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# Revealing out of equilibrium hidden phases in $\text{Sr}_3\text{Ru}_2\text{O}_7$ by applying stress

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We predict that the application of biaxial tensile strain uncovers an antiferromagnetic metallic *hidden phase* in  $\text{Sr}_3\text{Ru}_2\text{O}_7$ . By using hybrid density functional theory we applied uniaxial and biaxial strains and identified a variety of phases. We found that tensile strain can reduce by up to half the stress needed to expose hidden phases as compared to the use of uniaxial compressive strain. In addition, our results demonstrate that while elongation and compression of the octahedra induce magnetic phase transitions, tilting of the octahedra leads to a metal-to-insulator transition, indicating that the different hidden phases can be accessed by applying strain.

**PACS numbers:**

## I. INTRODUCTION

The search for hidden phases in complex materials is of significant importance to the materials community, since it could lead to new structures that display fundamentally interesting and technologically desirable properties ranging from high-strength ductile alloys to colossal magnetoresistance and high temperature superconductivity. In fact, hidden phases are key ingredient for understanding materials under extreme environments (e.g., high pressure, temperature, strain, or high magnetic or electric fields) where controlling the behavior of materials driven far from their equilibrium is crucial for their performance under operating conditions. In addition, creating a surface can tip the delicate balance between the structural, charge, orbital, and spin degrees of freedom, thereby offering insights for uncovering possible hidden phases with sought-after properties in their corresponding bulk materials.

Creating a surface in  $\text{Sr}_3\text{Ru}_2\text{O}_7$  breaks the inversion symmetry, which naturally occurs between the two double-octahedral layers. The most prominent effect at the surface is the octahedral tilt and increased rotation [1]. In our previous study we found that electronic and magnetic properties are not coupled with octahedra rotations but tilting of the octahedra produces a less conducting state at the surface [2]. This result lead us to apply uniaxial compressive strain along the [001] direction to force tilting of the octahedra throughout the structure and found two hidden phases. One transition is structural where the  $Bbcb$  structure transforms into the  $Bbmm$  and leads to the emergence of octahedra tilts at 1.5 GPa, while the other involves a ferromagnetic (FM) metallic to antiferromagnetic (AFM) insulator phase transition at 21 GPa.

In this work we investigate the application of in-plane uniaxial and biaxial tensile strains on  $\text{Sr}_3\text{Ru}_2\text{O}_7$ . The study was motivated by our recent results on applying uniaxial compressive strain along the  $c$ -axis where in-plane lattice parameters were progressively expanded ul-

timately yielding to metal-to-insulator (MIT) and magnetic phase transitions [2]. This lead us to the hypothesis that in-plane tensile strain could produce similar phase transitions but at a lower stress. Indeed, tensile strain not only reduces the stress needed to expose hidden phases as compared to uniaxial compressive strain, but it also allowed to uncover an AFM metallic hidden phase. Specifically, by applying tensile strain along the [010] direction the system undergoes the same structural phase transition but at a stress of only 0.6 GPa while the FM metal to AFM insulator transition is predicted at  $\simeq 17$  GPa and the AFM metallic phase at 10 GPa. The induced AFM phase is an AFM A-type state (AFM-A) that is characterized by Ru atoms that are coupled ferromagnetically in-plane and antiferromagnetically out-of-plane in each bilayer of the system (Fig.1c). This AFM configuration is different from the ground-state AFM-I phase found in our previous investigation [3].

$\text{Sr}_3\text{Ru}_2\text{O}_7$  continues to attract high interest due to its wide range of interesting properties and intriguing phases including metamagnetic transitions [4], and quantum critical phenomena [5]. Moreover certain number of parameters including the amount and type of defects and alloying [6–11], pressure [12, 13], temperature [14], or magnetic and electric fields [15] can give access to a wide range of electronic and magnetic properties. This is a consequence of the subtle interplay between charge, lattice, and spin degrees of freedom, which opens the possibility of controlling the properties of this compound. We will show here how applying strain on particular directions provides a way to control the structural properties of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  to induce a variety of phase transitions.

Neutron powder diffraction measurements and convergent-beam electron diffraction experiments on single crystals of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  found an  $Bbcb$  [16, 17] (# 68) orthorhombic space group structure with lattice parameters  $a \simeq b$ . In fact, there is another space group that describes this system as well, the  $Pban$  (# 50) space group [18], which is a super group of the  $Bbcb$  space group. The advantage of using the  $Pban$  space

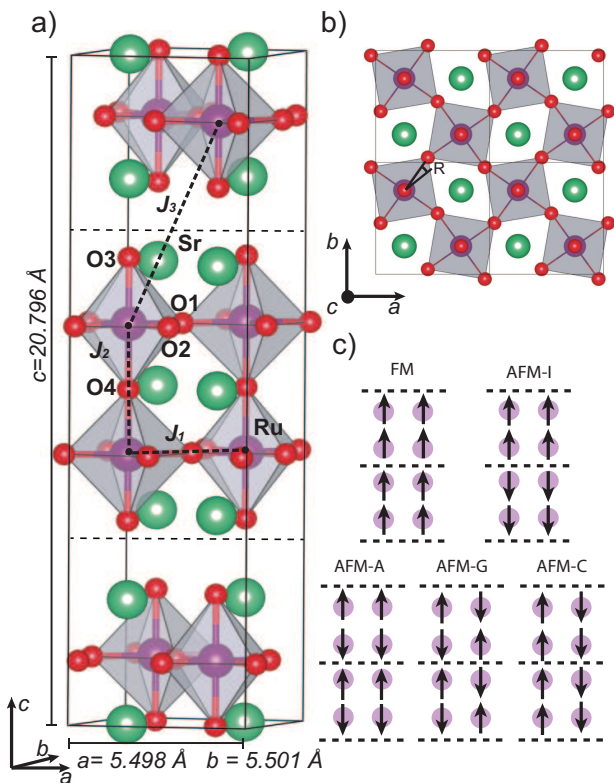


FIG. 1. Side and top views of the orthorhombic  $Bbcb$  structure of  $\text{Sr}_3\text{Ru}_2\text{O}_7$ . The  $\text{RuO}_6$  octahedra are rotated alternately clockwise and counter-clockwise about the  $c$ -axis. Dashed lines delimit the  $\text{Sr}_3\text{Ru}_2\text{O}_7$  bilayer.  $J_1$ ,  $J_2$ , and  $J_3$  are the magnetic couplings studied in this work. O1 and O2 refer to the in-plane oxygens, while O3 and O4 are the two different apical oxygens in the system. b) Top view showing the octahedral rotations. R indicates the rotation angle. c) Relevant magnetic phases studied in this work. The experimental cell parameters displayed in the figure have been extracted from Ref. 16.

group is that a larger number of AFM configurations can be generated for broader investigation of magnetic structures [3]. The bilayered perovskite is formed by two layers of  $\text{RuO}_6$  octahedra connected by sharing one apical oxygen and separated by two  $\text{SrO}$  layers (Fig.1). Each  $\text{RuO}_6$  octahedral is rotated about the  $c$ -axis by  $7.855^\circ$  while neighboring octahedra rotate by the same amount but in the counter clockwise direction [17]. It is important to recall here that in the bulk structure no octahedral tilts are observed.

