sqrt{4(t_{aa} - t_{bb}) + (\Delta - J)^2 + 4t_{ab}^2}$. As ω is increased through $\Delta - J$, the density of states has a step up. For $t_{bb} = 0$, the hybridization vanishes along a line in \vec{k} space which intersects the van-Hove point, causing the density of states $N(\omega)$ to diverge as $N(\omega \approx \Delta - J) \sim (\omega - \omega^*)^{-1/2} \ln[1/(\omega - \omega^*)]$ as $\omega \rightarrow \omega^* = \Delta - J$ from above. A nonzero t_{bb} eliminates the square-root divergence and moves the van-Hove singularity away from $\omega = \Delta - J$. Thus the leading edge of the sharp peak in the density of states fixes $\Delta - J$ and the upper and lower band edges determine t_{ab} and t_{aa} . Changing t_{bb} from 0.05 eV to 0 changes the best fit t_{ab} from 0.5 eV to 0.4 eV, and cause the density of states in the $\omega \sim \Delta$ region to be dominated by the $(\ln \omega)/\sqrt{\omega}$ singularity, making it asymmetric (unlike the published band structure calculation.⁵) For later use we note that the “ t_{aa} -only” bandwidth is slightly less than the “ t_{ab} -only” bandwidth.

The band structure is strongly spin-polarized. In the majority spin sector, one band (dominantly B , i.e., Fe states) is full and the other band is empty; In the minority spin sector one band (dominantly A , i.e., Mo/Re) is partly filled and the other (B) is empty. In other words, the B -site adopts a fully polarized filled-shell configuration, and motion of A carriers onto B sites depends on the spin, providing the connection between carrier motion and spin alignment which favors ferromagnetism.

One sees from Ref. 5 that in the majority-spin sector the A -derived states form a much narrower band than do the A -derived states in the minority sector. This shows that virtual processes which take the B site from d^5 to d^4 state are

much less important than those which take the B site from d^5 to d^6 . Further, Hund’s rules indicate that a d^4 or d^6 state of less than maximal Fe spin must be even less favorable than a maximal spin Fe d^4 configuration. Therefore, the local physics on the $B(Fe)$ site is described by

$$H_{loc}^B = \sum_{i \in B, \alpha\beta} b_{i\alpha}^\dagger (-\Delta + J\hat{S}_i \cdot \vec{\sigma}_{\alpha\beta}) b_{i\beta}, \quad (2)$$

where \hat{S} is a unit vector representing the direction of the spins on the Fe. Here we have chosen the zero of energy to be the A -level energy and have restricted to cubic symmetry. Our approximation treats the d^5 -maximal spin d^6 energy splitting correctly but is only an approximate representation of the unimportant higher energy states. We further argue that the small filling and high degree of spin polarization of the $A(Mo/Re)$ site means that we may neglect electron-electron interactions on this sublattice. Thus we propose the many body Hamiltonian

$$H = H_{xy}^{\text{hop}} + H_{xz}^{\text{hop}} + H_{yz}^{\text{hop}} + H_{loc}^B. \quad (3)$$

We solve this model via the dynamical mean field approximation (DMFT).⁹ This method has been widely applied to models, such as the Hubbard or Kondo-lattice model, with one atom per unit cell. In this situation, one formulates a local problem specified by the local action $S_{loc} = \sum_{\omega} g(\omega) c^\dagger(\omega) c(\omega) + H_{int}$, where $g(\omega)$ is a mean field function to be determined by a self-consistency condition. To generalize this structure to the situation of present interest we introduce two mean field functions, $\mathbf{a}(\omega)$ and $\mathbf{b}(\omega)$ for the A and B sublattices, respectively. We use boldface to denote tensors depending on spin and orbital indices. Our choice of interaction Hamiltonian allows us to integrate over the fermion fields, yielding

$$S_{loc} = \text{Tr} \ln[\mathbf{a}] + \text{Tr} \ln[\mathbf{b} + \Delta + J\vec{S} \cdot \vec{\sigma}]. \quad (4)$$

Here the trace is over the frequency, spin and orbital indices, and an average over the orientation of the core spin must still be performed. We now write the self-consistency conditions. Because an electron on site A may hop to either another A -site ion or to another B -site ion but the spin and orbital indices are conserved by the band part of H , we require three couplings (W_{AA} connecting A site to A bath; W_{AB} connecting A site to B bath and conversely, and W_{BB} connecting B site to B bath). We define the local Green functions $\mathbf{G}_a = \langle \mathbf{a}^{-1} \rangle$ and $\mathbf{G}_b = \langle (\mathbf{b} + \Delta + J\vec{S} \cdot \vec{\sigma})^{-1} \rangle$ ($\langle \rangle$ means average over the partition function constructed from S_{loc}) and obtain

$$\mathbf{a} = \omega + \mu - W_{AA}^2 \mathbf{G}_a - W_{AB}^2 \mathbf{G}_b, \quad (5)$$

$$\mathbf{b} = \omega + \mu - W_{AB}^2 \mathbf{G}_a - W_{BB}^2 \mathbf{G}_b. \quad (6)$$

These equations are the generalization to the present case of the widely-used semicircular density of states equations.^{9,10} They differ from the equations successfully used to describe CMR manganites^{10,11} in that the “core spin” interaction occurs only on the B site. Note that because H^{hop} is diagonal in the orbital index, these equations

are diagonal as well. However, the partition function which determines the spin average involves all orbitals. We shall consider only ferrimagnetic states with magnetization direction specified by a unit vector \hat{m} , for which it is convenient to express the spin dependence as $a_{\alpha\beta}(\omega) = a_0(\omega) + a_1(\omega)\hat{m} \cdot \vec{\sigma}_{\alpha\beta}$ (and similarly for \mathbf{b}).

