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THEORETICAL AND EXPERIMENTAL STUDY OF NON-STOICHIOMETRIC $SrRuO_3$: A ROLE OF OXYGEN VACANCIES IN ELECTRON CORRELATION EFFECTS

Š. Masys [a*], V. Jonauskas [a], S. Grebinskij [b], S. Mickevičius [b], V. Pakštas [b], and M. Senulis [b]

[a] *Institute of Theoretical Physics and Astronomy, Vilnius University, A. Goštauto 12, LT-01108 Vilnius, Lithuania*
E-mail: sarunas.masys@tfai.vu.lt
[b] *State Scientific Research Institute Center for Physical Sciences and Technology, A. Goštauto 11, LT-01108 Vilnius, Lithuania*

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We present a theoretical and experimental study of the electronic structure of $SrRuO_3$ after introduction of vacancies. Theoretically, the modeling of non-stoichiometric variations of $SrRuO_3$ was performed by removing appropriate atoms or their combinations, whereas in the experiments the annealing treatment at moderate temperatures in ultra-high vacuum was applied. At comparison of the obtained results allows us to draw an important conclusion that the formation of oxygen vacancies may be closely related to the manifestation of strong correlation effects in $SrRuO_3$.

Keywords: perovskite crystals, density functional theory, ultraviolet photoemission spectroscopy

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1. Introduction

Strontium ruthenate $SrRuO_3$ is a metallic perovskite oxide of extraordinary scientific interest. The compound's resistance to many chemical solutions, outstanding electrical and magnetic properties, good thermal conductivity, and low lattice mismatch with various functional perovskite oxides makes its use highly appealing in technological applications such as oxide electronics and spintronics [1–6].

Although about 1000 papers spanning the physics, materials science, and applications of $SrRuO_3$ have been published over the last two decades [1], a comprehensive understanding of this perovskite is still lacking. One of the most important issues in the physics of $SrRuO_3$ is its degree of electron correlation and what factors control it. Having in mind that a highly extended nature of 4d orbitals is common for transition metal oxides, one would naturally expect a weak manifestation of correlation effects in $SrRuO_3$. However, in the literature there are some studies indicating the presence of strong electron correlation [7–9] based on the observation of the incoherent part of the spectrum dominating over the coherent one. It is widely assumed that the coherent feature at the Fermi level (E_F) essentially represents the extended states of Ru 4d orbitals, whereas the incoherent feature at ~1.2−1.5 eV should be attributed to the presence of the localized electronic states and therefore taken as direct evidence of the existence of strong correlation effects.

In a recent paper [10], we have revealed that a shift in the spectral weight towards the incoherent Ru 4d peak may strongly depend on experimental data handling techniques and/or relevant preparation of the samples. The obtained data allowed us to conclude that $SrRuO_3$ is a weakly correlated material. By claiming this, we would like to continue our efforts in trying to understand what can possibly induce the change of the degree of electron correlation in $SrRuO_3$. As it was summarized by Koster et al. [1], the question of correlation effects can be related to the systematic investigation of the influence of thin film thickness, strain, and stoichiometry. Indeed, Toyota et al. [11] have shown that the electronic structure of $SrRuO_3$ highly depends on thin film thickness with the sharp peak in the vicinity of E_F occurring only at the sample thickness of 15 monolayers. Vailionis et al. [12] have demonstrated that the increase in tensile strain forces a thin film to undergo a room temperature phase transition strongly affecting the electronic and magnetic properties of $SrRuO_3$. Siemons et al. [13] have revealed that the intensity of the coherent peak is much more pronounced in stoichiometric specimens compared to non-stoichiometric ones, whereas Rondinelli et al. [6] have pointed out that electronic behaviour of $SrRuO_3$ thin films might be influenced by defects formed during the film deposition process.

