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Strain Induced Magnetism in $SrRuO_3$ Epitaxial Thin Films

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Abstract:

Epitaxial $SrRuO_3$ thin films were grown on $SrTiO_3$, $(LaAlO_3)_{0.3}(SrAlO_3)_{0.7}$ and $LaAlO_3$ substrates inducing different biaxial compressive strains. Coherently strained $SrRuO_3$ films exhibit enhanced magnetization compared to previously reported bulk and thin film values of 1.1-1.6 μ_B per formula unit. A comparison of (001) and (110) $SrRuO_3$ films on each substrate indicates that films on (110) oriented have consistently higher saturated moments than corresponding (001) films. These observations indicate the importance of lattice distortions in controlling the magnetic ground state in this transitional metal oxide.

Lattice distortions in transition metal complex oxides significantly alter their electronic and magnetic properties. For example, in bulk doped manganites exposure to hydrostatic or chemical pressure shifts their Curie temperature and impacts the colossal magnetoresistance effect.[1, 2] The effect of lattice distortions induced by epitaxial strain due to film-substrate mismatch has been also extensively studied in doped manganite thin films.[3] These studies suggested that the biaxial epitaxial strain imposed by the substrate can give rise to behavior distinct from those obtainable through bulk strain states. With recent advances in thin-film deposition techniques with atomic scale precision, we are now in a position to separate microstructural effects from interfacial and strain effects.

Among the transition metal oxides, the itinerant ferromagnet $SrRuO_3$ (SRO) is a model system in which effects of lattice distortions on electronic and magnetic properties can be studied in detail. SRO has been shown to grow coherently on miscut (001) $SrTiO_3$ (STO) substrates but very little is know about its growth on other substrates and other surface orientations.[4] Recently, thin films of SRO have been shown to exhibit surprising properties, including a metal-to-insulator transition in ultra-thin films as well as strong magnetic anisotropy effects and spin-glass behavior.[5, 6] Theoretical work on SRO films on (001) and (110) STO predicts saturation magnetization values for (001) SRO films under compressive epitaxial strain on (001) STO substrates smaller than the bulk and (110) SRO films on STO exhibiting even lower saturation magnetization values.[7] By varying the degree and orientation of compressive strain, it should therefore be possible to alter the magnetic ground state of SRO thin films.

SRO is the only known 4d transition metal oxide that is ferromagnetic and metallic. It has an orthorhombic crystal structure with a_{bulk} = 5.57 Å, b_{bulk} = 5.53 Å, c_{bulk} = 7.84 Å but is also well-described as a distorted cubic perovskite structure.[8, 9] Thus, throughout this paper we will refer to SRO's pseudocubic lattice parameters of a' = b' = c' = 3.93Å.[4,10] In bulk, SRO has a Curie temperature of ~160K and saturated moment of 1.1-1.6 μ_B/Ru.[8,11-13] This moment is significantly reduced from the theoretically predicted moment (2 μ_B/Ru) resulting from a Ru^{4+} ion in the low spin configuration. The difference is generally attributed to spin delocalization in itinerant ferromagnetism [8]

In this paper we report on enhancement of saturation magnetization in $SrRuO_3$ thin films resulting from substrate-imposed lattice distortions with various magnitudes and symmetries. Growing (001) and (110) oriented SRO films on STO, $(LaAlO_3)_{0.3}(SrAlO_3)_{0.7}$ (LSAT) and $LaAlO_3$ (LAO), we have systematically varied the strain state of the SRO films. We find strongly strain-dependent magnetism that is enhanced from bulk values and is consistent with improved relative alignment of the Ru^{4+} spins.

Epitaxial SRO films were deposited by pulsed laser deposition on (001) and (110) STO, LSAT, and LAO substrates, introducing compressive strains of 0.64%, 1.53%, and 3.56%, respectively. Films were grown with a laser fluence of ~1.29 J/cm^2 in 60 mtorr of O_2 at 700 °C and post annealed in atmospheric pressure O_2 at 600 °C to reduce the occurrence of oxygen vacancies. Film thicknesses were in the 55-80nm range. Atomic force microscopy on (001) oriented films showed extremely flat surfaces with atomic terraces. RMS roughness values increased with increasing film-substrate mismatch from 0.3nm in SRO on STO to 2nm on LAO. (110) oriented films displayed rougher morphologies consistent with island or columnar growth; RMS

roughness values on the order of 0.5nm on STO and 4.8nm on LAO. As with the (001) films, roughness increased with increasing film-lattice mismatch of the samples.

