

Experimental report

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Proposal: 5-24-693

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Title: Interplay of Jahn-Teller distortions and orbital order with lattice and local modes in $\text{LaMn}_{1-x}\text{GaxO}_3$

Research area: Chemistry

This proposal is a new proposal

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Samples: $\text{LaMn}_{(1-x)}\text{GaxO}_3$

Instrument	Requested days	Allocated days	From	To
D20	2	1	22/05/2023	23/05/2023
D2B	3	3	19/05/2023	22/05/2023

Abstract:

Understanding the emergence of colossal magnetoresistance (CMR) in optimally-doped $\text{La}_{1-x}\text{CaxMnO}_3$ ($x = 3/8$) is an ongoing active area of research in solid-state chemistry due to its potential technological relevance in data storage devices. Using a prototype system, we have recently discovered, coincident with the optimal doping regime for CMR, a novel state consisting of striping of orbital order (OO) with charge disorder (CD) occurring in a 1:3 ratio. This striped OO/CD potentially provides a new understanding of the microstructure in the CMR $\text{La}_{1-x}\text{CaxMnO}_3$ materials, and how this pattern of charge and orbital ordering may couple to the global lattice and strain modes. With our new insight we propose to undertake a variable temperature and composition neutron powder diffraction study on $\text{LaMn}_{1-x}\text{GaxO}_3$ to better understand how local geometric Jahn-Teller distortions couple to global lattice modes, driving structural phase transitions in the CMR manganites. This will lead to a greater appreciation of how the structure, hence properties of materials with technologically relevant metal-to-insulator transitions, such as CMR, can be systematically tuned.

Interplay of Jahn-Teller distortions and orbital order with lattice and local modes in $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$

Background and Scientific Context

Understanding the emergence of colossal magnetoresistance (CMR) in optimally-doped $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO, $x = 3/8$) is an ongoing active area of research in solid-state chemistry primarily due to its potential technologically relevant uses in novel data storage devices. Maximal decrease in resistivity is believed to be caused by percolative phase segregation between orbital ordered metallic and orbital disordered insulating states.¹ Orbital order/disorder behaviour is intimately tied to the presence of Jahn-Teller (JT) distortions caused by the high-spin d^4 Mn^{3+} cation, resulting in C-type orbital order of metallic LCMO phases. However, the intrinsic phase segregation at certain doping regimes prevents an in-depth microstructural study of how charge and orbital ordering phenomena arise in these states. Thus, a definitive understanding of the structure-properties relationships in these materials has yet to be reached.

The solid-solution $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ (LMGO) acts as a prototype system of the LCMO materials for understanding how local geometric JT distortions couple to global lattice modes in driving orbital order-disorder phase transitions. Prior work we have conducted using high-resolution synchrotron powder diffraction data highlights an orbital order-disorder transition at $x \approx 0.6$, consistent with that reported in literature.^{2,3} However, by decomposing lattice degrees of freedom in terms of irreducible representations of the parent space group $Pm-3m$, which has not yet been demonstrated by the literature, we find a reduction of lattice distortions associated with C-type orbital order (M_3^+), as one might expect as the JT-active species Mn^{3+} is diluted out. More interestingly, a concomitant decrease of the in-phase octahedral rotation about the c -axis (M_2^+) suggests a strong coupling between these modes. This is exciting since it has recently been predicted by computational methods that LaMnO_3 is only unstable to orbital ordering when MnO_6 octahedra are significantly rotated.⁴ Our work hence hints at a geometric origin for this coupling. Using Landau theory, we have identified a variety of third and fourth order terms involving zone boundary modes and unit cell strains that could facilitate this coupling.

