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Electronic and magnetic properties of epitaxial SrRhO₃ films

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Abstract

Strong interplay of fundamental order parameters in complex oxides are known to give rise to exotic physical phenomena. The 4d transition metal oxide SrRhO₃ has generated much interest, but advances have been hindered by difficulties in preparing single crystalline phases. Here, we have epitaxially stabilized high quality single crystalline SrRhO₃ films and investigated their structural, electronic, and magnetic properties. We determine that their properties significantly differ from the paramagnetic metallic ground state that governs bulk samples and are strongly related to rotations of the RhO₆ octahedra.

The delicate balance between charge, spin, orbital, and lattice order parameters has proven to give rise to novel properties in many transition metal oxides (TMOs).^{1,2} In particular, the onset of unconventional *p*-wave superconductivity in Sr_2RuO_4 ³ was the first example of Type-II superconductivity in an oxide without copper and inspired much interest in other analogous *4d* TMOs such as rhodates and other ruthenate compounds.^{4,5} However, the synthesis of many of these compounds proved to be a formidable task, often requiring high pressure and high temperature; which in turn limited experimental efforts on many of these compounds to a few experimental studies with polycrystalline samples.⁵⁻¹⁰ Theoretical work predicted that the magnetic ground state of the orthorhombic perovskite SrRhO_3 is sensitive to its symmetry with the bulk orthorhombic structure forming a paramagnetic (PM) metallic state, while the high symmetry cubic perovskite structure would reveal a ferromagnetic metallic state.¹¹ In addition, SrRhO_3 has recently received attention for the potential to realize topologically protected states as a constituent material in artificial heterostructures and superlattices.^{12,13} The potential of SrRhO_3 to realize such exotic ground states has inspired us to overcome the technical challenges associated with creating phase pure SrRhO_3 by synthesizing epitaxial thin films.

In this manuscript, we report on the synthesis and basic physical properties of SrRhO_3 films grown on (001) SrTiO_3 (STO) substrates by pulsed laser epitaxy (PLE). Epitaxial stabilization by PLE is advantageous as meta-stable phases that are difficult, if not impossible, to grow can be synthesized.¹⁴⁻¹⁶ Here, the first single crystalline samples of the orthorhombic perovskite SrRhO_3 were synthesized. We grew films with a KrF excimer laser ($\lambda = 248\text{nm}$) with laser fluence, substrate temperature, and oxygen partial pressure of 1.0 J/cm^2 , 750°C , and 100 mTorr , respectively. The samples were characterized by x-ray diffraction (XRD), atomic force microscopy (AFM), *dc*-transport, scanning quantum interference device (SQUID)

magnetometry, x-ray absorption spectroscopy (XAS), and spectroscopic ellipsometry (SE). We confirmed from XRD studies that our SrRhO₃ films were epitaxial and coherently strained. At low temperature, the electronic and magnetic properties strongly deviate from the PM metallic ground state of bulk crystals, while there is an abnormally strong hybridization between the O 2*p* and Rh 4*d* orbitals. Density functional theory (DFT) calculations were conducted to better understand this material. Polycrystalline SrRhO₃ realizes a orthorhombic perovskite structure with lattice parameters $a = 5.5394 \text{ \AA}$, $b = 7.8539 \text{ \AA}$, and $c = 5.5666 \text{ \AA}$ (Space group *Pnma*) that result in a pseudo-cubic lattice constant of 3.93 \AA with RhO₆ octahedra that undergo a $a^+b^-b^-$ distortion,⁵ as illustrated in Fig. 1.

The quality of these SrRhO₃ samples is confirmed through AFM and XRD measurements. Topographic images of a SrTiO₃ substrate prior to and after deposition of a 12 nm thick SrRhO₃ film are shown in Fig. 1a and 1b, respectively. Note that after deposition of the film, step terrace features of the underlying substrate are clearly visible, and the RMS roughness of the surface is $\sim 2.2 \text{ \AA}$, indicating that the epitaxial film is of high quality. The phase purity and orientation of the films are confirmed by XRD measurements where a θ - 2θ scan is shown in Fig. 1c. Note that the even SrRhO₃ 00*l* reflections are clearly visible while the odd 00*l* reflections are expected to be less intense than the background and are thus not visible here. The positions of the SrRhO₃ peaks are consistent with a compressively strained perovskite film that is elongated along the *c*-axis. The rocking curves have a full width at half maximum less than 0.04° and the reciprocal space maps (data not shown) indicate the high crystallinity and coherent strain state of the SrRhO₃ films.

