Tailoring the magnetic landscape in Al-doped LaMnO₃: an experimental and computational perspective

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Abstract
We have reported the synthesis, structural and magnetic properties of LaAlₓMn₁₋ₓO₃ (x = 0.05, 0.15, 0.25) in this article. We have synthesized these compounds through the Sol-gel citrate method and performed the Rietveld refinement of X-ray diffraction data to determine the lattice parameters. The surface elemental composition and oxidation states of LaAl₀.₂₅Mn₀.₇₅O₃ are investigated using X-ray photoelectron spectroscopy (XPS) in a wide energy window of 0–1200 eV. The magnetic study shows the ferromagnetic transition of these materials. To understand the nature of magnetization from the experiments, we have studied the first principle density functional theory (DFT) and Monte-Carlo simulation. From the DFT calculations, we have confirmed the ferromagnetic structure in the ground state and studied the electronic structure of these materials. The Monte Carlo simulation has been done through the anisotropic Ising model to analyze the origin of magnetic phase transition. We have determined the anisotropy and the interaction constants from the DFT calculations. The double exchange interaction is mainly responsible for the ferromagnetic ground state.

1. Introduction

Rare-earth-based perovskite manganates have been in the centre of research intrigue due to their rich inter-related structural [1], electronic [2] and magnetic properties [3, 4], which account for their giant magnetoresistance [5], colossal magnetoresistance [6], magnetocapacitance [7] and high magnetocaloric [8, 9] and magnetodielectric effects [10] to name a few. The underlying physics which drives the unusual but rich physical properties of the manganites results from the array of different complex interactions like double exchange (DE) [11], superexchange (SE) [12], electron-phonon interaction [13], electron-electron interaction [14], etc. The manganates have the empirical formula of ABO₃, where A and B mainly belong to large rare-earth and transition metal cations respectively. The structure of these perovskites mostly deviated from high symmetry with the tilting and the distortion of the BO₆ octahedra being the main structural characteristics that affect their physical properties. The tunable cation-cation ordering (long-range and short-range) at the transition metal site is actively modulated by chemical doping at these active sites. Thus the combination of structural deviations and cation-cation ordering modulate the observed exotic properties in these perovskites which range from structural phase transitions [15], magnetic phase transitions [16], and electronic metal-insulator transitions [17] which have direct implications on their magneto-dielectric [10], magneto-caloric effect [9] and magneto-resistive effects [18] which are useful for switchable spintronics applications [19]. The hexagonal perovskite manganites belong to the multiferroic group of materials which show the electric (∼900 K) and magnetic (∼100 K) ordering simultaneously [20, 21].

Among the rare-earth manganites, LaMnO₃ is a highly studied material, which takes part as a parent compound due to its highly enriched and intense properties. Previous studies show that it belongs to the orthorhombic centrosymmetric space group [22, 23]. The MnO₆ octahedra become tilted and distorted due to the orthorhombic distortion of this material [24]. This leads to the cooperative John-Teller effect of this material
which lifts the degeneracy of d-orbital of Mn$^{3+}$-ion $[t_{2g}^2(d_{x^2}^1, d_{y^2}^1, d_{z^2}^1) \text{ and } e_g^1(d_{x^2-y^2}^1, d_{y^2-x^2}^0)]$. The spins (S = 2) of the magnetic Mn$^{3+}$-ions are ferromagnetically aligned through the O$^{2-}$ due to the Hund rule and the orbital ordering in the Basal plane. Now, the perpendicular planes show the antiferromagnetic alignment with this plane due to cooperative John-Teller (JT) distortion [25], which forms the A-type anti-ferromagnetism of this material [26]. A study shows that the system becomes ferromagnetic instead of antiferromagnetic if the cooperative JT distortion is absent [27, 28]. Later, it is studied that the doping of divalent atoms in the La-site removes the JT distortion and the system shows the ferromagnetic behaviour at low temperatures [29]. The doping of these cations generates the Mn$^{4+}$-ion in the material due to the charge neutrality; this whole process is called the double exchange (DE) mechanism [30]. So, the Mn$^{4+}$ is mainly responsible for FM transition in LaMnO$_3$.