As vacancies and their complexes – the dominant point defects in most perovskites – are directly related to the variation in stoichiometry, we have decided to concentrate on this line of investigation from both theoretical as well as experimental point of view. According to the scheme suggested by Shin et al. [2], experimentally vacancies might be introduced by annealing the air-exposed samples at moderate temperatures, since this process causes the desorption of SrO, Ru, O_2, and CO_2. We have performed the resonant ultraviolet photoemission spectroscopy (UPS) measurements of the annealed specimens and compared the obtained data to the theoretical calculations. Such a comparison allows us to draw an important conclusion on the stoichiometry-dependent nature of correlation effects in $SrRuO_3$.

2. Computational details

In this work, the theoretical calculations were carried out using the CRYSTAL06 code [14] with the initial structural parameters of the orthorhombic Pnma space group of $SrRuO_3$ taken from a neutron diffraction study [15]. A parallelized version of CRYSTAL06 was launched on a 8 core/16 thread workstation with the dual Intel Xeon E5620 processor running at 2.4 GHz and overall possessing 96 GB of RAM memory. Due to a highly extended nature of Ru 4d orbitals, we have applied the density functional theory (DFT) with the local density approximation proposed by Perdew and Zunger [16]. As for the modelling of vacancies, they were introduced by removing appropriate atoms or their combinations from the fully relaxed structure of $SrRuO_3$. Concerning the basis set, small-core Hay–Wadt pseudopotentials [17] (PPs) were adopted for the description of the inner-shell electrons ($1s^22s^22p^63s^23p^63d^{10}$) for both Sr and Ru atoms. The valence functions for Ru ($4s^24p^64d^75s^1$) were taken from the modifed LANL2DZ basis set [18] (also available at EMSL database [19]) and optimized in order to avoid numerical problems usually caused by too diffuse valence functions overlapping with the core functions of the neighbouring atoms in the densely packed solids. The optimization procedure was based on an attempt to minimize the total energy per unit cell while varying the outermost exponents of the adopted functions. The lattice constants and atomic positions remained fixed at experimental values. For the Sr atom, the already optimized valence part of the basis set ($4s^24p^65s^2$) was applied from the strontium titanate study [20]. For the O atom, the all-electron basis set was employed from the calcium carbonate study [21]. The reciprocal-space integration was performed with the shrinking factor of 8 that corresponds to 125–260 independent *k* points in the irreducible Brillouin zone for $SrRuO_3$ and its non-stoichiometric variations. In order to improve the self-consistence field convergence, the Kohn–Sham matrix mixing technique [14] together with Broyden's scheme [22] were applied. The default values of truncation criteria for bielectronic integrals were modified to tighter ones by setting the overlap thresholds for exchange and Coulomb integrals to 10^{-9}. The tolerance on change in total energy was set to 10^{-9} hartree.

3. Experiment

A thin $SrRuO_3$ epitaxial film was deposited using reactive DC magnetron sputtering onto monocrystalline (001)-plane oriented $SrTiO_3$ substrate. Sputtering was performed in an Ar and O_2 mixture (1:1) at the pressure around 15 Pa. To prevent the bombardment by high-energy ions during the deposition, $SrTiO_3$ substrate was positioned in "off-axis" configuration at a distance of 15 mm from the symmetry axis of the discharge and 20 mm over the target plane. The temperature of the substrate was set at 600 °C. The thickness of the film was about ~100 nm.

The epitaxy of the film was confirmed by X-ray diffraction (XRD) scans. θ–2θ patterns were measured using the Rigaku SmartLab X-ray diffractometer equipped with a 9 kW rotating Cu anode X-ray tube. High resolution XRD optics consisted of a multilayer X-ray mirror combined with a four-bounce Ge (220) monochromator. The sample was kept in horizontal position. θ–2θ scans showed a single phase and only the (00*l*) peaks of the $SrRuO_3$ thin film were observed. The full width at half maximum (FWHM) of Gaussian-like rocking curves of the (002) peak of the film was 0.05° (FWHM of the substrate was 0.03°). The temperature dependence of DC resistivity was obtained by a four-probe method. The estimated Curie temperature T_C was about 145 K. A more thorough analysis on the quality of the grown sample can be found elsewhere [10].