Interestingly, this system has a critical thickness ($\sim 15\text{nm}$) below which phase pure samples can be synthesized. Attempts to grow thicker films yielded an impurity phase that is most probably due to the onset of strain relaxation at this thickness which then results in one of the lower symmetry phases of strontium rhodate being more energetically favorable. In addition, this observation suggests that the in-plane compressive strain simulates the pressure required to produce the meta-stable high pressure perovskite phase of SrRhO_3 .

The electronic properties of these SrRhO_3 films were investigated by *dc*-transport measurements as shown in Fig. 2a. Notice that at high temperature, the sample exhibits a metallic behavior consistent with the bulk properties of SrRhO_3 . However, at low temperature, there is a weak upturn in the resistivity. At high temperature, there is a very weak temperature dependence indicating that the resistivity saturates near the Mott-Ioffe-Regel limit,^{17,18} however here this limit is roughly four times larger than the range of $100\text{--}200\ \mu\Omega\cdot\text{cm}$ that is commonly reported in the literature.¹⁹ Recall that the SrRhO_3 films are $\sim 12\ \text{nm}$ thick and thus the upturn in resistivity at low temperature is likely due to the finite thickness effect which is known to result in an insulating behavior in ultrathin films of other correlated metallic oxide films.²⁰⁻²⁴ The inset shows the Hall measurement results at $2\ \text{K}$, which displays a linear response with a carrier concentration and mobility of $3.8 \times 10^{21}\ \text{cm}^{-3}$ and $1.1\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$, respectively. The temperature dependent magnetoresistance (MR) is presented in Fig. 2b where there is a sign change at $\sim 110\text{K}$ that will be discussed below and an upturn at low temperature likely due to increased scattering off defects. The temperature dependent magnetization obtained from SQUID measurements is shown in Fig. 2c, which reveals a subtle anomaly at the same temperature as the sign change in MR, suggesting there is a change in the magnetic structure here and that this change is not ferromagnetic in origin.

In order to obtain a greater understanding of the low temperature properties that clearly differ from those of bulk crystals, DFT calculations were performed to determine the density of states (DOS) and magnetic ground state of these SrRhO₃ films. The crystal structure was refined using the lattice parameters of the coherently strained SrRhO₃ films of $a = b = 3.905 \text{ \AA}$ and $c = 4.043 \text{ \AA}$ with no RhO₆ rotations (space group *Amm2*). The atomic positions were then allowed to relax to the bulk-like orthorhombic structure with octahedral rotations (space group *Pnma*) while maintaining the thin film lattice parameters. Within this framework, the DFT calculations predict a ferromagnetic metal ground state which is strongly inconsistent with the SQUID data in Fig. 2. However, DFT calculations for the *Amm2* space group with no RhO₆ rotations ($a^0a^0a^0$) indicate that a C-type antiferromagnetic (AFM) ground state is energetically favorable, and the calculated DOS of this state is illustrated in Fig. 3a. There are two implications of this result. First, it provides further evidence of the high sensitivity of the magnetic ground state of SrRhO₃ to octahedra distortions,¹¹ Secondly, the octahedra in these SrRhO₃ films grown on cubic STO are not rotated due to the substrate, which transfers its symmetry across the heterointerface (i.e. cubic materials grown on orthorhombic substrates being orthorhombic and vice versa), similar to that observed in other systems.^{25,26} This result was quite surprising considering bulk SrRhO₃ is an orthorhombic perovskite. So to test this, we performed XRD reciprocal space mapping for the all variants of the STO 103 reflection by azimuthally rotating the sample (see Fig. 4) and observed no evidence of orthorhombic distortions (i.e. RhO₆ rotations) in this SrRhO₃ film which has a cubic-like structure that is quite consistent with conclusions discussed above. Combining these DFT calculations with the MR and SQUID data, we determine that SrRhO₃ likely is a C-type AFM with a Neel temperature of $T_N \sim 110 \text{ K}$. Supporting this interpretation, the DOS for the C-type AFM state indicates that despite a gap-like feature forming near the Fermi level (E_F),

it does not fully open and the DOS at E_F remains finite. This result is quite consistent with the weak rise in resistivity with decreasing temperature.

