Strain healing of spin–orbit coupling: a cause for enhanced magnetic moment in epitaxial SrRuO₃ thin films

Shekhar Tyagi, V G Sathe, Gaurav Sharma, D M Phase and V R Reddy

UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, India
E-mail: vasant@csr.res.in

Received 7 November 2019, revised 27 February 2020
Accepted for publication 27 March 2020
Published 5 May 2020

Abstract
Enhanced magnetic moment and coercivity in SrRuO₃ thin films are significant issues for advanced technological usages and hence are researched extensively in recent times. Most of the previous reports on thin films with enhanced magnetic moment attributed it to the high spin state. Our magnetization results show high magnetic moment of 3.3 μₛ/Ru ion in the epitaxial thin films grown on LSAT substrate against 1.2 μₛ/Ru ion observed in bulk compound. Contrary to the previous reports the Ru ions are found to be in low spin state and the orbital moment is shown to be contributing significantly in the enhancement of magnetic moment. We employed x-ray absorption spectroscopy and resonant valance bandspectroscopy to probe the spin state and orbital contributions in these films. The existence of strong spin–orbit coupling responsible for the de-quenching of the 4d orbitals is confirmed by the observation of the non-statistical large branching ratio at the Ru M₂,3 absorption edges. X-ray magnetic circular dichroism studies performed at the Ru M₂,3 edges provided direct evidence of significant contribution of orbital moment in the film grown on LSAT. The relaxation of orbital quenching by strain engineering provides a new tool for enhancing magnetic moment and strain disorder is shown to be an efficient mean to control the spin–orbit coupling.

Keywords: spin–orbit coupling, strain disorder, x-ray absorption spectroscopy, epitaxial thin films, resonant photoelectron spectroscopy, SrRuO₃

1 Supplementary material for this article is available online

1. Introduction
SrRuO₃ (SRO) [1, 2] is getting wide attention from the applied science community for its unique applications like electrodes [3] or conducting layers in epitaxial hetero-structures of functional oxides and magnetic tunnel junctions [4–6] due to the robust spin polarization at the interface of the ferromagnetic oxide and the metal. Few materials are available in literature that have such variety of properties. SRO shows itinerant ferromagnetism, unusual transport properties and Fermi liquid behavior at low temperatures [7], whereas, it shows bad metal behavior at high temperatures [8]. In thin films, it is reported to exhibit high-perpendicular remnant magnetization and large magneto-optical constant [9].

It is by now widely accepted that a small disorder in SrRuO₃ produces large variations in its physical properties. Previous reports suggest that the magnetic properties can be significantly modified by the introduction of strain [10–13]. These studies showed that the physical properties of SRO are dissimilar in strained and relaxed films. For example; Gan et al [13] showed that the transition temperature reduces with enhancement in substrate induced strain in films of SRO grown on (001) oriented substrate. In fully strained films, the in-plane and out-of-plane inter atomic distances are considerably dissimilar, resulting in variation in the overlap of Ru: t₂g and O: 2p orbitals in the two directions. This significantly modifies
the physical properties as the electronic conduction and magnetic properties are known to be associated with the degree of hybridization of the Ru: 4d orbitals and O: 2p orbitals.

Recently, there is a race among researchers for attaining enhancement in magnetic moment in the films of SRO. Bulk SRO shows low spin state and a magnetic moment of \( \sim 1.2 \mu_B/\text{Ru ion} \). Gruutter \textit{et al} \[14\] showed enhanced magnetic moment i.e. 1.7 \( \mu_B/\text{Ru} \) and 1.9 \( \mu_B/\text{Ru} \) in SRO films grown on (001) SrTiO\(_3\) and LSAT substrate, respectively. Importantly, the saturation moment was found to be insensitive to the film thickness and the lattice distortions are shown to be responsible for controlling the magnetic ground state in SRO films. This is in contrast to the ultrathin films (<5 unit cell thick) of SRO, where termination effects result in quantum confinement which significantly modifies its physical properties \[15–18\]. Murtaza \textit{et al} \[19\] reported a large saturation magnetic moment in the range of 2–2.4 \( \mu_B \) in Ru deficient films, which was attributed to the stabilization of the high spin Ru\(^{4+}\) state. Gruutter \textit{et al} \[20\] proposed that the high spin state of the Ru ions can be stabilized through controlled lattice distortion introduced by the compressive nature of the in-plane strain and the orientation of the film. It was stated that in the high spin state, the orbital overlapping decreases and an enhancement in the density of states at the Fermi level is observed due to newly split eg band. It was proposed that the growth in the (111) orientation is responsible for the stabilization of the high spin state. In contrast to this report, Bowha \textit{et al} \[21\] and Agrestini \textit{et al} \[22\] negated the role of orientation of the film growth in stabilization of the high spin state. Bowha \textit{et al} \[21\] advocated that the nearest neighbor distances of the Ru ions decides the magnetic properties of the SRO thin films and found no signatures of the high-spin states in their study on the (111)-oriented SRO thin films. Agrestini \textit{et al} \[22\] argued that the stabilization of the high spin state with \( S = 2 \) would be too costly in energy and hence, it is not possible to stabilize high spin state in Ru\(^{4+}\). They proved that the thin films of SRO grown on (111) and (001) oriented SrTiO\(_3\) substrates are in low spin states with quenched orbital moment. These authors ruled out the hypothesis of a compressive strain-induced spin state transition. However, recently Ning \textit{et al} \[23\] reported 4 \( \mu_B/\text{Ru} \) moment in the (111)-oriented SRO films grown on SrTiO\(_3\) substrate. They observed 2 \( \mu_B/\text{Ru} \) and 3 \( \mu_B/\text{Ru} \) moment in the (001) and (110)-oriented films, respectively. These magnetization values are attributed to the high-spin state, low-spin state and mixed (low and high) spin states of Ru ion in the (111), (001) and (110)-oriented SRO films, respectively. Hence, the origin of enhancement in the magnetic moment remains a controversial issue.