X-ray diffraction measurements confirmed that all SRO films exhibited excellent epitaxy, showing only diffraction peaks corresponding to the substrate orientation with typical mosaic spreads of approximately 0.06° on (001) STO, 0.11° on (001) LSAT and 0.45° on (001) LAO. Figure 1 shows reciprocal space maps (RSM) of (001) SRO/STO, (001) SRO/LSAT and (001) SRO/LAO films. The fact that the film and substrate peaks line up along the in-place reciprocal lattice direction (Q_{IP}) in (001) SRO/STO and (001) SRO/LSAT samples indicate that these films are coherently strained to their substrates. (001) SRO/LAO samples are fully relaxed. From RSM data, volume-preserving and non volume-preserving contributions to the strain can be easily calculated on (001) SRO/STO and SRO/LSAT samples. These results indicate that there is a significant volume-preserving tetragonal distortion as well as a smaller volume contraction. Films grown on (110) STO are fully strained while films on (110) LSAT and LAO are partially and fully relaxed, respectively. (110) SRO/STO films experience monoclinic distortions due to the symmetry of the biaxial epitaxial strain induced by the film/substrate lattice mismatch. Transport measurements of all SRO films exhibit metallic behavior with a kink corresponding to the spin state transition. Film residual resistivity ratios ranged in value from 4-5, well within the typical range for previous high-quality epitaxial SRO films.[14,15] Additionally, resistivity scaled well with film thickness, thus indicating that the electronic properties are not dominated by surface or interface effects.

The magnetic properties of these SRO films were investigated using SQUID magnetometry. X-ray absorption (XA) spectroscopy and X-ray magnetic circular dichroism (XMCD) measurements

were performed at the Advanced Light Source beamline 6.3.1 using a resistive electromagnet providing magnetic fields up to 2T collinear with the x ray beam.. The absorption spectra were measured in an applied field of 1.9T with the x ray beam of about 60% circular polarization impinging on the sample surface at an angle of 60° to the sample normal. The x ray be At 298K the XA spectra showed no features corresponding to magnetic impurities such as Ni, Fe, or Co, although small amounts of Ba (<0.2 %) were detected. However, Ba, a common substitutional impurity in Sr compounds is not magnetic and is unlikely to affect the magnetic properties of SRO in such small quantities. XA and XMCD spectra of the Ru $M_{3,2}$ edge showed a dichroism signal compatible with ruthenium in an octahedral environment expected in SRO (Figure XX).[16] Magnetic measurements were taken with a SQUID magnetometer as a function of field and temperature. We found that for all substrate types, (110) films had larger moments than (001) oriented films. In the case of (001) substrates, fully relaxed films on LAO exhibited moments around 1.23 μB/Ru, in agreement with bulk measurements, while films on (001) STO and LSAT exhibited moments of 1.73 and 1.92 μB/Ru. Films on (110) STO, LSAT, and LAO substrates exhibited saturated moment of 2.07, 3.03, and 1.7 μB/Ru, respectively. Figure 3 shows typical plots of magnetization (normalized per formula unit) vs. applied field in which the difference between SRO films on different substrates can be seen.

All films, including those showing enhanced magnetic moments, had Curie temperatures lower than bulk. For (001) oriented substrates the cCurie temperature of films grown on LSAT, , $T_{C\_LSAT,}$ is below the transition temperature od films deporited on STO, T_{C_STO} while the transition temperatures, T_{C_LAO},of the fully relaxed SRO/LAO films were consistently higher than both. In the case of (110) samples, T_{C_STO} of coherently strained SRO/STO samples were lower

than T_{C_LSAT} of partially strained SRO/LSAT which were, in turn, lower than T_{C_LAO} of fully relaxed SRO/LAO samples. Transition temperatures of films on (001) oriented substrates (126-140K) were significantly lower than those on (110) substrates (148-152K). With enhancement of the magnetic moment, a corresponding increase in the Curie temperature is expected. Although this trend is observed among our (001) and (110) films, all observed Curie temperatures have been lower than those observed in the bulk.

