Probing Temperature-Induced Metal-Insulator Transitions in $SmBaMn_2O_6$ Using Scanning Transmission Electron Microscopy

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Thin films of $SmBaMn_2O_6$ deposited upon a substrate of $LaGaO_3$ are host to intriguing phase transitions and electical properties, including temperature-induced metal-insulator and ferromagnetic-antiferromagnetic transitions and potential hybrid improper ferroelectricity. However, little is known regarding the mechanisms driving these transitions. Motivated by work done in density functional theory indicating a change in space group may be responsible, we report evidence of a partial structural phase transition in $SmBaMn_2O_6$ between room temperature and cryogenic temperatures ($\sim$100 K). We demonstrate evidence for this change via convergent beam electron diffraction both in ab initio multislice simulations and experimentally using a scanning transmission electron microscope.

I. INTRODUCTION

Rare earth double perovskite manganese oxides, of which $SmBaMn_2O_6$ is one, are of academic interest due to their numerous coupled and competing phases[**?**]. Of specific interest is the transition from metal to insulator at around 200 K undergone by A-site ordered $SmBaMn_2O_6$, demonstrated in Fig. 1. Theoretical work

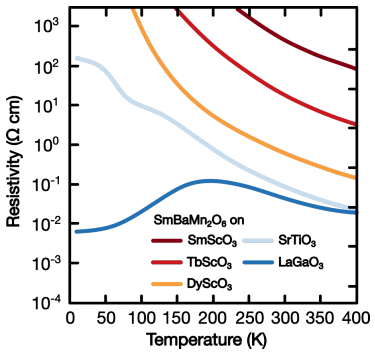

FIG. 1. Electrical resistivity as a function of temperature for thin films of $SmBaMn_2O_6$ grown by molecular beam epitaxy upon different substrates. A metal-insulator transition is present only upon LaGaO3, around 200 K. The rest exist entirely in the insulating regime, where resistivity decreases as a function of temperature. Courtesy of Yorick Birkholzer.

done by Nowadnick et al. using density functional theory demonstrated that A-site ordered $SmBaMn_2O_6$ is stable in a conducting Cmmm space group configuration for compressive strains exceeding approximately 0.8%, and stable in an insulating $P_{21}am$ space group for small compressive strains and tensile strains[**?**]. Thin films of $SmBaMn_2O_6$ experience a compressive epitaxial strain of approximately 0.7% when grown on $LaGaO_3$, and as such there is some theoretical precedent to suspect that a transition from the Cmmm space group at low temperature to the $P_{21}am$ space group at higher temperatures may be responsible for the metal-insulator transition seen in Fig. 1.

In this paper, we search for evidence of this structural phase transition using the ab initio multislice simulation package abTEM, and subsequently using cryogenic scanning transmission electron microscopy. Our results suggest that a partial structural phase transition does occur, but likely not one between the Cmmm and $P_{21}am$ space groups. In the future, a broader survey of potentially stable space group configurations of $SmBaMn_2O_6$ could elucidate the exact nature of this transition.

II. METHODS

The space groups $P_{21}am$ and Cmmm exhibit only very subtle differences that are infeasible to detect using conventional real space imaging techniques. Instead, we investigate diffraction data so as to more directly probe reciprocal space for detectable differences. In the software package abTEM, which uses a multislice approach to model an electron probe proceeding through a sample in a manner that mimics a scanning transmission electron microscope, we produced position averaged convergent beam electron diffraction (PACBED) simulations over a survey of zone axes on both $P_{21}am$ and Cmmm.

A difference in the number of higher order Laue zone lines, which form from the intersection of the Ewald sphere with consecutive planes of the crystal's reciprocal lattice, was detected between the $P_{21}am$ and Cmmm space groups imaged along the orthorhombic and pseudocubic zone axes and used as a quantitative diagnostic for subsequent experimental diffraction measurements. A scanning transmission electron microscope equipped with a liquid nitrogen cryogenic holder to obtain temperatures of $\sim$100 K and an electron microscope pixel array detector was used to image along the orthorhombic and pseudocubic zone axes of samples of A-site ordered $SmBaMn_2O_6$ on $LaGaO_3$, producing PACBED data to

be compared to the previously created simulations.

An important caveat to our experimentally obtained data concerns the A-site ordering of our $SmBaMn_2O_6$ samples. When exhibiting perfect A-site ordering, we expect alternating rows of samarium atoms and barium atoms occupying the A-sites of $SmBaMn_2O_6$'s double perovskite structure. However, when grown on $LaGaO_3$, this expected ordering is only present in domains on the order of 20 nm, as can be seen in part (d) of Fig. 2. The A-site configuration outside of these domains is as yet unclear, and the effect that this has on the results of our diffraction also has not been explored.