During the synthesis of LaMnO$_3$, the uncontrolled sintering and annealing create some vacancy of the cationic sites which produces some extra amount of non-stoichiometric oxygen ($3+\delta$) to balance the charge neutrality [31]. As a result of this procedure, the system creates some Mn$^{4+}$-ion, which is called self-doping [32]. This generates the DE ferromagnetic interaction in the materials. If the system crosses the certain limit of self-doping, it becomes fully ferromagnetic. So, the lower value of $\delta$ enhances the super-exchange (SE) which creates the canted A-AFM magnetic structure. The DE interaction (FM) wins the competition for higher $\delta$ values. If the $\delta \geq 0.1$, the crystal structure changes from orthorhombic to rhombohedral [32].

In the case of magnetic cations (M = Fe, Ni, Co) doping in the Mn site lead to the Orthorhombic crystal structure with ferromagnetic transition [33–35]. The exchange interactions between Mn$^{3+}$ and M$^{3+}$ are responsible for the ferromagnetic behaviour of these materials. But doping of the non-magnetic tetravalent Ti$^{4+}$-ion shows the Rhombohedral R-3c structure and the material creates Mn$^{5+}$-ion for charge neutrality [36]. The DE interaction between Mn$^{3+}$ and Mn$^{2+}$ generates ferromagnetism in this material. In this context, we have studied the effect of non-magnetic trivalent Al-doping in the Mn-site of LaMnO$_3$. The detailed structural properties have been studied through X-ray diffraction and X-ray Photo-electron Spectroscopy (XPS) method, which supports the presence of Mn$^{4+}$ state in this sample. The detailed magnetic analysis has been performed through the M-T and M-H curves and the DFT calculations with the magnetic Monte-Carlo simulations. The magnetic spin structure in the ground state is determined from DFT calculations, which are shown schematically in figure 1.

### 2. Experimental details

Al-doped LaMnO$_3$ is prepared through the sol-gel citrate method. Firstly all the nitrates La(NO$_3$)$_3$,6H$_2$O, Mn(NO$_3$)$_3$,9H$_2$O, and Al(NO$_3$)$_3$,6H$_2$O were taken with the calculated stoichiometric ratio in a de-ionised water medium with the appropriate molar ratio of citric acid and ethylene glycol. Then, the solution is stirred and heated to achieve a gel and fluffy ash-like powder. The obtained powder is calcined and sintered at 1173 K and 1223 K to get the final material. LaAl$_{x}$Mn$_{1-x}$O$_3$ ($x = 0.05, 0.15, 0.25$) are prepared with the help of the above-
described method. The room temperature X-ray diffraction (XRD) pattern of these materials is obtained from an X-ray powder diffractometer (Rigaku Miniflex II, Cu-Kα: λ = 1.54 Å), where the range of 2θ is 10° to 80° at a scanning rate of 0.02° per step. We get the crystal structure and the lattice parameters from the Rietveld refinement analysis of the XRD data using the Fullprof suite program [37]. The X-ray photoelectron spectroscopy spectra of \( \text{LaAl}_{0.25}\text{Mn}_{0.75}\text{O}_3 \) are taken by X-ray photoelectron spectroscopy (XPS). The magnetic measurements are performed using the vibrating sample magnetometer (VSM; Lakeshore).

3. Computational details

3.1. Ab-initio calculations

The electronic and magnetic properties of Al-doped LaMnO\(_3\) have been thoroughly investigated through the full-potential linearized augmented plane wave (FPLAPW) method as implemented in WIEN2K [38, 39]. The crystal structure of LaMnO\(_3\) is being optimized through spin-polarized general gradient approximation (GGA) with the Coulomb repulsion U (GGA+U) method. We have taken five magnetic spin configurations for the optimization process such as ferromagnetic (FM), non-magnetic (NM), and three antiferromagnetic (AFM) [A-AFM, C-AFM, G-AFM]. Now we have made the supercell for the other three Al-doped systems. In the supercell, we have replaced the Mn through the Al atoms in the appropriate percentage. All the structures are being optimized through the above-described process. The Hubbard parameter \( U_{eff} \) for Mn-d orbital is fixed to 3eV for all structures. The self-consistent criteria for energy and charge convergence have been set to \( 10^{-4} \) Ry and \( 10^{-5} \) e, respectively.

