



## Research articles

# Half-metallic ferromagnetism and metal–insulator transition in Sn-doped SrRuO<sub>3</sub> perovskite oxides

Namwook Kim<sup>a</sup>, Rokyeon Kim<sup>b</sup>, Jaejun Yu<sup>c,\*</sup>

<sup>a</sup> Computational Science Interdisciplinary Program, Seoul National University, Seoul 08826, Republic of Korea

<sup>b</sup> Center for Correlated Electron Systems, Institute for Basic Science, Seoul 08826, Republic of Korea

<sup>c</sup> Center for Theoretical Physics, Department of Physics and Astronomy, Seoul National University, Seoul 08826, Republic of Korea



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## ABSTRACT

We investigate the electronic and magnetic properties of SrRu<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub> by carrying out density-functional-theory calculations to show that a half-metallic ferromagnetic ground state emerges for the Sn doping of  $x \gtrsim 0.5$ . To examine the effect of on-site Coulomb interactions for the Ru *d* orbitals, which was suggested to enhance the half-metallicity in SrRuO<sub>3</sub>, we employed both the local spin-density approximation (LSDA) as well as the LSDA + *U* method. For all the possible configurations of Sn doping for  $x = 1/8, 1/4, 1/2, 5/8, 3/4,$  and  $7/8$  within the  $2 \times 2 \times 2$  unit cell, we monitor the Ru *t*<sub>2g</sub> bandwidth as well as the valence band maximum in the majority-spin channel and demonstrate that the Ru *d* electron hopping is blocked by the Sn-substituted sites so that the Ru *t*<sub>2g</sub> bandwidth becomes reduced as the doping *x* increases. For  $x < 0.5$ , the valence band maximum still touches the Fermi level so that SrRu<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub> remains as a usual ferromagnetic metal. A further reduction of the Ru *t*<sub>2g</sub> bandwidth for the range of  $0.5 \lesssim x \lesssim 0.7$  turns it into a half-metallic ferromagnet. As for  $x > 0.7$ , the Ru *t*<sub>2g</sub> bandwidth gets so narrow that even a small on-site Coulomb interaction, e.g.,  $U_{\text{eff}} = 1.0$  eV induces a band-gap, which indeed corresponds to a gap of the Ru impurity bands in the SrSnO<sub>3</sub> oxide semiconductor.

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## 1. Introduction

Since the pioneering work on the Mn-based Heusler alloys by de Groot and co-workers [1], half-metallic ferromagnets (HMFs) have attracted considerable interest as a new class of materials with potential applications for its possible memory and spintronic device applications. An ideal half-metal has only one spin channel for conduction, that is, metallic behavior in one spin channel but an insulating gap in the other spin channel. However, while many different HMFs have been suggested, its fabrication has been challenging. Since the experimental verification of half-metallicity remains controversial, there are not many HMF materials other than NiMnSb with enough evidence for its half-metallic ferromagnetism [2]. Despite the controversies and challenges, there have been many theoretical attempts in searching for new half-metallic materials [2,3].

Besides Heusler alloys, perovskite oxides have been considered as a promising class of materials for HMFs. Recent advances in the growth technique of oxide heterostructures have made it possible to manipulate complex electronic structures having both metallic

and insulating characters. One of the first realizations of HMF was in doped manganites like La<sub>0.66</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> and La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>, where the double-exchange mechanism for the doped carrier leads to the half-metallic state and eventually to the colossal magnetoresistance behavior [3,4]. Later, the idea of double-exchange ferromagnetism in manganites was applied to a series of double perovskite structures as a new form of HMFs. The first series of double perovskites like Sr<sub>2</sub>FeMoO<sub>6</sub>, Sr<sub>2</sub>FeReO<sub>6</sub>, Sr<sub>2</sub>CrWO<sub>6</sub>, Sr<sub>2</sub>-CrFeO<sub>3</sub>, and La<sub>2</sub>VMnO<sub>6</sub> were predicted where the B-site magnetic ion is substituted by another magnetic ion so that an ordered double perovskite structure can be stabilized [5–9]. Also suggested were a double doping of both A- and B-sites in La(Sr,Ca,Ba)VRuO<sub>6</sub> [10] as well as the doping of the B-site magnetic ion with non-magnetic ions in Sr<sub>2</sub>Fe(Sn,Ti,Zr)O<sub>6</sub> [11]. Initially, Sr<sub>2</sub>FeMoO<sub>6</sub> was reported to be half-metallic exhibiting intrinsic tunneling-type magnetoresistance at room temperature. However, the half-metallicity of such double perovskite systems turns out to be sensitive to the ordering of anti-ferromagnetic ordered B-site ions, e.g., Fe<sup>3+</sup> and Mo<sup>5+</sup> ions. Even a small amount of disorder can be crucial to the half-metallicity in such double perovskite systems [5].