We fix parameters by comparing the calculated $T=0$ DMFT density of states to the tight-binding one. Our fits are shown in Fig. 1; we are able to reproduce the general structure, including the upper and lower band edges reasonably well, but there are some differences of detail. The DMFT always exhibits a square root singularity at $\omega = J - \Delta$. Because this is integrable, and indeed is above the chemical potential, it is not important for our subsequent considerations. The DMFT is more likely to exhibit a gap in

the density of states for ω slightly smaller than $J - \Delta$. In the band theory, the $A-B$ hybridization vanishes along lines in k space [for H_{xy}^{hop} , this is along $\cos(p_x) + \cos(p_y) = 0$]; this feature is absent in DMFT. Finally, van Hove singularities are present in the band theory but not in DMFT. The “ W_{AA} -only” $T=0$ bandwidth is $4W_{AA}$, the “ W_{AB} -only” bandwidth is $4W_{AB}$; comparison to the tight-binding model suggests $W_{AB} \sim 2W_{AA}$.

We now evaluate the magnetic transition temperature, T_c , which we define as the temperature at which the paramagnetic solution becomes linearly unstable to a ferrimagnetic one. The spin structure of the mean field parameters is expressed by the nonmagnetic (a_0) and the magnetic (a_1) components, and at T_c nonzero values of a_1, b_1 become possible. Linearizing the equations in a_1, b_1 we obtain for T_c

$$1 = - \sum_n 2J^2 \frac{W_{AB}^4 + (a_0^2 - W_{AA}^2)W_{BB}^2}{(a_0^2 - W_{AA}^2) \left[((b_0 + \Delta)^2 - J^2)^2 - \left((b_0 + \Delta)^2 - \frac{1}{3}J^2 \right) W_{BB}^2 \right] - W_{AB}^4 \left((b_0 + \Delta)^2 - \frac{1}{3}J^2 \right)}. \quad (7)$$

Our two different DMFT fits to the tight-binding model (Fig. 1), yield T_c 's of 495 K (DMFT fit 1) and 200 K (DMFT fit 2), for the band filling appropriate for Mo. Equation (7) is a mean-field result. Our previous experience comparing DMFT to Monte Carlo results for double-exchange models shows that the mean-field expression overestimates T_c by about 25%,¹⁰ implying physical T_c 's of 370 and 150 K for these two fits. It is interesting that T_c 's are comparable to or larger than T_c 's observed in the manganese perovskites. We attribute this to the higher orbital degeneracy (which allows each and to be partially filled, favoring ferromagnetism) and very strong Fe-Mo/Re overlap.

We see that the calculated T_c 's depend sensitively on parameters. To elucidate this, we study this dependence in more detail. We begin with the effects of varying W_{AA} shown in Fig. 2, considering first the limit $W_{AA} \gg W_{AB}$. In this case one has a wide band of A site carriers, weakly coupled to a spin-polarized “resonant level” on the B site, a situation familiar from heavy-fermion physics.¹² Known results for this problem imply a carrier-spin coupling $I \sim W_{AB}^2/(J - \Delta)$ and a $T_c \sim I^2/W_{AA}$. The DMFT equations can be solved in this limit, leading to precisely this behavior (shown as stars in Fig. 2). Thus T_c is maximized at $W_{AA} = 0$.

We now turn to the effects of varying the Fe- d^6 /Mo energy difference $J - \Delta$, and the carrier density, n . We measure the carrier density as number added beyond the Fe d^5 configuration; thus Mo corresponds to $n=1$ and Re to $n=2$. Numerical results are shown in Fig. 3; a complicated nonmonotonic behavior is evident, which may be understood by consideration of the simplifying limits $W_{AA} \rightarrow 0$ and $(\Delta + J) \gg W_{AB}$. In this “double-perovskite-double-exchange” limit carrier motion is strongly constrained by the need to

have carrier and core spins parallel. Now specialize further to the limit $|J - \Delta| \gg W_{AB}$, so that the carriers are essentially confined to one sublattice, with effective bandwidth $W_{AB}^2/|J - \Delta|$. The model then maps onto the standard double-exchange one, with three orbitals per cell and Hund's coupling $J + \Delta$. The standard arguments¹⁰ then show that at low n one has a ferromagnet with a T_c determined by bandwidth (so increasing as $|J - \Delta|$ decreases), while as $n \rightarrow n_{\text{orb}}$ (one electron per orbital) some other nonferromagnetic (probably