The initial thin film surface was prepared by relatively low ($T \approx 200$ °C) heating under ultra-high vacuum (UHV) conditions ($P \sim 10^{-10}$ Torr) in order to remove the adsorbed surface contaminants. Then the sample was gradually annealed up to 400 °C by applying DC resistance heating. The temperature was measured with the optical pyrometer and the completion of the sample degassing process was checked by controlling the UHV system pressure. Finally, the $SrRuO_3$ thin film was sputtered with the Ar^+ ion beam for a full destruction of the surface.

Resonant UPS measurements were carried out in the synchrotron radiation laboratory HASYLAB, Hamburg (Germany). Synchrotron radiation obtained from the storage ring DORIS III was monochromatized with the FLIPPER II plane grating vacuum monochromator designed for the photon energy range of 15–200 eV. The spectrometer was equipped with a cylindrical mirror electron energy analyser. The total energy resolution was kept at 0.1 eV. The UPS experiments were done at the normal emission angle, allowing a large solid angle acceptance, which corresponds to an angle-integrated density of states (DOS). The base pressure during UPS measurements was 10^{-10} Torr. To compare our experimental spectra with the theoretical band-structure calculations, inelastic backgrounds were removed using the Shirley method [23]. The origin of the energy axis was set at the Fermi level as measured for a reference metallic sample.

4. Results and discussion

A set of $SrRuO_3$ valence band (VB) spectra for the photon energy near Ru 4p → 4d resonance ($h\nu = 60$ eV) and antiresonance ($h\nu = 46$ eV) conditions [10] measured after the appliance of different thin film treatment are shown in Fig. 1. All spectra were normalized to the intensity of con-

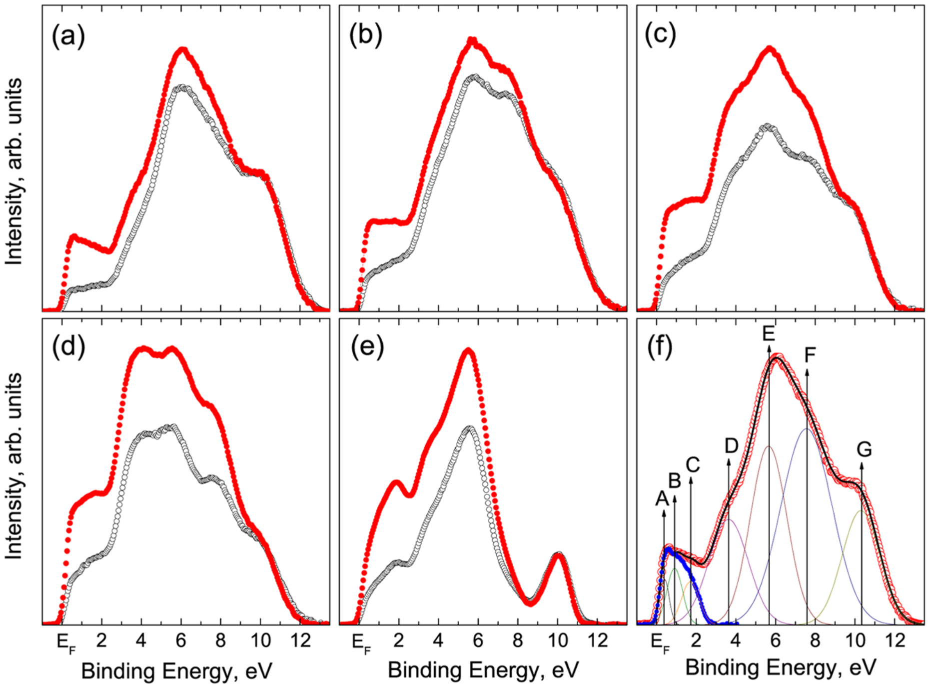

Fig. 1. VB spectra of $SrRuO_3$ thin film measured near resonance ($h\nu = 60$ eV, filled circles) and antiresonance ($h\nu = 46$ eV, open circles) after annealing in ultra-high vacuum at (a) 200 °C, (b) 250 °C, (c) 300 °C, (d) 400 °C, and (e) argon sputtering; (f) demonstrates an example of VB spectrum fitting for the thin film annealed at 200 °C ($h\nu = 60$ eV). Open circles correspond to the raw data, the thick line is the spectral envelope, thin lines are the spectral components, and filled circles represent the Ru 4d region (see the text).

