Electronic and Magnetic Properties of the Candidate Magnetocaloric-Material Double Perovskites  
La$_2$MnCoO$_6$, La$_2$MnNiO$_6$ and La$_2$MnFeO$_6$

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The search for room-temperature magnetocaloric materials for refrigeration has led to investigations of double perovskites. In particular, a puzzle has appeared in the La$_2$MnNiO$_6$, La$_2$MnCoO$_6$ and La$_2$MnFeO$_6$ family of compounds. They share the same crystal structure, but while La$_2$MnNiO$_6$ and La$_2$MnCoO$_6$ are ferromagnets below room temperature, La$_2$MnFeO$_6$, contrary to simple expectations, is a ferrimagnet. To solve this puzzle, we use density-functional theory calculations to investigate the electronic structure and magnetic exchange interactions of the ordered double perovskites. Our study reveals the critical role played by local electron-electron interaction in the Fe-d orbital to promote the Fe$^{3+}$ valence state with half-filled d-shell over Fe$^{2+}$ and to establish a ferrimagnetic ground state for La$_2$MnFeO$_6$. The importance of Hund’s coupling and Jahn-Teller distortion on the Mn$^{4+}$ ion is also pointed out. Exchange constants are extracted by comparing different magnetically ordered states. Mean-field and classical Monte-Carlo calculations on the resulting model give trends in $T_C$ that are in agreement with experiments on this family of materials.

I. INTRODUCTION

The magnetocaloric effect leads to an increase of the temperature when certain materials are exposed to a magnetic field and decreases when they are removed from it. In order to be suitable for room temperature magnetic refrigeration, magnetocaloric materials need to exhibit a large change in magnetization around room temperature. The most interesting materials for this technology are hence ferromagnets with a high netocaloric materials need to exhibit a large change in magnetic field and decreases when they are removed from it. In order to

parallel moments on neighboring Mn and Fe sites.$^{6,8}$

The difference in the ground state magnetic orders in LMFO and LMNO/LMCO is puzzling because all of these materials share the same crystal structure. The resulting double perovskite $A_2B'B'O_6$ structure stems from the perovskite structure $ABO_3$ where half of the transition metal sites (B) are occupied by Mn ions and the other half by Ni, Fe or Co ions.$^5$ In such a structure resulting from the solid solution of AB$'O_3$ and AB$''O_3$, the interaction between neighboring moments occurs through the oxygen-mediated superexchange interaction. Superexchange facilitates hopping of the electrons from the oxygen p shells to the magnetic ions d shell, leading to a reduction of the total energy due to a kinetic energy advantage. It can be antiferromagnetic (AFM) or ferromagnetic (FM), depending on structural parameters such as the B$'-O$-B$''$ bond angle and the B$'-O-B''$ bond length. Furthermore, crystal field splitting, Hund’s coupling and on-site electron-electron repulsion can also influence the superexchange interaction. The roles played by the latter parameters depend on the d shell occupancy.

Finally, the properties of double perovskites are strongly influenced by the level of cationic order. In the ordered phase, the 3d metal cations crystallize in the so-called rock-salt structure in which Mn and Ni (Fe, Co) atoms occupy alternate positions in each spatial direction. In the pristine double perovskites, the space group symmetry becomes $P2_1/c$. In the disordered phase, for which not only B$'-O$-B$''$ but also B$'-O$-B$'$ and B$''$-O-B$'$ bonds are present, the materials have been reported to crystallize in the $Pbnm$ space group.$^{3,4,11}$ For example in La$_2$MnCoO$_6$, the ferromagnetic Mn-O-Co bonds are diluted in a matrix of antiferromagnetic Co-O-Co and Mn-O-Mn bonds. Depending on the growth parameters, we measure two distinct transitions in a bulk sample as shown in Fig. 1 for La$_2$MnCoO$_6$ and La$_2$MnNiO$_6$, demonstrating a mixture of the ordered and the disordered domains. Tuning the growth parameters allows us to tune the proportion of both phases and eventually to remove completely the low tem-
temperature transition associated to the cation-disordered phase and leaving only the high temperature transition of the cation-ordered phase. In the present theoretical study, we will focus on the magnetic properties of the cation-ordered phase while trying to explain the absence of a high temperature transition in La$_2$MnFeO$_6$ as shown also in Fig. 1.

