Theory of Transition Temperature of Magnetic Double Perovskites

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We formulate a theory of double perovskite compounds such as Sr\(_2\)FeReO\(_6\) and Sr\(_2\)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 \(T_c\).

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, the development of new magnetic recording media, and perhaps the construction of improved sources of spin-polarized electrons for 'spintronics' applications. One promising family of materials are the 'double perovskites'. These are compounds of chemical formula \(A(B'FeO_x\) \(y\) \(z\) \(BFe\) \(p\)ounds of chemical formula \(ABO_3\), 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 seem 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 \(Ca\). Mis-site \((B-B')\) disorder has a pronounced effect.

In this paper we take a step towards a theoretical understanding for these materials. We derive a many-body Hamiltonian, using band theory calculations 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. The conduction bands are derived from transition metal \(B\)-site \(t_{2g}\) d-orbitals, in agreement with quantum chemical considerations. There are six conduction bands per spin direction per unit cell; roughly, one triplet arises mainly from the \(d_{xy,zz,zy}\) orbitals on the \(Fe\) and the other from the same orbitals on \(Mo/Fe\). 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 sublattices, which we denote as \(A(Mo/Re)\) and \(B(Fe)\). On each site we include 3 \(t_{2g}\) orbitals, \(d_{xy,zz,zy}\). A good fit to the band structure requires both first and second neighbor hoppings, probably because the Mo/Re conduction electrons come from the 4\(d\) 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 \(H_{\text{band}} = H_{\text{on-site}} + H_{\text{hop}} + H_{\text{hopping}}^\text{data}\), with \(a_{\text{data}}^\dagger\) creates an electron on site \(i\) of orbital state \(m\) and spin \(\sigma\). The on-site term \(H_{\text{on-site}}\) consists of an \(A-B\) site energy difference, which has a spin-independent term \(\Delta_m\) (independent of orbital \(m\) in cubic symmetry) and a spin dependent term \(J\sigma\).

\[
H_{\text{hop}} = \sum_{p,\sigma} \left( a_{p(xy)\sigma}^\dagger b_{p(xy)\sigma} + b_{p(xy)\sigma}^\dagger a_{p(xy)\sigma} \right) \left( -4t_{ab} \cos(p_x) \cos(p_y) - t_{ab} \sin(p_x) \sin(p_y) \right) + \left( a_{p(xy)\sigma}^\dagger b_{p(xy)\sigma} + b_{p(xy)\sigma}^\dagger a_{p(xy)\sigma} \right) \left( t_{ab} \cos(p_x) + 2t_{ab} \cos(p_y) \right)
\]

(1)
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. 1 are shown in Fig. 1, with uncertainties of 10 – 15% on all quantities.

![Image of density of states from tight-binding model and DMFT calculations.](image)

**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, $J = 1.85$ 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, $J = 2.5$ eV and $\Delta = 2.0$ eV). The first DMFT fit gives a $T_e$ 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 $\frac{1}{2}\sqrt{(\Delta - J - 4t_{aa} + t_{bb}) \pm \frac{1}{2}\sqrt{[4(t_{aa} - t_{bb}) + (\Delta - J)]^2 + 4t_{ab}^2}}$. As $\omega$ is increased through $\Delta - J$, the density of states has a step up. For $t_{bb} = 0$, the hybridization vanishes along a line in $k$-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 1). 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. Re/Mo) 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. 1 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 $d^3$ to $d^4$. Further, Hund’s rules indicate that a $d^4$ or $d^5$ 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

$$H_{loc}^B = \sum_{i \in B, \alpha \beta} b_{iaa}^\dagger (-\Delta + J \hat{S}_i \cdot \sigma_{a\beta}) b_{ia\beta}$$