3.2. Monte Carlo simulations

Monte-Carlo simulation is a very useful technique to study magnetic properties theoretically [40–43]. We have used the anisotropic Ising model for this simulation [44]. The anisotropy comes from the two types of Mn ions, Mn\(^{3+}\) and Mn\(^{4+}\), which are verified by XPS spectra, discussed later. So, the Hamiltonian, we have taken for the computation of the magnetic properties, is described in the following.

\[
H = -J_1 \sum_{\langle i,j \rangle} S_i S_j - J_2 \sum_{\langle i,k \rangle} S_i S_k - \Delta \sum_i S_i^z - h \sum_i S_i
\]

(1)

Where \( h \) and \( \Delta \) are the external field and the anisotropic constant, respectively. \( J_1 \) and \( J_2 \) are the interaction constants for the nearest neighbour (NN) and next nearest neighbour (NNN) interaction, respectively. Due to the two types of Mn-ions, we have used two spins value \( S = 2 \) and 1.5 for Mn\(^{3+}\) and Mn\(^{4+}\), respectively. The value of these constants is determined from the first principle calculations described in the later part of this article. The details of Monte-Carlo simulation are given in the supplementary section.

4. Results and discussions

4.1. Crystallographic information

The crystal structure of these materials is determined from XRD, described in figures 2(a)–(d). The main peak near 32° as well as next to this split into two parts, which indicates that it might be fitted with the R3\(_c\) (space group 167) symmetry. The lattice parameter, atomic coordinates, and the goodness of fit (χ\(^2\)) are given in table 1. Figure 2(d) represents the zoomed view of the main peaks and the next two other peaks of La\(_{1-x}\)Al\(_x\)Mn\(_{3-x}\)O\(_3\) (x = 0.05, 0.15, 0.25). 3%, 15%, and 25% Al-doped compounds are named LAM95, LAM85, and LAM75 respectively, which are used in the later part of the manuscript. The splitting of main peaks is going to abolish with higher Al concentration. For 75% Mn, the 32° peak almost merges into one peak. From our previous study of LaAl\(_{0.5}\text{Mn}_{0.5}\text{O}_3\), there is no sign of splitting of peaks (figures 2(d)–(d)) [45]. This 50% Al-doped material’s symmetry also completely changes to Monoclinic P2\(_1\)/n. So, this material has a structural phase transition from R3\(_c\) to P2\(_1\)/n with increasing Al-concentration.

The surface elemental composition and oxidation states of LaAl\(_{0.25}\text{Mn}_{0.75}\text{O}_3\) are investigated using X-ray photoelectron spectroscopy (XPS) in a wide energy window of 0–1200 eV. The survey spectrum of LaAl\(_{0.25}\text{Mn}_{0.75}\text{O}_3\), in figure 3(a) shows the presence of La(3d), Al(2p), Mn(2p) and O(1s). The high-resolution core level XPS spectra for La 3d and Mn 2p are presented in figures 3(b), and (c), respectively showing their formal oxidation valence states. The XPS spectra of La-3d in figure 3(b) show two sets of spin-orbit split peaks (834.6 eV; 838.1 eV) corresponding to La 3d\(_{5/2}\) and (851.4 eV; 855.0 eV) corresponding to La 3d\(_{3/2}\) respectively, which are known-markers for the +3 oxidation state for La. The core-level XPS spectra of Mn-2p, shown in figure 3(c) demonstrate a mixed or variable oxidation state for Mn. The double splitting of individual peaks

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**References:**

[37] H J S S J S S S h S

[38] Bhowmik et al. Phys. Scr. 98 (2023) 025806

[39] Rigaku Mini

[40] et al.: LaAl\(_{0.25}\text{Mn}_{0.75}\text{O}_3\)

[41] XRD

[42] Al-doped LaMnO\(_3\)

[43] GGA

[44] AFM

[45] C-AFM

[46] FPLAPW
corresponding to Mn 2p3/2 at \( \sim 643 \) eV and Mn 2p1/2 at \( \sim 653 \) eV marks the presence of two oxidation states for Mn, namely Mn\(^{3+}\) and Mn\(^{4+}\). The lower binding energies corresponding to 642.2 eV and 652.6 eV mark the presence of the Mn\(^{3+}\) state whereas the higher binding energies at 644.8 eV and 654.8 eV correspond to the Mn\(^{4+}\) oxidation state. In addition, satellite peaks for 2p3/2 and 2p1/2 occur at 529.7 eV, and 531.2 eV, respectively. The system has 30% of Mn\(^{4+}\) state in the Mn-site, which means the excess of non-stoichiometric oxygen (\( \delta \)) is 0.3. The presence of heterogeneous oxidation states of Mn is important to gain insights into the intriguing magnetic landscape of the materials which will be discussed in the subsequent sections.