The understanding of the microscopic mechanisms at play in LMFO could lead to the design of new materials that could be more suitable for magnetic refrigeration than LMNO and LMCO.

We first investigate the ground states of LMNO, LMCO and LMFO with density functional theory (DFT) calculations in Sec. (II). We compare the structural, electronic and magnetic properties of the three materials in order to understand the impact of electron-electron interaction and structural distortion on the ground state of LMFO. In Sec. (III), electronic structure calculations for different types of magnetically ordered ground states allow us to extract exchange coupling constants and corresponding mean-field transition temperatures. In Sec. (IV), we improve the estimates of the Curie temperature using Monte-Carlo calculations. The method specific to each section is described in the opening subsection.

II. ELECTRONIC STRUCTURE FOR La$_2$MnNiO$_6$, La$_2$MnCoO$_6$ AND La$_2$MnFeO$_6$

We first describe the method, then present results for LMNO and LMCO in Sec. (II B). The puzzling case of LMFO is presented in Sec. (II C).

A. Method

The GGA(+U) calculations are performed within the full-potential all electron basis set as implemented in the WIEN2k code, using the PBE functional. In GGA+U calculation, the effective interaction $U_{eff} = U - J$ has been set to 3.0 eV for Mn, Ni, Co and Fe $d$ orbitals (except when specified otherwise in the text). We use the GGA+U(SIC) method with an approximate correction for the double-counting. Structure optimization is performed on LMNO, LMCO and LMFO using the $P2_1/c$ space group. In order to confirm the ground state magnetic order, structure optimization is performed using two different magnetic alignments of Mn and Fe moments: ferromagnetic (FM), and (G-type) antiferromagnetic (AFM). A plane-wave cut-off of $R_{mt}K_{max}$ = 8.1 – 8.3 and a $k$-mesh of 50 points in the Brillouin zone are used for self-consistent calculations presented in Sec. (II B) and Sec. (II C). We check the convergence with respect to the number of $k$ up to 250 points in the irreducible Brillouin zone and to $R_{mt}K_{max}$ cutoff up to 8.1 for LMNO and LMCO, and 8.3 for LMFO. In supercell calculations, a $R_{mt}K_{max}$=7 and 60 $k$-points were used (Sec. (III)).

B. La$_2$MnNiO$_6$ and La$_2$MnCoO$_6$

Starting with La$_2$MnNiO$_6$, our ab initio electronic structure calculations confirm that the orbital occupancy of Mn-$d$ and Ni-$d$ are very close to the nominal ones. The oxidation state of Mn and Ni are Mn$^{3+}$ and Ni$^{2+}$ with $3d^{5}_{x}d^{6}_{y}$ and $3d^{6}_{x}d^{5}_{y}$ electronic configurations, where $\sigma = -\sigma$. Hence, the predicted total magnetic moment is $\approx 5\mu_B$/f.u., which is in good agreement with experimental data. The energy difference between AFM and FM configurations is 0.13 eV/f.u. in GGA calculations, and 0.16 eV/f.u. in GGA+U calculations. Fig. 2 (a) and (d) show partial density of states (DOS) of LMNO calculated from GGA and GGA+U methods respectively. The calculation is done in a FM magnetic moment configuration. Partial DOS of up (down)-component is denoted by positive (negative) value. Both methods predict an insulating ground state. Although the charge gap increases between GGA and GGA+U calculations, the partial charge occupations and the magnetic moments of the transition metal ions do not depend sensitively on effective Coulomb interaction. The overlap between partial DOS of transition metal and oxygen above the Fermi level indicates which virtual hopping processes can be realized in the system. The partial DOS above the Fermi level for LMNO illustrates good overlap between Ni-$e_g$ and O-$p$, in particular for down spin. Similarly, Mn-$e_g$ up and O-$p$ partial DOSs overlap well above the Fermi level. The optical gap predicted by GGA calculations is around 0.8 eV and, above the Fermi level, the states are dominated by the Mn-$e_g$ orbitals, as shown in Fig. 2 (a). Including the electron-electron interaction through GGA+U calculation pushes the Mn-$e_g$ states to higher energies, hence, just above the Fermi level, the states become dominated by the O-$p$ orbitals. The charge gap also increases to 1.7 eV, as shown in Fig. 2 (d).