As can be seen from the significantly decreased moments on the relaxed (001) and (110) films on LAO, strain plays an important role in determining the magnetic ground state of SRO. Fully strained films on (001) STO and LSAT exhibit increasing moments with increasing compressive strain. This trend is also observed in the case of (110) samples. With one significant exception, all films have saturation magnetic moment values that are understood within the context of better alignment of moments in a low spin Ru^{4+} state. Such moments have a theoretical value of approximately 2.2-2.3 μ_B per Ru ion, assuming perfect alignment of spins (2 μ_B) and 10-15% orbital moment (0.2-0.3 μ_B). However, SRO on (110) LSAT has a saturated moment exceeding 3 μ_B per formula unit, beyond the theoretical limit of a low spin Ru^{4+} ion configuration. It is very difficult to obtain a precise picture of the distortions in this case, as the strain state of such films is one with differing degrees of partial relaxation along the (001) and (1-10) directions. Thus, it is possible that changes in symmetry occur and, more specifically, rotation of the Ru-O octahedra may produce a transition in Ru to the high spin state (4 μ_B). Unfortunately, confirmation of such distortions is problematic as it is extremely difficult to measure bond angles in single crystalline thin films.

The larger enhancement of magnetization in (110) SRO films compared to (001) films dictates that monoclinic distortions induced by the biaxial strain in the (110) plane is more effective in enhancing magnetization than tetragonal distortions induced by biaxial strain in the (001) plane. In any case, the experimentally observed enhancement is at odds with recent theoretical calculations that predict suppression of magnetization in either case.[7] However, if octahedral tilt distortions could be taken into account theoretically, their agreement with our experiment might improve.

In summary, we have found significant elevation of the saturated magnetic moments in coherently strained SRO thin films compared to the bulk. These findings demonstrate the importance of the magnitude and symmetry of epitaxial strain in determining the magnetic state of SRO. As the vast majority of thin film devices must incorporate some form of epitaxial strain, it is important to not only understand the effects strain imposes but also to develop our ability to engineer these effects to improve device effectiveness.

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Figures:

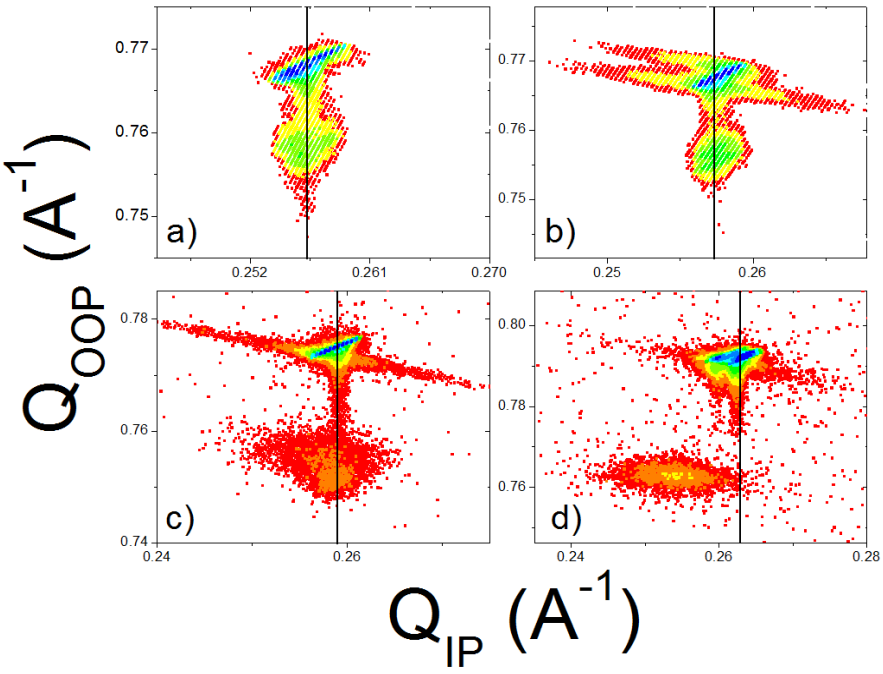
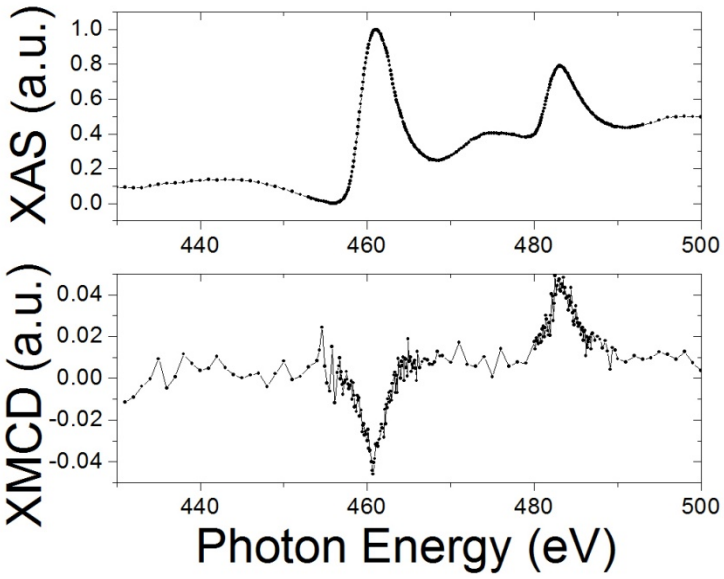


Figure 1 – Reciprocal space maps of the (103) reflections of a) 60nm thick SRO on (001) STO b) 120nm thick SRO on (001) STO c) 50nm thick SRO on (001) LSAT d) 70 nm thick SRO on (001)

LAO. If the vertical black line passes through the film peak as well as the substrate peak, pseudomorphic growth has occurred. If not, relaxation has occurred.



{ I suggest to change the displayed photon energy range to start near 450eV. There is no need to show the featureless pre-edge region.}

Figure XX –Ru $L_{3,2}$ XA and XMCD spectra in SRO on (001) STO. The XA spectrum is compatible with an octahedral coordination of Ru^{4+}, while the XMCD shows magnetism originating in the Ru.