Our study begins by presenting an extended and more detailed analysis of our previous investigation on uniaxial compressive strain. This allowed us to gain additional understanding of the coupling between degrees of freedom and contributed to support our hypothesis to apply in-plane tensile strain to expose hidden phases at a lower stress. We will show that the magnitude and direction of the strain applied to the system is key to induce different

hidden phases. Finally, a guide for experimentalists in search of hidden phases is provided.

## II. COMPUTATIONAL DETAILS

We have performed first-principles DFT calculations using the CRYSTAL14 computational package [19, 20]. CRYSTAL14 employs atom-centered Gaussian type orbital (GTO) basis sets to build Bloch functions, which are used to expand the one-electron crystalline orbitals. The GTO basis sets for each atom comprising the  $\text{Sr}_3\text{Ru}_2\text{O}_7$  system were taken from Ref. 21. For Ru and Sr, the small-core HayWadt pseudopotentials [22] were adopted for the description of the inner-shell electrons ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ ). The valence functions for Ru were based on the modified LANL2DZ basis [23]:  $4s^2 4p^6 4d^7 5s^1$ , while the  $4s^2 4p^6 5s^2$  was used for Sr. Finally, for O atoms we used the 8-411d all-electron basis set constructed by Corà [24]. The effects of spin-orbit coupling and phonon properties have not been considered in this work. For all calculations we have used a hybrid functional based on a mixing of 10% HFX with 90% PBESol [25] exchange potential (PBES-10). This particular functional has been shown to accurately capture the electronic, magnetic, and structural properties of bulk [3] and surface  $\text{Sr}_3\text{Ru}_2\text{O}_7$  [2].

For our calculations a  $8 \times 8 \times 8$  Monkhorst-Pack mesh [26] was utilized to generate a 170 k-point sampling of the irreducible Brillouin zone. The thresholds controlling the accuracy in the evaluation of Coulomb and exchange integrals were set to  $10^{-7}$  (ITOL1, ITOL2, ITOL3, and ITOL4, using notations from Ref. 20) and  $10^{-14}$  (ITOL5), while the SCF energy threshold was set to  $10^{-6}$  au.

To study the electronic structure and magnetic properties of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  under uniaxial pressure, we performed constrained geometry relaxation where we fixed the  $c$  lattice parameter and relaxed the  $a$  and  $b$  lattice parameters and all atomic coordinates. We manually changed the value of  $c$  to investigate the effect of different compressive strains applied parallel to the [001] direction on the electronic and magnetic properties. The study of the application of in-plane tensile strains was carried out for different values of  $a$  and/or  $b$  lattice parameters, that we kept fixed while relaxing the  $c$  parameter and all atomic positions. The convergence criterion on gradient components and nuclear displacements in both studies was set to 0.0003 Ha/Bohr and 0.0012 Bohr respectively. Total energy convergence threshold between geometry optimization steps was set to  $10^{-6}$  Ha. By using these parameters we obtain converged total energies within 1-2 meV per unit cell.

In this study, we will only consider a homogeneous chemical and magnetic phase regardless of the amount of strain applied. Nevertheless, the real system may

respond by decomposing the material in different polymorph phases or binary metal oxides ( $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ ) [27, 28].

The estimation of the uniaxial pressure applied to the system was obtained by analyzing the stress tensor as reported in the supplemental materials of Ref. 2.

### III. RESULTS AND DISCUSSION

Recent experimental measurements in  $\text{Sr}_3\text{Ru}_2\text{O}_7$  indicate that the emergence of octahedral tilts at the surface drives the system towards a less conducting state than in the bulk [1]. The same study suggests that applying uniaxial compressive strain along the  $c$ -axis in the bulk structure will stimulate the emergence of octahedral tilts in the entire structure, ultimately leading to a phase transition. Octahedra tilting starts to develop at  $\simeq 1.5$  GPa of uniaxial pressure while the MIT and magnetic phase transitions occur at a higher pressure of about 21 GPa.

To uncover hidden phases we first investigated the competition between different magnetic configurations as a function of compressive strain along the [001] direction by varying the  $c$ -lattice parameter (Subsection A). This allowed us to determine the lowest energetic state as a function of strain. Then we studied the structural (Subsection B), magnetic, and electronic (Subsection C) properties also as a function of uniaxial compressive strain to understand the physical mechanisms that trigger these phase transitions. The results obtained lead us to study an alternative procedure to drive the MIT and magnetic phase transitions in  $\text{Sr}_3\text{Ru}_2\text{O}_7$  which consists in the application of in-plane tensile strains (Subsection D).

#### A. Competition between different magnetic phases under uniaxial compressive strain

In this section we study the evolution of magnetism in the system as a function of uniaxial compressive strain along the  $c$ -axis. The results obtained can provide hints on how to reproduce the reported hidden phases at a lower stress. We considered the FM phase and four different AFM spin orderings, which include the A, G, C, and I types of arrangements (see Fig. 1c). The total energy difference between FM and AFM-X (where X is A, G, C, or I) displayed in Table I is defined as  $\Delta EX = E_{AFM-X} - E_{FM}$ .