Figure 2. The XRD data and the Rietveld refinement of LaAl\(_{x}\)Mn\(_{1-x}\)O\(_3\)\( [x = (a) 0.05, (b) 0.15, (c) 0.25]\). (d) The zoomed view of the main perovskite peaks of these materials and the 4th one is for the LaAl\(_{0.5}\)Mn\(_{0.5}\)O\(_3\), taken from our previous study.

Table 1. Atomic coordinates and lattice parameters of LaAl\(_{x}\)Mn\(_{1-x}\)O\(_3\)\( [x = 0.05, 0.15, 0.25]\) were determined from the Rietveld Refinement method.

| Sample | Atom | x   | y   | z   | Lattice parameters (Å) | Reliability factors | Occupancy | Wyckoff site |
|--------|------|-----|-----|-----|-----------------------|---------------------|------------|--------------|
|        |      |     |     |     | a = 5.505(2)          | \( \chi^2 = 1.23 \) | 1.00(0)    | 6a           |
| LAM95  | La   | 0   | 0   | 0.25| b = 5.505(2)          | R\(_p\) = 7.90     | 0.991(2)   | 6b           |
|        | Mn   | 0   | 0   | 0   | c = 13.311(6)         | R\(_{wp}\) = 10.3   | 0.021(1)   | 6b           |
|        | Al   | 0   | 0   | 0   | \( \gamma = 120^\circ \) | R\(_{exp}\) = 8.67  | 1.128(5)   | 18e          |
|        | O    | 0.456(3) | 0   | 0.25| \( \gamma = 120^\circ \) | R\(_{exp}\) = 8.67  | 1.128(5)   | 18e          |

| Sample | Atom | x   | y   | z   | Lattice parameters (Å) | Reliability factors | Occupancy | Wyckoff site |
|--------|------|-----|-----|-----|-----------------------|---------------------|------------|--------------|
| LAM85  | La   | 0   | 0   | 0.25| a = 5.486(2)          | \( \chi^2 = 1.18 \) | 1.00(0)    | 6a           |
|        | Mn   | 0   | 0   | 0   | b = 5.486(2)          | R\(_p\) = 7.33     | 0.933(1)   | 6b           |
|        | Al   | 0   | 0   | 0   | c = 13.288(6)         | R\(_{wp}\) = 9.74   | 0.054(2)   | 6b           |
|        | O    | 0.451(4) | 0   | 0.25| \( \gamma = 120^\circ \) | R\(_{exp}\) = 8.44  | 1.161(1)   | 18e          |

| Sample | Atom | x   | y   | z   | Lattice parameters (Å) | Reliability factors | Occupancy | Wyckoff site |
|--------|------|-----|-----|-----|-----------------------|---------------------|------------|--------------|
| LAM75  | La   | 0   | 0   | 0.25| a = 5.471(3)          | \( \chi^2 = 1.16 \) | 1.00(0)    | 6a           |
|        | Mn   | 0   | 0   | 0   | b = 5.471(3)          | R\(_p\) = 7.46     | 0.891(1)   | 6b           |
|        | Al   | 0   | 0   | 0   | c = 13.275(1)         | R\(_{wp}\) = 9.67   | 0.055(2)   | 6b           |
|        | O    | 0.452(4) | 0   | 0.25| \( \gamma = 120^\circ \) | R\(_{exp}\) = 8.97  | 1.184(3)   | 18e          |
4.2. Magnetic properties

The temperature dependency of magnetization in ZFC (zero field cooled) mode is plotted in figure 4(a). The value of magnetization decreases gradually with increasing temperature for all three materials. The magnetic moment should be decreased with the decreasing Mn concentration. But we have seen that the value of magnetization for $x = 0.15$ is greater than the $x = 0.05$ in the lower temperature. This happens due to the increasing percentage of Mn$^{4+}$ ions in the $x = 0.15$ sample. The magnetization versus temperature plot clearly indicates the ferromagnetic transition of these materials. The transition temperatures are $T_{C0.05} = 135$ K, $T_{C0.15} = 110$ K, and $T_{C0.25} = 85$ K which are determined from the minimum point of the 1st derivative of the M-T curve.

