Theory of magnetism in La$_2$NiMnO$_6$

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The magnetism of ordered and disordered La$_2$NiMnO$_6$ is explained using a model involving double exchange and superexchange. The concept of majority spin hybridization in the large coupling limit is used to explain the ferromagnetism of La$_2$NiMnO$_6$ as compared to the ferrimagnetism of Sr$_2$FeMoO$_6$. The ferromagnetic insulating ground state in the ordered phase is explained. The essential role played by the Ni-Mn superexchange between the Ni $e_g$ electron spins and the Mn $t_{2g}$ core electron spins in realizing this ground state, is outlined. In presence of antisite disorder, the model system is found to exhibit a tendency of becoming a spin-glass at low temperatures, while it continues to retain a ferromagnetic transition at higher temperatures, similar to recent experimental observations [D. Choudhury et al., Phys. Rev. Lett. 108, 127201 (2012)]. This reentrant spin-glass or reentrant ferromagnetic behaviour is explained in terms of the competition of the ferromagnetic double exchange between the Ni $e_g$ and the Mn $e_g$ electrons, and the ferromagnetic Ni-Mn superexchange, with the antiferromagnetic antisite Mn-Mn superexchange.

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I. INTRODUCTION

The double perovskite (DP) La$_2$NiMnO$_6$ (LNMO), has generated a lot of interest for its magnetodielectric properties, making it a promising candidate for potential device applications. There have also been suggestions of topological phases for LNMO formed in LaNiO$_3$-LaMnO$_3$ superlattices. The pure compound is supposed to be a ferromagnetic semiconductor, with a Curie temperature very close to room temperature ($T_C \approx 280K$). Recently, there has been reports of reentrant spin-glass behaviour in partially disordered LNMO at low temperatures, along with a disordered ferromagnetism at higher temperatures. In this paper, a simple theoretical model for LNMO is proposed which can explain the ferromagnetic insulating behaviour of the ordered compound, as well as provide insight into the low temperature spin-glass behaviour observed in the disordered case. Since there is supposed to be significant contribution of the relative spin-orientation dependent asymmetric hopping between the transition metal sites to the dielectric constant, hence the colossal magnetodielectricity is closely related to the magnetism. Hence an understanding of the magnetic and electronic properties of this material is essential to the understanding of the magnetodielectricity in this material.

II. THE MODEL HAMILTONIAN

In La$_2$NiMnO$_6$ the Nickel is in $Ni^{3+}$ state ($t_{2g}^5 e_g^2$) and has two $e_g$ electrons, while the Manganese is in $Mn^{4+}$ state ($t_{2g}^3 e_g^0$) and has three $t_{2g}$ electrons. As the $t_{2g}$ electrons are more localized, and are parallel due to strong Hund coupling, they may be thought of as a core classical spin $S = 3/2$. Nickel has a filled $t_{2g}$ shell, and net $t_{2g}$ spin $S = 0$, hence this compound can be thought of as a manganite where half the sites do not have a core spin. When Nickel $e_g$ electrons hop on to the vacant $e_g$ orbitals of Manganese, they have an exchange with the large Mn $t_{2g}$ core spins as usual, but the difference with most other DP-s like Sr$_2$FeMoO$_6$ (SFMO) and Sr$_2$CrOsO$_6$ (SCOO) is that this exchange coupling is ferromagnetic rather than antiferromagnetic. A model with somewhat similar ingredients had been proposed in Refs, but they only considered the ordered case numerically, and at zero temperature. A detailed understanding of the magnetism of LNMO including the case of antisite disorder is lacking so far. We propose the following simple model Hamiltonian for the ordered case:

\[
H_{ord} = \epsilon_N \sum_{i,\sigma} c_{N,i\sigma}^\dagger c_{N,i\sigma} + \epsilon_M \sum_{i,\sigma} c_{M,i\sigma}^\dagger c_{M,i\sigma} \\
+ t_{MN} \sum_{<ij><\sigma} c_{M,i\sigma}^\dagger c_{N,j\sigma} + J_H \sum_{i,\alpha,\beta} c_{M,i\alpha}^\dagger \bar{e}_{\alpha\beta} c_{M,i\beta} \cdot \vec{S}_i \\
+ J_{super} \sum_{<ij>} c_{N,i\alpha}^\dagger \bar{e}_{\alpha\beta} c_{N,j\beta} \cdot \vec{S}_i \tag{1}
\]