The enhancement in the magnetic moment of the SRO films can arise due to two mechanisms; first one is the stabilization of the high spin state of the Ru ions with \( S = 2 \) and the second one is due to significant orbital moment contribution. The second mechanism is operative only when the orbital quenching is disrupted.

We thought of that the quenching of the orbital moment can be disrupted by weakening the crystal field effect. This can be achieved by lowering the local symmetry of the oxygen octahedra surrounding the Ru\(^{4+}\) ion by the introduction of large disorder. Large disorder in films can be created by creating defect states but in that case the spin moment is also expected to decrease significantly. The other method is to introduce large strain disorder in films during growth, which will not affect the spin moment but is expected to affect the local crystal field. It has previously been reported that the orbital angular moment weakness due to reduction in hybridization of Ru\(^{4+}\) ions with the surrounding oxgens \[24\].

In order to address above issues and to achieve strain disorder, thin films of SrRuO\(_3\) of various thicknesses were grown on (001) oriented SrTiO\(_3\) and LSAT substrates providing different strain relaxation states. Intentionally, films with strain disorder were chosen for the investigation of their magnetic properties. Our study show that both the films remain in low spin state with different degrees of orbital quenching resulting in enhanced magnetic moment in the film grown on LSAT.

2. Experimental techniques

The bulk SrRuO\(_3\) is prepared by standard solid state reaction method and characterized by x-ray diffraction and Raman spectroscopy. It is found to be single phase in nature and showed the ferromagnetic transition at 160 K, exactly matching with the literature \[25–27\]. A dense pellet of 20 mm diameter was prepared and was used as a target during deposition of thin films of SrRuO\(_3\) on (001) oriented single crystal substrates of SrTiO\(_3\) and LSAT commercially procured from MTI-corp. USA, using pulsed laser deposition technique. A pulsed Excimer laser with 248 nm wavelength (pulse width = 20 ns) providing an energy density of 3.6 J.cm\(^{-2}\) and repetition rate of 10 Hz was used for the deposition. The substrates were kept at 750 °C during deposition in the presence of oxygen gas partial pressure of 0.13 mbar. After several test depositions the cooling rate after deposition was kept at 40 °C per minute that resulted in best quality films. For confirming the phase purity x-ray diffraction was carried out using Bruker D2 phaser (Cu K\(\alpha\) radiation). The reciprocal space mapping and x-ray reflectivity measurements were carried out using Bruker D8-discover high resolution x-ray diffractometer (HRXRD). Magnetic properties of the films were examined using 7-Tesla SQUID-vibrating sample magnetometer (SVSM; Quantum Design Inc., USA). Valence band spectroscopy was performed at angle-integrated photoemission spectroscopy (AIPES) beamline on Indus-1 synchrotron radiation source at RRCAT, Indore, India. To measure the valance band spectra the base pressure in the experimental chamber was of the order of \(10^{-10}\) Torr. The Ar\(^+\) ion sputtering was performed for removing surface contamination at very low energy of 500 eV (ion current 2 \( \mu \) amp) for 2 min so that it does not influence the composition of the film and bulk sample. Spectra were collected at 300 K with incident photon energy of 48 eV (off-resonance) and 52 eV (on-resonance). Fermi level was aligned by recording the valence band spectra of the Ag foil, which is also mounted along with the sample on the holder. Electronic properties of both the films and the bulk compound was analysed using x-ray absorption spectroscopy (XAS) technique measured in total electron yield (TEY) mode across Ru M\(_{2,3}\) edges and O(oxygen) K-edge at soft x-ray absorption
Figure 1. The reciprocal space mapping (RSM) plot recorded at the symmetric (002) and asymmetric (103) plane: (a) and (b) shows the RSM plot corresponding to the LSAT/SRO(S1) film while (c) and (d) shows the RSM plot corresponding to the STO/SRO(S2) epitaxial thin film. The circles illustrates the broadening of the reciprocal lattice point and arrows indicates amount of peak broadening perpendicular and parallel to the reflecting plane.