Figure 3. (a) The whole XPS spectra of LaAl$_{0.25}$Mn$_{0.75}$O$_3$ and fitted data are shown for (b) La and (c) Mn atoms.

Figure 4. (a) The $M$ versus $T$ curve in ZFC mode for LaAl$_x$Mn$_{1-x}$O$_3$ ($x = 0.05, 0.15, 0.25$). (inset) The inverse susceptibility and its linear fitted curve with respect to the temperature in the paramagnetic region. (b) The magnetic hysteresis for these materials at 80 K and its zoomed view at origin (inset).
The inverse of the dc susceptibility is plotted in the inset of figure 4(a). The linear part (paramagnetic region) of this curve is fitted through the Curie-Weiss law, \( \chi = C/(T - \Theta_{\text{CW}}) \). The positive value of \( \Theta_{\text{CW}} \) indicates the ferromagnetic ordering of these materials at lower temperatures. The effective magnetic moments are 3.76 \( \mu_B/\text{f.u.} \), 3.51 \( \mu_B/\text{f.u.} \), and 3.32 \( \mu_B/\text{f.u.} \), calculated from the Curie constant \( C \). The spin-only moment value of Mn\(^{3+} \) is 4.9 \( \mu_B \). So, the theoretical magnetic moments for \( x = 0.05 \), 0.15, and 0.25 are 4.66 \( \mu_B/\text{f.u.} \), 4.17 \( \mu_B/\text{f.u.} \), and 3.68 \( \mu_B/\text{f.u.} \), respectively. It is clearly seen that there is a difference between experimental and theoretical moment values. In the octahedral environment, the d-orbital of Mn\(^{3+} \) ion is separated to \( e_g \) and \( t_{2g} \) due to the crystal field effect. This discrepancy of the moment arises due to the much stronger crystal field interaction than the spin-orbit interaction. But with lower Mn-concentration this difference at the moment is small due to the presence of extra Mn\(^{4+} \) in the system, which is proved from the XPS data previously. In this case, the crystal field interaction creates less impact because there is no \( e_g \) electron in Mn\(^{4+} \)-ion. The origin of the ferromagnetic character of these materials is mainly due to the double exchange interaction (DE) between Mn\(^{3+} \) and Mn\(^{4+} \) through the \( O^2- \)-ion. One \( t_{2g} \) electron of Mn\(^{3+} \) transfers through the \( O^2- \)-ion to Mn\(^{4+} \), creating the ferromagnetism in these materials.

Figure 4(b) and its inset figure represent the magnetic hysteresis loop and its zoomed view of these three materials at 80 K. For \( x = 0.05 \), the loop behaves like a ferromagnet as magnetization saturates in a high 10 kG magnetic field. The value of coercivity \( H_C = 333 \text{ Oe} \) and the remanent magnetization \( M_r = 0.25 \mu_B/\text{f.u.} \) suggest the ferromagnetic behaviour of this material. In the case of \( x = 0.15 \), the curve also saturates at high field and coercivity \( H_C = 78.15 \text{ Oe} \) and the remanent magnetization \( M_r = 0.11 \mu_B/\text{f.u.} \), which indicates the ferromagnetic character of this material. But for the \( x = 0.25 \) sample, we have seen the paramagnetic type behaviour at 80 K.

### 4.3. Electronic and magnetic structure: DFT

The electronic and magnetic structure of the material plays a crucial role in the different transport properties of the materials. To know the better physics of the material, the first principle density functional theory is the most accurate tool in this regard. The crystal structure should be optimized to get accurate results. The minimization of the energy with respect to the volume is the best way to achieve an optimized structure. However, we have taken the atomic coordinates and lattice parameters of the Rhombohedral R-3c LaMnO\(_3\) and optimized this structure through the WIEN2K structure optimization. We have used four different spin configurations (FM, A-AFM, C-AFM, and G-AFM). Among these we have seen that FM has the lowest energy, so the LaMnO\(_3\) is ferromagnetic (figure S2). Then we introduced the Al-atom by replacing some Mn-ion with an appropriate proportion of 5\%, 15\%, and 25\% in the B-site of the perovskites. All the structures have shown the ferromagnetic in the ground state.