However, because these lattice modes involve intricate, coordinated displacement of oxygen atoms within BO_6 octahedra, large differences in X-ray scattering factors of La and O mean that X-ray diffraction techniques alone will not be sufficient to robustly extract the true nature of these subtle distortions. The neutron scattering length of O, which is of similar magnitude to La, will allow for an unambiguous determination of oxygen positions and thermal displacement parameters. Therefore, further work using powder neutron diffraction (PND) techniques is needed to explore the complex interplay of unit cell strain and local and lattice modes to understand how they arise in orbital ordering phenomena in terms of both temperature and composition dependencies. To achieve this, PND measurements were obtained on the instruments D2B and D20.

Preliminary Results

From measurements collected on D2B, compositions in the LMGO solid-solution for $x = 0.2, 0.375, 0.5$ and 0.7 were studied and PND data were collected within the temperature range $10 \text{ K} \leq T \leq 300 \text{ K}$. Figure 1 shows the results of Rietveld refinements of $Pnma$ structural models against datasets obtained at 10 K for these compositions, demonstrating the good quality fits to the data. By consideration of the symmetry-motivated crystallographic approach to investigating orbital order-disorder behaviour in these samples, resulting tetragonal and orthorhombic unit cell strain, Γ_3^+ and Γ_5^+ respectively, and Jahn-Teller distortion, M_3^+ , modes are plotted in Figure 2 for each composition and temperature-

