Real-Space Study of Charge and Orbital Ordering in $La_{0.6}Sr_{2.4}Mn_2O_7$ Manganite Single Crystal

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Charge and orbital ordering often occur in strongly correlated materials involving cations with multi-valence states. This order is related to various interesting physical phenomena in perovskite-structured and related oxides, such as superconductivity and colossal magnetoresistance [1,2]. The $n = 2$ Ruddlesden-Popper phase $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (LSMO), which is comprised of perovskite-like (La, Sr)MnO_3 bilayers separated by a rock-salt-like (La, Sr)O layer along [001], represents one of the most interesting manganites where its charge and orbital ordering can be tuned by varying x. In its phase diagram [3,4], previous studies revealed a narrow region with $0.66 \leq x \leq 0.72$ that showed no long-range magnetic ordering, while the regions with x below 0.66 and above 0.72 exhibited clear different long-range magnetic ordering behaviors owing to charge/orbital ordering in the lattice.
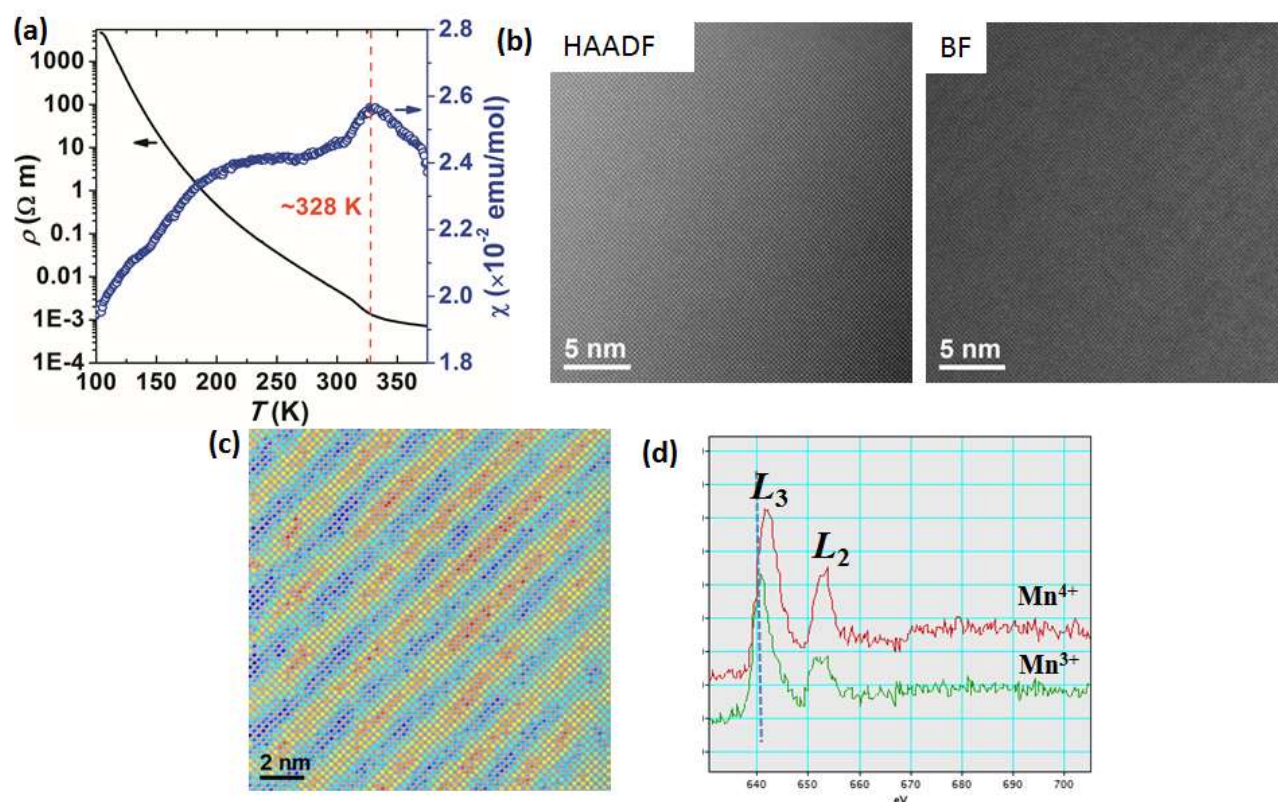
However, our resistivity and magnetic susceptibility measurements on a single crystal with $x = 0.7$ ($La_{0.6}Sr_{2.4}Mn_2O_7$) (Figure 1a) revealed a transition at around 328 K and bright-field-scanning transmission electron microscopy (BF-STEM) imaging (Figure 1b, right) showed the appearance of superstructure in this crystal at room temperature, indicating the possible appearance of local charge/orbital ordering and phase competition in the region of $0.66 \leq x \leq 0.72$. The sensitivity of properties to such minute compositional change and possible short-range ordering motivated us to study the complex interplay and competition between different degrees of freedom in this quantum material.

Our recent microscopy research revealed that charge and orbital ordering in perovskite-related structured materials can be visualized by picometer resolution strain maps (PRSM) utilizing atomic-resolution aberration-corrected STEM. The quantitative sub-Å analysis of HAAD-STEM images (Figure 1b, left) for the $La_{0.6}Sr_{2.4}Mn_2O_7$ single crystal depicts local periodic PRSM (Figure 1c) associated with subtle cation displacements. Analysis of the valence states of Mn in different strain stripes using the $L_{2,3}$ ratio method [5,6] for electron-energy loss spectra (EELS) revealed that they involve different Mn valence states (Figure 1d), i.e. charge-ordering. The orbital pattern was then inferred from PRSM determined from HAADF-STEM images, combined with single column EELS mapping of the distribution of the Mn^{3+} and Mn^{4+} valence states. In this pattern, due to $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbital ordering in each stripe, the oxygen octahedra are compressed along y (or x) while elongated along x (or y), causing their surrounding cations to move in the same direction, i.e. a simple-shear transverse lattice deformation.

Such PRSM analyses also directly visualized two types of nanoscale domains in this single crystal. The competition and interaction between these two types of short-range ground states accounts for the bulk properties of the $La_{0.6}Sr_{2.4}Mn_2O_7$ crystal. This work underscores the role of subtle structural distortions in determining the functionalities in correlated quantum materials and furthermore highlights the importance of real-space local probes to visualize charge and orbital ordering and nanoscale phase competition [7].

References:

[1] E H da Silva Neto *et al*, Science (2013), p. 1243479.
[2] Y Moritomo *et al*, Nature **380** (1996), p. 141.
[3] C D Ling *et al*, Phys. Rev. B **62** (2000), p. 15096.
[4] J F Mitchell *et al*, J. Appl. Phys. **89** (2001), p. 6618.
[5] M Varela *et al*, Phys. Rev. B **79** (2009), p. 085117.
[6] H Tan *et al*, Ultramicroscopy **116** (2012), p. 24.
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Figure 1. (a) Temperature-dependence resistivity and susceptibility for the $La_{0.6}Sr_{2.4}Mn_2O_7$ single crystal both show transition temperatures at around 328 K due to the appearance of charge and orbital ordering below it. (b) HAADF-STEM (left) and BF-STEM (right) images along [001] zone axis for the same region. The latter one reveals the appearance of superlattice in the structure while the former one does not show visible lattice displacements. (c) Local picometer resolution strain maps (PRSM) caused by charge and orbital ordering. (d) EEL spectra for two atomic columns in different strain stripes, respectively. Chemical shift of Mn L-edge and different $L_{2,3}$ ratios both indicate different Mn valence states.