In LMNO, the main factor determining the ground state magnetic structure is the kinetic energy gain due to superexchange interaction. This is illustrated schematically in Fig. 2 (g) where the position of the atomic levels roughly corresponds to their position in the DOS. Assuming that the electronic configuration of Mn is $3d^{5}_{3}d^{1}_{1}$, then the O-$p_1$ electron...
FIG. 2. (Color online) Spin-resolved partial density of states for Mn-\(e_g\), Mn-\(t_{2g}\), Ni (Co, Fe)-\(e_g\), Ni (Co, Fe)-\(t_{2g}\) and O-\(p\) from GGA calculations (top row) and GGA+U (middle row) calculations. GGA+U calculations are performed with \(U_{\text{eff}} = 3\text{eV}\). The upper part in each panel is majority-spin DOS result, and the lower the minority-spin one. GGA calculations predict an insulating ferromagnetic ground state for (a) LMNO and (b) LMCO, and a metallic ferromagnetic ground state for (c) LMFO. GGA+U calculations predict an insulating ferromagnetic ground state for (d) LMNO and (e) LMCO, and an insulating ferrimagnetic ground state for (f) LMFO. Bottom row: Schematic representation of the superexchange interaction in (g) LMNO, (h) LMCO and (i) LMFO. The figures represent schematically the weight of each orbital with respect to the others and are derived from the partial DOS plots and partial charge data. In LMFO, \(e_g\) electrons are more itinerant than the \(t_{2g}\) electrons and therefore repulsion \(U\) has a smaller impact on them. This leads to a smaller energy splitting between up- and down-spin states of \(e_g\) electrons and in turn to positioning of \(e_g\) states between \(t_{2g}\) states.

A higher hopping amplitude to Mn-\(e_g\) states than the O-\(p\) electron because Hund’s coupling between \(t_{2g}\) and \(e_g\) states of Mn favors parallel alignment. On the other hand, the \(t_{2g}\) states of Ni are fully occupied. The extra two electrons reside in \(e_g\) states and have parallel spins due to Hund’s coupling. Since O-\(p\) contributes in a superexchange mechanism with the \(e_g\) states of Ni, a spin-up configuration is preferred for Ni-\(e_g\) electrons. This explains why La\(_2\)MnNiO\(_4\) is a ferromagnet. It is worth noting that the alternative Mn\(^{3+}\) and Ni\(^{2+}\) oxidation states would have led to an AFM configuration, but it is not energetically favorable due to the large crystal field splitting on Mn ions (see Sec. (III)).

GGA and GGA+U calculations performed on LMCO lead to similar results. Fig. 2 (b) and (e) show the partial DOS of LMCO. The charge gap is very small in GGA, around 0.1 eV. Adding \(U\) splits the Co-\(t_{2g}\) states and enhances the charge gap to \(\approx 1.3\) eV. Both types of calculations predict a ferromagnetic insulating ground state with \(\approx 6\mu_B/\text{f.u.}\), which is in agreement with the experimental data. The energy difference between AFM and FM configurations is 0.14 eV/f.u. in GGA calculations, and 0.18 eV/f.u. in GGA+U calculations. The superexchange mechanism in LMCO is similar to the one described for LMNO, with the difference that Co has a 3\(d_{\uparrow}\)\(s_d\)\(d_{\uparrow}\) electronic configuration (see Fig. 2 (h)). Similarly to LMNO, properties such as charge occupation or partial moments of Mn and Co atoms do not vary sensibly between GGA and GGA+U calculations.