Figure 2. The magnetization ($M$) as a function applied magnetic field ($H$) for LSAT/SRO (S1) and STO/SRO (S2) thin films measured at 5 K. The error bars ($\pm 45$ emu/cc) are comparable to the size of the symbol.

Figure 3. The soft x-ray absorption spectroscopic spectra recorded on the LSAT/SRO (S1), STO/SRO (S2) and bulk SRO at the oxygen 1s (K-edge) presented in the right panel. For better information the valance band spectra recorded at the ‘on’ resonance condition as a function of relative energy to the Fermi energy ($E_F$) is also presented in the left panel.

3. Results and discussions

In order to probe the effect of strain disorder, mainly three samples were investigated. Thin films of SrRuO$_3$ grown on LSAT substrate (S1), SrTiO$_3$ substrate (S2) and pellet of bulk SrRuO$_3$ were investigated using HR-800 micro-Raman set-up equipped with 632.8 nm excitation laser source, an 1800 gr mm$^{-1}$ grating and a Peltier cooled CCD detector. Linkam make stage with temperature stability of $\pm 0.1$ K was used for temperature variation of the sample.
SrRuO$_3$. The films were thoroughly characterized using x-ray diffraction technique used in various modes and the film thickness was estimated using x-ray reflectivity (XRR) measurements. The XRR data of the films of smaller thickness was fitted (see supplementary figure S1, available online at stacks.iop.org/JPhysCM/32/255802/mmedia) which provided us the deposition rate. From this the thickness of the S1 and S2 films were deduced and found to be 186 ± 1 nm. Both the films were rectangular in shape with dimensions of (4.12 mm × 5.54 mm) and (3.28 mm × 6.54 mm) for S1 and S2 respectively. The x-ray reciprocal space map analysis was carried out at the symmetric (002) and asymmetric (103) reflection which provided details of strain disorder and epitaxy. Figures 1(a) and (b) shows the RSM carried out on S1 film while figures 1(c) and (d) shows RSM carried out on the S2 film along the (002) and (103) planes, respectively. The in-plane ‘a’ and out-of-plane ‘c’ lattice parameters deduced from the RSM analysis are $a = 3.926$ Å, 3.920 Å; and $c = 3.924$, 3.926 Å for the S1 and S2 films respectively. The strain values resulted from the lattice parameters in the in-plane direction are $−0.07\%$ and $−0.22\%$ while in the out-of-plane direction the values are $−0.12\%$ and $−0.09\%$ for the S1 and S2 films, respectively. The RSM study thus suggests that both the films are nearly relaxed with nominal strain values. The asymmetric reciprocal lattice point corresponding to the films showed significant broadening as indicated by a circle (figures 1(b) and (d)). The length of the tangential arrows with the circle represents the amount of peak broadening perpendicular (mosaic spread) and parallel (lateral correlation length) to the reflecting plane. From the RSM measurements the mosaic spread representing the angular range of the low-angle grain boundaries were calculated. The calculated angular values are $1.10°$ and $0.22°$ corresponding to the S1 and S2 films, respectively. We have also calculated the lateral correlation length that are found to be quite different in the two films. The calculated lateral correlation length is found to be 3.45 Å in S1 film and 15.44 Å in S2 film which suggests that the strain is getting modulated in the adjacent unit cell in S1 film while after four unit cells in S2 film.

Thus, it can be concluded that the local strain disorder is larger in S1 film than in S2 film.

To find out the saturation magnetic moment, we have carried out the magnetization vs magnetic field (M–H) measurements at 5 K for both the films (figure 2) in zero field cooled protocol. The diamagnetic contribution arising from the substrate have been subtracted using standard procedure [30]. The saturated magnetic moment calculated from the M–H curves was found to be 3.3 ± 0.06 $\mu_B$/Ru$^{4+}$ for S1 film and 1.5 ± 0.06 $\mu_B$/Ru$^{4+}$ for S2 film, the errors are estimated from the error in estimation of the volume of the films. The magnetization values are significantly higher when compared to the bulk. In the bulk SRO, a magnetic moment of $\sim 1.2$ $\mu_B$/Ru$^{4+}$ was reported that is attributed to low-spin state configuration due to the large crystal field splitting [20]. Importantly, the coercivity of the hysteresis loop was found to be ~0.65 and ~0.46 T in S1 and S2 film, respectively. A large value of the coercivity in S1 can be attributed to the higher local strain disorder as deduced from the RSM study, as it is likely to enhance the domain pinning.

The enhanced magnetic moment can arise either due to Ru$^{4+}$ ion in high spin state or due to enhanced orbital contribution when Ru$^{4+}$ is in low spin state. Generally, the orbitals are assumed to be fully quenched in 4d compounds.

