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Atomic Scale Crystal Field Mapping of Polar Vortices in Oxide Superlattices

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Polar vortices in oxide superlattices can be utilized as potential candidates for data storage applications due to their unique polarization topologies.[1] The structure and dipole arrangement in polar vortices has been studied via X-ray scattering techniques, (scanning) transmission electron microscopy ((S)/TEM) and computational calculations.[1] However, the fundamental correlation between the atomic structure and the electronic structure (which is manifested in the chemical bonding) has heretofore not been explored. The hybridization between nominally empty d orbitals on the B-site with the occupied O $2p$ orbitals favors the condensation of a polar (ferroelectric) state in ABO_3 perovskite oxides.[2] The complex, continuously rotating local polarization texture of the vortices, in turn, can result in especially intricate d-orbital interactions. Soft X-ray spectroscopy can probe these interactions at the transition metal L-edge, but these techniques do not have the spatial resolution to resolve variations within one vortex (~5 nm region). Electron energy loss spectroscopy (EELS) in the STEM mode uses inelastically scattered electrons to probe the core-shell excitations (empty density of states) of transition metals at atomic resolution.

We studied the crystal field of the Ti L-edge in polar vortices formed in $[(PbTiO_3)_{16}/(SrTiO_3)_{16}]_8$ (PTO/STO) superlattices with a combination of high-resolution monochromated STEM-EELS mapping using a state-of-the-art direct electron detector and spectrometer (Gatan Continuum with a K3 detector), first-principles calculations, and crystal field multiplet theory. Changes in the crystal field of the Ti^{4+} cations in the PTO/STO superlattices are mapped as the spontaneous displacement of Ti^{4+} (and its corresponding $3d$ orbitals) rotates within the vortices.[3]

Figure 1(a) shows the zoomed-in schematic of a polar vortex where the continuous rotation of polarization affects the corresponding orbital hybridization. We first mapped out the presence of vortices using displacement vector mapping of the A sites in HAADF-STEM images (Figure 1 b,c). The atomic resolution EELS map was used to identify the Ti atoms (Figure 1d). The orbital hybridization within a vortex structure was experimentally identified by fine-structure of Ti L-edge spectra from different areas in STO, vortex edge and core (areas marked in Figure 1b). Within the PTO layer, the e_g peak in the Ti L-edge spectra has a negative shift as we move from vortex edge to core (Figure 1f). We fitted two gaussians (e_g' and e_g'') to e_g peak to understand this variation. We could map out the vortex core regions using the e_g'' peak in the Ti L-edge spectra (Figure 1e). To examine the origin of subtle differences between Ti L edge spectra at the vortex core and edge, we employed crystal field multiplet EELS calculations in combination with density of states (PDOS) calculations. Figure 2a shows that the c/a ratio changes as the

polarization rotates. We used the e_g, t_{2g} and crystal field splitting parameters at different points in the oxide superlattices as inputs to calculate crystal field multiplet EELS spectra. We find that with the variation of strain (position 1 and 2), orbital rotation (position 1 and 3) and polarization magnitude (position 5 and 4) affects the local e_g and t_{2g} splitting and crystal field splitting of Ti *3d*-O *2p* orbitals, creating a pseudo Jahn Teller effect (Figure 2b). Mapping of the Ti 3*d* orbital rotation and hybridization at high resolution will serve as a stepping-stone to understand the microscopic consequences of physical phenomena such as chirality and negative permittivity that have been reported in such polar textures [1][4].

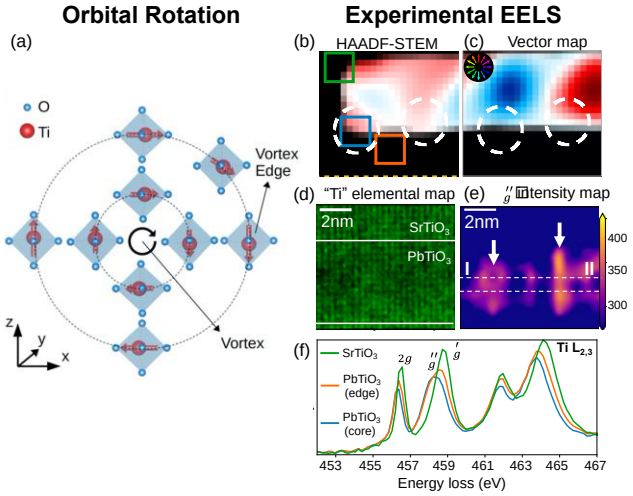

Figure 1: (a) Schematic representing the rotation of TiO_6 octahedra within one vortex domain. (b) Simultaneously acquired HAADF-STEM image. (c) The corresponding A site displacement vector map displaying the presence of the vortices in white circles. (d) Atomic resolution Ti L edge EELS map. (e) Intensity of the e_g'' peak of the Ti-L_3 edge obtained via Gaussian fitting after binning by position. (f) De-noised Ti *L* edge spectra of STO (green solid box), PTO at the vortex core (blue box), and edge (orange box).

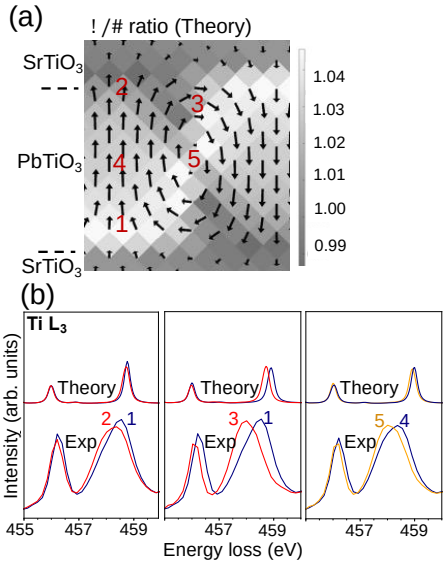

Figure 2: (a) Theoretical local polarization profile of polydomain structures in PTO/STO superlattices. Background gray scale represents the local tetragonality. (b) Comparison of multiplet calculated EEL spectra using parameters in crystal field, e_g and t_{2g} splitting as inputs and experimental EEL spectra for the five Ti^{4+} positions.

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