The electronic properties of SrRhO_3 films were further investigated through XAS and SE measurements as presented in Fig. 5. Since these spectra were collected at room temperature, we expect that the PM DOS (Fig. 3b) will be most representative of the data since we anticipate a PM ground state here. Note that the PM and C-type AF DOS are qualitatively similar with the major distinction between the two being a suppression of states near E_F in the latter. The XAS measurements were performed on beamline 4-ID-C at the Advanced Photon Source of Argonne National Laboratory and were obtained at room temperature with an angle of incidence of $\sim 25^\circ$ while simultaneously monitoring both fluorescence (TFY) and electron yields (TEY) near the O K edge. Recall that the samples are quite thin ($t \sim 12$ nm) so the TFY signal is strongly influenced by the underlying STO substrate as evident in the strong similarities between TFY and STO data in Fig. 1a. However even though TEY is known to be a surface sensitive probe, the similarities between both TFY and TEY at low energy indicates that TEY well represents the properties of the bulk of the film and is also shown in Fig. 5b. It is important to note that this data is somewhat distinct from similar measurements on polycrystalline SrRhO_3 ,²⁷ which also supports the claim that the physical properties of SrRhO_3 are highly sensitive to the local RhO_6 environment. First note that there is a small peak at ~ 523 eV that is due to the Rh M -edge and is too weak to be observed in TFY whereas all other features are due to the O K -edge. The hybridization between the O $2p$ and the Rh $4d$ as indicated by the partial DOS (see Fig. 3) enable d states to be investigated here. The three peaks shown in Fig. 5b are due to the Rh $4d$ manifold. The small peak at ~ 528.5 eV is t_{2g} in character while the others at ~ 530.5 and ~ 532.5 eV are e_g in character. This interpretation is in great agreement with the line shapes of the partial DOS

(Fig. 3b), where the states near E_F have strong contributions from both Rh d and O p orbitals, whereas there is a strong peak ~ 7 eV above E_F that is mostly Sr d in character. Making comparison to SrCoO_3 ²⁸ and SrIrO_3 that are respectively the $3d$ and $5d$ analogs of SrRhO_3 , we find that peaks associated with d orbitals are much broader for SrRhO_3 , implying that hybridization of the O p and Rh d manifolds is likely quite strong here. Combining this with the fact that recent experimental studies have revealed that both SrCoO_3 ²⁹ and SrIrO_3 ³⁰ have significantly improved catalytic activity in oxygen evolution reactions as compared to Pt and IrO_2 , respectively and that for the former this behavior is accompanied by such hybridization implies that SrRhO_3 has great promise for enhanced oxygen kinetics while such investigations are part of our continued work that is beyond the scope of this study.

The electronic properties were further investigated by SE (Fig. 5c) and for SrRhO_3 we observed a nearly linear response, however if one considers the calculated DOS in this energy range both above and below E_F it is approximately constant which should yield a nearly featureless optical conductivity signal. Despite this, there does appear to be a weak broad peak at roughly 2 eV. Comparing this spectra to that of SrIrO_3 (SrCoO_3),³¹ we observe a much sharper peak at 3.3 eV (1.8 eV) that is due to p - d optical transitions. Thus, there is a systematic shift of this feature to higher energy with increasing atomic number and similar to XAS data, it is much broader than in either counterpart. Therefore, there is great agreement between both spectroscopic techniques and our DFT calculations.