In order to estimate the spin state of the Ru$^{4+}$ ions in these samples, the oxygen K-edge x-ray absorption spectra (XAS) was recorded and is presented in figure 3. The resonant photoemission spectra (PES) recorded in the on-resonance ($h\nu = 52$ eV) condition is also presented in the same figure giving complete electronic structure of Ru band. It is well known that the O 1s XAS spectra provides direct information about unoccupied Ru bands (4d) through the hybridization [31, 32]. We carried out the analysis of the O 1s XAS spectra of the bulk SRO compound by following the terminology used in refs. [27, 28, 33]. Accordingly, the features (A, B and C) near the edge are attributed to the Ru 4d bands in figure 3. The Ru 4d band is known to split into $t_2g$ and $e_g$ sub-bands due to the octahedral crystal-field effect. The $e_g$ band further splits due to the intra-atomic exchange into a majority and a minority band.

The feature A corresponds to the localized $t_{2g}$ sub-band ($\pi$-bonding) while features B and C corresponds to the delocalized $e_g$ sub-band ($\sigma$-bonding). The features D and E correspond to the Sr 3d bands, whereas the feature F are attributed to the metal (Ru + Sr) sp bands due to the (Ru + Sr) sp–O 2p interactions.

Interestingly, the film S1 and S2 shows major differences in the O 1s XAS spectra when compared to spectra shown by the bulk compound. It is noted that the position of the feature A is nearly same in the bulk and the films, however, the relative intensity of the A peak reflecting Ru $t_{2g}$ band show significant enhancement in the films when compared to the bulk compound. This peak is relatively broad in S1 film than in S2 and bulk. The shape profile of B and C features reflecting Ru $e_g$ band show a drastic variation in the films than in the bulk. The two features merge completely in films forming a single band which shows a shift towards lower binding energy without any change in the intensity.

These changes in the spectrum suggests that the degree of hybridization of the O 2p states with the Ru 4d states is substantially different in the thin films as compared to in bulk. The crystal field splitting is significantly lower in films (3.56 eV for S1 film and 3.63 eV for S2 film) than in the bulk (4.58 eV). One of the plausible reasons for the decrease in the crystal field splitting can be reduction in $\sigma$-bonding and enhancement in $\pi$-bonding due to variation in octahedral distortions in the films. The mutual exchange of the strength between the bonding of orbitals decide the change in the crystal field splitting.

Compared to the bulk, the enhanced intensity of the feature A in the films indicate that the unoccupied density of state in Ru $t_{2g}$ band are getting enhanced in the films, particularly in S1. The change in the shape profile of the Ru $e_g$ band indicates the modulation in the exchange effects between the majority and the minority spin contributions [34]. The XAS spectra at higher binding energy of the bulk and the films show significant change in spectral character which reveals modification in the hybridization state of the Sr 4d bands. This indicates that the strain and strain disorder present in the films induces modification in the hybridization between the Sr 4d bands and the
O 2p states in films. Finally, there are also subtle variations in the metal-sp bands in both the films with respect to the bulk.

The XAS spectra provided important information about the spin state of the Ru ions. It is noted that the crystal field splitting is reduced in the films (it is lowest in S1 film). As a consequence, the spin state of the Ru ions may change. However, the intensity of the eg band is found to be the same in the two films and the bulk compound suggesting that the unoccupied states in the eg bands are same in all the three samples. In case of a spin state variation i.e. from low spin state in bulk to high spin state in films, the unoccupied density of state of the eg band in the films should have shown a dramatic decrease. This should have reflected in the decrease in intensity of the eg band in the films which is contrary to the observation. Thus, it can be concluded that the films remain in the low spin state. The intensity of the t2g band on the other hand showed a systematic increase from bulk compound to S2 to S1. The increment in unoccupied density of states of the t2g can arise due to spin state variation or charge transfer. As mentioned above the possibility of high spin state is ruled out, thus charge transfer between metal ion (Ru t2g) and oxygen ligand (O 2p) is the only remaining possibility. The effect of charge transfer is not merely reforming the nominal charges of the metal ions but complete change in the crystal field produced by the modified local oxygen environment as observed. It is well known that the charge transfer mechanism requires strong orbital overlapping. In order to probe the orbital overlap and the electronic structure near the Fermi level, the valance band spectra was recorded. In figure 3, the valance band panel presents the resonant photoemission spectra at 52 eV for S1, S2 film and bulk. We observed that the position of the O 2p bands is shifted towards the Ru 4d: t2g band or the Fermi level while the binding energy of the Ru 4d: t2g band remains unaffected in the films when compared to the bulk. This clearly indicates a relative change in the magnitude of the ligand-to-metal charge transfer energy Δ (the energy difference between the O 2p band and Ru 4d: t2g in the conduction band). It is found to be ~7 eV in the bulk compound while ~6 eV in the films. This shows that the O 2p orbitals are strongly modified in thin films. The electronic structure is expected to get affected significantly due to the modifications in Ru 4d and O 2p orbital overlap. In order to probe the changes in electronic structure, we analysed the electronic structure using photoemission spectroscopy. The Ru 4p–4d resonant photoemission spectra of S1 and S2 films along with bulk SRO are measured in the on-resonance (52 eV) and the off-resonance (48 eV) condition at room temperature and is illustrated in figures 4(a)–(c), respectively. We followed the well-established electronic structure of SrRuO3 in literature [30] and assigned the bands. Accordingly, the experimental features observed between ~-4 eV and ~-1 eV are assigned to the Ru 4d band and from ~-8 eV to ~-3 eV are assigned to the O 2p-derived band. A finite density of states of Ru 4d band at the Fermi level (E_F = 0 eV) is observed in both the films and bulk SRO that is expected for a compound with good conductivity.