FIG. 1. (colour online) Crystal structure of La$_2$NiMnO$_6$
In Ni-Mn a single orbital model which can explain the magnetism of LNMO, we consider Mn. In our attempt to find the simplest Hamiltonian introduces for LNMO the Ni-Mn energy.

\[ H_{\text{ord}}^{(1)} = \epsilon_N \sum_{i \sigma} c_{N,i\sigma}^\dagger c_{N,i\sigma} + \epsilon_M \sum_i m_i^\dagger m_i + t_{MN} \sum_{<ij>} \left( \cos \frac{\theta_i}{2} m_i^\dagger c_{N,j\uparrow} + \sin \frac{\theta_i}{2} e^{i\phi_i} m_i^\dagger c_{N,j\downarrow} \right) + J_{\text{super}} \sum_{<ij>} c_{N,i\sigma}^\dagger \sigma_{\alpha\beta} c_{N,j\beta} \cdot \vec{S}_i \]  

where \( m_i^\dagger \) represents spinless Mn degree of freedom, \( \theta_i \) is the polar angle between the spin \( \vec{S}_i \) at i-th Mn site with z-axis, \( \phi_i \) is the azimuthal angle, and charge transfer energy is given by \( \Delta = \tilde{\epsilon}_M - \epsilon_N \). This represents the minimal model for understanding the magnetism of ordered LNMO. It is to be noted that this Hamiltonian has majority spin hybridization between Mn and Ni, i.e., in case of a fully ferromagnetic arrangement of the B-site (Mn) core spins (\( \theta_i = 0 \), \( \phi_i = 0 \) \forall i), B-B' (Mn-Ni) hybridization in the DP A2BB'06 (La2NiMnO6) is only possible in the majority spin channel, rather than in the minority spin channel as in DP-s like SFMO15 and SCOO12 (See Appendix).

Antisite disordered regions (with B,B' interchanged) have strong antiferromagnetic superexchange between two nearest-neighbour B site ions, e.g., half-filled Fe3+ ions in case of SFMO15, or half-filled Mn4+ ions in case of LNMO. Hence in the disordered case, the following terms are added18:

\[ H_{\text{disord}} = t_{MM} \sum_{<ij>} \left[ \cos \frac{\theta_i}{2} \cos \frac{\theta_j}{2} \right] m_i^\dagger m_j + \epsilon_i^{(\phi_i-\phi_j)} \sin \frac{\theta_i}{2} \sin \frac{\theta_j}{2} \right] m_i^\dagger m_j + t_{NN} \sum_{<ij>\sigma} c_{N,i\sigma}^\dagger c_{N,j\sigma} + J_{\text{AS}} \sum_{<ij>} \vec{S}_i \cdot \vec{S}_j \]  

where \( J_{\text{AS}} \) is an antiferromagnetic superexchange in the antisite region between two neighbouring Mn \( t_{2g} \) core spins (see Fig 2), while \( t_{MM} \) and \( t_{NN} \) represent hopping between two neighbouring Mn and two neighbouring Ni \( e_g \) levels respectively.

III. ORDERED CASE: DISPERSION AND DOS

In the ordered case, in the limit \( |J_H| \to \infty \), the dispersion can be obtained analytically from Eq 2 in the ferromagnetic phase. There are 3 \( e_g \) bands, given by

\[ \epsilon_1 = \epsilon_N - \frac{J_{\text{super}} S}{2} \]  

\[ \epsilon_{\pm} = 0.5 \left[ (\epsilon_M + \epsilon_N) + \frac{(J_H + z J_{\text{super}})S}{2} \right] \pm \sqrt{\left\{ (\epsilon_M - \epsilon_N) + \frac{(J_H - z J_{\text{super}})S}{2} \right\}^2 + 4\epsilon_k^2} \]
where $\epsilon_k = 2t_{MN}(\cos k_x + \cos k_y)z$.

