The ordering of oxygen vacancies constitutes a new avenue towards finding novel physical phenomena and new functionalities in transition metal oxides. Ordered arrays of vacancies may not only enhance or suppress existing properties, but also lead to collective states absent in the perfect crystallographic phase, or in samples with randomly distributed defects. Along these lines, epitaxial strain in thin films can be used to tune ordering phenomena not present in the bulk, which may result in unusual properties. For example, epitaxial LaCoO₃ (LCO) thin films under tensile strain, e.g., grown on SrTiO₃, are ferromagnetic (FM) at low temperatures, while the bulk material is non-magnetic [1]. The origin of the observed FM ordering has been debated extensively on the basis of theoretical calculations and complementary experimental data. Competing interactions of comparable magnitude permit Co atoms to present low-spin (LS), intermediate spin (IS) or high-spin (HS) [2,3]. Different types of Co spin states and ordering have been proposed in strained films, but the layers have been assumed stoichiometric and no O deficiency has been considered [4,5]. Here, we demonstrate, using atomic resolution electron microscopy and electron energy-loss spectroscopy (EELS), that epitaxial LCO thin films contain ordered arrays of oxygen vacancies (Figure 1). The epitaxial strain is relaxed through the local lattice expansion at ordered oxygen-deficient atomic planes. The vacancies lead to excess electrons in the Co d-states and thus to the charge order of Co ions, as demonstrated by EELS through the Co L₂₃ ratio. Density-functional calculations show a spin state ordering not present in bulk that results in a net magnetic moment [6].


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Fig. 1: Atomic resolution EELS mapping of the LCO film. High resolution Z-contrast image with O K map as the inset. The profile of O K map (yellow graph) shows the O vacancy ordering. Bottom right: Model showing the magnetic ordering, according to DFT calculations. Green arrows denote the spin orientation for the high spin Co. Adapted from reference [6]