By investigating LMNO and LMCO, we identify a key player in promoting the FM ground state: it is the Mn\(^{3+}\) oxidation with three electrons in \(t_{2g}\) states that allows the Hund’s
coupling to become effective and to reduce the total energy of FM state with respect to AFM state.

C. La$_2$MnFeO$_6$

In light of the previous results, we move to the interesting case of LMFO. The GGA calculations predict a metallic ferrimagnetic ground state for LMFO with finite Fe-$d$ spectral weight at the Fermi level as seen from the density of states of Fig. 2 (c). The total moment predicted by GGA calculations is $\sim \tau \mu_B$/f.u., which corresponds to high-spin Mn$^{3+}$ and Fe$^{2+}$ states. The energy difference between the AFM and the FM configuration is 0.09 eV/f.u. These results are not in agreement with the available experimental data. Indeed, experiments on high-order films (B-site order $\approx$ not in agreement with the available experimental data. In-...
Curie temperature, $T_c = 280K$, in this family.

III. MAGNETIC EXCHANGE COUPLINGS AND CURIE TEMPERATURE

Another important factor in designing magnetocaloric materials is the Curie temperature, $T_C$. Estimating $T_C$ from ab initio calculations is a challenging task. One approximate way, which we follow here, is to derive a spin Hamiltonian for the system and then evaluate its transition temperature. In the following subsection we present the method. The results follow.

A. Extracting the exchange constants

We neglect the induced magnetic moment of oxygen because it is very small in comparison to magnetic moments of the transition metal ions. The magnetic exchange interaction can be evaluated by mapping the DFT total energy to the Ising model,

$$H = -\sum_{ij} J_{ij} S_i^z S_j^z,$$  \hspace{1cm} (1)

where $J_{ij}$ is the exchange interaction between spins $S_i^z$ and $S_j^z$ residing at the $i$th and $j$th sites, respectively. Here, we assume that the exchange couplings have energy units, hence the spin values are divided by the Bohr magneton. To obtain the long range exchange interactions, we first consider a $2 \times 2 \times 2$ supercell. The primitive unit cell contains two Mn ions and two Ni(Fe, Co) ions, hence the supercell contains 32 magnetic ions. We consider six independent exchange pathways connecting various Mn and Ni(Fe, Co) sites. $J_1$ and $J_2$ are the nearest-neighbor in-plane and out of plane couplings between Mn and Ni(Fe, Co), while $J_3(J_4)$ and $J_5(J_6)$ are the next nearest-neighbor in-plane and out of plane couplings between Mn(Ni, Fe, Co) magnetic moments. The exchange couplings are illustrated in Fig. 3 (a).

In order to reduce the errors, we work with the total energy differences with respect to the ground state rather than the absolute total energy values. We fixed the structure and changed the magnetic order between eight different spin configurations and calculated their total energy. We assumed the exchange couplings have energy units, hence the spin values are divided by the Bohr magneton. To obtain the long range exchange interactions, we first consider a $2 \times 2 \times 2$ supercell. The primitive unit cell contains two Mn ions and two Ni(Fe, Co) ions, hence the supercell contains 32 magnetic ions. We consider six independent exchange pathways connecting various Mn and Ni(Fe, Co) sites. $J_1$ and $J_2$ are the nearest-neighbor in-plane and out of plane couplings between Mn and Ni(Fe, Co), while $J_3(J_4)$ and $J_5(J_6)$ are the next nearest-neighbor in-plane and out of plane couplings between Mn(Ni, Fe, Co) magnetic moments. The exchange couplings are illustrated in Fig. 3 (a).

In order to reduce the errors, we work with the total energy differences with respect to the ground state rather than the absolute total energy values. We fixed the structure and changed the magnetic order between eight different spin configurations and calculated their total energy. The spin configurations are chosen by adopting different configurations for each transition metal sublattice. Each sublattice can have the following spin configurations: (i) in-plane and out of plane FM (ii) in-plane FM and out of plane AFM (iii) in-plane AFM and out of plane FM. The chosen spin configurations are given in Table I. Because of the symmetries common to all the magnetic orders considered in the calculations, we were able to reduce the $2 \times 2 \times 2$ supercells to smaller ones that are twice as big as the primitive ones. These reduced supercells contain 4 non-equivalent Mn and 4 non-equivalent Ni(Fe, Co) atoms, hence a total of 8 magnetic ions.

