Quantifying Nanoscale Coexistence of Competing Phases In Ca_2RuO_4

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2022 Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials Research Experience for Undergraduates Program at Cornell University (PARADIM REU @ Cornell)

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Primary Source of PARADIM REU @ Cornell Funding: Support for PARADIM is provided under NSF Grant # DMR-2150446 as part of the Materials Innovation Platform Program

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Abstract:

The 2D Perovskite Ca_2RuO_4 exhibits a strain tunable metal-insulator transition which is accompanied by a structural transition. In a compressively strained film grown on $LaAlO_3$ cooled to cryogenic temperature and imaged with cryogenic scanning transmission electron microscopy, the metallic and insulating phases have been found to coexist. These phases have differing lattice parameters that allow their structure to be differentiated throughout the film. Quantifying these structural differences in Ca_2RuO_4 is key to understanding the metal-insulator transition and phases. The variations in the lattice parameters are measured using algorithms implemented in Python and visualized. We find that Ca_2RuO_4, across its metal/insulator interface~~,~~ exhibits a gradual change in lattice parameters across several nanometers. Visualizing these changes helps quantify the changes undergone at cryogenic temperatures.

Introduction:

While most materials are either metallic or insulating, some materials exhibit metal-insulator transitions (MIT), phase transitions where the material switches from a metal to an insulator accompanied by a change in atomic structure. Metal-insulator transition materials have the potential to enable emerging technologies such as neuromorphic computing, but this will require a deep understanding of how these materials can be controlled by various external stimuli. The 2D perovskite oxide Ca_2RuO_4 exhibits a metal-insulator transition, and the transition temperature can be tuned with epitaxial strain along with other stimuli such as electric fields [1,2,3]. Notably, compressively strained films grown on $LaAlO_3$ do not have a uniform transition in between phases, resulting in coexisting metallic and insulating areas of the film below the transition temperature. These phases can be differentiated by a change in lattice parameters — the metallic phase is stretched along the out of plane [001] direction [4]. Here, this phase coexistence was measured with cryogenic scanning transmission electron microscopy (STEM), allowing the atomic scale features of the metal-insulator nanostructure to be characterized.

Methods:

Images of a Ca_2RuO_4 film grown on $LaAlO_3$ were acquired on the [010] orthorhombic zone axis with cryogenic high angle annular dark field STEM at ~100 K to directly characterize the film's atomic structure. The STEM images went through a variety of processing steps to precisely identify the positions of the most prominent atom, Ruthenium, with the Python package STEMTool [5]. Several algorithms were then developed to identify local~~ly~~ variations in the film structure. In particular, distances and angles between ruthenium sites were calculated allowing local changes in the lattice parameters to be seen, visualizing the coexisting metallic and insulating domains present in the material.

Distances and angles between neighboring sites were calculated using their x and y coordinates, then plotted on the images. The spatial distribution of inter-site distances and angles are visualized with a colormap, where the color corresponds to the distance or angle of a site relative to its neighbors.

Results:

Visualizing the measured spacings of each Ruthenium site to its neighbors normal to the (001) plane ("out of plane") and in the (001) plane ("in plane"), striped domains with shorter out of plane and longer in plane lattice parameters can be seen revealing the phase coexistence present in the film(Fig. 1 a,b). The change in lattice parameters is consistent with the narrow stripes belonging to the insulating S phase, while the surrounding film is the metallic L phase. Mapping the local rotation of the lattice, a corresponding mis-orientation is measured along each of the stripes (Fig. 1 c,d). To investigate the nature of the interface between the coexisting phases, the out of plane Ru-Ru distance was profiled along the stripes, visualizing the change in the lattice parameter inside and outside of the stripes (Fig. 2). Consistent with the maps of the lattice parameter, the stripes are clearly marked by a significant reduction in the out of plane lattice parameter from ~1.255 nm in the L phase matrix to ~1.230 nm in the S phase stripes. Intriguingly, the interfaces between the phases are not sharp — instead, the lattice parameter gradually changes over 2-5 unit cells.

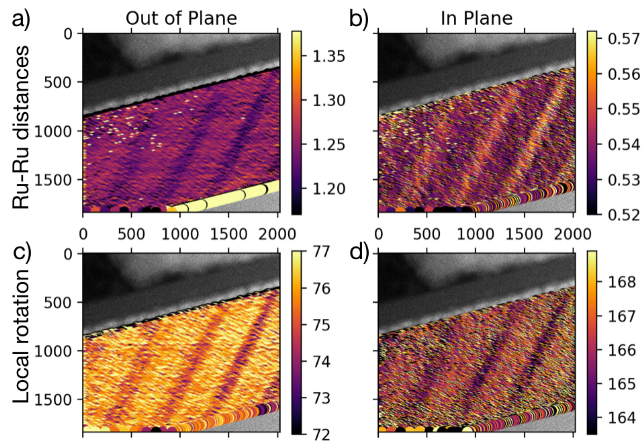

Figure 1: Maps of local structural parameters overlaid on atomic resolution STEM image revealing phase coexistence. a) out of plane inter-Ruthenium distance, b) in plane inter-Ruthenium distance, c) local out of plane rotation, d) local in plane rotation.

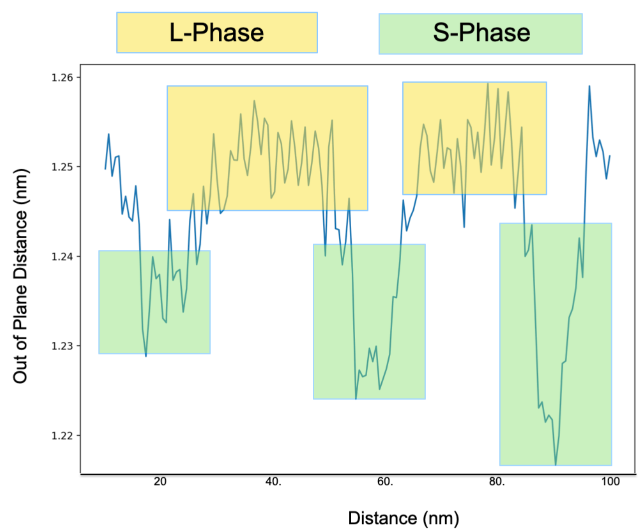

Figure 2: Profile of out of plane Ruthenium-Ruthenium spacing along the strip direction showing significant change in lattice parameter and gradual change spanning several unit cells at the interface.

Conclusions:

Characterizing the coexisting metallic and insulating phases and quantifying the nanoscale structure of Ca_2RuO_4 helps us to understand the material's metal-insulator transition. Looking forward, this work will be expanded upon to characterize the structure and in particular the interfaces with higher precision. In addition, for this study other areas of the film were not able to be analyzed because of severe defects in the atomic structure, however the phase coexistence in these areas must also be characterized to understand how the transition is modulated by defects in the lattice.

Acknowledgements:

I would like to thank my mentor Noah, PI Dr. Lena Kourkoutis, and their entire group for welcoming me into their workspace and providing a very exceptional summer experience.

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