Theory of Half-metallic Ferrimagnetism in Double Perovskites

Onur Erten,1 O. Nganba Meetei,1 Anamitra Mukherjee,1 Mohit Randeria,1 Nandini Trivedi,1 and Patrick Woodward2

1Department of Physics, The Ohio State University
2Department of Chemistry, The Ohio State University

(Dated: August 21, 2018)

We present a comprehensive theory of the temperature- and disorder-dependence of half-metallic ferrimagnetism in the double perovskite Sr2FeMoO6 (SFMO) with \( T_c \) above room temperature. We show that the magnetization \( M(T) \) and conduction electron polarization \( P(T) \) are both proportional to the magnetization \( M_S(T) \) of localized Fe spins. We derive and validate an effective spin Hamiltonian, amenable to large-scale three-dimensional simulations. We show how \( M(T) \) and \( T_c \) are affected by disorder, ubiquitous in these materials. We suggest a way to enhance \( T_c \) in SFMO without sacrificing polarization.

Double perovskites (DPs) \( A_2BB'O_6 \) are an important family of complex oxides, derived from the simple ABO3 perovskite structure by a three-dimensional (3D) checkerboard ordering of B and B’ ions. One of the best studied examples is Sr2FeMoO6 (SFMO), a half-metallic ferrimagnet with \( T_c \approx 420 \text{K} \), well above room temperature \([1,3]\). Clearly SFMO, and other DPs, can have enormous technological impact if their stoichiometry and ordering can be controlled.

From a theoretical point of view, we argue that DPs are simple systems for understanding metallic ferromagnetism, despite their apparent complexity. First, in contrast to iron, there is a clear separation of the local-magnetism, despite their apparent complexity. First, in contrast to the manganites, DPs include \( B \) sites with spin \( 3/2 \) states; see Fig. 1(a). The results of previous theoretical calculations on SFMO differ from both the Heisenberg and Anderson-Hasegawa models \([8]\). We show that the magnetization \( M(T) \) of localized Fe spins. This result is significant because, while \( M(T) \) is easy to measure, it is \( P(T) \) that is of crucial importance for spintronic applications.

We make detailed comparisons with and predictions for SFMO. Our main results are:

1. We show that both the total magnetization \( M(T) \) and the conduction electron polarization \( P(T) \) at \( E_f \) are proportional to the magnetization \( M_S(T) \) of localized Fe spins. This result is significant because, while \( M(T) \) is easy to measure, it is \( P(T) \) that is of crucial importance for spintronic applications.

2. Our main theoretical advance is the derivation and validation of an effective classical spin Hamiltonian \( H_{\text{eff}} \) [see eq. (2)] for DPs, which differs from both the Heisenberg and Anderson-Hasegawa models \([8]\). We show that \( H_{\text{eff}} \) describes the full \( T \)-dependence of the magnetization \( M_S(T) \), and hence that of \( M(T) \) and \( P(T) \).

3. We present the results of simulations of \( H_{\text{eff}} \) on large 3D lattices, including disorder effects, thus going beyond all previous theoretical calculations on SFMO.

4. We compute \( M(T) \) and \( T_c \), using microscopic band-structure parameters as input, and see how these are affected by deviations from stoichiometry and by anti-site (AS) disorder, ubiquitous in real materials. Ours is the first theory to show that \( T_c \) is insensitive to AS disorder, in excellent agreement with experiments, even though \( M(0) \) is suppressed.

5. We conclude with a novel proposal to enhance \( T_c \) of SFMO without sacrificing polarization, using a combination of disorder and doping.

Model Hamiltonian: For large Hund’s coupling \( J_H \), the \( Fe^{3+} \) (3d\(^5\)) site has a \( S=5/2 \) “core spin” or local moment. The \( Mo^{5+} \) (4d\(^1\)) contributes a \( t_{2g} \) electron which hybridizes via O with the \( Fe \) \( t_{2g} \) states. Symmetry implies that \( d_{x\beta} \) electrons delocalize only in the \((\alpha, \beta)-\text{plane}\) \([10]\). Thus the motion of electrons in the 3D system decouples into three 2D planes. The “double exchange” Hamiltonian \([3,4]\) describing itinerant electrons interacting with core spins is:

\[
H = -t \sum_{\langle i,j \rangle,\sigma} (\epsilon_{i\sigma} d_{i\downarrow}^\dagger c_{j\sigma} + h.c.) -t' \sum_{\langle j,j' \rangle,\sigma} c_{j\downarrow}^\dagger c_{j'\sigma} + \Delta \sum_i d_{i\downarrow}^\dagger d_{i\uparrow} \quad (1)
\]