We use GGA calculations to find the energy of each configuration in the LMNO and LMCO phases. In the case of LMFO, since GGA does not predict the right ground state, we use GGA+U with $U_{eff} = 3.0$ eV in Mn-3d and Fe-3d shells to find the energies.

The corresponding total energy mapped to the Ising model can be obtained as follows. The primitive unit cell contains two Mn and two Ni (Co, Fe) ions. Each Mn (Ni, Co, Fe) has four in-plane and two out of plane nearest-neighbors which belong to the other sublattice. The number of in-plane and out of plane next-nearest neighbors are eight and four, respectively, and they belong to the same sublattice. Therefore, letting $S^z$ and $S'^z$ denote the $z$-component of the spin on B' and B" sublattices, the nearest-neighbor interaction contributes $-4J_1S^zS'^z - 2J_2S^zS'^z$ per magnetic ion to the total energy while the next-nearest-neighbor interaction contribution depends on the sublattice and is given by $-4J_3S^zS'^z - 8J_4S^zS'^z$ or $-4J_3S^zS'^z - 8J_4S^zS'^z$ per magnetic ions. Therefore, the total energies of the above spin configurations for primitive

| Configuration | Sublattice B’ | Sublattice B” | Spin alignment |
|---------------|---------------|---------------|----------------|
| FM | i | i | in phase |
| AFM1 (G-type) | i | i | out of phase |
| AFM2 (A-type) | i | i | in phase |
| AFM3 (C-type) | i | i | out of phase |
| AFM4 | iii | iii | (see caption) |
| AFM5 | ii | ii | n.a. |
| FiM | i | ii | n.a. |
| AFM6 | i | iii | n.a. |

TABLE I. Spin configuration of the sublattices used in the 8 magnetic configurations. The transition metal sublattice spin configurations are: (i) in-plane and out of plane FM (ii) in-plane FM and out of plane AFM and (iii) in-plane AFM and out of plane FM. For AFM4, the spin alignment of the sublattices is chosen in such a way that the out of plane nearest neighbor alignment is AFM. Spin alignment of the sublattices in configurations AFM5, AFM6 and FiM does not influence the expression of the total energy since there is no net contribution of nearest neighbor (Mn-Fe/Co/Ni) interaction to the total energy. Uncommon configurations AFM4, AFM5, FiM and AFM6 are illustrated in Fig. 3 (b) to (e).
These equations should be multiplied by 2 to obtain the total energy of the supercell considered here. They yield seven energy differences; six of them are used to calculate the exchange couplings and the last one is used to verify their validity.

B. Calculated exchange constants and mean-field Curie temperatures

The calculated magnetic exchange interactions for LMNO are presented in Table II. The nearest-neighbor exchange couplings are FM-type and sizable while the next-nearest-neighbor magnetic moments are coupled antiferromagnetically. The rather short-range magnetic interaction is a consequence of the rather localized 3d electron wave functions. The next-nearest neighbors are identical ions with half-filled shells and their AFM coupling can be understood in terms of a simple Hubbard model: The AFM alignment of the magnetic moment allows for hopping of the electron between these sites and reduces kinetic energy.

The exchange couplings for LMCO are also listed in Table II. One can notice that the Mn-Co couplings are smaller than the Mn-Ni ones, which is in agreement with the discussion of the superexchange mechanism in these materials of Sec. (II B) and Sec. (II C). We argued that, due to the superexchange interaction, the ideal situation to promote an FM phase over an AFM one in the family of compounds studied is the 3d5-3d8 case. This situation occurs in LMNO and it could explain why the exchange couplings are larger in this material, and also why its experimental T_C is the largest in this family even though its total moment is not the largest. Once again, the next-nearest neighbor couplings are smaller than J_1 and J_2 by one or two orders of magnitude due to the localization of 3d wave functions. Note that Co-Co exchange couplings are FM. In contrast with LMNO, in which direct hopping between Ni ions only occurs between e_g states, in LMCO the direct hopping processes between t_{2g} states are allowed as well. Hence, a simple argument based on half-filled Hubbard model is not applicable to Co ions.