In the off-resonance condition, the spectrum is only due to the direct photoemission process:

\[
\text{Ru} : 2p^64d^n + h\nu \rightarrow \text{Ru} : 2p^64d^{n-1} + e^- 
\]

whereas, in the on-resonance condition, the spectral features are enhanced due to intra-atomic excitation process or indirect excitation process:

\[
\text{Ru} : 2p^64d^n + h\nu \rightarrow [2p^53d^{n+1}]^+ \rightarrow \text{Ru} : 2p^54d^{n-1} + e^- .
\]

We subtracted the valence band spectra recorded in off-resonance condition from the valance band spectra recorded in off-resonance condition, to deduce the direct contribution of the Ru 4d derived states in the valence band. Such subtracted spectra contains positive and negative contributions as shown in the bottom panel of the figure 4. The positive contributions originate from the Ru 4d component due to the resonant enhancement. On the other hand the O 2p cross section decreases when going from hv = 48 eV to hv = 52 eV photon energy resulting in negative contributions of the derived states in the subtracted spectra. It transpires that the distribution of Ru derived states are different in S1, S2 films and bulk.

Figure 4 suggests that Ru derived states contribute prominently to the entire VBS in the S1 film, while its prominence is limited to the binding energy range of 1–7 eV for the S2 film and bulk.

A careful observation of this figure suggests that the Ru 4d t2g band is broader in S1 and S2 films when compared to that in bulk. The photoemission intensity around E_F is also weaker in the films than in the bulk. A direct visual evidences of these inferences are provided in the inset of figure 3, where the valence band spectra of the three samples near E_F is projected in a zoomed condition. The broadening of the d band and decrease in the density of states at E_F is considered as a hallmark of the presence of spin–orbit interactions [35, 36].

The presence of spin–orbit interactions in the films give clue about the enhanced magnetic moment observed in films. As the spin state transition is ruled out, the only possibility for enhancement in the magnetic moment is the contribution from the orbital moment. Generally, orbital moment is fully quenched in all the d-transition metal ions. However, when the
spin–orbit coupling is strong, it disrupts the orbitals quenching. The signatures of the charge transfer observed in the XAS spectra collected at O K-edge also provides an evidence of the presence of spin–orbit coupling in the system. In order to estimate quantitatively, the spin–orbit coupling present in the system, XAS at the M_{2,3} edges of the Ru^{4+} ions is carried out and is presented in figure 5. Van der Laan and Thole [37–39] showed that the intensity ratio of the white line features at L_{2,3} or M_{2,3} edges of the respective transition metal ion is directly proportional to the expectation value of the spin–orbit operator \langle \mathbf{L} \cdot \mathbf{S} \rangle = \sum_i (l_i S_i). This method was successfully used in quantitative analysis of the spin–orbit coupling in iridium-based 5d compounds [40, 41]. The intensity ratio I(M_1)/I(M_2) = BR is defined as the branching ratio, where I(M_{1,2}) is the integrated intensity of the white line feature at the respective absorption edge [36, 37, 42, 43]. The expectation value of the spin–orbit operator \langle \mathbf{L} \cdot \mathbf{S} \rangle is related with the branching ratio by the expression: BR = (2 + r)/(1 − r), where r = \langle \mathbf{L} \cdot \mathbf{S} \rangle/\langle m_h \rangle and \langle m_h \rangle refers to the average number of 4d holes which is taken as 5.2 as estimated by detailed cluster calculations [22, 34]. The value of \langle \mathbf{L} \cdot \mathbf{S} \rangle is expressed in units of [(h/2\pi)^2]. According to Van der Laan and Thole, a large \langle \mathbf{L} \cdot \mathbf{S} \rangle does imply the presence of strong spin–orbit coupling effects, however, the converse is not necessarily true. When the orbitals are fully quenched, the spin–orbit coupling strength is nearly zero giving the statistical average value of 2 for the BR, while when the spin–orbit coupling is large the BR is expected to show higher values. The white line was fitted by taking an arc tangent function for background contribution along with a Gaussian function following the method described in [36]. The fitting of the S1, S2 and bulk is presented in figures 5(a)–(c). The values thus obtained were used to calculate the BR which resulted in 2.7, 2.2 and 2.0 for S1, S2 and bulk SRO, respectively. It is noted that the value of the BR is significantly higher than the average statistical value of 2 in film S1 confirming presence of strong spin–orbit coupling. This explains the de-quenching of the orbitals resulting in enhanced magnetic moment in the S1 film.