Fig. 2 displays the energy of the AFM-A, AFM-C, and AFM-G configurations as well as the FM state relative to the FM ground-state energy as a function of decreasing  $c$ . On one hand, we notice that total energies involving AFM-C are higher than other AFM phases when decreasing  $c$ -lattice parameter and thus, it does not compete as a potential new state in the parameter range considered. On the other hand, the total energy of the AFM-I phase,

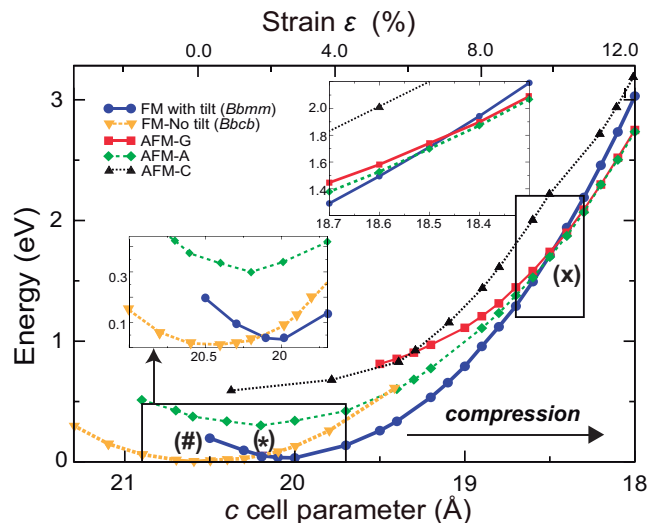


FIG. 2. Energy of FM (with and without tilt), AFM-A, AFM-C, and AFM-G magnetic orderings relative to the FM ground-state energy as a function of decreasing the  $c$  lattice parameter. The symbols: (#), (\*), and (x) indicate ground-state, first transition (structural), and second transition (electronic and magnetic), respectively.

which is characterized by FM bilayers coupled antiferromagnetically, is higher in energy than the FM state and it does not show much variation in total energy as a function of decreasing  $c$ -lattice parameter. This phase has not been included in Fig. 2 due to the small energy difference with the FM phase ( $\Delta EI$  ranges between 0 to 10 meV during the entire range of compressive strains before the transition) which is a consequence of the fact that Ru atoms in different bilayers do not interact significantly. This narrow range of energy differences could indicate the possibility of having a mixed state where bilayers are coupled either ferromagnetically or antiferromagnetically but with all Ru atoms in each bilayer coupled ferromagnetically.

We observe a structural transition from  $Bbcb$  to  $Bbmm$  that occurs at  $c = 20.2$  Å (marked by the symbol “(\*)” in Fig. 2) with the emergence of octahedra tilts and a considerable reduction of rotations (subsection B). Further uniaxial compressive strain along the  $c$ -axis significantly reduces the total energy difference between AFM-A and AFM-G states and the FM phase. At a critical value of  $c = 18.5$  Å, a transition from metallic FM to an insulating AFM-A state occurs, corresponding to a compressive strain of approximately 10% (marked by the symbol “(X)”, in Fig. 2). Further application of compressive strain increases the stability of the AFM-A phase without significant changes in the bandgap (subsection C).

The FM - AFM-A phase transition has been observed in other systems such as  $\text{RBaMn}_2\text{O}_6$  ( $R=\text{Pr}, \text{Nd}$ ) [29] or  $\text{LaMnO}_3$  [30] when temperature goes below Néel temperature. In those cases the phase transition is associ-

TABLE I. Calculated  $a$  and  $b$  cell parameters ( $\text{\AA}$ ), volume  $V$  ( $\text{\AA}^3$ ),  $\text{RuO}_6$  octahedra tilt and rotation angles (deg), and  $\Delta\text{EX} = E_{\text{AFM-X}} - E_{\text{FM}}$  (meV) as a function of compressive strain along the  $c$ -axis.

$c$	$a$	$b$	$V$	Rot	Tilt	$\Delta\text{EA}$	$\Delta\text{EG}$	$\Delta\text{EC}$	$\Delta\text{EI}$
20.796 <sup>a</sup>	5.477	5.477	623.8	8.05	0.00	-	-	-	-
20.73 <sup>b</sup>	5.498	5.501	626.9	7.85	0.00	-	-	-	-
20.6*	5.49	5.49	620.8	9.70	0.00	370	501	681	3.8
20.5	5.49	5.50	619.3	9.40	0.00	360			
20.4	5.51	5.51	619.7	8.97	0.00	354	527	608	4.4
20.3	5.52	5.53	619.4	8.34	0.00	346			
20.2	5.51	5.61	624.2	2.1	8.56	338	264	735	
20.0	5.52	5.63	620.6	2.0	8.84	308	298	857	1.1
19.7	5.53	5.66	616.6	1.3	9.61	283	492	542	6.0
19.4	5.54	5.70	612.2	1.1	10.22	266			2.0
19.2	5.54	5.72	608.5	1.0	10.70	239	388	425	
18.9	5.55	5.77	604.8	1.0	11.66	151			
18.8	5.55	5.78	603.6	1.0	12.05	114	194	320	1.5
18.6	5.56	5.81	601.3	0.8	12.65	29	87	305	
18.5	5.64	5.85	610.4	0	12.55	-12	30	291	-6
18.4	5.65	5.87	610.1	0	12.45	-75	-43		
18.3	5.65	5.89	609.6	0	12.47	-125	-101		
18.2	5.66	5.91	608.5	0	12.65	-160	-151	258	-12
18.1	5.67	5.93	607.7	0	12.76	-230	-213		
18.0	5.68	5.94	607.4	0	12.80	-294	-270	155	-5

<sup>a</sup>: Experimental results from Ref. 18

<sup>b</sup>: Experimental results from Ref. 16

\*: Fully relaxed

ated with the  $d_{x^2-y^2}$  orbital order and consistent with the change of lattice parameters where in-plane parameters are expanded while the out-of-plane parameter is contracted. This result provided the first indication that the FM to AFM-A phase transition could also be generated by applying in-plane tensile strain. In order to gain additional understanding of this phase transition, we analyze in the next section the structural changes induced by the application of compressive strain and their connections with the magnetic phase transition.

## B. Structural properties under uniaxial compressive strain

As we apply uniaxial compressive strain along the  $c$ -axis (making the  $c$  parameter shorter), the structural properties of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  change. In Fig. 3a we show the evolution of the  $a$  and  $b$  lattice parameters and volume as a function of reducing the  $c$  parameter. For small compressive strains ( $\epsilon < 2\%$ ),  $a$  and  $b$  show the same linear increase with the reduction of  $c$ . At a critical compressive strain of  $\simeq 2\%$  (where  $c = 20.2 \text{ \AA}$  and uniaxial pressure is  $\simeq 1.5 \text{ GPa}$ )  $b$  experiences a sharp elongation of about  $0.1 \text{ \AA}$ , giving rise to uneven in-plane lattice parameters and an increase in volume that yields a larger volume structure than in the ground-state. This result is a consequence to the emergence of tilts in the system (Fig. 3b).  $\text{RuO}_6$  octahedra become tilted by  $8.6^\circ$  and

the rotations are highly reduced due to the expansion of the in-plane lattice parameters. Further increases in uniaxial compressive strain causes  $a$  and  $b$  to increase but with  $b$  increasing slightly more than  $a$ , indicating a slight anisotropic effect on the structure while octahedra tilts continue increasing and rotations progressively disappear.