taminant carbon monoxide peak [8, 24] centred at ~10 eV. Our theoretical band-structure calculations for stoichiometric $SrRuO_3$, presented in Fig. 2, reveal that the features located between E_F and ~2.5 eV may be mainly attributed to the Ru 4d states, whereas the structures at higher binding energies may be largely assigned to the O 2p states. The relative variation of VB spectra measured at resonance and antiresonance conditions is much higher for the Ru 4d region compared to the O 2p region, confirming that Ru 4d states dominate at low (<2.5 eV) binding energies. Therefore, we concentrate our attention on this binding energy region.

By comparing VB spectra presented in Fig. 1(a–d), one can notice that the sharpness of the feature in the vicinity of E_F gradually decreases with increasing annealing temperature, qualitatively indicating that the intensity of the coherent peak at E_F decreases with increasing deviation in stoichiometry [2]. It is also seen that the decrease of the coherent feature is accompanied by the formation of the broad structure at higher binding energies. The shape of VB spectra drastically changes after Ar^+ sputtering (see Fig. 1(e)) revealing the radical reconstruction of the electronic structure at the surface.

In order to perform a semi-quantitative analysis, VB spectra were fitted with seven Gaussian peaks marked by A, B, C, D, E, F, and G (see Fig. 1(f)). Peaks A, B, and C at binding energies of 0.4, 0.92, and 1.7 eV, respectively, approximately represent the dominant Ru 4d region, while peaks D, E, and F at binding energies of 3.6, 5.6, and 7.6 eV, respectively, correspond to the 2p region. The last feature G located at 10.2 eV is due to the contaminations. It should be noted that even at Ru 4p → 4d resonance peaks A, B, and C representing Ru 4d states contain a small but finite admixture of the O 2p states, thus the ratio of the peak intensities (see Fig. 3) only provide a rough semi-quantitative picture of the evolution of different Ru 4d spectral components under heat and sputtering treatment. According to our band-structure calculations (Fig. 2), the sharp peak A (FWHM = 0.55 eV) in the vicinity of E_F may be assigned to the coherent part of the spectral function. The broader peak B (FWHM = 0.93 eV) may be recognized as the incoherent part of the spectral function [25, 26], not present in DFT calculations, whereas the broadest peak C (FWHM = 1.1 eV) may be attributed to the tail of asymmetric shape of the coherent feature and stronger admixture of O 2p states in the dominant Ru 4d region [10].

Figure 3 illustrates the evolution of relative intensities for different spectral components under heat treatment and subsequent argon sputtering. As it could be expected, the relative intensity of

