Atomic-Resolution Imaging of Phase Transitions in Strongly Correlated Oxides with Continuously Variable Temperature Cryo-STEM

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Atomic-Resolution Imaging of Phase Transitions in Strongly Correlated Oxides with Continuously Variable Temperature Cryo-STEM

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Cryogenic scanning transmission electron microscopy (cryo-STEM) provides unparalleled insight into nanoscale material structure at the low temperatures required to access strongly correlated phenomena in quantum materials. These high-resolution *in situ* measurements are necessary in materials such as oxides, where charge, orbital, and lattice degrees of freedom give rise to complex phase diagrams comprising inhomogeneous orderings spanning multiple length scales. For instance, in charge ordered manganites atomic-resolution cryo-STEM experiments have identified temperature-dependent phase inhomogeneity underlying the emergence of incommensurate order, as well as clarified the charge ordered ground state and role of lattice coupling [1,2]. However, cryo-STEM measurements at atomic resolution have conventionally been limited to one temperature set by the cryogen boiling point, due to instability from the loss of thermal equilibrium as heat is supplied to broaden the available temperature range. This presents a significant barrier towards understanding phases stable only over narrow temperature ranges and the dynamic evolution of temperature-dependent processes such as phase transitions. Recently, a novel holder design integrating MEMS devices which can locally heat the sample without destabilizing the holder has made atomic-resolution cryo-STEM imaging possible at continuously variable temperatures (CVT) from ~100 to 1000 K [3]. Here, we leverage this access to intermediate temperatures between liquid nitrogen and ambient temperature to build a microscopic understanding of low temperature phase transitions in two strongly correlated oxide systems.

The Ruddlesden-Popper ruthenate Ca_2RuO_4 is a Mott insulator which undergoes a metal-insulator transition (MIT) from the high-temperature L-Pbca to the low-temperature S-Pbca phase at 357 K [4]. This transition is extremely sensitive to external stimuli such as strain, and the MIT can be driven with a threshold electric field of only 40 V/cm at room temperature [5]. In a 40 nm epitaxial film grown on $(001)_{pc}$ $LaAlO_3$ the MIT temperature is suppressed to ~230 K, and diffraction experiments suggest a nanoscale domain structure develops upon cooling through the transition. Atomic-resolution high-angle annular dark-field (HAADF)-STEM imaging shows that upon cooling the uniform high-temperature L-Pbca structure incorporates coherent stripes of an S-Pbca like phase, distinguished by a reduced in-plane lattice parameter (Fig. 1 a-d). With atomic resolution imaging at a series of temperatures through the MIT with CVT cryo-STEM, we map this ferroelastic domain structure over hundreds of nanometers (Fig. 1e). The spatially inhomogeneous behavior through the transition and distinct stripe arrangement after cycling revealed by CVT cryo-STEM suggest the domains mediate the epitaxial strain and respond to the film's elastic boundary conditions rather than pinning sites in the lattice.

In a second example, we will focus on the melting of charge order in the manganites. Previous electron diffraction and imaging studies have associated this melting with incommensuration and a reduction in coherence length, but the microscopic nature of the ordering through the transition has not yet been conclusively determined [6]. Here, we study the melting of charge order in the prototypical ~2/3 hole-doped system $Bi_{.35}Sr_{.17}Ca_{.48}MnO_3$. At low temperature, the material possesses a 3-unit cell locally unidirectional charge ordering and associated well-ordered transverse sinusoidal periodic lattice displacements (PLDs) [1]. These picometer scale PLDs are mapped with CVT cryo-STEM through a series of temperatures below the melting onset in Fig. 2 a-h, where the sinusoidal ordering – and its period – are largely unchanged. Upon heating near room temperature, however, discommensurations emerge locally altering the period of the PLDs and suppressing the PLD amplitude. This is shown in the line profiles in Fig. 2i, where the uniform commensurate ordering is disrupted by a region with a longer period and suppressed amplitude. Probing these structural changes in the PLDs with CVT cryo-STEM as the charge order melts provides insight into the role of long-range interactions and localized defects in the transition [7].