Applying uniaxial compressive strain makes the non-tilted octahedra in the ground-state structure become tilted by the same amount in all bilayers of the system. This is opposed to the case when a  $[001]$  surface is created in the system and octahedra tilts only emerge within the first surface bilayer [2].

At  $c = 18.5 \text{ \AA}$  (10 % of compressive strain corresponding to  $\simeq 21 \text{ GPa}$  of uniaxial pressure) a second phase transition occurs where the system simultaneously undergoes a FM metallic to an AFM-A insulator where tilting of the octahedra increases up to  $12.6^\circ$  and rotations disappear completely. Fig. 3c shows the top and side views of the resulting structure. During this process,  $\text{RuO}_6$  octahedra are transitioning from elongated to compressed, which in combination with the octahedra tilts, are responsible for the electronic and magnetic changes.

From these results we formulate a hypothesis: could expansion of the  $a$  and  $b$  cell parameters be achieved via in-plane strain producing the same or even new hidden phases? In fact, we have shown that the  $b$  lattice parameter increases more than the  $a$  lattice parameter, suggesting that tensile strain could efficiently be applied to a particular direction to produce hidden phases with less amount of stress. Before we answer these questions we continue our study on applying compressive strain to analyze the electronic and magnetic properties and how are these connected to the structural changes.

## C. Electronic and magnetic properties under uniaxial compressive strain

In Fig. 4a we display the evolution of the total energy difference relative to the FM state ( $\Delta E = E_{\text{AFM-A}} - E_{\text{FM}}$ ) and bandgap as a function of decreasing  $c$  lattice parameter. As can be seen,  $\Delta E$  decreases from almost  $400 \text{ meV}$  to  $0 \text{ meV}$  as we reduce  $c$  from  $20.6$  to  $18.5 \text{ \AA}$ . At a critical strain of  $\epsilon \simeq 10\%$  the FM metallic character of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  becomes an insulator with a bandgap of  $\simeq 0.4 \text{ eV}$  and an A-type AFM configuration. Additional increases in uniaxial compressive strain further stabilizes the AFM-A insulating state without significant changes in the bandgap. The projected density of states for the FM metallic ground-state structure and the AFM-A insulator state are shown in Fig.4b. The ground-state structure features a half-metallic character where  $t_{2g}$  electrons participate in the conduction while  $e_g$  levels are empty.[3]

Fig. 4c displays the evolution of Ru-O bond distances as a function of decreasing  $c$  parameter through the insu-

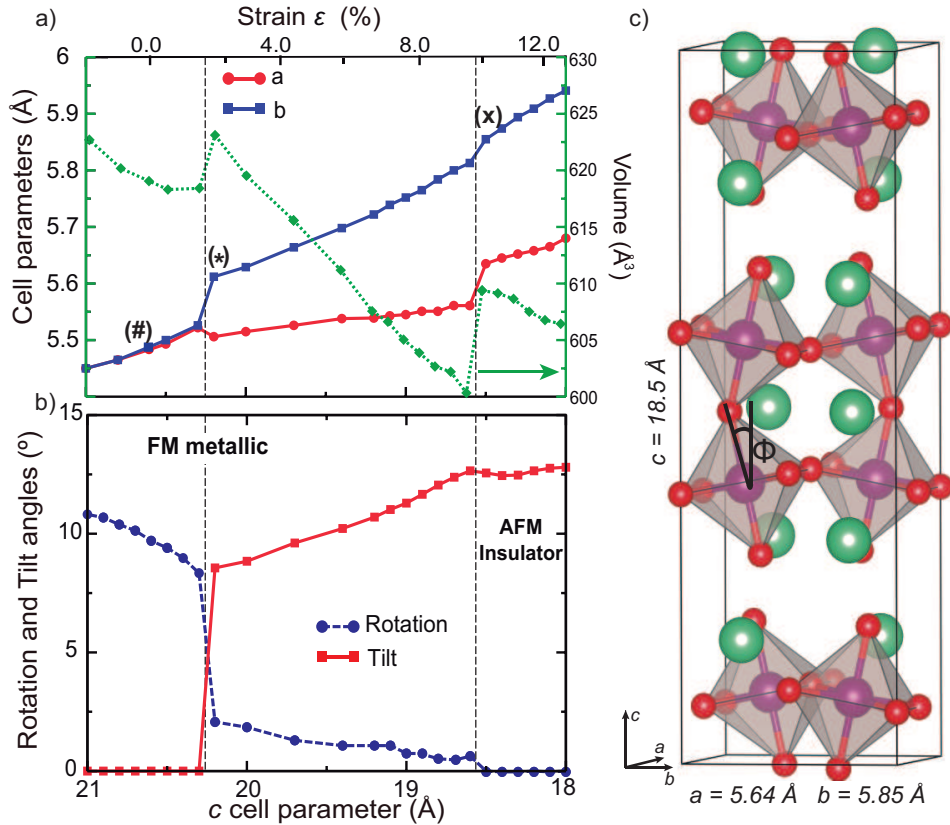


FIG. 3. a) Evolution of the volume,  $a$  and  $b$  cell parameters, and b) RuO<sub>6</sub> octahedra rotation and tilts (adapted from Ref. 2) as a function of reducing the  $c$  cell parameter. c) Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> structure under 21 GPa of uniaxial pressure where the system is characterized by an insulating AFM state.

lating AFM-A state ( $c = 18.5$  Å). We found that RuO<sub>6</sub> octahedra, that were elongated along the  $c$ -axis in the ground-state, become almost regular (that is, all Ru-O bond distances become identical) under uniaxial compressive strain of  $\simeq 2\%$  and then compressed under additional strain (Ru-O1 and Ru-O2 bond distances become longer than Ru-O3 and Ru-O4). The compression of the octahedra along with the emergence and increase of tilts in the system as we apply uniaxial compressive strain have important consequences in the orbital ordering and filling of the Ru(4d) and consequently, affect the electronic and magnetic properties of the compound.