X-ray magnetic circular dichroism spectroscopy was performed to detect substantial orbital moment which will essentially arise as an effect of the de-quenching of the 4d orbitals. We collected the XAS spectra at Ru M_{2,3} edges of S1 film under magnetic field of \pm 1.2 T (\sigma^+ and \sigma^-) using a constant helicity of the incident photon beam at 110 K. Figure 6(a) shows the averaged XAS spectra collected under 1.2 T magnetic field in opposite directions and figure 6(b) shows the corresponding XMCD signal.

By using the sum rules [44, 45], the orbital (m_o) and spin magnetic moments (m_s) per Ru ion in S1 film were deduced. Following equations were used to deduce the m_o and m_s:

\[ m_o = - \left( \frac{4}{3} \right) \left\{ \int_{E_2} \cdot (\sigma^+ - \sigma^-) \, dE - \int_{E_3} \cdot (\sigma^+ + \sigma^-) \, dE \right\} \times N_h \]

\[ m_s = \langle T_2 \rangle = - \left\{ \frac{6 \int_{E_3} \cdot (\sigma^+ - \sigma^-) \, dE - 4 \int_{E_2} \cdot (\sigma^+ + \sigma^-) \, dE}{\int_{E_2,3} \cdot (\sigma^+ + \sigma^-) \, dE} \right\} \times N_h. \]

For ions with octahedral symmetry, the magnetic dipole moment T_2 is very small when compared to m_o and hence can be neglected [46]. Here, N_h is the effective number of holes in the 4d shell which is taken as 5.2 [22, 34].

This resulted in \( m_o = 0.5 \mu_B/\text{Ru} \) and \( m_s = 1.2 \mu_B/\text{Ru} \). The \( M–H \) data was also collected at 110 K in out of plane direction (figure 6(c)) in order to facilitate comparison with the MCD results. This gave a magnetization value of 1.77 \pm 0.06 \mu_B/Ru. This is a direct evidence of the presence of significant orbital contribution in S1 film. The presence of significant contribution of the orbital magnetic moment in SrRuO_3 thin films was reported previously by Grutter et al [20] and by Kan et al [47] using XMCD measurements at the Ru M_{2,3} edges. On the other hand the XMCD studies on Ca_{1-x}Sr_xRuO_3 bulk compounds found negligible contribution of the orbital moment [48]. The observed substantial orbital moment in the S1 film is arising from the de-quenching of the 4d orbitals which stabilizes the spin–orbit coupling.

The results of the XAS and VBS studies clearly points out that the modification in the hybridization of the Ru 4d and O 2p band in S1 compared to bulk compound is responsible for the enhancement in the spin–orbit coupling. It is known that the degree of hybridization of the Ru 4d and O 2p bands is directly linked with the tilt and rotation of the RuO_6 octahedra. Raman spectroscopy is a useful tool to probe the rotation of the RuO_6 octahedra and has been used previously in perovskites to probe
the degree of rotation of the oxygen octahedra [49]. Therefore, we carried out temperature dependent Raman spectroscopy studies on both the films across magnetic ordering temperature. The Raman spectra of the films (figure 7(a)) matched with the previous report and the character of the modes were identified using [50].

We have fitted Raman spectra by using Lorentzian functions and deduced the Raman mode intensity. According to theoretical calculations, the Ag(3) Raman mode corresponds to the in-phase y-rotation of the oxygen octahedra while Ag(2) mode is not associated with the octahedra. Therefore, the intensity ratio Ag(3)/Ag(2) is a hallmark of the modification in the rotational degree of octahedra due to temperature variation. The normalized intensity of the Ag(3) mode is plotted as a function of temperature in figures 7(b) and (c) for film S1 and S2 respectively. Interestingly, the intensity of this mode show a sudden jump at ~150 K in S1 film, a temperature where ferromagnetic order sets in (see figure S2 in supplementary material for magnetization vs temperature curve). On the other hand the intensity showed monotonous increase with decreasing temperature for S2 film. This provides a direct evidence that the hybridization of the Ru 4d and O 2p is strong and the oxygen octahedral rotation is getting significantly altered in S1 due to magnetic ordering.

The mechanism responsible for the enhancement of the spin–orbit coupling stimulating de-quenching of the orbitals is presented in a schematic (figure 8). In bulk compound, where the oxygen octahedral are arranged in a regular manner, the axial d-orbitals of the Ru ions (dx^2−y^2 and dz^2) are strongly hybridized with oxygen axial orbitals (px, py and pz) leading to strong σ-bond (left panel of figure 8) which is responsible for the orbital quenching.