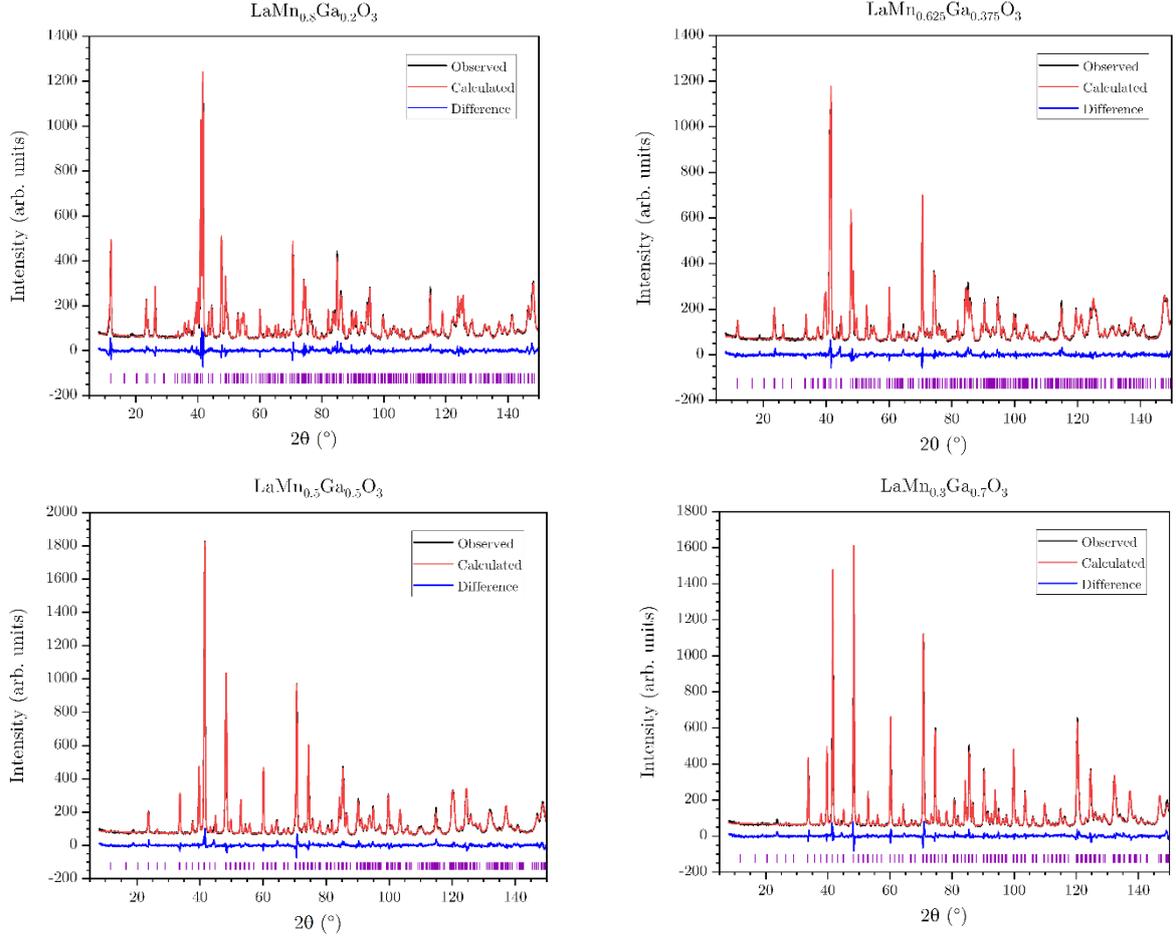


Figure 1: Rietveld refinements of $Pnma$ structural models of $LaMn_{1-x}Ga_xO_3$ ($x = 0.2, 0.375, 0.5$ and 0.7) against PND data obtained on D2B at 10 K. Plots correspond to the samples of composition $x = 0.2$ (top left), $x = 0.375$ (top right), $x = 0.5$ (bottom left) and $x = 0.7$ (bottom right). Black, red and blue traces represent observed, calculated and difference profiles respectively. Purple ticks indicate peak positions of the $Pnma$ structural model.

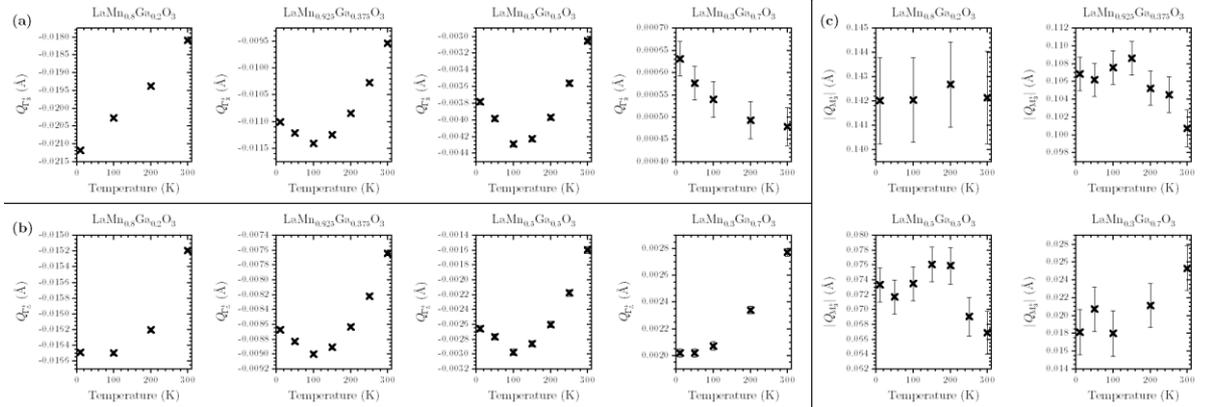


Figure 2: Resulting symmetry-adapted mode and strain amplitudes obtained from Rietveld refinements of $Pnma$ structural models against D2B PND datasets for each composition studied as a function of temperature. (a) Tetragonal unit cell strain Γ_3^+ for compositions left to right $x = 0.2, 0.375, 0.5, 0.7$. (b) Orthorhombic unit cell strain Γ_5^+ for compositions left to right $x = 0.2, 0.375, 0.5, 0.7$. (c) Jahn-Teller distortion M_3^+ for compositions top left to bottom right across the columns $x = 0.2, 0.375, 0.5, 0.7$.

dependent measurements. These initial results show that both tetragonal and orthorhombic strain increase in negative amplitude up to $T \approx 80$ K, whereby for temperatures below this an inflection in unit cell strain is observed. This temperature point is coincident with the onset of (anti)ferromagnetic transitions occurring in these materials which is corroborated by both D20 measurements, shown later,

and with literature.^{2,3} Furthermore, we observe that the M_3^+ mode amplitude remains essentially invariant as a function of temperature for each composition. This means that we are able to show that the strength of the Jahn-Teller effect remains essentially constant as a function of decreasing temperature, and that the important feature driving orbital order-disorder behaviour in the LMGO system is the concentration of Jahn-Teller active species.