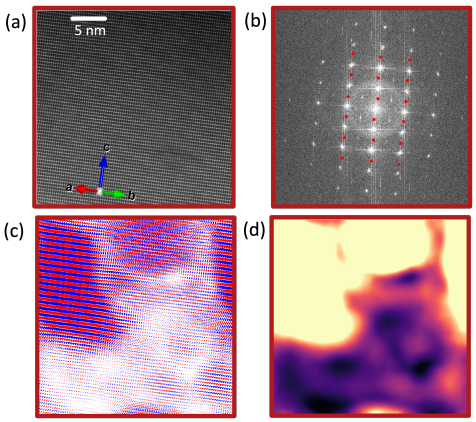

FIG. 2. The process of identifying A-site ordering in $SmBaMn_2O_6$ using reciprocal space mapping. In (a), a high angle annular dark field (HAADF) image along the [110] zone axis is obtained. This image is Fourier transformed in (b), and the half-ordered peaks associated with A-site ordering are identified in red. These peaks are masked, and the image is converted back to real space with an inverse Fourier transform. In (c), an intensity map of the difference between the original HAADF image and the Fourier masked image, which exhibits no A-site ordering, is shown. Regions where the difference is large indicate the original HAADF image had the expected ordering. In (d), the magnitude of the intensity map in (c) is taken and a Gaussian filter is applied to remove short-range modulations and obtain a domain map indicating where the $SmBaMn_2O_6$ sample exhibits A-site ordering.

III. RESULTS AND DISCUSSION

Diffraction results in simulation and in the microscope are shown in Fig. 3. In both, a change in the number of higher order Laue zone lines is visible, indicating a structural phase transition. However, we expect the room temperature phase of $SmBaMn_2O_6$ to correspond to $P_{21}am$, and instead see the opposite. As $SmBaMn_2O_6$ is host to many structural orders, it is likely that the transition we observe is instead a transition between some other set of space groups. Magnetic measurements of our $SmBaMn_2O_6$ samples, on top of our existing understanding of its electrical transport, would help clarify the potential nature of this transition and narrow the scope of potential participating space groups. The existence of

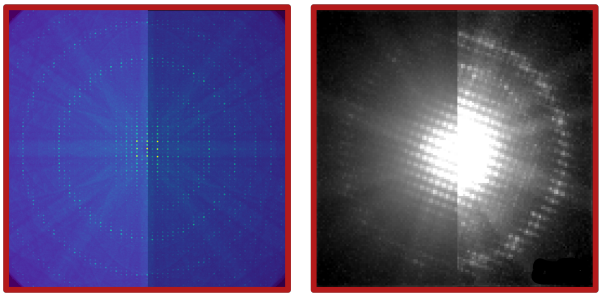

FIG. 3. PACBED data using the simulation package abTEM (left) and in the microscope using a pixel array detector (right). The simulated image is split in half, comparing the Cmmm space group (left) with the P_21am space group (right). The experimental image is similarly split comparing room temperature (left) with cryogenic temperature (right). In both, a change in the number of higher order Laue zones lines is present; however, we see additional zones experimentally where we should instead expect fewer to appear; it is likely that a different space group transition is occuring than that initially suggested by theory.

the additional higher order Laue zone line seen on the far right of Fig. 3 is spatially heterogeneous. In Fig. 4, the presence of this Laue zone line is maped throughout the sample, indicating phase coexistence. Further research could include imaging at a more granular set of temperatures, to gauge whether the domain exhibiting a structural transition grows with decreasing temperature.

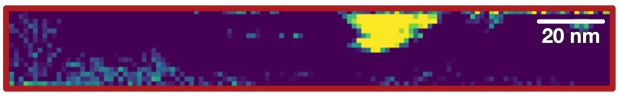

FIG. 4. A map over the $SmBaMn_2O_6$ film of the intensity of the additional HOLZ line indicative of a change in space group at cryogenic temperature. A region of high intensity can be seen, indicating the phase transition has occurred but is limited to domains, with phase coexistence present.

IV. CONCLUSIONS

In this paper, evidence for a temperature-induced structural phase transition in $SmBaMn_2O_6$ on $LaGaO_3$ in the form of a change in the number of higher order Laue zone lines is reported. This transition is inconsistent with prior conjecture that the material's metal-insulator transition was driven by change between the Cmmm and $P_{21}am$ space groups, and instead suggests that a transition between a different set of space groups is responsible. Future work includes obtaining magnetic measurements for $SmBaMn_2O_6$ as a function of temperature and conducting PACBED simulations for additional candidate space group configurations such as Pnam.

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