From the previous study, we have seen that the Orthorhombic Pnma LaMnO\(_3\) shows the A-type antiferromagnetic spin configuration in the ground state [22–26]. So, we have taken this structure and optimized it for four different spin configurations. The result of this study shows that the A-AFM has the lowest energy among them. Figure S1 represents the energy minimization curve of Pnma symmetry. LaMnO\(_3\), and 5\% Al-doped LaMnO\(_3\) have shown the A-type AFM ground state whereas the other two compounds show the ferromagnetic state. So, the structural symmetry has responsible for the magnetic structure in this case. The magnetic moments for all materials with individual atoms are shown in table 2. The moments of the Mn atoms in LAM95 for the Pnma space group are opposite to each other, conmmagnetic moments for all materials with individual atoms are shown in table 2. The moments of the Mn atom in ferromagnetic state. So, the structural symmetry has responsible for the magnetic structure in this case. The reason, the magnetization curve of LAM95 ground state. For R-3c symmetry, the ground state magnetic moment of LAM95 is lower than LAM85. For that character of these materials is mainly due to the double exchange interaction Mn\(^{3+} \)-O-Mn\(^{3+} \). Now, for the 5\% Al-doped LaMnO\(_3\) (Pnma), shows the A-AFM magnetic structure in the ground state. But the

| Symmetry | Materials | \( \mu_{L,M} \) | \( \mu_{Al} \) | \( \mu_{3d} \) | \( \mu_{Mn} \) | \( \mu_{O} \) | \( \mu_{tot} \) | \( \mu_{all} \) |
|----------|-----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Pnma     | LAM95     | 0.01           | 0.007          | 3.23           | -3.24          | -0.06          | -0.51          | 3.99           |
|          | LAM85     | 0.01           | 0.006          | 3.37           | 3.40           | 0.02           | 3.23           | 27.98          |
|          | LAM75     | 0.02           | 0.003          | 2.86           | 3.01           | 0.04           | 2.44           | 11.99          |
| R-3c     | LAM95     | 0.01           | 0.008          | 2.96           | 2.58           | 0.05           | 2.51           | 30.00          |
|          | LAM85     | 0.01           | 0.009          | 3.76           | 3.68           | -0.02          | 1.83           | 28.00          |
|          | LAM75     | 0.01           | 0.015          | 3.70           | 3.69           | -0.01          | 0.76           | 12.00          |

Table 2. Calculated magnetic moments of each atom, interstitial, and cell for Al-doped LaMnO\(_3\) in \( \mu_B \) unit.
other two materials have shown the FM ground state. The doping of non-magnetic Al-atom (above 5%) breaks the superexchange AFM interaction between NN Mn$^{3+}$-ions. The bond lengths of Mn-O in MnO$_6$ octahedra derived from DFT are 1.69 Å, 2.09 Å, and 2.24 Å for the Pnma LAM95 structure. Whereas these bond lengths become 1.91 Å, 1.96 Å, and 2.18 Å for Pnma LAM85. So, clearly, the John-Teller effect is dominated in the 1st case which leads to the antiferromagnetic ground state of 0.05% Al-doped LaMnO$_3$. The John-Teller effect lifts the degeneracy of e$_g$ orbital and the system shows the orbital ordering, which is responsible for long-range AFM ordering of Mn-ions here. This is called the cooperative John-Teller effect. In the second case, the cooperative JT effect disappears which means the system is no longer antiferromagnetic. For, LaGa$_{1-x}$Mn$_x$O$_3$, the antiferromagnetic state is progressively destroyed above the 30% of Ga-doped LaMnO$_3$ and the compound becomes ferromagnetic just like in our case [46].