PND measurements on D20 were collected on the compositions $x = 0.375$ and $x = 0.5$ within a temperature range $6 \text{ K} \leq T \leq 275 \text{ K}$ in roughly 1.6 K intervals in a ‘sweep’ mode. Heatmaps of the data collected, given in Figure 3, show the emergence of (anti)ferromagnetic superstructure peak evolution which starts at the temperature $T \approx 80 \text{ K}$ for both compositions. With these much finer temperature point increments compared to D2B we will be able to accurately track the distortion mode amplitude evolution of these compositions by performing Rietveld refinements against these datasets.

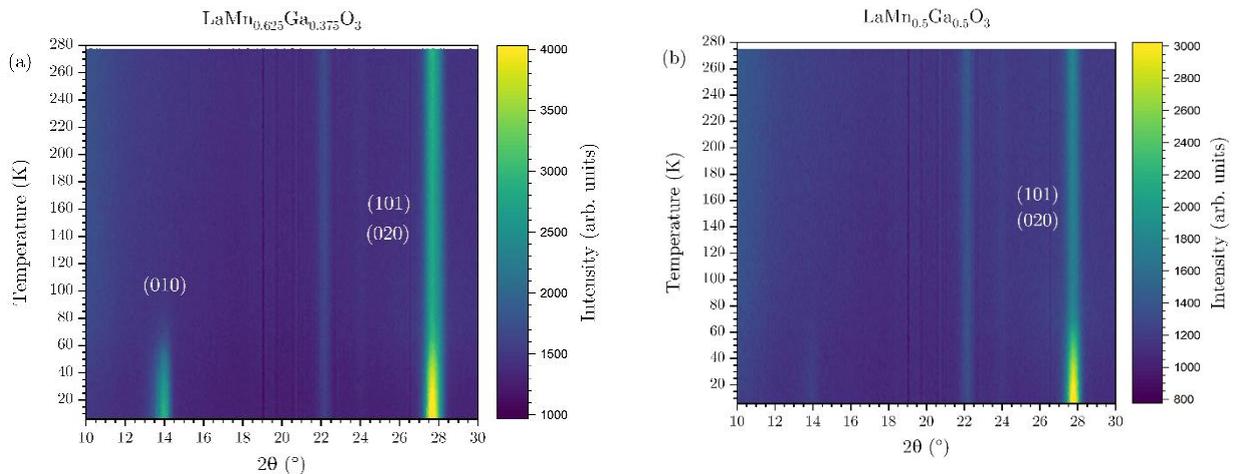


Figure 3: Heatmaps of variable temperature PND data in the temperature range $6 \text{ K} < T < 275 \text{ K}$ for $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ with the compositions $x = 0.375$ (a) and $x = 0.5$ (b) obtained on D20. The emergence of (anti)ferromagnetic peak intensity, with indices given with respect to the $Pn'ma'$ magnetic space group, begin to appear at $T = 80 \text{ K}$, consistent with magnetisation measurements from literature.^{2,3}

Continued Work

Continuing analysis of these data include the sequential refinement of D20 PND datasets against $Pnma$ structural models of the manganite perovskites, highlighting the fine evolution of structural and magnetic distortions that drive orbital order-disorder and magnetic transitions in the LMGO solid-solution. Furthermore, optimising the refinements of PND datasets obtained on D2B will be performed in order to confirm the trends in unit cell strain and Jahn-Teller distortion mode amplitudes already demonstrated.

References

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