Here \( d_{i\sigma} (c_{i\sigma}) \) are fermion operators on the \( Fe \) (\( Mo \)) sites with spin \( \sigma \). At the Fe sites \( i \), we choose local axes of quantization along \( S_i \) and Pauli exclusion prohibits an \( \uparrow \) electron. For all the \( Mo \) sites \( j \), we choose the same (global) axis of quantization. The orientation \((\theta_i, \phi_i)\) of the classical spins \( S_i \) then affects the \( Mo-Fe \) hopping via \( \epsilon_{ij} = -\sin(\theta_i/2) \exp(i\phi_i/2) \) and \( \epsilon_{ij} = \cos(\theta_i/2) \exp(i\phi_i/2) \).

The parameters in \( H \) are the hopping amplitudes \( t \), between nearest neighbor (Fe-Mo) sites, and \( t' \), between two \( Mo \) sites, and the charge transfer energy \( \Delta \) between \( Fe \) \( t_{2g} \) and \( Mo \) \( t_{2g} \) states; see Fig. 1(a). The results are independent \([4]\) of the sign of \( t \). For now, we choose \( t = 1 \) as our unit of energy. Symmetry dictates \( t' > 0 \). We choose \( t'/t = 0.1 \) and \( \Delta/t = 2.5 \), using realistic band...
The magnetic properties of the core spins by generalizing the two-site Anderson-Hasegawa [8] analysis for manganites to double perovskites.

To derive $H_{\text{eff}}$, we find the exact solution of $H_{\text{eff}}$ for two unit cells. The Hilbert space, for a given $t_{2g}$ orbital, has three states per unit cell: Fe $t_{2g\uparrow}$ and Mo $t_{2g\uparrow\downarrow}$. The smallest accessible filling is $n = 0.5$ (per plane), i.e., one electron in two unit cells [11]. We analytically find the lowest eigenvalue as a function of the angle $(\theta_1 - \theta_j)$ between spins. Working in two different geometries, we find [12] the nearest-neighbor ($J_1$) and next-nearest-neighbor ($J_2$) interaction energies; see inset in Fig. 2(c).

Expressing these in terms of $S_i \cdot S_j$, where each $S_i$ is a unit vector, we obtain the effective Hamiltonian

$$H_{\text{eff}} = -J_1 \sum_{\langle i,j \rangle} F_1 (S_i \cdot S_j) - J_2 \sum_{\langle\langle i,j \rangle\rangle} F_2 (S_i \cdot S_j)$$

where the functions $F_1 (x) = 8\sqrt{2 + \sqrt{2 + 2x}}$ and $F_2 (x) = (5 + \sqrt{5})\sqrt{6 + 2\sqrt{3 + 2x}}$. Our two-unit cell analysis gives explicit expressions [12] for $J_1$ and $J_2$, both of which are ferromagnetic with their scale set by the kinetic energy $t$ of delocalization. We emphasize that the double square-root form of $H_{\text{eff}}$ is quite different from the (single square-root) Anderson-Hasegawa model.

Next we need to understand how we can use $H_{\text{eff}}$ going beyond the simple two-unit cell derivation. Specifically: (i) How can we relate $J_1$, $J_2$ to $t$, $t'$, $\Delta$ and the filling $n$? (ii) To what extent does $H_{\text{eff}}$ capture the essential physics of the full Hamiltonian $H$?

