

Probing the Structural and Electronic Couplings in Rare-earth Nickelate Superlattices by STEM-EELS

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During the last decade, the scanning transmission electron microscopy (STEM)-based combination of annular bright field (ABF) imaging and electron-energy loss spectroscopy (EELS) has been consolidated as one of the key techniques for characterizing coherent interfaces, where novel phenomena are expected to arise due to the mutual interaction between two neighboring compounds. [1] While ABF images, acquired simultaneously to high-angle annular dark field (HAADF) images, allow the atomic columns of both heavy and light elements to be visualized together, EELS can provide atomic-scale information about the chemical and electronic modulations of the probed material. Together, they enable the direct, real space study of local structural, chemical, and electronic changes across such boundaries with sub-Å resolution, which cannot be achieved by other means.

The use of this combination has revolutionized the research field of transition metal oxide perovskite compounds, whose electronic and magnetic properties are highly sensitive to subtle modulations of their atomic structure. A paradigmatic example is the family of rare-earth nickelate oxides, whose compounds (except LaNiO_3) display a sharp metal–insulator transition (MIT) and a Néel transition at transition temperatures that depend on their characteristic Ni-O-Ni bond angles. [2] Although their physical properties have been widely studied, little was known about the characteristic length-scales over which their distinct electronic phases can be established. This aspect was addressed in a recent work where a series of $[(\text{NdNiO}_3)_m/(\text{SmNiO}_3)_n]$ superlattices (SLs) were investigated, with m and n being, respectively, the number of pseudocubic (PC) unit cells in each nickelate layer and the total amount of repetitions of the periodic unit. In these SLs, a novel type of electronic coupling was found, which was attributed to the interfacial energetics of the system. [3]

In this work, we use STEM-EELS to thoroughly investigate the nature of this novel electronic coupling and the associated length-scales. For the data acquisition, we use a double-corrected FEI Titan Themis 60-300 instrument operated in STEM-mode at 200/300 kV and equipped with an X-FEG source, a monochromator and a Gatan GIF Quantum ERS spectrometer. This experimental set-up provides us reasonably good energy resolution (~ 0.4 eV zero-loss peak FWHM for an energy dispersion of 0.1 eV) while keeping a relatively high current (around 80-120pA) atomic resolution probe for fine-structure analysis in the core-loss regime. First, we acquire atomically-resolved EELS compositional maps to demonstrate that the nickelate interfaces are atomically sharp with a minimal degree of cationic intermixing. Second, we determine the length-scale associated to the structural couplings established at the nickelate interfaces by measuring the evolution of the Ni-O-Ni bond angle across them. For this, we simultaneously acquire a series of HAADF and ABF images from the same film area, each frame rotated 90° respect the previous one. Then, the HAADF images are cross-correlated and corrected for linear and

non-linear scan distortions using the Smart-Align software. [4] These corrections, generated from incoherent scattering images, are next applied to the phase-contrast ABF image series. The average of this series gives a high-quality ABF image, from which the Ni-O-Ni bond angle is estimated at each film monolayer from the atomic column coordinates associated to the oxygen sublattice. Their central positions are obtained by using multiple 2D Gaussian fittings using Atomap. [5] A remarkably short coupling length is observed of just 1 PC unit cell, which is much shorter than that associated to their displayed electronic coupling (around 8 PC unit cells).

Motivated by this difference in structural and electronic coupling length scales, we next use the SLs to test the ability of EELS to locally determine the electronic state of each individual nickelate layer, by looking at specific spectral signatures present in the Ni *L* edge and O *K* edge fine-structures. The subtle changes in spectral fingerprints – as usually observed only with X-ray absorption spectroscopy – together with the low intensity of the measured peaks, forces us to find a good balance between energy resolution, probe current and beam damage. The resulting EELS spectrum images not only enable us to determine the electronic state of each individual nickelate layer, in two SLs having distinct electronic behaviors, but also to generate electronic phase maps with ~single unit cell resolution (pixel size around 4 Å). The width of the metallic-insulating phase boundaries is also estimated from these maps, which is observed to be remarkably short (around 2–4 PC unit cells). [6] Moving forwards from this analysis, we will also present first results of ongoing experiments where we make such EELS measurements at different temperatures using a high-stability *HennyZ* stage. These measurements promise to open new avenues for studying the structure–electronic property relationships in nickelate oxides.

References:

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