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Harnessing Local Sample Variations to Generate Self-Consistent EELS References for Stoichiometry Quantification

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The ability to grow crystallographically perfect and stoichiometrically precise samples is crucial for realizing the most exotic materials-by-design. Especially when lattice-scale variations enhance or quench materials properties, high-resolution STEM EELS is a powerful tool to both characterize and understand these materials. Some phenomena such as charge transfer or local bonding can be quantified by tracking changes in the fine structure of a single relevant edge [1]. Quantifying subtle stoichiometric variations, however, requires comparison between the relative weights of two or more distinct edges, necessitating proper accounting of other factors that contribute to the overall EELS signal, such as differing sample thickness, beam conditions, contamination, etc. This is particularly difficult for novel materials where standardized calibration samples or substrates are not available. Furthermore, signal improvements offered by recent developments to direct electron EELS detectors [2, 3] have granted practical access to many minor or low-signal edges for which sufficient references may not yet exist. Here, we describe an internally-referenced EELS approach used to quantitatively probe local stoichiometric variations in superconducting (SC) thin films of Sr_2RuO_4.

Historically studied in bulk single crystals, the report of Sr_2RuO_4 thin films with SC transition temperatures (T_c) comparable to that of bulk is notable given the sensitivity of its superconductivity to crystalline defects [4]. But while some samples exhibit the highest reported T_cs, others show no signs of superconductivity despite XRD data that suggest high structural perfection. High-resolution STEM reveals that a single SC film may include significant inclusions of higher-n Ruddlesden-Popper (RP) phases $Sr_{n+1}Ru_nO_{3n+1}$ (Fig. 1a). These inherent local variations in stoichiometry will skew the overall ratio of Ru/Sr in a given sample as measured by bulk spectroscopic techniques. In contrast, lattice-resolved EELS allows us to selectively probe only the $n = 1$ layers which are most relevant to superconductivity. Although they appear to have little effect on SC properties, the high-n inclusions provide an ideal reference for calibrating EELS data across a stoichiometric series. Compared to typical approaches relying on a series of reference samples, here all references are recorded from a single TEM sample, thereby avoiding variations due to separate sample preparations. The fine structure of the O-K edge can be used to track different RP phases (Fig. 1b), but the SNR obtainable for localized measurements is insufficient to distinguish between the SC and non-SC phases. The neighboring Sr-$M_{2,3}$ and Ru-$M_{4,5}$ edges, however, show a clear trend in relative intensity depending on the local concentration ratio of the two elements (Fig. 1c). Because all the spectra are collected from nearby regions on the same lamella, no further controls are needed to account for variations in overall sample condition. The ratios of integrated Ru/Sr edges cleanly fit to a linear trend when compared to the corresponding structural ratios $n/(n+1)$ (Fig. 1d). Using the resulting trend as a self-calibrated reference, the corresponding Ru/Sr EELS ratio for the non-SC film can be used to estimate the actual Ru/Sr ratio at around 0.35 (up to ~30% deficient), suggesting a very high density of Ru point defects [5].

