Poster

Competition between *G*-type, *C*-type and *CE*-type orbital ordering modes in Na- and Ca-doped Hg-quadruple manganite perovskites

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Manganite perovskites exhibit a plethora of different charge and orbital ordering schemes, all of which control the emergence of various technologically-relevant properties such as metal-insulator transitions, magnetism and colossal magnetoresistance (CMR). $La_{1-x}Ca_xMnO_3$ (LCMO) shows a maximum in the CMR effect, large changes in resistivity under an applied magnetic field, for precise compositions with $x = 3/8$ believed to be caused by percolative phase segregation between metallic and insulating states [1-2], producing an average Mn *B*-site oxidation state $\langle Mn_B \rangle = +3.375$. Hence, understanding the nature of ordering phenomena for these optimally-doped perovskites is critical in order to aid the improvement and design of novel functional materials.

However, many competing complexities occur simultaneously in LCMO which precludes an accurate understanding of how each can control ordering phenomena. Examples of these complexities include mixed Mn oxidation states, electronic band-narrowing phenomena, and different degrees of Jahn-Teller distortions and tolerance factor effects. By using quadruple perovskites $Na_{1-x}Ca_xMn_3Mn_4O_{12}$ (structural form $AA'_3B_4O_{12}$, Figure 1) as prototypic systems of LCMO that tunes electronic effects, at precise x ($x = 0.5$) giving $\langle Mn_B \rangle = +3.375$ we have recently observed a novel orbital order:charge disorder (OO:CD)-stripe state [3]. It is proposed that this novel OO:CD-stripe state, and the structural distortions that accompany it, is a likely candidate to successfully describe ordering phenomena occurring in insulating LCMO that competes with the itinerant conducting state.

Following from the success of studying these quadruple perovskites, we have found the novel synthesis of Hg-equivalent quadruple perovskites, $HgMn_3Mn_4O_{12}$, exhibit a polar ground state due to charge transfer between *A'*- and *B*-sites with a concomitant evolution of *G*-type charge and orbital order (Figure 1) [4]. Both the polar ground state and *G*-type ordering are uncommon in manganite perovskites. Ca- and Na-equivalents of these quadruple perovskites result in different types of orbital order: 'disordered' *C*-type and *CE*-type, respectively, which means that the character of the Hg^{2+} electronic configuration ($4f^{14}\ 5d^{10}$) acts to expand the richness of the physical properties and ordering regimes demonstrated throughout the manganites.

Noting the striking differences between different charge and orbital order states *via* subtle variations in the chemistry of these manganite perovskites, we present results of a systematic study investigating the evolution of different types of orbital ordered states in the series $Hg_{1-x}(Na/Ca)_xMn_3Mn_4O_{12}$. By careful Rietveld analysis of synchrotron powder *X*-ray diffraction data, employing symmetry-adapted distortion mode formalism, we show that for the Na-doped series, tuning the average Mn_B oxidation state, the polar ground state and *G*-type ordering regime is preserved for compositions up to $x = 0.3$, with an observed coexistence of *G*-type and OO:CD-stripe states for $0.4 \leq x \leq 0.5$. On the other hand, we find that in the isoelectronic Ca-substituted series, the effective 'polarisability' of the *A*-site is tuned evident by the suppression of the polar *G*-type state to the 'disordered' *C*-type state of the Ca end member for compositions of $x \geq 0.2$.

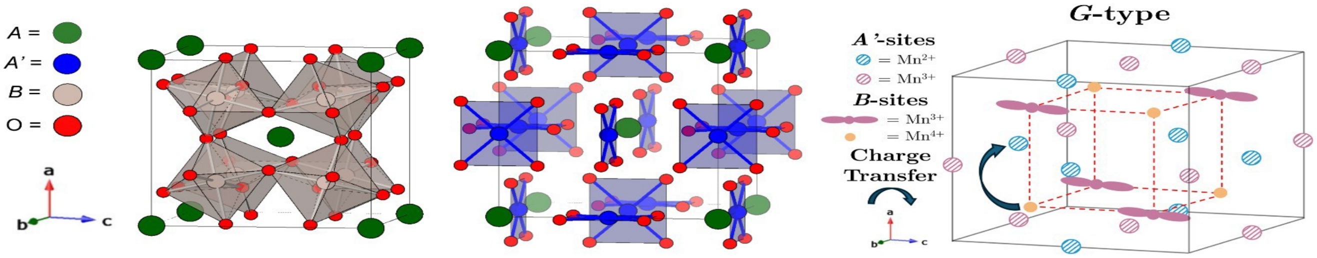

Figure 1. (Left, Middle) Structure of the quadruple perovskites $AA'_3B_4O_{12}$. BO_6 octahedral and $A'O_4$ square planar motifs are shown separately for clarity. (Right) *G*-type charge and orbital order observed in the ground-state Hg-quadruple perovskites. Black and red dashed lines represent the unit cell and sub-unit containing *G*-type charge and orbital order at the *B*-site, respectively. *A*- and O-sites are omitted for clarity.

S. W. Cheong and H. Y. Hwang, in *Colossal Magnetoresistance Oxides*, edited by Y. Tokura (Gordon and Breach, London, 2000) Chap. 7. **[2]** M. Uehara *et al.*, *Nature*, **399**, 560 (1999). **[3]** W. -T. Chen *et al.*, *Nat. Commun.*, **12**, 1 (2021). **[4]** W. -T. Chen *et al.*, *Phys. Rev. B*, **97**, 144102 (2018).