We display in Fig. 4d how Ru(4d) electron occupancy ( $\alpha + \beta$ ) evolves as a function of  $c$  lattice parameter. At  $c = 20.6$  Å (0 GPa),  $xz$  and  $yz$  orbitals are doubly degenerated while  $xy$  forms a singlet at higher energy (relative to the doublet) and thus, it is less occupied. This  $t_{2g}$  symmetry breaking into a doublet and a singlet is a consequence of the elongated octahedra. The first transition (structural) occurs at  $c = 20.2$  Å and leads to a symmetry breaking of the  $xz$  and  $yz$  orbitals. This occurs along with a crossover where the  $xy$  orbitals are now at a lower energy and more occupied than the  $xz$  and  $yz$

orbitals. This is a consequence of the emergence of tilts in the system, which changes the polarization between orbitals and therefore, the Ru(4d) electron occupancies. This effect can also be seen in the  $z^2$  and  $x^2-y^2$  orbitals (although these orbitals are less populated than the  $t_{2g}$ ). A low-spin state is observed for the entire range of uniaxial strains.

As the uniaxial pressure increases (reduction of the  $c$  lattice parameter) the orbital fillings do not show appreciable changes until the metal-to-insulator and magnetic phase transitions occur at  $c = 18.5$  Å ( $\simeq 21$  GPa). At this point, the energy splitting between  $xy$  and the  $xz$  and  $yz$  orbitals increases leading to a significant change in filling in favor of the  $xy$  orbitals. The compressed and tilted RuO<sub>6</sub> octahedra under this pressure makes the superexchange dominate the Ru-O-Ru out-of-plane interaction and the system stabilizes in the AFM-A insulating state.

To gain additional insight into this transition we plot in Fig. 5 the charge densities of the FM metallic (ground-state) and the AFM-A insulating (at  $c = 18.5$  Å) structures. Examining these densities allow us to understand how the electrons are arranged in these systems and how orbitals look like. The system under pressure, unlike the

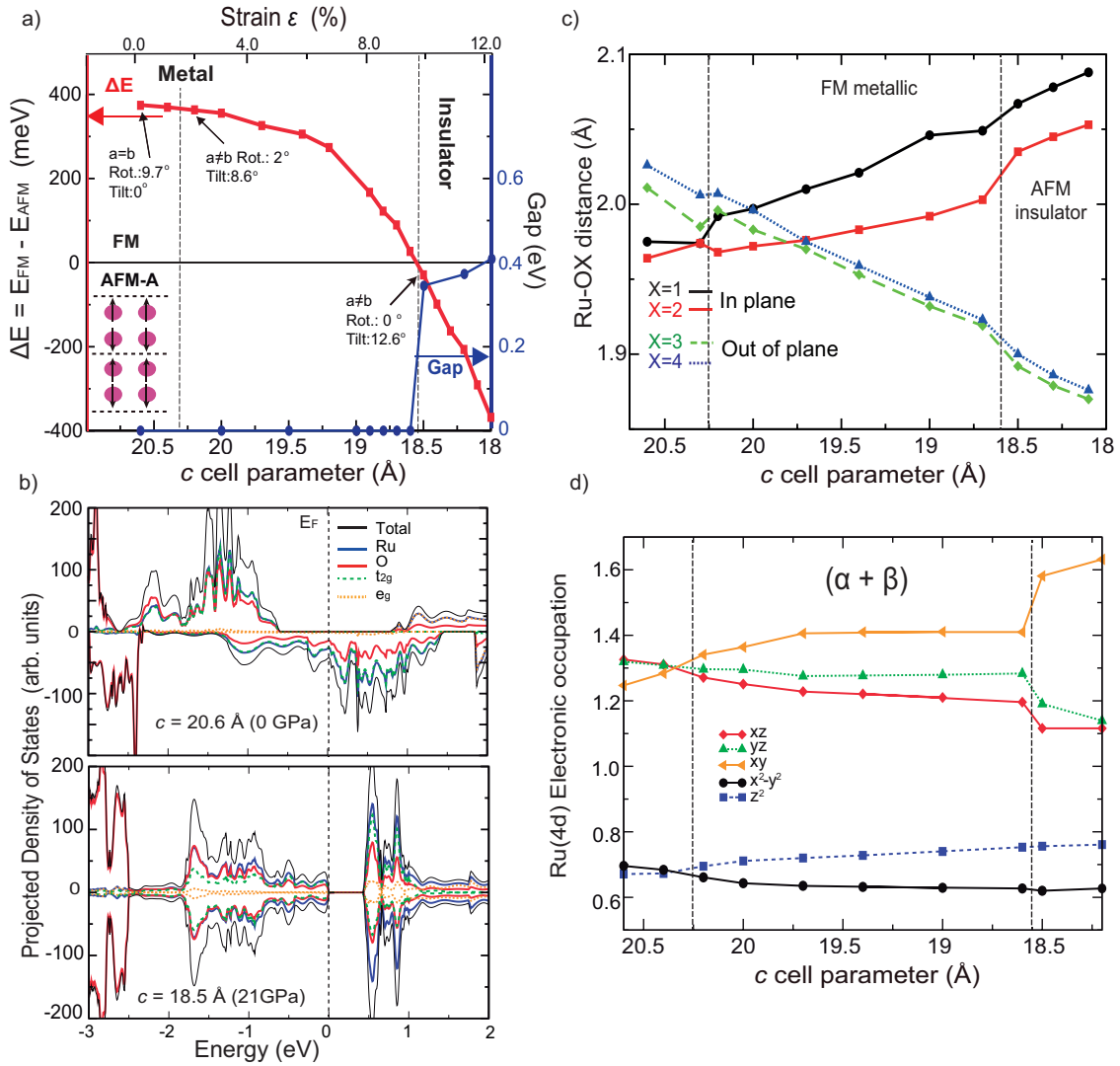


FIG. 4. a) Phase diagram of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  showing the evolution of  $\Delta E$  and bandgap as a function of  $c$  cell parameter and strain. (adapted from Ref. 2). b) Projected density of states for the FM metallic ground-state and AFM-A insulator structures. c) Evolution of Ru-OX bond distances in the octahedra and d) Evolution of the Ru(4d) electronic occupations ( $\alpha + \beta$ ) as a function of  $c$  lattice parameter (adapted from the Supplemental materials in Ref. 2).

ground-state, features antiferro-orbital correlations between Ru atoms in-plane and out-of-plane due to the different Ru(d) filling between  $xz$  and  $yz$  orbitals. However, the most remarkable feature is in the O atoms connecting octahedra layers along the  $c$ -axis. Contrary to the ground-state structure, in the system under 21 GPa the O- $p_z$  orbitals overlap the Ru- $xz$  and Ru- $yz$  orbitals, leading to an out-of-plane AFM coupling by a superexchange interaction.