At half-filling of the Ni $e_g$ orbital in this single orbital model in the ferromagnetic state with all the core spins $S$ pointing up, the Ni $e_g$ band in only one spin channel (the majority spin channel) is fully filled, and so the Fermi energy lies in a gap. This gap can be estimated in the limit of Ni-Mn $e_g - e_g$ hopping $t_{MN} = 0$, when the bands shrink to levels. Then $\epsilon_1 = \epsilon_Ni - \frac{zJ_{\text{super}}S}{2}$, $\epsilon_+ = \epsilon_{Mn} + \frac{J_H}{2}S$, and $\epsilon_- = \epsilon_{Mn} - \frac{J_{\text{super}}S}{2}$. $\epsilon_1$ and $\epsilon_-$ now represent the two spin-split Ni $e_g$ down (minority) and up (majority) levels respectively, while $\epsilon_+$ represents the energy of the up (majority) Mn $e_g$ orbital. The down (minority) Mn $e_g$ orbital is shifted out to $\infty$ due to the $J_H \to -\infty$ limit being taken. Hence the energy gap in the majority spin channel between the occupied Ni orbital given by $\epsilon_-$ and the unoccupied Mn orbital given by $\epsilon_+$ is given by

$$E_g = \epsilon_+ - \epsilon_- = \Delta - \frac{zJ_{\text{super}}S}{2}$$

(6)

Hence the gap in the majority spin channel can be estimated as $\Delta - \frac{zJ_{\text{super}}S}{2}$. Thus, a necessary condition for the Ferro-Insulating state is $\Delta > \frac{zJ_{\text{super}}S}{2}$. If the Ni-Mn hopping is turned on, then this condition becomes more stringent:

$$\Delta - \frac{zJ_{\text{super}}S}{2} > 8t_{MN}$$

(7)

However, if there was no Ni-Mn superexchange, the two Ni $e_g$ levels for up and down spins would have coincided, and the Ni $e_g$ band being half-filled, the system would have been metallic. In presence of the Ni-Mn superexchange, the Ni $e_g$ levels are spin-split. The condition for non-overlapping of the Ni $e_g$ bands can be estimated as $\epsilon_1 - \epsilon_- > 0$, which gives $-zJ_{\text{super}}S > 0$. This along with the inequality $\Delta$ are the conditions for the realization of a Ferromagnetic Insulator (FI) ground state. Hence the Ni-Mn superexchange, introduced in a model for LNMO in Eq 4 and Eq 5 is an important and essential component for obtaining the ferromagnetic insulating ground state in the ordered case. Thus electron correlations are an essential criterion for the realization of the FI ground state in this model of LNMO.

In the case of finite $J_H$, there are $4 e_g$ bands. In Fig 4 the DOS is plotted for $J_H = -0.98eV$ by numerically solving the $4 \times 4$ eigenvalue problem from Eq 4 in the ferromagnetic ground state for each $\vec{k}$ and using $\rho(E) = \frac{1}{V} \sum_k \delta(E - \epsilon_k)$. The $t_{2g}$ bands for Mn and Ni do not appear in the DOS as the $t_{2g}$ electrons for Mn$^{4+}$ and Ni$^{2+}$ have been considered to be classical core spins of $S=3/2$ and $S=0$ respectively. With the Mn core $t_{2g}$ spin considered to be in up state at all sites, it is found that the minority (down) spin Ni $e_g$ band and the majority (up) spin Mn $e_g$ band lie in between the majority (up) spin Ni $e_g$ and the minority (down) spin Mn $e_g$ bands, as in the DFT DOS of Re$^{2+}$. The Fermi energy lies in between the Ni $e_g$ and the Mn $e_g$ majority spin bands. Thus the ferromagnetic insulating state is explained. The separation between the Ni $e_g$ and Mn $e_g$ bands in the minority spin channel is almost twice that in the majority spin channel, once again similar to the DFT DOS. The band gap in the majority spin channel (\approx 1eV) is also reproduced. Thus the relative band positions are roughly similar to that of the published DFT results$^{20}$. 

IV. ORDERED CASE: MAGNETISM

Exact Diagonalization-Monte Carlo (ED-MC) simulations were performed with the hamiltonian $H_{\text{ord}}^{(1)}$ given by Eq 2 and a system size of $8 \times 8$ in 2D, and $8 \times 8 \times 8$ in 3D. The moments at the Nickel site, Manganese site and the total moment are plotted in Fig 4. It is observed that the B and B' site moments are parallel to each other, rather than antiparallel as in SrFeMoO$_6$. 

FIG. 4. (colour online) Mn $t_{2g}$ core spin, Ni $e_g$ electron spin and total moment as a function of temperature in the ordered case.