In summary, we have successfully synthesized high quality epitaxial films of SrRhO_3 by PLE and have investigated their electronic and magnetic properties through various experimental and theoretical techniques. We conclude that the magnetic ground state in SrRhO_3 is highly sensitive to rotations of the RhO_6 octahedra and C-type AFM is the energetically favorable state at zero

temperature, which drastically differs from that of bulk crystals. It has an ordering temperature of roughly 110 K and likely originates from substrate induced high symmetry phase where the octahedra are not rotated ($a^0a^0a^0$), thus providing an example where the octahedral distortions are tunable and strongly coupled to physical properties. We have made a number of comparisons between these experimental and theoretical results and find them to be highly self-consistent. In addition, these SrRhO_3 films exhibit abnormally strong hybridization between the O $2p$ and Rh $4d$. Thus, SrRhO_3 displays great potential for novel functionalities and synthesis of high quality single crystal samples is no longer a hurdle for experimentalists.

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References

- 1 E. Dagotto, *Science* **309**, 257 (2005).
- 2 Y. Tokura and N. Nagaosa, *Science* **288**, 462 (2000).
- 3 Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, *Nature* **372**, 532 (1994).
- 4 K. Yamaura and E. Takayama-Muromachi, *Physica C* **445–448**, 54 (2006).
- 5 K. Yamaura and E. Takayama-Muromachi, *Phys. Rev. B* **64**, 224424 (2001).
- 6 K. Yamaura, Q. Huang, D. P. Young, Y. Noguchi, and E. Takayama-Muromachi, *Phys. Rev. B* **66**, 134431 (2002).
- 7 K. Yamaura, Q. Huang, D. P. Young, and E. Takayama-Muromachi, *Chemistry of Materials* **16**, 3424 (2004).
- 8 K. Yamaura, Y. Shirako, H. Kojitani, M. Arai, D. P. Young, M. Akaogi, M. Nakashima, T. Katsumata, Y. Inaguma, and E. Takayama-Muromachi, *J. Am. Chem. Soc.* **131**, 2722 (2009).
- 9 Y. Shirako, H. Kojitani, M. Akaogi, K. Yamaura, and E. Takayama-Muromachi, *Physics and Chemistry of Minerals* **36**, 455 (2009).
- 10 C.-Q. Jin, J.-S. Zhou, J. B. Goodenough, Q. Q. Liu, J. G. Zhao, L. X. Yang, Y. Yu, R. C. Yu, T. Katsura, A. Shatskiy, and E. Ito, *Proceedings of the National Academy of Sciences* **105**, 7115 (2008).
- 11 D. J. Singh, *Phys. Rev. B* **67**, 054507 (2003).
- 12 J.-M. Carter, V. V. Shankar, M. A. Zeb, and H.-Y. Kee, *Phys. Rev. B* **85**, 115105 (2012).
- 13 D. Xiao, W. Zhu, Y. Ran, N. Nagaosa, and S. Okamoto, *Nat Commun* **2**, 596 (2011).
- 14 Y. X. Liu, H. Masumoto, and T. Goto, *Materials Transactions* **46**, 100 (2005).
- 15 S. Havelia, K. R. Balasubramaniam, S. Spurgeon, F. Cormack, and P. A. Salvador, *Journal of Crystal Growth* **310**, 1985 (2008).
- 16 J. Nichols, O. B. Korneta, J. Terzic, G. Cao, J. W. Brill, and S. S. A. Seo, *Appl. Phys. Lett.* **104**, 121913 (2014).
- 17 N. F. Mott, *Philos. Mag.* **26**, 1015 (1972).
- 18 A. F. Ioffe and A. R. Regel, *Prog. Semicond.* **4**, 237 (1960).
- 19 N. E. Hussey, K. Takenaka, and H. Takagi, *Philos. Mag.* **84**, 2847 (2004).
- 20 M. Takizawa, D. Toyota, H. Wadati, A. Chikamatsu, H. Kumigashira, A. Fujimori, M. Oshima, Z. Fang, M. Lippmaa, M. Kawasaki, and H. Koinuma, *Phys. Rev. B* **72**, 060404 (2005).
- 21 Y. J. Chang, C. H. Kim, S. H. Phark, Y. S. Kim, J. Yu, and T. W. Noh, *Phys. Rev. Lett.* **103**, 057201 (2009).
- 22 B. Kim, D. Kwon, J. H. Song, Y. Hikita, B. G. Kim, and H. Y. Hwang, *Solid State Commun.* **150**, 598 (2010).
- 23 J. Son, J. M. LeBeau, S. J. Allen, and S. Stemmer, *Appl. Phys. Lett.* **97**, 202109 (2010).
- 24 T. L. Meyer, L. Jiang, S. Park, T. Egami, and H. N. Lee, *APL Mater.* **3**, 126102 (2015).
- 25 J. M. Rondinelli, S. J. May, and J. W. Freeland, *MRS Bulletin* **37**, 261 (2012).
- 26 Z. Liao, M. Huijben, Z. Zhong, N. Gauquelin, S. Macke, R. J. Green, S. Van Aert, J. Verbeeck, G. Van Tendeloo, K. Held, G. A. Sawatzky, G. Koster, and G. Rijnders, *Nat Mater* **15**, 425 (2016).
- 27 N. Han-Jin, B. J. Kim, S. J. Oh, J. H. Park, H. J. Lin, C. T. Chen, Y. S. Lee, K. Yamaura, and E. Takayama-Muromachi, *Journal of Physics: Condensed Matter* **20**, 485208 (2008).
- 28 H. Jeon, W. S. Choi, M. D. Biegalski, C. M. Folkman, I. C. Tung, D. D. Fong, J. W. Freeland, D. Shin, H. Ohta, M. F. Chisholm, and H. N. Lee, *Nat Mater* **12**, 1057 (2013).
- 29 J. R. Petrie, C. Mitra, H. Jeon, W. S. Choi, T. L. Meyer, F. A. Reboredo, J. W. Freeland, G. Eres, and H. N. Lee, *Advanced Functional Materials* **26**, 1564 (2016).
- 30 R. Tang, Y. Nie, J. K. Kawasaki, D.-Y. Kuo, G. Petretto, G. Hautier, G.-M. Rignanese, K. M. Shen, D. G. Schlom, and J. Suntivich, *J. Mater. Chem. A* **4**, 6831 (2016).