The idea of double-exchange ferromagnetism for the half-metallicity in double perovskite systems was quite intriguing, but its realization is still hampered by the requirement of the strict

\* Corresponding author.

E-mail address: [jyu@snu.ac.kr](mailto:jyu@snu.ac.kr) (J. Yu).

B-site ordering. As an alternative to the double-exchange idea, here we attempt to find a way of transforming a simple perovskite ferromagnetic metal into half-metal with the substitution of B-site ions. We draw special attention to SrRuO<sub>3</sub> because it is known to be the only ferromagnetic metal ( $T_c \approx 160$  K) among the 4d transition-metal oxides [12–14]. Early on, Katsnelson and co-workers [2] has pointed out that SrRuO<sub>3</sub> has all the ingredients for HMF, where a low-spin state of Ru occurs with the almost full  $t_{2g}$  majority-spin band and the partially filled  $t_{2g}$  minority-spin band. Even there was a theoretical claim of a half-metallic ground state with Jahn–Teller distortion based on the LDA +  $U$  calculation with a large value of  $U$ , [15] but, unfortunately, there has been no experimental report of either Jahn–Teller distortion or half-metallicity [12]. Rondinelli and co-workers made an extensive theoretical investigation on the ground state properties of SrRuO<sub>3</sub> and concluded that the on-site Coulomb interaction parameter  $U_{\text{eff}}$  needs to be set to be larger than 2 eV to achieve the half-metallic ground state in SrRuO<sub>3</sub>, which is inconsistent with the absence of orbital ordering in experiment as well as the theoretical estimation of  $U_{\text{eff}}$  by the self-interaction-correction calculations [16].

On the other hand, there has been an interesting suggestion of inducing the half-metallicity by doping Ti atoms in SrRuO<sub>3</sub>. Following up the experimental observation of a metal–insulator transition in SrRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> ( $x \sim 0.3$ ), which was attributed to both the disorder and on-site Coulomb correlations at the Ru-site, [17,18] a GGA +  $U$  calculation for SrRu<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> has suggested the presence of half-metallic state for  $x > 0.1$  with a metal–insulator transition near  $x \sim 0.65$  [19]. Although the  $U_{\text{eff}}$  parameter used in the calculation was a bit too large to be realistic, [16] it may be considered as a meaningful suggestion for a possible route of doping SrRuO<sub>3</sub> into HMF.

Here we propose the Sn-doped SrRuO<sub>3</sub> perovskite oxide as a candidate material for HMF. SrRuO<sub>3</sub> is one of the most frequently used oxide electrode materials. It has high chemical stability and good thermal properties, which are advantageous for integration with other oxide materials into heterostructures [20]. Because of the similar ionic sizes of Ru<sup>4+</sup> and Sn<sup>4+</sup> ions, the substitution of Ru by Sn atoms in SrRuO<sub>3</sub> is quite feasible. Indeed, it has been demonstrated that the epitaxial Sr(Ru<sub>0.48</sub>Sn<sub>0.52</sub>)O<sub>3</sub> thin film exhibits an excellent lattice match with the (100)-oriented KTaO<sub>3</sub> [21]. At the endpoints of SrRu<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub>, SrRuO<sub>3</sub> is a ferromagnetic metal while SrSnO<sub>3</sub> is a large gap semiconductor with the optical gap of around 4 eV [22,23]. Since the band gap of SrSnO<sub>3</sub> is larger than the Ru  $t_{2g}$  bandwidth of less than 3 eV in SrRuO<sub>3</sub>, the Sn atom at the Ru site is expected to block the hopping of Ru  $d$  electrons effectively. As results, by controlling the amount of doping  $x$  in SrRu<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub>, one can change the Ru  $t_{2g}$  bandwidth which results in a ferromagnetic-metal-to-half-metal transition near  $x \approx 0.5$  and a metal-to-insulator transition as well for  $x > 0.7$ .

## 2. Methods and computational details

To investigate the electronic structure and properties of Sr(Ru<sub>1-x</sub>Sn<sub>x</sub>)O<sub>3</sub> as a function of  $x$ , we carried out density functional theory (DFT) calculations by using the full-potential projected augmented wave method [24] as implemented in the VASP package [25,26] with the local spin-density approximation (LSDA) [27] and the LSDA +  $U$  scheme [28] as well. We adopted the spherically averaged form of the rotationally invariant LSDA +  $U$  introduced by Dudarev and co-workers, [29] where only one parameter  $U_{\text{eff}} = U - J$  is used for the description of effective on-site Coulomb interactions for Ru  $d$  orbitals. In the LSDA +  $U$  calculations, we employed  $U_{\text{eff}} = 1.0$  eV for Ru  $d$  by benchmarking the calculated magnetic ground state against the previous DFT works and experiments [16]. The plane-wave energy cutoff of 520 eV was used and