FIG. 5. (colour online) Left : $M$-$T$ plot for the ordered case in 2D. Right: Curie Weiss fit to the reciprocal susceptibility for the ordered case.
This is a consequence of the majority spin hybridization between B and B' site electrons in the Hamiltonian of Eq.\(^2\) for LNMO, as opposed to minority spin hybridization as in SFMO\(^1\). This explains why LNMO is ferromagnetic, as opposed to SFMO, which is ferrimagnetic. This is also supported by the fact that the Nickel \(e_g\) up and down spin bands do not lie within the exchange gap of the Mn \(e_g\) bands (see DOS of Fig.\(^3\)), as opposed to SFMO where the spin-split Mo orbitals lie within the exchange gap of Fe, inducing a moment in Mo opposite to Fe\(^2\). The magnetization (M) versus temperature in 2D plotted in left panel of Fig.\(^5\) shows a single transition with a \(T_c\) around 360K, while the Curie-Weiss fit of the inverse susceptibility gives a \(T_c\) around 250K. The M vs T plot in 3D is shown in the left panel of Fig.\(^7\). The \(T_c\) is similar (around 350K). The parameters used were: \(t_{MN}=0.125\) eV, \(\Delta=1.9\) eV, \(J_{super,S}=-7.5\) meV (2D) and -5 meV (3D)\(^22\). The ordered moment reaches 90% of the maximum value at a temperature of about 1 K.

The effective exchange for an effective B-site (Mn) core spin-only model can be calculated from the Hamiltonian of Eq.\(^2\) by integrating out the B' (Ni) sites of the DP La\(_2\)NiMnO\(_6\), using the procedure of Self-Consistent Renormalization (SCR)\(^14\). As in Ref.\(^8\), if we assume a on-site anisotropy on the Ni site then the \(J_{super}\) term in Eq.\(^2\) becomes diagonal. In the case of all spins lying parallel to this anisotropy axis (\(\theta = 0\) or \(\theta = \pi\)), the effective exchange for a Mn core spin-only model\(^8,14\)

\[
H = \sum_{ij} J_{ij}^{eff} \sqrt{\frac{1 + S_i S_j}{2}}
\]

can be evaluated as (considering majority spin hybridization with \(J_H \rightarrow -\infty\) rather than minority spin hybridization with \(J_H \rightarrow \infty\) as in Ref.\(^8\)):

\[
J_{ij}^{eff} = \sum_k \frac{1}{2} [E_{k+} n_F(E_{k+}) + E_{k-} n_F(E_{k-})] e^{i \vec{k} \cdot (\vec{r}_i - \vec{r}_j)}
\]

where \(E_{k\pm} = \frac{\Delta - J_{super}}{2} + \frac{\sqrt{(\Delta - J_{super})^2 + 4\epsilon^2}}{2} \Rightarrow J_{super} = \frac{\epsilon}{\sqrt{\frac{4\epsilon^2}{(\Delta - J_{super})^2} + 1}}\)

\[
\epsilon = -z J_{super} S / 2.
\]

However, since the the Ni-Mn superexchange \(J_{super}\) is ferromagnetic, \(J_{super}^f < 0\), unlike the Cr-Os superexchange \(J_2\) as defined in Ref.\(^8\) which is antiferromagnetic, \(J_2 > 0\). Hence the effective exchange expression becomes identical to that of Ref.\(^8\) with \(J_{super}^f\) instead of \(|J_2|\).

In LNMO, only the lowest band out of the 3 bands given in Eq.\(^5\) is occupied: this signifies the Nickel \(e_g\) majority spin band. Shifting the energies of the 3 bands by \(-z J_{super} S\), and putting \(\epsilon_{Mn} = \epsilon_{Mn} + \frac{J_{super} S}{2} = \Delta\) and \(\epsilon_{Ni} = 0\), the dispersions of the 3 shifted bands become:

\[
\epsilon_\pm = \frac{\Delta - \frac{z J_{super} S}{2}}{2} \pm \sqrt{\left(\frac{\Delta - \frac{z J_{super} S}{2}}{2}\right)^2 + 4\epsilon^2}
\]