- ³¹ W. S. Choi, H. Jeon, J. H. Lee, S. S. A. Seo, V. R. Cooper, K. M. Rabe, and H. N. Lee, *Phys. Rev. Lett.* **111**, 097401 (2013).

Figure Captions

Figure 1 AFM topographic images of $3 \times 3 \mu\text{m}^2$ area of the STO substrate obtained (a) before and (b) after deposition of a ~ 12 nm thick SrRhO_3 film. (c) XRD θ - 2θ scan of SrRhO_3 film..

Figure 2 (a) The temperature dependence of the longitudinal resistivity (ρ_{xx}). (inset) The field dependence of the transverse resistivity (ρ_{xy}) obtained at $T = 2$ K. (b) The temperature dependent magnetoresistance ($MR = [R(H) - R(0)]/R(0) \times 100\%$) obtained at $\mu_0 H = 5$ T. (inset) The field dependent MR obtained at $T = 2$ K. (c) The temperature dependent magnetization (M) obtained while warming with $\mu_0 H = 0.1$ T after cooling in the same and zero field.

Figure 3 Calculated total and partial DOS of SrRhO_3 at $T = 0$ K for (a) C-type AF and (b) PM magnetic ground states obtained with an ideal thin film crystal structure with undistorted ($a^0 a^0 a^0$) RhO_6 octahedra (space group $Amm2$). The dashed gray line marks $\text{DOS} = 0$ and the inset shows a magnification near E_F .

Figure 4 X-ray diffractions reciprocal space maps near 103, 013, 103, and 013 reflections of STO.

Figure 5 (a) Room temperature XAS spectra near the O K edge of both SrRhO_3 and SrTiO_3 where there is a vertical offset for clarity. (b) Room temperature XAS spectra (TEY) near the O K edge of SrIrO_3 , SrRhO_3 , and SrCoO_3 . (c) Optical conductivity (σ_1) of SrRhO_3 film obtained at room temperature along with SrCoO_3 (from Ref. 31) and SrIrO_3 .