We also determined the coupling strength between different neighboring Ru atoms as we apply uniaxial compressive strain and compare them with the ground-state structure. This allowed us to understand the effect of uniaxial pressure on the magnetic property. The magnetic couplings considered here are:  $J_1$ , coupling between

Ru nearest neighbors;  $J_2$ , coupling between next nearest neighbors localized out-of-plane in the bilayer; and  $J_3$ , coupling corresponding to the nearest Ru atoms localized in different bilayers (see Fig. 1a). We calculated these parameters by mapping the energy differences of different spin arrangements to the Ising Hamiltonian [31] as we did in a previous work [3].

The results obtained after solving the equations reported in Ref. 3 can be seen in Table II for the system under different  $c$  parameters (different compressive strains). The ground-state structure has an in-plane FM coupling  $J_1 > 0$ , and an out-of-plane FM coupling  $J_2 > 0$ . The latter is the strongest coupling in the system (51 meV in comparison to 30 meV for  $J_1$ ). This can be understood as a consequence of the stronger polariza-

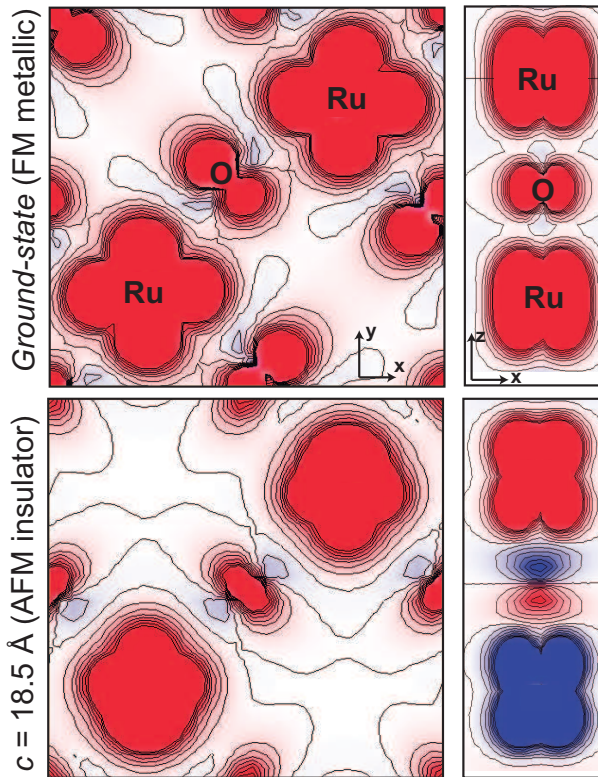


FIG. 5. Charge density of the FM metallic ground-state structure and the AFM insulator state observed under pressure. Different colors indicate different spin orientations.

TABLE II. Magnetic coupling parameters (meV) for different  $c$ -axis parameters (Å). <sup>a</sup>: Calculated ground-state structure.

$c$	$J_1$	$J_2$	$J_3$
20.6 <sup>a</sup>	30	51	0.2
19.5	18	31	0.1
18.5	15	-0.7	-0.3
18.1	10	-46	-0.5

tion between Ru and O through the  $180^\circ$  Ru-O-Ru angle in comparison to the Ru-O-Ru angle in-plane forming  $160^\circ$ . As we apply uniaxial compressive strain along the  $c$ -axis, the system evolves from elongated non-tilted octahedra to tilted compressed octahedra. This corresponds to breaking the  $180^\circ$  angle between Ru-O-Ru atoms out-of-plane making the out-of-plane Ru-O bonds shorter and the in-plane Ru-O bonds longer, ultimately leading to the FM-AFM phase transition.

$J_2$  is the most sensitive magnetic coupling parameter when uniaxial pressure along the  $c$ -axis is applied to the structure. This parameter evolves from 51 meV (ground state) to -0.7 meV at the transition (18.5 Å) and down to -46 meV when further compressive strain is applied to the structure. We noted that  $J_3$  also changes from FM to AFM character, indicating that AFM-I becomes lower in energy than FM at  $c = 18.5$  Å. However, AFM-A is the

lowest energetic state when the transition is triggered.

The mechanism associated with the AFM-A insulating phase transition can be understood via the inverse Goodenough-Kanamori interaction [32]. Where the Ru-O-Ru intrabilayer angle along the  $c$  axis is reduced from  $180^\circ$  to  $\simeq 155^\circ$  along with a reduction of the corresponding Ru-O bond lengths. This produces a reduction of the magnetic coupling that satisfies the Goodenough-Kanamori rules [33, 34] ultimately, leading to the FM-AFM phase transition.

We have now tied octahedra distortions to the electronic and magnetic properties of the system. Therefore, we expect that applying in-plane tensile strain will induce similar structural distortions that will eventually trigger phase transitions in the system. One advantage of applying in-plane tensile stress is that one has an extra degree of freedom to use to manipulate the octahedra in the search for new hidden phases.

#### D. In-plane tensile stress

The reported results in the previous sections have allowed us to support our hypothesis to apply in-plane tensile strain to uncover hidden phases in  $\text{Sr}_3\text{Ru}_2\text{O}_7$ . In this next section we will analyze the properties of the system when it is under uniaxial or biaxial tensile strain.

In Fig. 6a we show the evolution of  $\text{RuO}_6$  octahedral tilts as a function of in-plane surface area when tensile strain along [100], [010] and a combination of both (biaxial, [100]+[010]) is applied to the system. The stress produced in all of these cases increases the in-plane area of the system and triggers a structural transition where octahedra become tilted (as we found by applying compressive strain along the [001] direction). However, the required stress to drive this transition depends on the direction of the application and is lower along the [010], reducing the 1.5 GPa obtained by compressive strain to 0.6 GPa. In Fig. 6b we display the energetics of the Bbcb (non-tilted) and the Bbmm (tilted) symmetry structures as the surface area of the unit cell increases due to the application of tensile strain along different  $x$  and  $y$  directions. As it can be seen, the tilt of the octahedra is a key structural distortion that leads to more stable structures when in-plane tensile strain is applied to the system.

