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Nanoscale STEM/EELS and Theory Investigations of Vibronic Properties of Superlattices

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As the size of nanostructures decreases, the structural and chemical heterogeneity associated with interfaces approach the importance of the constituent materials and the local phenomena associated with interfaces can alter the macroscopic response of the material. Vibrational electron energy-loss spectroscopy (EELS), atomic-resolution imaging, and integrated differential-phase contrast (iDPC) in a scanning transmission electron microscope (STEM) provide a unique opportunity to simultaneously probe the atomic scale structure, chemical composition, and vibrational response of complex nanostructures [1], [2]. Here we combine these and other experimental techniques with density-functional-theory (DFT) calculations to describe the localized vibrational response associated with the atomic structure of interfaces in four and twenty- seven unit-cell (SL4, SL27) $SrTiO_3$-$CaTiO_3$ (STO-CTO) superlattices.

Figure 1 shows a cropped region of annular darkfield (ADF) and iDPC images along with an enlarged region-of-interest at the interface of each superlattice. Single symmetric STO oxygen columns are seen at the top of the enlarged iDPC image of SL27. In SL4 the STO oxygen columns become elliptical and some are split indicating coupled tilting to the CTO layer and an overall more uniform tilt pattern.

Off-axis vibrational EELS and DFT calculations were used to measure the spatial extent of structurally driven localization in the superlattices. We show that the layers of the superlattices systematically change with the number of unit-cells per layer in accordance with the symmetry seen in imaging, as shown in Figure 2. The emergent vibronic response of the superlattices as their layer thickness decrease below certain values demonstrates the importance for both quantitative atomic and local vibrational characterization to understand the origin of macroscopic behavior.

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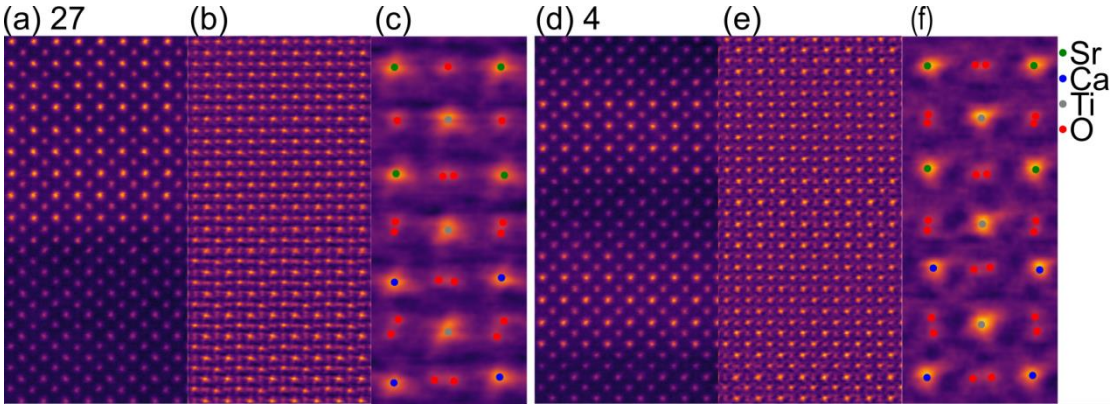

Figure 1. Figure 1. (a,d) ADF, (b,e) iDPC images, and (c,f) enlarged interface region-of-interest from iDCP images for superlattice (a-c) twenty-seven and (d-f) four.

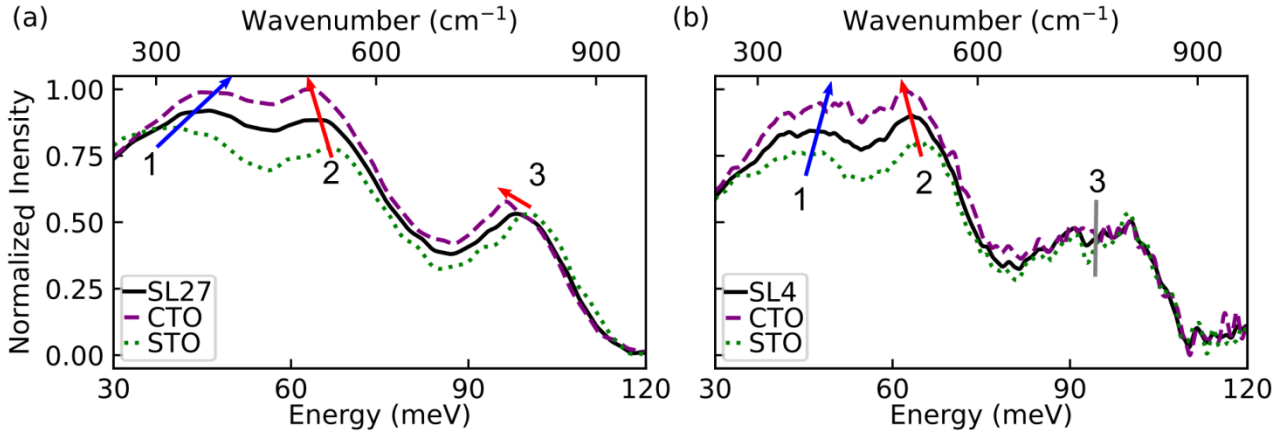

Figure 2. Figure 2. Layer-averaged off-axis vibrational EELS in (a) SL27 and (b) SL4 with arrows indicating the energy shift of peaks from STO to interface to CTO

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