Hence there are 3 shifted bands centered at \(\approx 0\), \(-z J_{super} S\) and \(\left(\frac{\Delta - \frac{z J_{super} S}{2}}{2}\right)\). Out of these, in LNMO, only the lowest Ni \(e_g\) band, signified by \(\epsilon_\pm\), is occupied, as the electron filling is 1 per Ni \(e_g\) orbital (this is a single orbital model). Hence in the expression for effective exchange between Mn core \(t_{2g}\) classical core spins given by Eq.\(^8\) only the Fermi function for \(E_{k-}\) is non-zero at T=0. In the limit of small Ni-Mn hopping compared to Ni-Mn charge transfer energy and superexchange (\(t_{2g}^2 / (\Delta - J_{super}) \rightarrow 0\)), \(E_{k-} \rightarrow \frac{1}{2} (\Delta - J_{super}^f) \left[1 - \sqrt{1 + \frac{4\epsilon^2}{(\Delta - J_{super}^f)^2}}\right] \rightarrow \frac{1}{2} (\Delta - J_{super}^f) \left[1 - \left\{1 + \frac{2\epsilon^2}{(\Delta - J_{super}^f)^2}\right\}\right] \rightarrow -\epsilon^2\).

Hence

\[
J_{ij}^{eff} \rightarrow \frac{1}{2} \sum_k E_{k-} e^{i \vec{k} \cdot (\vec{r}_i - \vec{r}_j)}
\]
FIG. 8. Variation of the two temperatures of the kink anomalies in the magnetization with parameters, obtained from ED-MC simulations. Left: Variation of temperature $T_1$ of lower temperature anomaly with $t_{MN}^2$, for constant $J_{super}$. Right: Variation of temperature $T_2$ of higher temperature anomaly with $J_{super}$, for constant $t_{MN}$.

$$\sum_k \frac{-\epsilon_k^2}{2(\Delta - J_{super})} e^{i\vec{k}.(\vec{r}_i - \vec{r}_j)} \to -h_{ij} \frac{-h_{ij}}{2(\Delta - J_{super})}$$

where $h_{ij} = t_{MN}^2 \sum_{x,y} \delta_{2x \pm j} + 2 \sum_{x,y} \delta_{2x \pm j} + 4 \delta_{ij}$ is the Fourier transform of $t_{2g}^2$ defined in Ref. [24]. It involves a third neighbour term, a next-nearest neighbour term, and an onsite term. Hence the effective exchange between large B site classical core spins (Mn $t_{2g}$ core spins) in LNMO, with a filling of one electron per Ni $e_g$ orbital, is ferromagnetic, just like that (between Cr $t_{2g}$ core spins) in SCOOC, which has a filling of one electron per Os orbital. Thus the core spin ferromagnetism of LNMO arises from a similar interplay of double exchange $J_H$ and superexchange $J_{super}$ as in SCOOC, except that these are both ferromagnetic in the former, while both are antiferromagnetic in the latter. Thus when the B’ sites are included, these two exchanges produce overall ferromagnetism in LNMO, and overall ferrimagnetism in SCOOC.

V. DISORDERED CASE: REENTRANT SPIN-Glass TRANSITION

ED-MC simulations with $H = H_{ord}^{(1)} + H_{disord}$ for the case of 25% random antisite disorder were performed with a maximum system size of 16×16 in 2D, and 8×8×8 in 3D. The results are shown in Fig 9, the right panel of Fig 8 and in Fig 9 and Fig 10. ZFC and FC plots for the magnetization are shown in the left panel of Fig 8 for 2D. Parameters chosen are similar to the ordered case. The 3D results for the ZFC and FC plots of the magnetization are shown in the right panel of Fig 7. The ZFC magnetization shows a kink at around 250K corresponding to a transition to a disordered ferromagnetic state, followed by another kink at around 50K, signifying the onset of a new frustrated regime, where the system exhibits a tendency to become a spin-glass at low temperatures. This is similar to the signature of the reentrant spin-glass transition observed experimentally by D. Choudhury et al. 2. The ZFC-FC diverges throughout this temperature range, and the moment reaches only about 45-48% of its saturation value. The Curie Weiss fit to the high temperature susceptibility gives a $T_c$ of about 320K while the low temperature kink anomaly in the magnetization starts around 150K, and the highest value of moment is reached around 50K, indicative of the frustration in the system.