In the case of LMFO, Mn and Fe magnetic moments are coupled antiferromagnetically, with |J_1| and |J_2| smaller than what we found previously for LMNO and LMCO. Finally, the Curie temperatures evaluated from a mean-field treatment of

![Diagram](attachment:image.png)

FIG. 3. (Color online) Top panel: (a) Reduced supercell with the 4 non-equivalent Mn (blue) and Ni(Co, Fe) (red) atoms. The gray atoms are on the Mn sublattice and the black ones on the Ni(Co, Fe) sublattice. The lattice vector a denotes the out of plane direction, while the lattice vectors b and c generate the plane. Bottom panel: Spin configuration for Mn (blue) and Ni(Co, Fe) (red) sublattices in (b) AFM4, (c) AFM5, (d) AFM6 and (e) FiM phases.
the Ising model are given in Table IV. For the details of the mean-field calculation, see appendix A. The mean-field theory overestimates the Curie temperatures. However, it gives the correct trend.

Finally, in order to examine the accuracy of the exchange couplings, we used them to evaluate the energy differences of a new magnetic configuration with respect to FM state and compare the results with those found directly from the ab initio calculations. The configuration AFM6, given in Table I, was not used in the calculation of the couplings. The energy difference from the ab initio calculations and from the Ising model using exchange couplings from Table II are listed in Table III. The agreement is very good in the case of LMNO (less than 1% of disparity), and relatively good in the cases of LMCO and LMFO (respectively 5% and 11% of disparity).

### IV. TRANSITION TEMPERATURE FROM MONTE-CARLO CALCULATIONS

The mean field treatment of the spin Hamiltonian does not take into account fluctuations hence overestimates the Curie temperatures $T_C$. In order to get better approximations, we perform classical Monte-Carlo calculations with the GT-GPU method on a cubic lattice\(^\text{17}\) using the $J$ and extreme spin values listed in Table II.

### A. Monte Carlo methodology

Genetic Tempering is a Monte-Carlo algorithm that uses many copies of the Metropolis-Hastings algorithm\(^\text{18-20}\) to generate highly precise statistical measurements and eliminate auto-correlation error. To ensure accuracy, initial state samples are chosen from unconverted samples surrounding the target answer. Running another round of Monte-Carlo sampling on these initial states gives a partial cancellation of the relaxation error.\(^\text{21}\) The $T_c$ is obtained from Binder’s cumulant,\(^\text{20}\) $B(T, L) = 1 - \langle M^4 \rangle_L / (3 \langle M^2 \rangle_L^2)$, with $L$ the linear lattice size. In the thermodynamic limit, $L \to \infty$, the Binder’s cumulant tends towards $2/3$ for $T < T_c$ and $0$ for $T > T_c$, hence it is discontinuous in this limit. In simulation with finite $L$, the intersection point of the Binder’s cumulants for different system sizes determines $T_c$ and usually depend only rather weakly on those sizes.

| $E_{AFM6} - E_{FM}$ | From $J$ values | From ab initio calculations |
|---------------------|-----------------|---------------------------|
| LMNO                | 0.154           | 0.155                     |
| LMCO                | 0.176           | 0.185                     |
| LMFO                | -0.181          | -0.202                    |

**TABLE III.** Energy difference between AFM6 phase and FM phase in eV.

| Transition temperature (K) | Mean-field Monte-Carlo Experimental |
|----------------------------|------------------------------------|
| LMNO                       | 527 419 280 \([2]\)               |
| LMCO                       | 505 399 226 \([3]\)               |
| LMFO                       | 418 329                             |