On the other hand in films that possess large local strain inhomogeneity (as in S1 film in present case) the situation is different. In this case, the oxygen octahedra are locally distorted in order to accommodate locally fluctuating strain state, leading to irregular tilts and rotations of the oxygen octahedra. This leads to reduction in the strength of the σ-bond and increase in the strength of the π-bond resulting in partial de-quenching of the orbital moment. In this schematic we have shown isotropic picture however, in unquenched orbital case,
the 4d orbitals can be represented as mixed orbitals as given in [51, 52] for Ca$_2$RuO$_4$. It is known that SrRuO$_3$ exhibits significant magneto-structural coupling and our study provides a strong evidence of it.

4. Conclusions

Enhanced magnetic moment (3.3 $\mu_B$/Ru$^{4+}$) is demonstrated in the epitaxial film of SrRuO$_3$ grown on LSAT. In previous reports high spin state was attributed for the enhanced magnetic moment. In contrast, our results provide an evidence of low spin state and contribution of orbital angular moment responsible for the enhancement in the magnetic moment. As a rare experimental evidence the de-quenching of the orbital angular momentum is demonstrated in 4d transition metal oxide. The strong spin–orbit coupling introduces the dequenching of the orbitals in this system. The strain disorder also modifies other magnetic properties like coercivity apart from the enhanced magnetic moment without disturbing the itinerant character of the films which has many applications.

Acknowledgments

We would like to thank Dr S R Barman for fruitful discussions and suggestions. Dr R J Choudhary is acknowledged for magnetization measurements. Mr Avinash Wadikar and Mr Rakesh Kumar are gratefully acknowledged for their help in recording XMCD data.

ORCID iDs

V G Sathe https://orcid.org/0000-0002-7743-8321
Gaurav Sharma https://orcid.org/0000-0002-0573-9416

References

[1] Randall J J and Ward R 1959 J. Am. Chem. Soc. 81 2629
[2] Koster G, Klein L, Siemons W, Rijnders G, Dodge J S Eom C B, Blank D H A and Beasley M R 2012 Rev. Mod. Phys. 84 253
[3] Eom C B, Vandover R B, Phillips J M, Werder D J, Marshall J H, Chen C H, Cava R J, Fleming R M and Fork D K 1995 Appl. Phys. Lett. 63 2570
[4] Mieville L, Worledge D, Geballe T H, Contreras R and Char K 1998 Appl. Phys. Lett. 73 1736
[5] Worledge D C and Geballe T H 2000 Phys. Rev. Lett. 85 5182
[6] Takahashi K S, Sawa A, Ishii Y, Akoh H, Kawasaki M and Tokura Y 2003 Phys. Rev. B 67 094413
[7] Mackenzie A P, Reiner J W, Tyler A W, Galvin L M, Julian S R, Beasley M R, Geballe T H and Apitulnik A 1998 Phys. Rev. B 58 R13–318
[8] Klein L, Dodge J S, Ahn C H, Snyder G J, Geballe T H, Beasley M R and Kapitulnik A 1996 Phys. Rev. Lett. 77 2774
[9] Klein L, Dodge J S, Geballe T H, Kapitulnik A, Marshall A F, Antognazza L and Char K 1995 Appl. Phys. Lett. 66 2427
[10] Choi K J, Baek S H, Jung H W, Beikeny L J, Lyubchenko M and Eom C B 2010 Adv. Mater. 22 759
[11] Maria J P, McKinstry H L and Trollet-McKinstry S 2000 Appl. Phys. Lett. 76 23
[12] Lee B W, Jung C U, Kawasaki M and Tokura Y 2008 J. Appl. Phys. 104 103909
[13] Gan Q, Rao R A, Eom C B, Garrett J L and Lee M 1998 J. Appl. Phys. Lett. 72 8
[14] Grutter A J, Wong F, Arenholz E, Liberati M and Suzuki Y 2010 J. Appl. Phys. 107 09E138
[15] Toyoda D, Ohkubo I, Kumiagaara H and Oshima M 2005 Appl. Phys. Lett. 87 162508
[16] Chang Y J, Kim C H, Phark S H, Kim Y S, Yu J and Noh T W 2009 Phys. Rev. Lett. 103 057201
[17] Gupta K, Mandal B and Mahadevan P 2014 Phys. Rev. B 90 125109
[18] Autieri C 2016 J. Phys. Condens. Matter 28 426004
[19] Bohra M C, Wu P, Yeh H J, Cheng Y H, Peng C C and Chou H 2011 J. Appl. Phys. 109 07D728
[20] Grutter A J, Wong F J, Arenholz E, Vailionis A and Suzuki Y 2012 Phys. Rev. B 85 134429
[21] Lee B, Kwon O-U, Shin R H, Jo W and Jung C U 2014 Nanoscale Res. Lett. 9 8
[22] Agrestini S et al 2015 Phys. Rev. B 91 075127
[23] Ning X K, Wang Z J and Zhang Z D 2015 J. Appl. Phys. 117 093907
[24] Grutter A J, Wong F J, Jenkins C A, Arenholz E, Vailionis A and Suzuki Y 2013 Phys. Rev. B 88 214410
[25] Bushmeleva S N, Pomjakushin V Y, Pomjakushina E V, Sheptyakov D V and Balagurov A M 2006 J. Magn. Magn. Mater. 305 491
[26] Kanbayasi A 1976 J. Phys. Soc. Japan 41 1876
[27] Kumar P S A, Joy P A and Date S K 1999 Physica B 269 356
[28] Phase D M, Gupta M, Potdar S, Behera L, Sah R and Gupta A 2012 J. Alloys Compd. 577 25–8
[29] Phase D M, Panchal G, Ravat R, Tiwari S, Prakash R, Jain D and Choudhary R J 2019 J. Magn. Magn. Mater. 48 296
[30] Kolesnik S, Yoo Y Z, Chmaissem O, Dabrowski B, Maxwell T, Kimball C W and Genis A P 2006 J. Appl. Phys. 99 08F501
[31] Abbate M, Zampieri G, Okamoto J, Fujimori A, Kawasumi S, Takeshita T, Kimball C W and Apitulnik A 2006 Adv. Mater. 18 269
[32] Abbate M, Zampieri G, Okamoto J, Fujimori A, Kawasumi S, Takeshita T, Kimball C W and Apitulnik A 2006 Adv. Mater. 18 269
[33] Phase D M, Gupta M, Potdar S, Behera L, Sah R and Gupta A 2012 J. Alloys Compd. 577 25–8
[34] Phase D M, Panchal G, Ravat R, Tiwari S, Prakash R, Jain D and Choudhary R J 2019 J. Magn. Magn. Mater. 48 296
[35] Kolesnik S, Yoo Y Z, Chmaissem O, Dabrowski B, Maxwell T, Kimball C W and Genis A P 2006 J. Appl. Phys. 99 08F501
[36] Abbate M, Zampieri G, Okamoto J, Fujimori A, Kawasumi S, Takeshita T, Kimball C W and Apitulnik A 2006 Adv. Mater. 18 269
[37] Abbate M, Zampieri G, Okamoto J, Fujimori A, Kawasumi S, Takeshita T, Kimball C W and Apitulnik A 2006 Adv. Mater. 18 269
[38] Phase D M, Panchal G, Ravat R, Tiwari S, Prakash R, Jain D and Choudhary R J 2019 J. Magn. Magn. Mater. 48 296
[39] Kolesnik S, Yoo Y Z, Chmaissem O, Dabrowski B, Maxwell T, Kimball C W and Genis A P 2006 J. Appl. Phys. 99 08F501