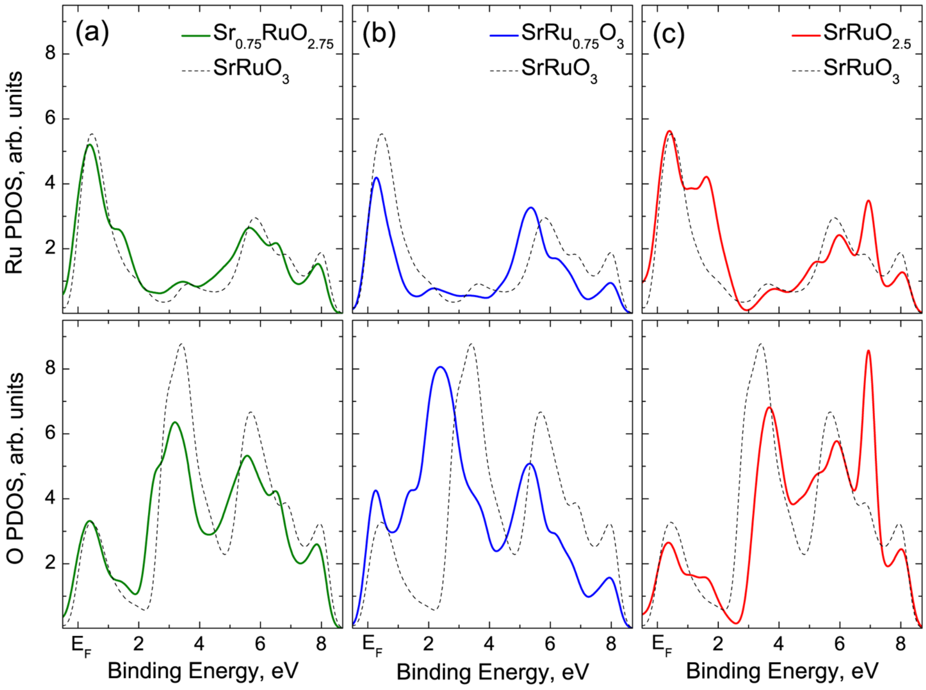

Fig. 2. The PDOS of Ru and O in $SrRuO_3$ after the removal of (a) SrO, (b) Ru, and (c) O_2 atoms.

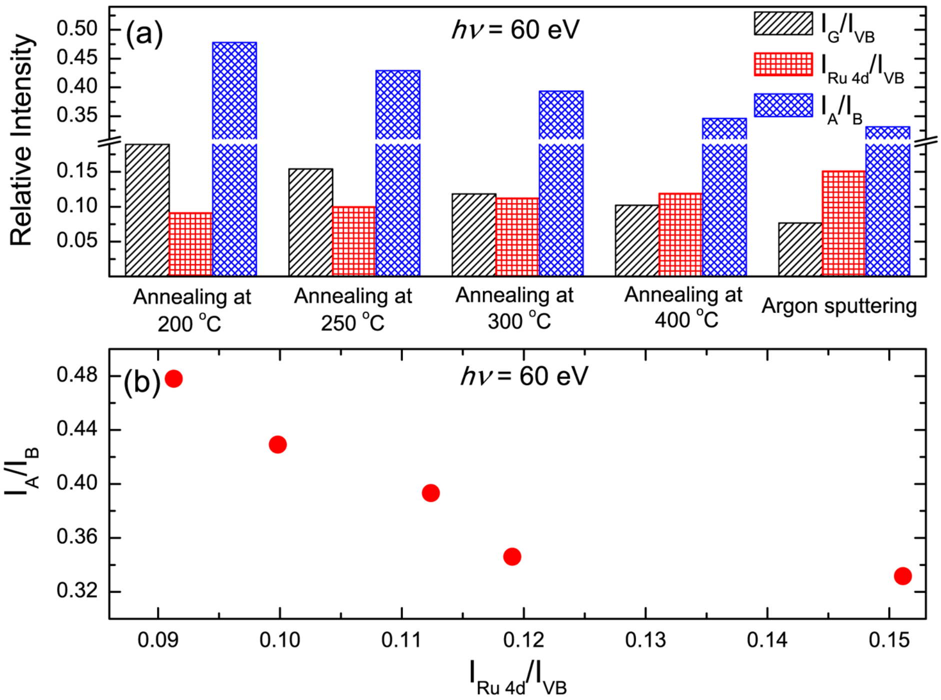

Fig. 3. (a) Evolution of relative intensities for different spectral components under varying thin film treatment. (b) Anticorrelation between the relative intensities of Ru 4d/VB and A/B ratios. Here I_k (k = A..G) corresponds to the intensity of the individual spectral components (see Fig. 1 (f)), $I_{VB} = (I_A + I_B + I_C + I_D + I_E + I_F)$ is the total intensity of ruthenium and oxygen peaks in VB spectra, and $I_{Ru\ 4d} = (I_A + I_B + I_C)$ represents the intensity of the Ru 4d region.