The dependence of $J_1$ and $J_2$ on microscopic parameters can be obtained by matching the spin-wave (SW) spectra of $H_{\text{eff}}$ and $H$. This comparison is shown in Fig. 2(c) along certain symmetry directions. We find SW dispersion for $H$ using ED to compute the energy of electrons moving in a "frozen" spin-wave background. The SW analysis for $H_{\text{eff}}$ is straightforward, since for small deviations from the FM ground state, $H_{\text{eff}}$ reduces to a nearest and next nearest neighbor FM Heisenberg model $H_{\text{Heis}}$. The low energy scale of 0.1t for spin dynamics (see Fig. 2(c)) justifies a posteriori our assumption of "slow" spins and "fast" electrons, whose bandwidth is of order $t$ (see Fig. 1(b)). The same separation of energy scales also justifies the use of $T$-independent exchange couplings $J_1$ and $J_2$ for all $T < T_c$, as we discuss next.
To validate the effective classical model $H_{\text{eff}}$ we show in Fig. 4(d) that it reproduces the magnetization $M(T)$ of the full Hamiltonian $H$ over the entire range of temperatures. We note that the corresponding Heisenberg model $H_{\text{Heis}}$ gives quite different results, except in the $T \to 0$ limit with small spin deviations. In other words, the $T$-dependent magnetization of DP’s cannot be modeled by a Heisenberg Hamiltonian. But the (highly non-linear) $H_{\text{eff}}$ that we have derived gives an excellent description of the ED-MC results for the full $H$.

The classical $H_{\text{eff}}$ can be easily simulated on large 3D lattices, unlike the full $H$, and the results are shown in Fig. 3. We note the linear drop in $M(T)$ at low $T$, due to classical spin-waves, followed by a rapid suppression of $M$ at the phase transition [13]. We estimate $T_c$ in the infinite volume limit using finite size scaling; see Fig. 3(b). For $t'/t = 0.1$ and $\Delta/t = 2.5$, we find $T_c = 0.14t$. Comparing this to $T_c = 420K$ for pure SFMO, we obtain $t = 0.27$ eV, consistent with ref. [2].

**Disorder:** $H_{\text{eff}}$ permits us to model various kinds of disorder and deviations from stoichiometry [12]. (i) Excess Fe is modeled with an extra spin (at a Mo site) that interacts with its neighboring spins with a large antiferromagnetic (AF) superexchange $S(S + 1)J_{\text{AF}} \approx 34$ mev [14]. (ii) Excess Mo is modeled by removing an Fe spin from the lattice. Both (i) and (ii) also require reevaluation of $J_1$ and $J_2$ due to change in carrier density $n$. (iii) Here we focus on anti-site (AS) disorder, the most common form of disorder in DP’s, with Fe and Mo interchanged and no change in $n$.

We see from Fig. 4 that AS disorder systematically reduces $M(0)$ without affecting $T_c$, in excellent agreement with experiments [16, 17]. We quantify AS disorder using $\delta$ the fraction of Fe atoms that are on the Mo sublattice. The observed magnetization $M(0)\mid\{1-2\delta\}$ arises from the loss of two moments for each AS defect. One from the moment lost at the Mo (on the Fe sublattice) and the other from the Fe (on the Mo sublattice) antiferromagnetically coupled to its neighbors via $J_{\text{AF}}$.

There are two opposite effects of AS disorder on $T_c$, that appear to balance each other. The strong Fe-Fe superexchange $J_{\text{AF}}$ pins the spins surrounding the Fe-defect, and makes the magnetic order more robust against thermal fluctuations. On the other hand, the Mo-defect leads to
broken $J_1, J_2$ bonds which weaken the magnetism. The net effect is a $T_c$ insensitive to $\delta$ for moderate levels of AS disorder, which is exactly what experiments observe.

We note that while the loss of $M(0)$ with AS disorder has been explained earlier \cite{16, 18, 19}, ours is the first theory to correctly account for $T_c$; previous theories either found a drop \cite{16} in $T_c$ or an increase \cite{16}.

**Raising $T_c$:** We conclude with a proposal to raise the ferromagnetic $T_c$ without sacrificing the conduction electron polarization $P$; see Fig. 5. In brief, it involves adding excess Fe and compensating for the loss of mobile carriers by La substitution on the Sr site.

To see how this works, let us first consider excess Fe without any compensation: $\text{Sr}_2\text{Fe}_{1+y}\text{Mo}_{1-y}\text{O}_6$. In this case, $M_S(0)$ decreases like $y$ due to the AF alignment of excess spins. $T_c$ also decreases with $y$ because the loss of carriers $n = (1-3y)/3$ dominates over the enhanced pinning of moments by $J_{AF}$ in the vicinity of defects. For the uncompensated case, the calculated $T_c(y)$ in Fig. 5(b) is in reasonable agreement with experiments \cite{20}.