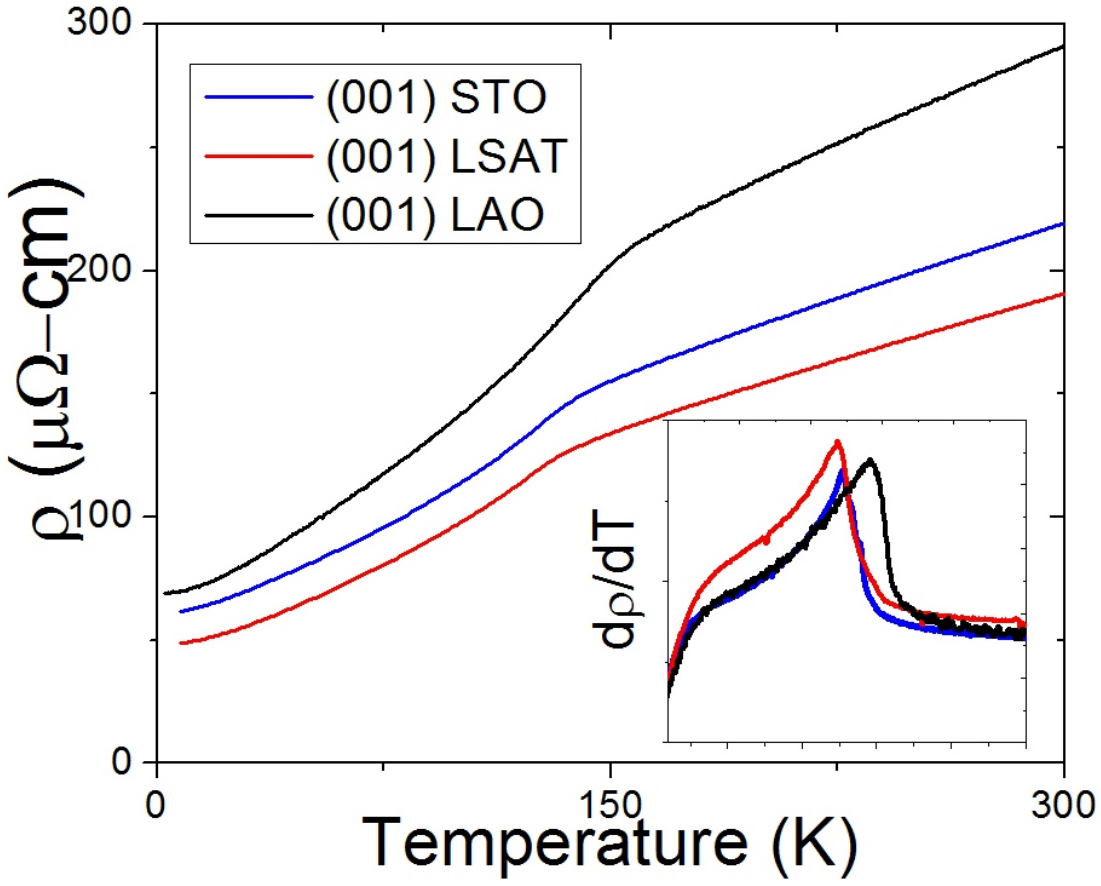


Figure 2 – Resistivity vs. Temperature for SRO films on (001) STO, LSAT, and LAO. (Inset) dρ/dT vs. Temperature for films on (001) STO, (001) LSAT, and (110) LAO. The difference in transition temperature as a function of substrate orientation can be clearly seen in the location of the "kink" in these curves.

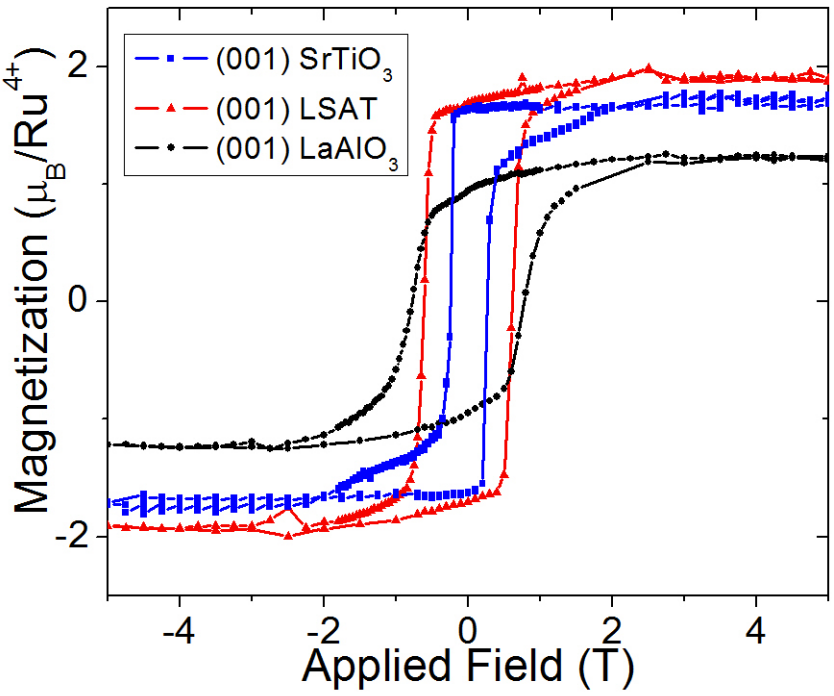


Figure 3 – Normalized Magnetization vs. Applied Field for SRO films on (001) STO, LSAT, and LAO. The difference in saturated magnetization between substrates can be seen, with the relaxed film on LAO exhibiting significantly lower moment than those on STO and LSAT.