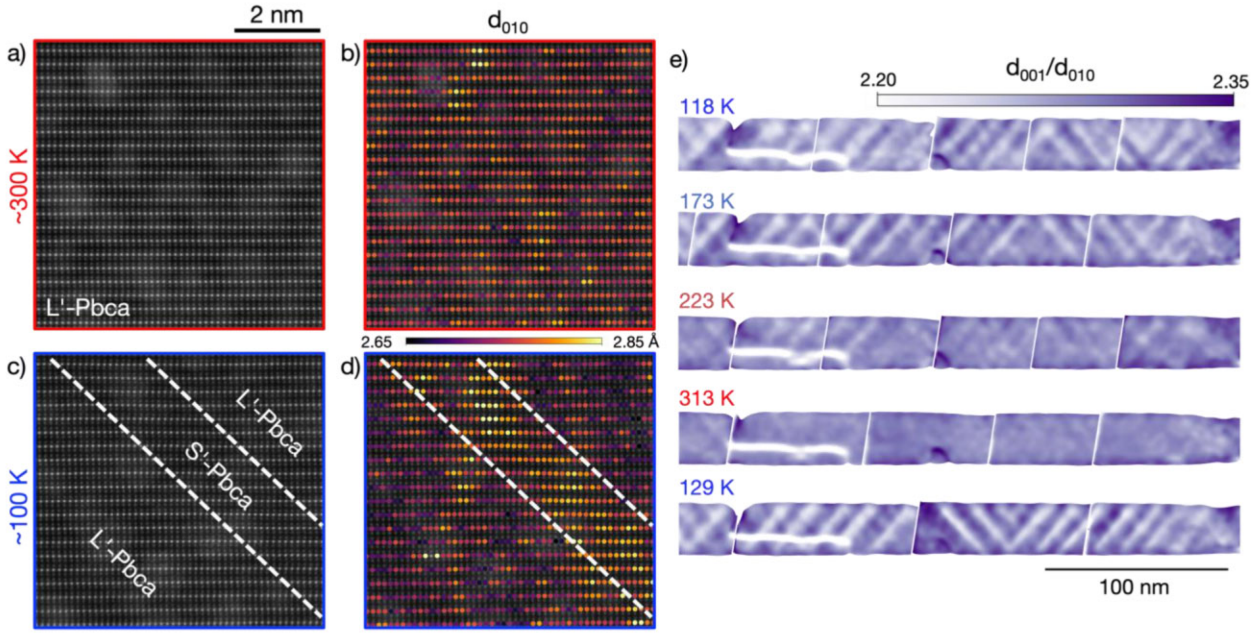

Fig. 1. Emergence of ferroelastic stripe texture in 40 nm thick Ca_2RuO_4 on $(001)_{pc}$ $LaAlO_3$. HAADF-STEM images acquired at (a) 300 K and (c) 100 K and corresponding in-plane lattice parameter maps (b,d) reveal the emergence of S'-Pbca insulating domains. e) The ratio of the out-of-plane to in-plane lattice parameter extracted from montaged HAADF-STEM images through a temperature cycle shows the disappearance and reemergence of the ferroelastic domain structure.

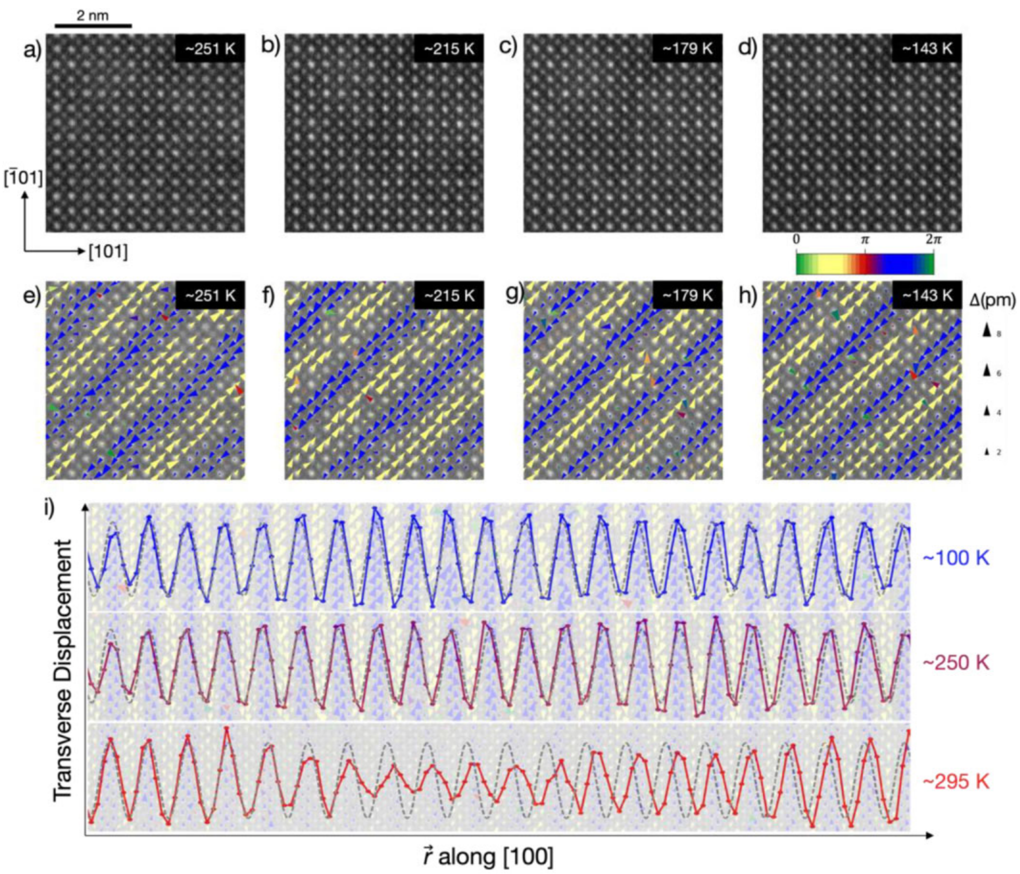

Fig. 2. Atomic-resolution mapping of periodic lattice displacements in $Bi_{.35}Sr_{.17}Ca_{.48}MnO_3$ at intermediate cryogenic temperatures. (a-d) Atomic-resolution HAADF-STEM images acquired at a series of intermediate cryogenic temperatures. (e-h) Corresponding PLD maps reveal picometer scale stripe patterns measured at each temperature. i) PLD profiles reveal discommensuration of the PLD with the atomic lattice upon heating near room temperature.

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