We can compensate for the carriers by A-site substitution: $\text{La}_x\text{Sr}_{2-x}\text{Fe}_{1+y}\text{Mo}_{1-y}\text{O}_6$ with electron density $n = (1-x-3y)/3$ per plane. Choosing $x = 3y$ counters the doping-dependent drop in $T_c$ that dominated above and we find that $T_c$ can be significantly enhanced over that of pure SFMO due to just the local pinning of moments at excess Fe sites. This increase in $T_c$ goes hand-in-hand with an unchanged $M_S(0)$; see Fig. 5(a).

We also note that the polarization $P(0)$ remains 100%. When the Fe spins cant at finite $T$, electrons depolarize by mixing of up and down states, however, no such processes are permitted at $T=0$, even in a disordered Fe-rich system. We have checked using the full Hamiltonian \cite{16} that, even though the strict proportionality between $M_S(T)$ and $P(T)$ is not observed in the presence of disorder, the high temperature $P$ is still enhanced over the clean system due to the large increase in $T_c$.

An alternative way to enhance $T_c$ is to add mobile electrons using La doping, which, however, has been shown to lead to considerable increase in AS disorder \cite{15}. In principle, compensated doping as proposed here should introduce less AS disorder \cite{21}.

In conclusion, while we have focused here on SFMO, our theory provides a general framework for understanding half metallic ferrimagnetism in DP's. Interesting directions for future work include A-site substitution, Coulomb correlations on B', which may become increasingly important for larger carrier concentrations, and spin-orbit coupling on B' for 5d elements.

**Acknowledgments:** Our research was supported by the Center for Emergent Materials, an NSF MRSEC (Award Number DMR-0820414). We thank R. Mishra, O. Restrepo, and W. Windl for discussions and acknowledge use of the computational facilities of the Ohio Supercomputer Center.

\[1\] For a recent review, see: D. Serrate, J. M. De Teresa and M. R. Ibarra, J. Phys. Cond. Mat. 19, 023201 (2007).

\[2\] K. I. Kobayashi et al., Nature 395, 677 (1998).

\[3\] D. D. Sarma et al., Phys. Rev. Lett. 85, 2549 (2000).

\[4\] A. Chattopadhyay and A. J. Millis, Phys. Rev. B 64, 024424 (2001).

\[5\] J. L. Alonso et al., Phys. Rev. B 67, 214423 (2003).

\[6\] L. Brey et al., Phys. Rev. B 74, 094429 (2006).

\[7\] P. Sanyal and P. Majumdar Phys. Rev. B 80, 054411 (2009).

\[8\] P. W. Anderson and H. Hasegawa, Phys. Rev. 100, 675 (1955).

\[9\] Flipping the sign of $t$ only interchanges the bonding and antibonding bands shown in Fig. 1(b).

\[10\] A. B. Harris et al., Phys. Rev. B 69, 035107 (2004).

\[11\] For the two unit cell geometry, $n = 0.5$ is the closest we can get to the SFMO filling $n = 0.33$. We also ignore $t'$ in this geometry.

\[12\] A detailed derivation will be published elsewhere.

\[13\] Note: (i) the qualitative difference between the sharp transition found in 3D (Fig. 3(a)) with the smooth behavior in 2D (Fig. 2(d)), (ii) the factor of three difference in $T$ scales between 3D (FCC) and 2D (square lattice) arising from the increased number of neighbors.

\[14\] We use $S(S + 1)J_{EF} = k_BT_N/2$ for the AF insulator LaFeO$_3$ with $T_N = 750$K.

\[15\] J. Navarro et al., Phys. Rev. B 64, 092411 (2001).

\[16\] A. Ogale et al., Appl. Phys. Lett. 75, 537 (1999).

\[17\] J. Navarro et al., Phys. Rev. B 67, 174416 (2003).

\[18\] B. Aguilar, O. Navarro and M. Avignon, Europhys. Lett. 88 67003 (2009).

\[19\] R. Mishra et al., Chem. Mater. 22, 6092 (2011).

\[20\] D. Topwal et al., Phys. Rev. B 73, 094419 (2006).

\[21\] La doping of $x = 1$ gives rise to a 15% increase of $T_c$, but also a large change in Mo valence (+5 to +4), which adversely impacts cation ordering, leading to large AS disorder. In contrast, in our proposal a 25% increase in $T_c$ is obtained for $y = 0.25$ and $x = 0.75$, with an average Mo valence of only +4.66.