the Brillouin zone was sampled with a  $10 \times 10 \times 8$  Monkhorst–Pack  $\mathbf{k}$ -point mesh [30] for  $\sqrt{2} \times \sqrt{2} \times 2$  supercell of orthorhombic SrRuO<sub>3</sub> and SrSnO<sub>3</sub> and with  $8 \times 8 \times 6$   $\mathbf{k}$ -points for the  $\sqrt{2} \times \sqrt{2} \times 2$  supercell of Sr(Ru<sub>1-x</sub>Sn<sub>x</sub>)O<sub>3</sub> and with  $6 \times 6 \times 6$   $\mathbf{k}$ -points for the  $2 \times 2 \times 2$  supercell of Sr(Ru<sub>1-x</sub>Sn<sub>x</sub>)O<sub>3</sub>. For each configuration, we obtained optimized lattice structures as well as internal atomic positions through the relaxation steps below 5 meV/Å of the Hellmann–Feynman forces. For the Brillouin-zone integrations, the tetrahedron method with Blöchl corrections [31] was used for the better description of Fermi levels.

## 3. Results

### 3.1. LSDA band structures of Sr(Ru<sub>1-x</sub>Sn<sub>x</sub>)O<sub>3</sub> ( $x = 0.0, 0.25, 0.5, \text{ and } 0.75$ )

Among various 4d transition metal oxides, bulk SrRuO<sub>3</sub> is the only 4d ferromagnetic metal-oxide. Since the 4d electrons are less localized than 3d, SrRuO<sub>3</sub> is considered to be a candidate of Stoner-type band ferromagnetism [14]. The structural optimization of pristine SrRuO<sub>3</sub> within LSDA calculations leads to an orthorhombic GdFeO<sub>3</sub>-type structure with four formula units per cell as shown in Fig. 1. The orthorhombic distortion and the internal positions of atoms are found to be consistent with the previous work [16]. The calculated band structure of SrRuO<sub>3</sub> is a ferromagnetic metal where the Ru  $t_{2g}$  bands crossing the Fermi level in both majority- and minority-spin channels with an exchange split of about 0.25 eV. The main features of band structure are consistent with the previous works [16,32].

The top panel of Fig. 2 illustrates the LSDA results for the projected density-of-states (pDOS) of pristine SrRuO<sub>3</sub>. The valence band is composed mainly of O 2p states hybridized with Ru 4d. The significant presence of Ru 4d  $e_g$  components in the lower region of the valence band between  $-8$  eV and  $-6$  eV below the Fermi level, which is set at  $E_F = 0$  eV, and in the conduction band between 1 eV and 5 eV indicates the strong  $dp\sigma$  hybridization of Ru 4d  $e_g$  and O 2p orbitals. The bands crossing the Fermi level ranging from  $-2$  eV and 1 eV consist of the Ru 4d  $t_{2g}$ -O 2p  $dp\pi$  hybridized orbitals. Since all of the Ru  $t_{2g}$  orbitals form two-dimensional (2D) networks of individual  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals hybridized with the O 2p orbitals in the  $xy$ -,  $yz$ -, and  $zx$ -planes, respectively, the pDOS features of the  $t_{2g}$  bands can be understood in terms of a superposition of 2D tight-binding bands. Consequently, the characters of Van Hove singularities inherent in the 2D band structure contribute to the large peaks in the density of state near the Fermi level, thereby being responsible for the Stoner-type ferromagnetic instability in SrRuO<sub>3</sub> [33].

Now the introduction of a Sn atom into the Ru site plays a role in removing the Ru 4d  $t_{2g}$  orbital states from the site with the Sn substitution. The absence of the pDOS near the Fermi level at the Sn-substituted site is obvious when considering that SrSnO<sub>3</sub> is a large band-gap semiconductor, the band-gap of which is even larger than the Ru  $t_{2g}$  bandwidth of SrRuO<sub>3</sub>. Therefore, the broken passage of the Ru 4d  $t_{2g}$ -O 2p  $dp\pi$  hybridization blocks the hopping of Ru  $t_{2g}$  electrons in the 2D tight-binding bands and, consequently, results in a reduced bandwidth of the Ru  $t_{2g}$  bands for the finite doping  $x$ . Fig. 2 shows the  $x$ -dependence of the pDOS, which affects mostly the bandwidths and positions of the Ru  $t_{2g}$  bands in the majority- and minority-spin channels, respectively. It is interesting to note that, as  $x$  increases, the bandwidth gets narrow significantly and, at the same time, the exchange split between two spin channels becomes enhanced. So the centers of the bands for each spin channel appears to remain almost unchanged. The reduction of the bandwidth, especially in the majority-spin channel causes the majority-spin  $t_{2g}$  band to shift downward relative to the Fermi

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