In order to explore the systematics of the two kink anomalies in the magnetization vs temperature curve, ED-MC simulations were carried out for the 25% disordered systems with varying parameter sets (not just the parameter set obtained from DFT data of Ref. [27,28] quoted before). The results are shown in Fig 8. It is observed that the temperature $T_1$ for the low temperature anomaly occurring varies as the square of the Mn-Ni hopping amplitude $t_{MN}$ (left panel of Fig 5), when $J_{super}$ is maintained constant. Whereas, the temperature $T_2$ at which the high temperature anomaly occurs varies proportional to $J_{super}$ (right panel of Fig 5), when $t_{MN}$ is maintained constant.

In order to confirm the spin-glass behaviour of this disordered system, the spin-glass susceptibility $\chi_{SG0}$ is plotted versus temperature in the left panel of Fig 9 in 2D for system sizes 4×4, 8×8 and 16×16 respectively. It is found to diverge at low temperatures, confirming that the system is indeed a spin-glass. Finite size scaling has been undertook in the right panel of Fig 9. Upon scaling the spin-glass susceptibility as $\chi_{SG0}(T)/\eta \nu$, and plotting this versus $(T - T_{SG})^{1/\nu}$ (where $T$ is expressed in eV), the data for the 3 different system sizes are found to collapse to the same curve for the choice

$$\eta = 0.076, \nu = 1.92 \ (T \ in \ eV)^{\frac{1}{2}}.$$
\( T_{SG} < 116K, \eta = -0.076, \nu = 1.92^{30-32} \). The scaling exponents \( \eta \) and \( \nu \) are intermediate between those for the disordered 2D Ising model\(^{28}\) and the disordered 3D classical Heisenberg model\(^{31}\).

As the ordering temperature for the high temperature ferromagnetic phase is \( \approx 250-300K \), which is close to the \( T_c \) of the ferromagnetic phase in the ordered case, this ordering scale is clearly set by the Mn-Ni superexchange \( z J_{\text{super}} S \) (\( \approx 300K \)). The low temperature frustrated phase accompanied by a kink anomaly in the magnetization, is presumably due to the competition of the ferromagnetic Mn-Mn effective double exchange scale set by \( \frac{t_i^2}{2(\Delta - J_{\text{super}})} \) (\( \approx 50K \), from \( J_{ij}^{\text{eff}} \) in Eq \(^{10}\), with the antiferromagnetic antosite Mn-Mn superexchange \( J_{AS} \). The presence of two ferromagnetic scales, namely due to Mn-Ni superexchange and effective Mn-Mn double exchange along with the antiferromagnetic antosite Mn-Mn superexchange \( J_{AS} \) in LNMO presumably leads to the reentrant spin-glass or reentrant ferromagnetic behaviour. Such a competition between double exchange and superexchange leading to reentrant spin-glass behaviour have also been observed in other materials\(^{33}\). Thus, a rough estimate of the two scales related to the reentrant spin-glass transition, can be obtained as \( T_2 \approx z J_{\text{super}} S \) corresponding to a transition to a high temperature superexchange dominated regime and \( T_1 \approx \frac{t_i^2}{2(\Delta - J_{\text{super}})} \), signifying the onset of a low temperature double exchange dominated regime\(^{34}\). The observed dependence of the two kink anomalies in the magnetization upon parameters \( t_{MN} \) and \( J_{\text{super}} \) (namely \( T_1 \approx t_{MN} \) and \( T_2 \propto J_{\text{super}} \)), obtained from ED-MC simulations (Fig \(^{5}\)) as discussed before, is consistent with this picture. This establishes that the observed kink anomalies in the magnetization are indeed signatures of a changeover from a superexchange dominated to a double exchange dominated regime.

It is to be noted that the two transitions as observed in the ZFC happen in a single homogeneous phase involving Ni\(^{2+}\)-Mn\(^{4+}\) ions and not two phases consisting of Ni\(^{2+}\)-Mn\(^{4+}\) and Ni\(^{3+}\)-Mn\(^{3+}\) respectively, as suggested in some previous works.\(^{3}\) As evident from Fig \(^{4}\) the moment on the \( e_g \) orbitals resides almost entirely on the Nickel, and very little on the Manganese site. Thus, the Nickel maintains its Ni\(^{2+}\) character and the Manganese its Mn\(^{4+}\) character, as reported in Ref\(^{2}\). Thus our results support the idea of a reentrant spin-glass transition within a single homogeneous phase of disordered La\(_2\)NiMnO\(_6\), as proposed in Ref\(^{2}\).