Figure 8. Schematic showing modifications in the hybridization of Ru 4d and O 2p orbitals due to strain disorder leading to disruption in the orbital quenching.
[40] Clancy J P, Chen N, Kim C Y, Chen W F, Plumb K W, Jeon B C, Noh T W and Kim Y 2012 J. Phys. Rev. B 86 195131
[41] Laguna-Marco M A, Haskel D, Souza-Neto N, Lang J C, Krishnamurthy V V, Chikara S, Cao G and van Veenendaal M 2010 Phys. Rev. Lett. 105 216407
[42] Cho D-Y, Park J, Yu J and Park J-G 2012 J. Phys.: Condens. Matter 24 055503
[43] Chapon L C and Lovesey S W 2011 J. Phys.: Condens. Matter 23 252201
[44] Thole B T, Carra P, Sette F and van der Laan G 1992 Phys. Rev. Lett. 68 1943–6
[45] Chen C T, Idzerda Y U, Lin H-J, Smith N V, Meigs G, Chaban E, Ho G H, Pellegrin E and Sette F 1995 Phys. Rev. Lett. 75 152–5
[46] Teramura Y, Tanaka A and Jo T 1996 J. Phys. Soc. Japan 65 1053
[47] Kan D, Mizumaki M, Nishimura T and Shimakawa Y 2016 Phys. Rev. B 94 214420
[48] Okamoto J et al 2007 Phys. Rev. B 76 184441
[49] Iliev M N, Abrashev M V, Laverdière J, Jandl S, Gospodinov M M, Wang Y-Q and Sun Y-Y 2006 Phys. Rev. B 73 064302
[50] Iliev M N, Litvinchuk A P, Lee H-G, Chen C L, Dezaneti M L, Chu C W, Ivanov V G, Abrashev M V and Popov V N 1999 Phys. Rev. B 59 3393
[51] Das L et al 2018 Phys. Rev. X 8 011048
[52] Jain A et al 2017 Nat. Phys. 13 633–7