**TABLE IV.** Magnetic phase transition temperature in Kelvin obtained from different methods for LMB"O.

### B. Improved Curie temperatures

The Curie temperatures obtained from Monte-Carlo are shown in Table IV and compared with mean-field values and experimental ones. The transition temperature of bulk ordered LMFO is not known but the magnetization measurements indicate a lower $T_C$ than LMCO, as seen in Fig. 1. As can be seen from Table IV, both mean-field and Monte-Carlo give consistent trend with experimental data but overestimate them. The Monte-Carlo prediction is closer to experimental transition temperatures. It is worth mentioning that Curie temperature of LMNO and LMCO are affected by the (AF) next-nearest neighbor exchange coupling: they have smaller magnitude in comparison with nearest neighbor exchange coupling, but the number of next-nearest neighbor is larger. Finally, capturing the correct trend allows both mean-field and Monte-Carlo methods to be used reliably in material design.

### V. CONCLUDING REMARKS

We used GGA and GGA+U calculations in order to understand the ground state electronic and magnetic properties of double perovskite La$_2$MnFeO$_6$. This material is predicted to be an insulating ferrimagnet, unlike similar compounds La$_2$MnCoO$_6$ and La$_2$MnNiO$_6$, which are insulating ferromagnets. The present study helped us understand the important role played by electron-electron interactions in the determination of the ground state of this material. We also showed that the interplay between crystal field, Mn-O-Fe bonding angle and electron-electron interactions also needs to be taken into consideration when analyzing the superexchange mechanism in LMFO.

Large electron-electron interactions in Fe 3$d$ shells promote Mn$^{3+}$ and Fe$^{3+}$ oxidation states and AFM ground state in LMFO. In contrast, we also saw that Mn-O-Fe bonding angles superior to $\approx 165^\circ$ promote a FM ground state with Mn$^{4+}$ and Fe$^{2+}$ oxidation states. From these observations, we believe that studying two different new materials could be of interest in the global topic of magnetic refrigeration.

First, in order to avoid the strong electronic repulsion in 3$d$ shells that promote an AFM ground state in LMFO over an FM one, one could study the double perovskite La$_2$MnRuO$_6$ (LMRO). Valence orbitals in Ru are 4$d$, which are more extended in space than Fe-3$d$ orbitals. Smaller correlations in LMRO could lead to a FM ground state with Mn$^{4+}$ and Ru$^{2+}$.
oxidation states. However, experiments on disordered LMRO (space group $Pnaa$) have found this material to be a ferromagnet with trivalent Mn in high-spin configuration and trivalent Ru in low-spin configuration. The effect of the ordering of Mn and Ru atoms still needs to be investigated.

The second option is to get rid of an excess electron in Fe by hole-doping the compound, which could lead to Mn$^{3+}$ and Fe$^{3+}$ oxidation states. If both Mn and Fe are in high-spin configuration, these oxidation states would lead to a ferromagnetic superexchange interaction. Moreover, the substitution of La$^{3+}$ cations with larger divalent cations would increase the tolerance factor of the material, which would in turn reduce the amount of octahedral tilting. This avenue will be explored further in work to come.

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Appendix A: Mean-field theory for Curie temperature

In this section we recall mean-field theory for double perovskites, which allows us to estimate the Curie temperature. The magnetic system of LMNO, LMCO and LMFO can be modeled by the Ising model, Eq. (1). The mean field approximation is to replace the configurational energy by the energy of a non-interacting system of spins each experiencing a field $h_{MF}$. The mean field Hamiltonian can be obtained by substituting $S_i^z = \langle S_i^z \rangle + \delta S_i^z$ with $\delta S_i^z \equiv S_i^z - \langle S_i^z \rangle$ and neglecting terms of order $(\delta S_i^z)^2$ in Eq. (1). For the FM configuration, the mean-field energy is

$$E_{MF}^F = - \sum_i h_{MF} S_i^z - \sum_j h'_{MF} S_j^z,$$

$$h_{MF} = 2(4J_1 + 2J_2)m' + 2(4J_3 + 8J_4)m,$$

$$h'_{MF} = 2(4J_1 + 2J_2)m + 2(4J'_3 + 8J'_4)m',$$

where magnetizations per spin are $m = (1/2N) \sum_i \langle S_i^z \rangle$ and $m' = (1/2N) \sum_i \langle S_i^z \rangle$ and $2N$ denotes the total number of sites of a given type. Recall that $h_{MF}$ and $h'_{MF}$ depend on temperature through the temperature dependence of $m$ and $m'$.

