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Authors
Susarla, Sandhya
García-Fernández, Pablo
Ophus, Colin
et al.

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Atomic Scale Crystal Field Mapping of Polar Vortices in Oxide Superlattices

Sandhya Susarla[1,2], Pablo García-Fernández[3], Colin Ophus[1], Sujit Das[2], Pablo Aguado-Puente[4], Margaret McCarter[2], Peter Ercius[1], Lane W. Martin[2], Ramamoorthy Ramesh[1,2,5] and Javier Junquera[3]

[1:] National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA
[2:] Department of Materials Science and Engineering, University of California, Berkeley, CA, 94720, USA
[3]: Departamento de Ciencias de la Tierra y Física de la Materia Condensada, Universidad de Cantabria, Cantabria Campus Internacional, Avenida de los Castros s/n, 39005, Santander, Spain
[4:] CIC nano GUNE BRTA, Donostia - San Sebastián, 20018, Spain
[5:] Department of Physics, University of California, Berkeley, CA, 94720, USA

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].

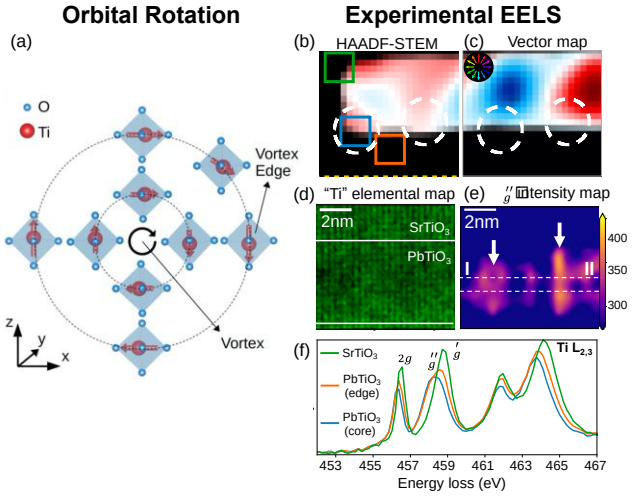

Figure 1: (a) Schematic representing the rotation of TiO_6 octahedra within one vortex domain. (b) Simultaneously acquired HAADF-STEM image. (c) The corresponding A site displacement vector map displaying the presence of the vortices in white circles. (d) Atomic resolution Ti L edge EELS map. (e) Intensity 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).

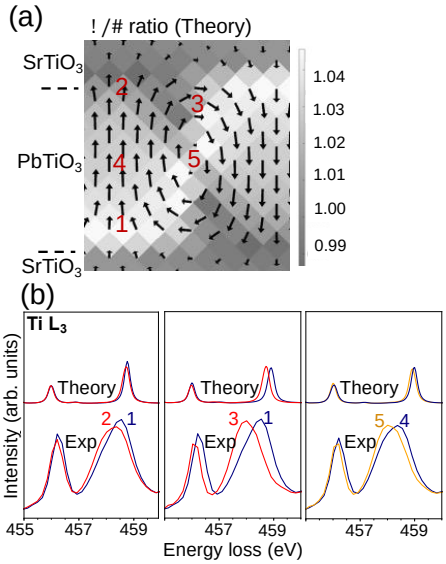

Figure 2: (a) Theoretical local polarization profile of polydomain structures in PTO/STO superlattices. Background gray scale represents the local tetragonality. (b) Comparison of multiplet calculated EEL spectra using parameters in crystal field, e_g and t_{2g} splitting as inputs and experimental EEL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

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