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

$$H = H_{xy}^{hop} + H_{zz}^{hop} + H_{yz}^{hop} + H_{loc}^B$$

We solve this model via the dynamical mean field approximation (DMFT). 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 $S_{loc} = \Sigma_{\omega} g(\omega) c_\omega^\dagger(\omega) c_\omega + H_{int}$, 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, $a(\omega)$ and $b(\omega)$ 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

$$S_{loc} = Tr \ln[a] + Tr \ln[b + \Delta + J \hat{S} \cdot \sigma]$$

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...
more likely to exhibit a gap in the density of states for tant for our subsequent considerations. The DMFT is indeed is above the chemical potential, it is not impor-
gularity at

general structure, including the upper and lower band
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k hybridization vanishes along lines in

to be partially filled, favoring ferromagnetism) and very
fully used to describe CMR manganites [10,11] in that

Known results for this problem imply a carrier-spin cou-
lings

\[ \begin{align}
\mathbf{a} &= \omega + \mu - W_{AA}^2 \mathbf{G}_a - W_{AB}^2 \mathbf{G}_b \\
\mathbf{b} &= \omega + \mu - W_{AB}^2 \mathbf{G}_a - W_{BB}^2 \mathbf{G}_b
\end{align} \]

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 success-

\[ \begin{align}
\mathbf{a} &= \omega + \mu - W_{AA}^2 \mathbf{G}_a - W_{AB}^2 \mathbf{G}_b \\
\mathbf{b} &= \omega + \mu - W_{AB}^2 \mathbf{G}_a - W_{BB}^2 \mathbf{G}_b
\end{align} \]

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 import-
for our subsequent considerations. The DMFT is
more likely to exhibit a gap in the density of states for $\omega$
slightly smaller than $J - \Delta$. In the band theory, the $A - B$
hybridization vanishes along lines in $k$-space (for $H_{\text{hop}}$, this is along $\cos(p_x) + \cos(p_y) = 0$); this feature is ab-
sent in DMFT. Finally, van Hove singularities are present in
the band theory but not in DMFT. The "$W_{AA}$-only"

\[ \begin{align}
1 &= -\sum_n 2J^2 (a_n^2 - W_{AA}^2) \left[ ((b_0 + \Delta)^2 - J^2)^2 - ((b_0 + \Delta)^2 - \frac{1}{3}J^2) W_{BB}^2 \right] - W_{AB}^4 \left( (b_0 + \Delta)^2 - \frac{1}{3}J^2 \right)
\end{align} \]

Our two different DMFT fits to the tight-binding model
(Fig. 1), yield $T_c$’s of 495K(DMFT fit 1) and
200K(DMFT fit 2), for the band filling appropriate for
Mo. Eq. (1) is a mean-field result. Our previous ex-
perience comparing DMFT to Monte Carlo results for
double-exchange models shows that the mean-field ex-
pression overestimates $T_c$ by about 25% [10], implying
physical $T_c$’s of 370 and 150K for these two fits. It is in-
teresting 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

\[ T = 0 \text{ bandwidth is } 4W_{AA}, \text{ the "} W_{AB}-\text{only} \text{" bandwidth is } 4W_{AB}; \text{ comparison to the tight-binding model suggests } W_{AB} \sim 2W_{AA}. \]
$T_c$ 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 $d^6$ configuration; thus Mo corresponds to $n = 1$ and Re to $n = 2$. Numerical results are shown in Fig. 3, a complicated non-monotonic behaviour 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 $W_{2B}^2/(J - \Delta)$. The model then maps onto the standard double-exchange one, with three orbitals per cell and Hund’s coupling $J + \Delta$. The standard arguments [14] 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 $n \rightarrow n_{orb}$ (one electron per orbital) some other non-ferromagnetic (probably incommensurate cf [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 [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 ferri-magnetic $T_c$s, essentially because of other competing forms of magnetic order. We therefore suggest that a search for higher $T_c$ materials focus on 4$d^1$ systems and on ways to reduce the same sublattice hopping, as well as to more closely match the Fe $d^6$ and B$^\prime$ site energies. On the other hand, systems based on 4$d^2$ ions are more likely to exhibit interesting many-body physics and non-trivial 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 $t_{2g}$ orbitals [5] can be computed by allowing the site energy $\Delta$ 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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