\section*{VI. CONCLUSION}

In conclusion, a plausible explanation for the ferromagnetic insulating ground state of ordered La\(_2\)NiMnO\(_6\) along with the reentrant spin-glass behaviour observed in presence of antisite disorder, is provided in a unified framework. The importance of the Ni-Mn superexchange in realizing the correlated ferro insulating state in the ordered case is established. Salient features of the DFT DOS are explained using this simple model Hamiltonian. The relevant energy scales which dictate the magnetism are identified. The underlying physics of the reentrant spin-glass transition is explained in terms of a changeover from a high temperature ferromagnetic superexchange dominated regime to a low temperature ferromagnetic double exchange dominated regime, in competition with the antiferromagnetic antosite superexchange. A novel mechanism of majority spin hybridization is proposed to explain the ferromagnetic behaviour of ordered LNMO as opposed to ferrimagnetic behaviour of many other DP-s like SFMO.

\section*{VII. APPENDIX: MAJORITY SPIN HYBRIDIZATION}

Let us consider a two-sublattice Kondo lattice model suitable for double perovskites, of the form of Eq \(^{11}\) for simplicity without the superexchange term.

\[
H_{\text{ord}} = \epsilon_{N_i} \sum_{\sigma} c_{N,i,\sigma}^\dagger c_{N,i,\sigma} + \epsilon_{M_n} \sum_{\sigma} c_{M,i,\sigma}^\dagger c_{M,i,\sigma} + t_{MN} \sum_{\langle ij \rangle,\sigma} c_{M,i,\sigma}^\dagger c_{N,j,\sigma} + J \sum_{\alpha,\beta} c_{M,i,\alpha}^\dagger \sigma_{\alpha\beta} c_{M,i,\beta} \cdot \vec{S}_i
\]

Then the Kondo coupling term \( J \sum_{\alpha,\beta} c_{M,i,\alpha}^\dagger \sigma_{\alpha\beta} c_{M,i,\beta} \cdot \vec{S}_i \) can be diagonalized by using a transformation of the Fermion operators \( c_{M,i,\uparrow} \) and \( c_{M,i,\downarrow} \) as follows\(^{18}\).

\[
\begin{align*}
    c_{M,i,\uparrow} &= \cos \frac{\theta}{2} m_{i\uparrow} + \sin \frac{\theta}{2} m_{i\downarrow} \\
    c_{M,i,\downarrow} &= \sin \frac{\theta}{2} e^{i\phi} m_{i\downarrow} - \cos \theta e^{i\phi} m_{i\uparrow}
\end{align*}
\]

For DP-s like Sr\(_2\)FeMoO\(_6\) (SFMO), an antiferromagnetic Kondo coupling (\( J > 0 \)) is considered\(^{18}\), and hence in the limit \( J \to \infty \), all terms involving \( m_{i\sigma} \) operators are neglected. Then \( m_{i\uparrow} \) is set equal to spinless operator \( m_i \). The hybridization terms of such a \( J \to \infty \) model (as in Ref\(^{18}\)), written in the same notation convention as followed in this manuscript, is given by:

\[
t_{MN} \sum_{\langle ij \rangle} \theta_i \theta_j m_{i\uparrow}^c c_{N,j,\uparrow} + \epsilon_{i\uparrow} m_{i\uparrow} + h.c. \tag{13}\]

Obviously, if all the B site core spins \( \vec{S}_i \) point upwards, \( \theta_i = 0, \phi_i = 0 \), whereupon the B-site spinless Fermions \( m_i \) hybridize only with the minority down spin B’ site electrons \( c_{N,j,\downarrow} \). Thus minority spin hybridization is obtained, which leads to ferrimagnetism in DP-s like SFMO, with the B’ site moment pointing opposite to the B site moment. This is because the minority B’ site electrons form a band due to hybridization which is partially or wholly occupied, while the majority B’ site electrons are localized, and hence remain above the Fermi energy.
On the other hand, the model for LNMO that is presented in Eq (1) considers a ferromagnetic Kondo coupling, which in this case is nothing but the Hund coupling \( J = J_H \). Then in the limit \( J \to -\infty \), the \( m_{\text{eff}} \) terms are neglected, and \( m_{\text{eff}} \) are set equal to the spinless Fermion operator \( m_i \). The resultant model as in Eq (2) has the following hybridization terms in the \( J \to -\infty \) limit:

\[
t_{MN} \sum_{\langle ij \rangle} \left( \cos \frac{\theta_i}{2} m_i m_j^\dagger + \sin \frac{\theta_i}{2} \hat{\phi}_i e^{i\phi_i} m_i m_j^\dagger \right) + \text{h.c.} \quad (14)
\]