The spin-polarised total DOS and the partial DOS of Al-doped LaMnO$_3$ ($x = 0.05$ and 0.25) are shown in figures 5(a)–(d). Figure 5(a) represents the DOS of LAM95 (Pnma symmetry). In the TDOS, we see symmetric states for up and down spin configuration, which proves the antiferromagnetic character present here. But for 25% Al-doped compound (figure 5(b)), we clearly have an asymmetric Total DOS, which confirms the

![Figure 5](https://example.com/figure5.png)

**Figure 5.** The spin-polarised DOS and PDOS curve for (a), (b) Pnma LaAl$_{x}$Mn$_{1-x}$O$_3$ ($x = 0.05, 0.25$) and (c), (d) R-3c LaAl$_{x}$Mn$_{1-x}$O$_3$ ($x = 0.05, 0.25$). The Fermi energy ($E_F$) is set to zero, shown with the vertical dotted line.
ferromagnetic ground state. For the Pnma space group, it shows some gap in the Fermi level for both spins, which indicates the semiconducting behaviour of these compounds. But for the R-3c space group (figures 5(c) and (d)), there is no gap in the up-spin states whereas the down-spin creates some gap for all compounds, which supports the half-metallic behaviour of these materials. It also shows the asymmetric DOS in the TDOS for up and down spins because of the ferromagnetic ground state of these compounds.

4.4. Magnetic properties: Monte-Carlo simulation

Now, we have studied the magnetic properties of Al-doped LaMnO$_3$ from the Monte-Carlo simulation. The magnetic properties of these materials arise from the Mn-atom, which is situated at the corner site of the unit cell. The interaction between the two nearest neighbours Mn-ion must be ferromagnetic for these cases. So, the interaction constant is a very important parameter to determine the magnetic state. We have calculated the nn and nnn interaction constants $J_1$ and $J_2$ from our DFT data.

$$ J_1 = \frac{E_{A-AFM} - E_{FM}}{2 \times Z \times (S_1 S_2)} $$

$$ J_2 = \frac{E_{G-AFM} - E_{G-AFM}}{2 \times Z \times (S_1 S_2)} $$

and the magnetic anisotropic constants are determined from this equation,

$$ \Delta = \frac{E_a}{\sum (S_i)^2} $$

Where, $E_{FM,IAFM}$ stands for the minimum energy of different spin configuration. The $Z$, $S_1$, and $S_2$ are coordination numbers and the spin of two types of Mn ions. $E_a$ is the magnetic an-isotropic energy, calculated from this literature [50]. The value of the nn interaction constants ($J_1$) is 0.69 meV, 0.52 meV, and 0.56 meV respectively for $x =$ 0.05, 0.15, and 0.25 samples. Whereas the nnn interaction constants ($J_2$) are 0.008 meV, 0.08 meV, and 0.01 meV respectively. The anisotropic constants are 0.017 meV, 0.013 meV, and 0.01 meV respectively. The experimental magnetic data shows long-range ferromagnetism for all three cases. From the DFT calculations, we have seen that the ferromagnetic configuration has the minimum energy for the Rhombohedral R-3c space group.

Figures 6(a)–(c) and (d) represent the temperature-dependent magnetic properties and magnetic hysteresis loop, derived with the help of these interaction constants from the Monte-Carlo simulation. The value of magnetization decreases sharply with increasing temperature for all three materials. The magnetization curves follow the experimental DC-magnetization. The comparison between the experimental and simulation magnetization curve is shown in figure 6(e). The magnetization for $x =$ 0.05 is lesser than the $x =$ 0.15 curve as
5. Conclusions

We have synthesized the LaAl$_x$Mn$_{1-x}$O$_3$ (x = 0.05, 0.15, 0.25) from the Sol-gel citrate method. The XRD data confirm the Rhombohedral R-3c symmetry for all the compounds. The mixed valance of Mn-ions (Mn$^{3+}$ and Mn$^{4+}$) is present in 25% Al-doped material. For balancing the extra oxygen (3+δ), the system introduces the Mn$^{4+}$-ion which is responsible for the ferromagnetic DE interaction. As a result, the experimental magnetic study shows the ferromagnetic transition of these materials at a lower temperature. The transition temperatures are $T_\text{C,0.05} = 135$ K, $T_\text{C,0.15} = 110$ K and $T_\text{C,0.25} = 87$ K. From DFT calculations, we have concluded that all the compounds are ferromagnetic and half-metallic in the ground state. We have performed the Monte Carlo simulation through the anisotropic Ising model to analyze the origin of magnetic transition. The interaction constants are calculated from the DFT calculations. It shows the ferromagnetic behaviour for all the compounds and the critical temperatures are 140 K, 110 K, and 87 K for x = 0.05, 0.15, and 0.25 respectively.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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