Further application of tensile strain along the [010] increases the octahedra tilt up to  $12.3^\circ$  and the system undergo a simultaneous electronic and magnetic phase transition similar to the system under uniaxial compressive strain (tilt of  $12.6^\circ$ ), but reducing the stress from  $\simeq 21$  GPa to 17 GPa. Octahedra find lower energetic structures by tilting along the  $y$ -axis (rotating about the  $c$ -axis) and therefore, expanding the system along the [010] direction produces the same effect as compressing along the [001] where  $b$  lattice parameter expands more than  $a$  (see section B). The application of tensile stress



TABLE III. Structural parameters ( $\text{\AA}$  and deg.) and magnetic and electronic phases obtained by applying tensile strain along  $[100]$ ,  $[010]$ , and biaxial ( $[100]+[010]$ ) directions. The lattice parameters that were fixed during the calculations are indicated with (\*). HM: Half-metallic, M: metallic, I: insulator

$[100]$					$[010]$					$[100]+[010]$				
a*	b	c	tilt	phase	b*	a	c	tilt	phase	a*	b*	c	tilt	phase
5.49	5.49	20.6	0.00	FM/HM	5.49	5.49	20.6	0.00	FM/HM	5.49	5.49	20.6	0.00	FM/HM
5.60	5.57	20.04	0.00	FM/HM	5.55	5.48	20.48	0.00	FM/HM	5.54	5.54	20.37	0.00	FM/HM
5.70	5.53	20.00	0.00	FM/HM	5.60	5.52	20.09	8.60	FM/HM	5.60	5.60	19.99	8.69	FM/HM
5.80	5.47	19.98	6.99	FM/HM	5.70	5.49	20.01	9.53	FM/HM	5.65	5.65	19.91	8.75	FM/HM
5.90	5.43	19.95	6.50	FM/HM	5.80	5.43	19.93	10.15	FM/HM	5.70	5.70	19.78	9.07	FM/HM
6.00	5.39	19.91	5.67	FM/HM	5.90	5.39	19.84	10.82	FM/HM	5.80	5.80	19.58	9.65	AFM/M
6.10	5.36	19.87	5.20	FM/HM	6.00	5.36	19.75	11.21	FM/HM	5.85	5.85	19.25	9.68	AFM/M
6.20	5.33	19.83	4.56	FM/HM	6.10	5.34	19.68	11.64	FM/HM	5.90	5.90	19.14	9.39	AFM/M
6.23	5.45	19.42	5.91	AFM/M	6.20	5.31	19.59	11.95	FM/HM	6.00	6.00	18.98	9.34	AFM/M
6.30	5.45	19.34	5.04	AFM/M	6.30	5.29	19.53	12.32	FM/HM	6.10	6.10	18.82	9.34	AFM/M
6.40	5.43	19.29	4.65	AFM/M	6.32	5.39	19.18	11.51	FM/HM	6.20	6.20	18.68	9.21	AFM/M
6.50	5.41	19.25	4.90	AFM/M	6.40	5.38	19.13	11.22	AFM/I					
6.60	5.39	19.22	4.76	AFM/M	6.50	5.37	19.07	10.81	AFM/I					
					7.20	5.31	18.65	8.35	AFM/I					

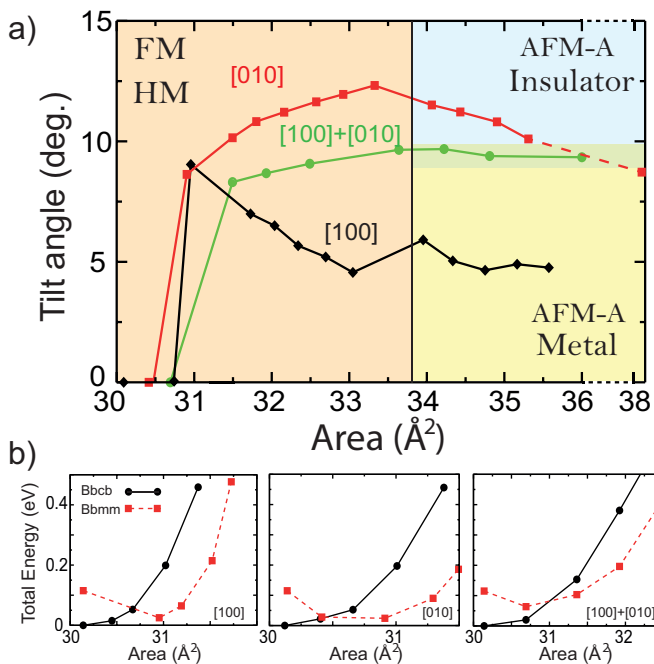


FIG. 6. a) Evolution of the  $\text{RuO}_6$  octahedra tilts as a function of in-plane surface area when tensile strain is applied along  $[100]$ ,  $[010]$  and  $[100]+[010]$ . The different magnetic and electronic phases highly depend on the tilt of the system. HM states for Half-metallic. b) Total energy difference between the Bbcb (non-tilted) and Bbmm (tilted) symmetries with the ground-state structure as a function of in-plane area in the range of  $30 \text{ \AA}^2$  to  $32 \text{ \AA}^2$ .

along  $[100]$  or  $[100]+[010]$  produce a magnetic phase transition by compressing the octahedra but the symmetry breaking of the orbitals, induced by tilting, was not large enough to generate the metal-to-insulator phase transi-

tion. For these cases we found a new non-equilibrium hidden phase characterized by an AFM metallic state. Table III displays the structural parameters and the different predicted phases for each direction where tensile stress is applied.

These results suggest that while the evolution of the  $\text{RuO}_6$  octahedra from elongated to compressed is related with the magnetic phase transition, the octahedral tilts are responsible for the metal-to-insulator transition. To support this idea we applied further tensile strain along the  $[010]$  direction to reduce the tilt to  $8.35^\circ$  and thus produce an AFM metallic system (Fig. 6).

In Fig. 7a we show the total energy difference between FM and AFM-A states as a function of tensile strain applied along  $[100]$ ,  $[010]$ , and  $[100]+[010]$ . We observe that less amount of strain along  $[100]$  ( $\approx 13\%$ ) than along the  $[010]$  directions ( $\approx 15\%$ ) is needed to drive the magnetic phase transition. This indicates the existence of a preferable direction to drive this transition smoothly. The reason for this difference is due to the different  $\text{Ru}(4d)$   $xz$  and  $yz$  orbital occupations, producing higher resistance to stress along the direction with more electronic density. The corresponding tensile stress values needed to trigger this transition are 16.1 GPa along the  $[100]$  and 17.3 GPa along the  $[010]$  directions. For the case where we apply biaxial tensile strain, about 6%, correspondent to 9.8 GPa along the  $[100]$  and 7.4 GPa along the  $[010]$  directions, will drive the FM to AFM-A transition in the system. This clearly contrasts with the 21 GPa of compressive stress along the  $[001]$  direction needed to drive the magnetic phase transition.