The magnetization per spin is given by $m = \sum S_i^z p(S_i^z) S_i^z$ where $p(S_i^z)$ denotes the single-spin Boltzmann distribution

$$p(S_i^z) = \left( \frac{1}{Z} \right) \exp(\beta h_{MF} S_i^z),$$

and $Z$ is the partition function

$$Z = \sum_{S_i^z} \exp(\beta h_{MF} S_i^z) \cdot \sum_{S_i^z} \exp(\beta h'_{MF} S_i^z).$$

It is straightforward to show that the magnetizations are given by Brillouin functions

$$m(T) = \frac{1}{\beta} \frac{\partial \ln(Z)}{\partial h_{MF}} = - \frac{1}{2} \coth(\beta h_{MF}/2) + (S^z + \frac{1}{2}) \coth(\beta h_{MF}(S^z + 1/2)),$$

$$m'(T) = \frac{1}{\beta} \frac{\partial \ln(Z')}{\partial h'_{MF}} = - \frac{1}{2} \coth(\beta h'_{MF}/2) + (S'^z + \frac{1}{2}) \coth(\beta h'_{MF}(S'^z + 1/2)),$$

where $S^z$ and $S'^z$ denote the extreme values of the spins. For example, for LMNO, they are $S_{Mn}^z = 3/2$ and $S_{Ni}^z = 1$. Note that one could have used $S_{Mn}^z = 3$ and $S_{Ni}^z = 2$ which renormalizes the exchange couplings but leaves Curie temperature invariant. These coupled equations can be solved to obtain $m$ and $m'$. For high $T$ (low $\beta$), the only solution is $m = m' = 0$ whereas for low $T$ there are possible non-trivial solutions. The solution with non-zero $|m|$ and $|m'|$ appears at Curie temperature. By expanding the coth functions in the limit of small $h_{MF}$ and $h'_{MF}$, the above equations give the eigenvalue problem

$$m(T) = \frac{S^z(S^z + 1)}{3k_B T} h_{MF}(T),$$

$$m'(T) = \frac{S'^z(S'^z + 1)}{3k_B T} h'_{MF}(T),$$

which yields the following equation for Curie temperature:
\[ 3k_B T_c = \left[ S^z(S^z + 1) h_2 + S'^z(S'^z + 1) h'_2 \right] + \frac{1}{4} \sqrt{4h_1^2 S^z(S^z + 1) S'^z(S'^z + 1) + [S^z(S^z + 1) h_2 - S'^z(S'^z + 1) h'_2]^2}, \]

where we have defined \( h_1 = 4J_1 + 2J_2 \), \( h_2 = 4J_3 + 8J_4 \) and \( h'_2 = 4J'_3 + 8J'_4 \). Note that in the case with identical moments, \( S^z = S'^z \), and only nearest neighbor coupling, the above equation reduces to textbook formula, i.e., \( 3k_B T_c = 2h_1 S^z(S^z + 1) \).

Assuming that LMFO undergoes a ferrimagnetic to paramagnetic transition at Néel temperature \( T_N \), then \( T_N \) can also be obtained from (A10). In this case, the only difference between the treatment of \( T_N \) and \( T_C \) is the sign of nearest-neighbor interaction \( h_1 \), which also appears in \( h_{MF} \) and \( h'_{MF} \). However, the sign of \( h_1 \) disappears in (A10). For the classical Ising model on bipartite lattices, it is well known that a simple relabeling of up and down for one of the sublattices maps the nearest-neighbor ferromagnetic model to the antiferromagnetic one.

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