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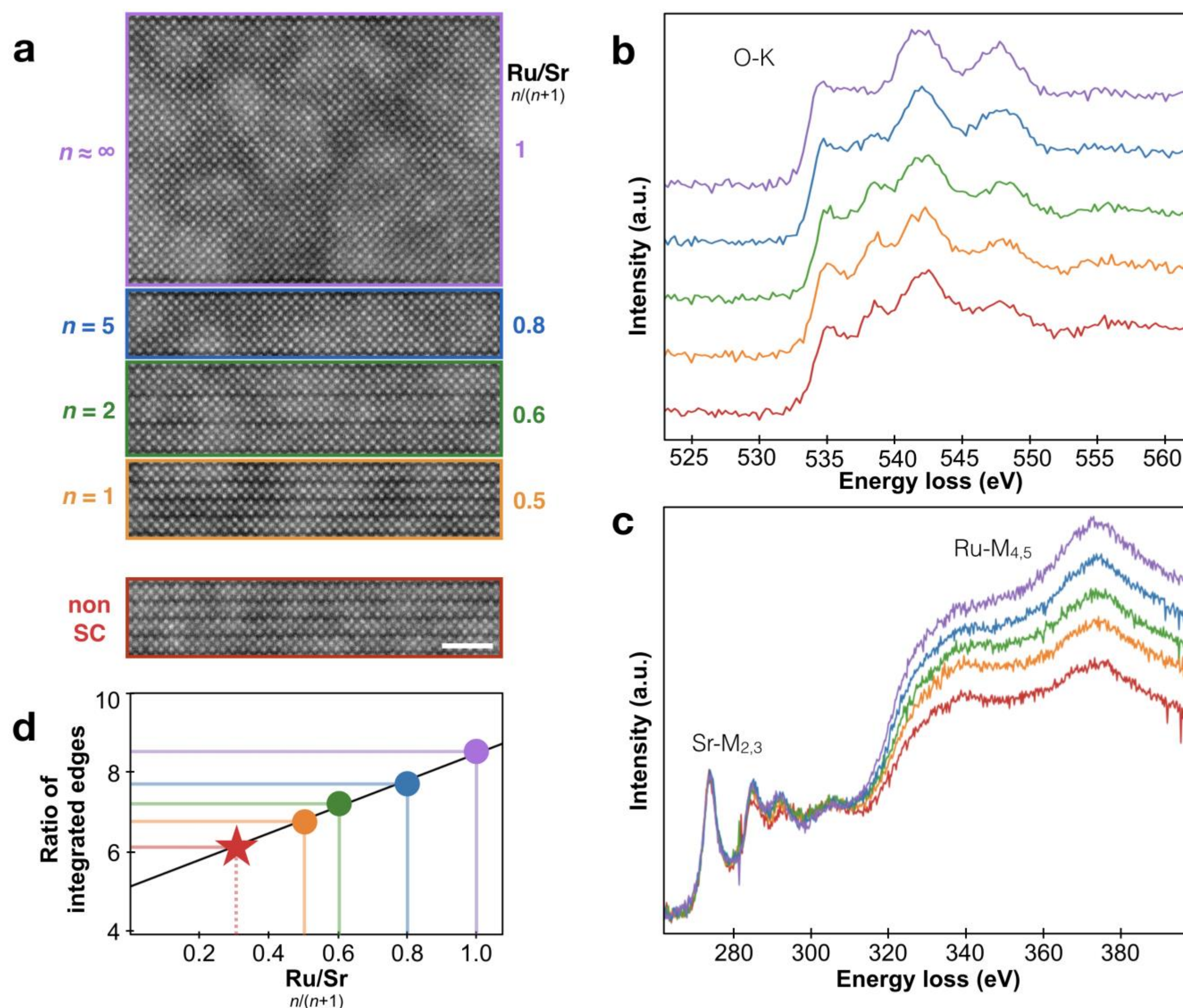

Figure 1. a) HAADF STEM images of regions with varying RP $Sr_{n+1}Ru_nO_{3n+1}$ phases in a single SC film and a nominally n = 1 phase in a non-SC film (red). Scale bar 2. **b)** Background-subtracted and normalized O-K edges across four different RP phases from the SC and an n = 1 phase of the non-SC (red) film regions in (a). Changes in the fine structure between distinct phases are clear, but SNR of the localized measurement is not sufficient to distinguish the SC and non-SC regions. **c)** Comparison of normalized and background-subtracted Sr-$M_{2,3}$ and Ru-$M_{4,5}$ edges. Normalized by the Sr-$M_{2,3}$ edge, spectra show a clear trend in the relative intensity of the Ru-$M_{4,5}$. **d)** The Ru/Sr ratios of integrated edges from (c) plotted as a function of the Ru/Sr $n/(n+1)$ ratio. Spectra from the SC sample are used as references to generate and calibrate the black linear fit. The EELS ratio of the non-SC film (red star) is then placed along the fit to estimate the local Ru/Sr stoichiometry at ~0.35.

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