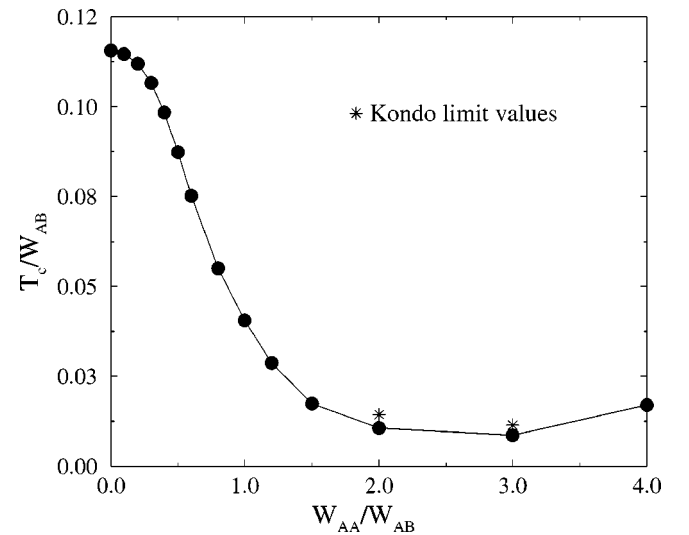


FIG. 2. Variation of magnetic T_c with the ratio of the hops W_{AA}/W_{AB} , as calculated from Eq. (7) using the “best-fit” value $(J - \Delta)/W_{AB} = 0.4$; $n = 1$. Band theory suggests $W_{AA}/W_{AB} \approx 0.6$. The values of T_c calculated in the Kondo limit described in the text are shown as stars. The upturn at $W_{AA}/W_{AB} > 3$ arises because the A band begins to mix with the majority B states.

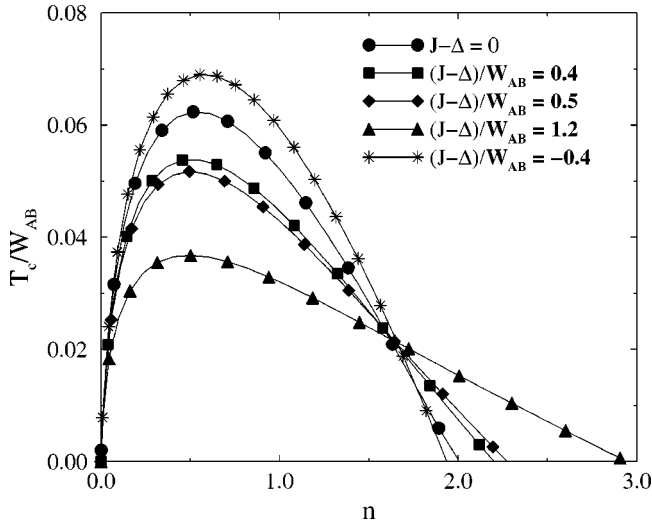


FIG. 3. Variation of magnetic T_c with band filling n , in the $(\Delta + J) \rightarrow \infty$ limit, for different values of $J - \Delta$ and $W_{AA}/W_{AB} = 0.6$; $W_{BB} = 0$.

incommensurate cf. Ref. 10) arrangement of spins becomes favorable. The density range over which a non-ferromagnetic ground state is preferred increases as $J - \Delta$ decreases, essentially because the greater effective bandwidth increases the energy gain from populating “wrong-spin” orbitals, and this accounts for the decrease in the ferromagnetic T_c with decreasing $|J - \Delta|$ at larger n . This trend is in qualitative agreement with the variation in T_c on changing Mo ($n = 1$) for Re ($n = 2$) in Ba and Sr-based double perovskites.^{6,13,14}

To summarize, we have formulated a many-body Hamiltonian which contains the essential physics of the Fe-based double perovskite compounds, and have used it to determine the factors affecting the ferro(or ferri)-magnetic transition temperature. Same-sublattice (Mo-Mo) hopping is not small in the actual materials, and acts to lower T_c . The higher band fillings of the Re compounds make it more difficult to realize high ferrimagnetic T_c 's, essentially because of other competing forms of magnetic order. We therefore suggest that a search for higher- T_c materials focus on $4d^1$ systems and on ways to reduce the same sublattice hopping, as well as more to closely match the Fe d^6 and B' site energies. On the other hand, systems based on $4d^2$ ions are more likely to exhibit interesting many-body physics and nontrivial ground states.

The Hamiltonian and approximation scheme we have proposed allows a number of immediate extensions. From the tight-binding band theory and the DMFT self-energy, the dc and optical conductivities may be calculated. The effects of a lattice distortion which lifts the degeneracy of the three t_{2g} orbitals⁷ can be computed by allowing the site energy Δ to depend on orbital index. Finally, the “cavity field” interpretation of dynamical mean field theory allows a straightforward investigation of the effects of mis-site (Re-Fe interchange) disorder. Work in all of these directions is in progress.

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