In this case, if all the B site core spins \( \vec{S}_i \) point upwards, i.e., \( \theta_i = 0, \phi_i = 0 \) then the B site spinless fermions \( m_i \) hybridize only with the majority spin B’ site electrons \( c_{N,j}^\dagger \). Hence the majority spin B’ site electrons form a band which in this case is fully occupied, while the minority spin B’ site electrons are mostly localized, and remain above the Fermi energy. Thus we get majority spin hybridization in the \( J_H \to -\infty \) model given by Eq (2) leading to ferromagnetism in LNMO, with the B’ moment pointing parallel to the B site moment.

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13. Re\(^{\text{\ldots}}\) distinguishes between the Ni-Mn \( e_g \) superexchange \( J(1) \) which is FM and the Ni-Mn \( e_g \) superexchange \( J(2) \) which is AFM and considers the net Ni-Mn superexchange \( J_{\text{net}} \) to arise as the additive effect of the two competing interactions \( J_{\text{net}} = J(1) + J(2) \). This net interaction \( J_{\text{net}} \) comes out to be FM and of magnitude \(-5\text{meV}\). However, the Ni-Mn \( e_g \) \( e_g \) superexchange cannot be considered in the present work as then the Hamiltonian ceases to have spin-Fermion interactions which are coupled classical-quantum interactions, and instead would have four-Fermion fully quantum mechanical interactions which can no longer be treated by the ED-MC method. The Ni-Mn \( e_g \) \( e_g \) superexchange can however, be treated using this method as that is between classical \( t_{2g} \) core spins and quantum Ni \( e_g \) Fermions. Hence this Ni-Mn \( t_{2g} \) \( e_g \) superexchange is used as \( J_{\text{super}} \) in the model of Eq (2) but instead considered as FM, and the value of the net superexchange \( J_{\text{super}} S = J_{\text{net}} = -5\text{meV} \) is used. While this is an approximation, it does not alter the physics greatly, as this \( J_{\text{super}} \) is taken as the only Ni-Mn superexchange, and hence the value as well as the sign of the net Ni-Mn superexchange as in the DFT paper of Ref 5 is preserved.
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$J_{\text{super } S}$ in 3D is $2/3$ of $J_{\text{super } S}$ in 2D, so that $z J_{\text{super } S}$ remains constant at the value given in Ref 6, where $z$ is the coordination number.

While the value of $J_{\text{super } S} = -5\text{meV}$ as in Ref 6 correctly reproduces the ferromagnetic $T_c$, larger values are required to match the separation between the Nickel majority and minority $e_g$ bands in the DFT DOS. The onsite Coulomb $U$ on the Nickel $e_g$ orbitals, neglected in this work, might have a role to play here.

The parameters used for the antisite disordered part are $t_{MN} = t_{MM} = t_{NN} = 0.125$, $J_{AS} = 0.025$, $h = 0.01$. The value of $J_{AS}$ used in this work is intermediate between the values of nearest neighbour Heisenberg Mn $t_{2g}$ core spin superexchange in rare-earth manganites (0.017 eV) as given in Ref 35, and the value of Fe-Fe antisite superexchange for the double perovskite Sr$_2$FeMoO$_6$ (0.035 eV) considered in Ref 18.

The next-nearest-neighbour B'-B' (Ni-Ni) superexchange which introduces an additional source of frustration even in the ordered case, like the Os-Os superexchange in SCO [34], has not been considered in this work.

Since the temperature scale in the data collapse plot is in eV, the error in determining $T_{SG}$ is about 0.01 eV for 2D. Hence the only definitive statement that can be made about $T_{SG}$ is that it is less than 116K in 2D.

While this temperature $T_1$ signifies the onset of a frustrated double exchange dominated regime, when the effective Mn-Mn double exchange begins to compete with the antisite Mn-Mn superexchange, and spin-glass correlations begin to proliferate, the actual spin-glass transition $T_{SG}$ may occur at lower temperatures.

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