We show in Fig. 7b the projected density of states per atom for the AFM phases obtained under minimum strain application along each direction. We observe that only the application of tensile strain along the  $[010]$  direction produces a metal-to-insulator transition.

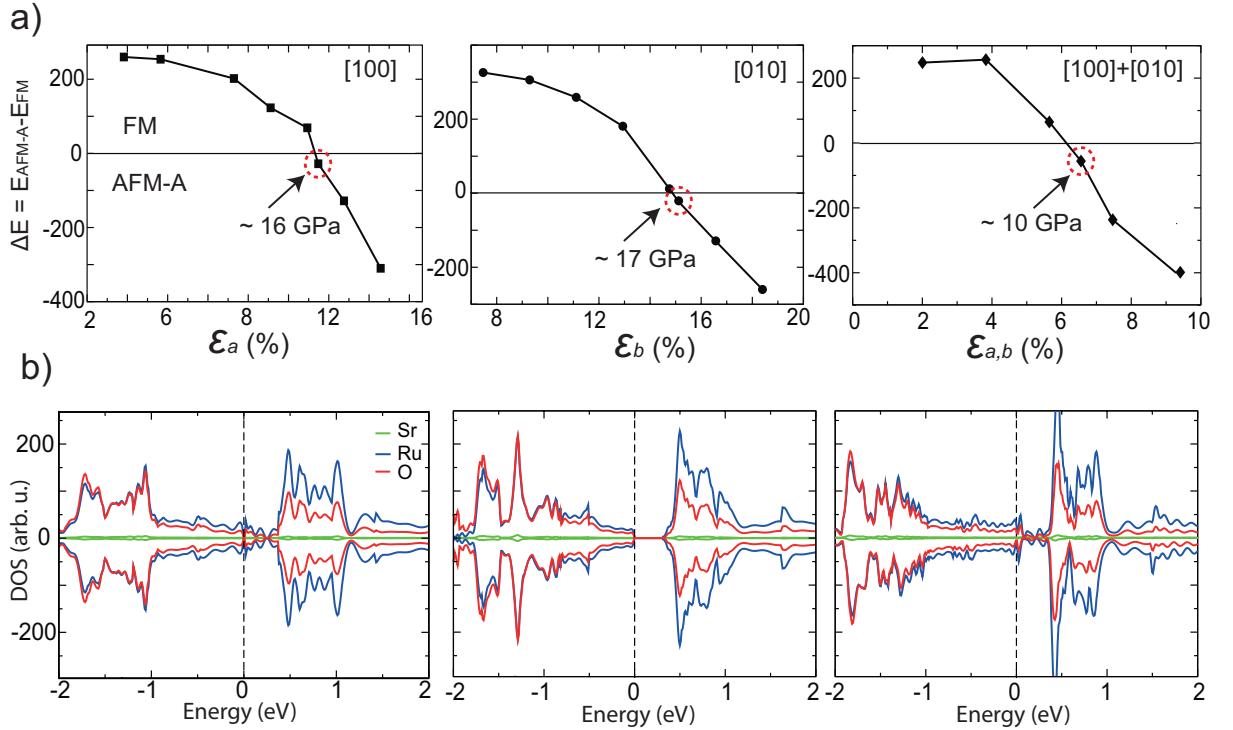


FIG. 7. a) Evolution of the total energy difference between FM and AFM-A states ( $\Delta E = E_{AFM-A} - E_{FM}$ ) as a function of tensile strain along [100], [010], and [100]+[010] directions. b) Projected density of states per atom for the AFM-A structures correspondent with the points indicated by a dotted circle right above.

In the other two cases the half-metallic character becomes metallic. The reason for that is the lack of tilt development as shown in Fig. 6. A detailed analysis of the electronic structure indicates that 4d- $e_g$  electronic contributions are responsible for this metallicity, which is related to the filling of electrons at lower energies when tilts are not large enough to break the symmetry of the orbitals that produces the MIT.

Finally, in order to provide a guide for experimentalists to epitaxially grow  $Sr_3Ru_2O_7$  on different size substrates we provide in Fig. 8 the magnetic state of  $Sr_3Ru_2O_7$  as a function of randomly applying stress along [100] and [010] directions. The size of the spots represent the total energy differences between FM and AFM states ( $\Delta E = E_{AFM-A} - E_{FM}$ ). We observe that when the in-plane area, which is associated with a specific combination of compressed and tilted octahedra, becomes larger than  $34 \text{ \AA}^2$  (represented by a dotted line), the system exhibits an AFM-A phase. Consequently, this shows the existence of a clear correlation between in-plane area and magnetic phases.

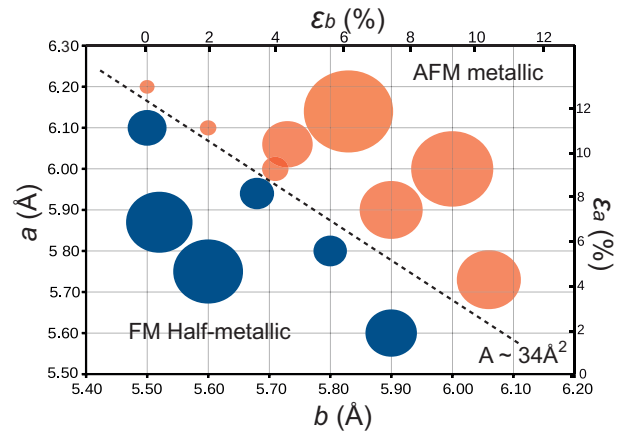


FIG. 8. Magnetic character obtained for structures with different  $a$  and  $b$  lattice parameters. The size of the circles indicate the absolute value of  $\Delta E$  magnitude. The dashed black line correspond to an in-plane area of  $34 \text{ \AA}^2$ . The larger circle corresponds to  $\Delta E = -470 \text{ meV}$ .

## CONCLUSION

We uncovered an antiferromagnetic metallic hidden phase in  $Sr_3Ru_2O_7$  by applying 10 GPa of biaxial ten-

sile strain. The hypothesis that motivated us to apply tensile strain is based on our recently reported results on uniaxial compressive strain along the  $c$ -axis, where the in-plane lattice parameters increased yielding two hidden phases. By using hybrid density functional theory we applied uniaxial and biaxial in-plane tensile strains as an alternative procedure. We not only found that these hidden phases were exposed at lower stress but we also were able to uncover a new hidden phase. Our results indicate that octahedra distortions (tilting, compression and elongation) can be controlled by applying in-plane tensile strain to expose hidden phases.

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