contaminant peak G decreases with increasing annealing temperature indicating that the contamination gases have been removed from the film surface. The opposite trend can be observed for the relative intensity of the Ru 4d region. Having in mind that Sr atoms occupy the negligible part of the spectra [10], one can make an assumption that oxygen vacancies are preferentially formed at the film surface during the heating in vacuum. Such an assumption is enhanced by the experiments of Shin et al. [2], in which the temperature of the initial and relatively small desorption of SrO and Ru is determined to be only ≈350 °C. Moreover, the band-structure calculations shown in Fig. 2 clearly demonstrate that the introduction of SrO or Ru vacancies into the crystalline structure of $SrRuO_3$ does not increase the partial DOS (PDOS) of the Ru 4d region. An increase of Ru PDOS at the incoherent peak position is prominent when O_2 vacancies are formed. Finally, the strong anticorrelation between the relative intensity of Ru 4d/VB and A/B ratios presented in Fig. 3(b) apparently confirms that the oxygen vacancies are responsible for the increase of the concentration of the incoherent states. Therefore, remembering the main purpose of our work, we can claim that the manifestation of strong correlation effects in $SrRuO_3$ may be closely related to the formation of oxygen vacancies during the growth and/or cleaning process of the samples.

5. Conclusions

In this paper, the effect of the introduction of vacancies into the structure of $SrRuO_3$ was studied theoretically and experimentally by means of DFT approach and resonant UPS. It was shown that the thin film heating at moderate temperatures in ultra-high vacuum evokes the formation of oxygen vacancies which in turn are responsible for the decrease of the coherent Ru 4d peak at E_F accompanied by the increase of the incoherent part of the spectrum. Having in mind that the ratio of the coherent and incoherent spectral components is usually taken as a measure of the strength of correlation effects in $SrRuO_3$, we can conclude that oxygen vacancies may be highly responsible for the manifestation of strong electron correlations in this perovskite-type material.

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TEORINIS IR EKSPERIMENTINIS NESTECHIOMETRINIO $SrRuO_3$ TYRIMAS: DEGUONIES VAKANSIJŲ ĮTAKA ELEKTRONŲ KORELIACIJAI

Š. Masys [a], V. Jonauskas [a], S. Grebinskij [b], S. Mickevičius [b], V. Pakštas [b], M. Senulis [b]

[a] *Vilniaus universiteto Teorinės fizikos ir astronomijos institutas, Vilnius, Lietuva*

[b] *Fizinių ir technologijos mokslų centro Puslaidininkių fizikos institutas, Vilnius, Lietuva*

Santrauka

Perovskitinis kristalas $SrRuO_3$ tyrėjus domina dėl puikių elektrinių ir magnetinių savybių, didelio atsparumo įvairių reakcijų terpėse, gero šiluminio laidumo ir išskirtinio struktūrinio suderinamumo su įvairiais funkciniais oksidais. Tai leidžia šį darinį panaudoti kuriant oksidų elektronikos ir spintronikos pagrindu veikiančius prietaisus.

Vienas iš svarbiausių klausimų, į kuriuos bandoma atsakyti tyrinėjant $SrRuO_3$ elektroninę sandarą, yra elektronų koreliacijos stipris šioje medžiagoje. Literatūroje galima rasti darbų, kuriuose teigiama, jog $SrRuO_3$ elektronų koreliacija yra stipri. Tačiau yra ir tokių darbų, kuriuose pateikiama priešinga nuomonė. Remdamiesi ankstesniais savo tyrimais, įrodančiais silpnai koreliuotą $SrRuO_3$ elektronų prigimtį, mes bandome atsakyti, kas gali sukelti elektronų koreliacijos stiprio pokytį. Teoriškai mes modeliuojame SrO, Ru ir O_2 vakansijų suformavimą $SrRuO_3$ kristalinėje struktūroje tankio funkcionalo teorijos artinio rėmuose. Eksperimentiškai vakansijos yra sukuriamos kaitinant plonųjų $SrRuO_3$ plėvelių bandinius vakuume. Teorinių ir eksperimentinių rezultatų palyginimas rodo, jog elektronų koreliacijos stiprio padidėjimą gali lemti deguonies vakansijų susidarymas bandinių auginimo arba paruošimo matavimams metu.