

# Manipulation of electronic structure via alteration of local orbital environment in $[(\text{SrIrO}_3)_m, (\text{SrTiO}_3)]$ ( $m = 1, 2, \text{ and } \infty$ ) superlattices

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## Abstract

We investigated the electronic structure of  $[(\text{SrIrO}_3)_m, (\text{SrTiO}_3)]$  ( $m = 1, 2, \text{ and } \infty$ ) superlattice (SL) thin films with optical spectroscopy and first-principles calculations. Our optical results confirmed the existence of the  $J_{\text{eff}} = 1/2$  states in SL samples, similar to the bulk Ruddlesden–Popper series  $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$  iridates. Apart from this similarity, in the SL samples we observed redshifts of the characteristic optical excitations in the  $J_{\text{eff}} = 1/2$  state and an enhancement of the low-energy spectral weight, which implies a reduction in the effective electron correlation for bands near the Fermi energy. The DFT+ $U$  calculations suggested that the  $\text{SrTiO}_3$  layer intervened between  $\text{SrIrO}_3$  layers in the SLs activates additional hopping channels between the Ir ions, thus increasing the bandwidth and reducing the effective strength of the correlations. This work demonstrates that fabrication of iridium-based heterostructures can be used to finely tune electronic structures via alteration of their local orbital environments.

## I. INTRODUCTION

Iridium oxides have attracted attention recently due to their large spin-orbit coupling. In the  $5d$  transition metal oxides, the spin-orbit coupling becomes large and comparable to other important interactions, such as electron–electron correlation and hopping. The subtle interplay between these competing interactions can lead to novel quantum phenomena, including relativistic Mott insulators [1–4], Weyl semimetals [5], and topological insulators [6,7]. An ideal system to explore such exotic physics is the Ruddlesden–Popper (RP) series of iridates, i.e., the  $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$  compounds. In quasi-two-dimensional  $\text{Sr}_2\text{IrO}_4$ , the large spin-orbit coupling leads to formation of the effective total angular momentum  $J_{\text{eff}} = 1/2$  Mott insulating state. Similar to two-dimensional cuprates, it was suggested that carrier doping could lead to superconductivity in the  $J_{\text{eff}} = 1/2$  square lattice of  $\text{Sr}_2\text{IrO}_4$  [8–12]. With increasing  $n$ , the  $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$  series exhibits an insulator-to-metal transition [13,14].

The intriguing ground states of  $5d$  transition metal oxides make them an appealing platform for artificial heterostructures and strain engineering. The RP series  $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$  can be viewed as a natural oxide superlattice (SL) itself; namely  $\text{SrIrO}_3$  thin slices, each composed of  $n$  layers, alternate with  $\text{SrO}$  layers. By substituting the  $\text{SrO}$  layers with alternative layers, we can easily create artificial RP-like iridate SLs, which do not exist in bulk form. During the last two decades, there have been significant advancements in the synthesis of atomic-scale oxide heterostructures [15] and numerous novel states created in artificial interfaces have been investigated [16–18]. Heterostructure construction can be used to control various parameters, such as lattice constants, dimensionality, and lattice geometry, which are critical in determining related quantum phenomena. Therefore, engineering artificial heterostructures of RP-like iridates can provide new insight into the physics of strongly spin-orbit-coupled Mott insulators.

Recently,  $[(\text{SrIrO}_3)_m, \text{SrTiO}_3]$  SL samples were synthesized, and their transport and magnetic properties were investigated [19]. In the  $[(\text{SrIrO}_3)_m, \text{SrTiO}_3]$  SL, the  $\text{SrO}$  layers of the RP  $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$  compounds are replaced by  $\text{SrTiO}_3$ . Transport measurements on the RP-like SL showed a semimetal–

insulator transition, analogous to the  $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$  series, and magnetic measurements revealed ground states also similar to those of RP compounds. Bulk  $\text{Sr}_2\text{IrO}_4$  is known to have a weak ferromagnetic moment due to canted in-plane antiferromagnetism (*ab*-AF) [20–22]. For the  $m = 1$  and  $m = 2$  SL, a weak ferromagnetic moment originating from canted *ab*-AF ordering was detected [19]. On the other hand, bulk  $\text{Sr}_3\text{Ir}_2\text{O}_7$  is known to have a weak ferromagnetic moment due to collinear out-of-plane antiferromagnetic ordering [23–26]. In contrast to transport and magnetic studies, no optical spectroscopic data for Ir-based SLs has been reported, and their electronic structure remains poorly understood.

In this study, we investigated the electronic structures of  $[(\text{SrIrO}_3)_m, \text{SrTiO}_3]$  SLs ( $m = 1, 2,$  and  $\infty$ ) by means of optical spectroscopy and first-principles calculations. The optical conductivity spectra of artificial RP-like SLs show two strong absorption peaks below 1.5 eV, a characteristic feature of the  $J_{\text{eff}} = 1/2$  state. Compared with the bulk RP series, however, the peaks are located at lower energies. In addition, we observed sizable low-energy spectral weight (*SW*) in the  $m = 1$  and 2 SLs, whereas the RP counterparts showed clear optical gaps. Our first-principles calculations indicated that the experimental data could be explained in terms of changes in the bandwidth due to increased hopping between Ir ions in the SLs. Our work demonstrates that artificial heterostructures provide a useful means of controlling the electronic properties of these intriguing materials.

## II. METHODS

We fabricated  $[(\text{SrIrO}_3)_m, \text{SrTiO}_3]$  ( $m = 1$  and 2) SLs and a  $\text{SrIrO}_3$  thin film on  $\text{SrTiO}_3$  (001) substrates using the pulsed laser deposition technique. Note that the perovskite  $\text{SrIrO}_3$  thin film corresponds to the SL with  $m = \infty$ . The total thickness of each sample was about 32 nm. All samples were grown epitaxially on the  $\text{SrTiO}_3$ (001) substrate, to allow the strain from the substrate to lock in the in-plane lattice constants of our SLs to be the same as those of bulk  $\text{SrTiO}_3$ , i.e., 0.3905 nm. Transport measurements showed the SL samples with  $m = 1$  and 2 to be insulators and the  $\text{SrIrO}_3$  film to be a semimetal. Detailed information on the sample growth and characterization was reported in

Ref. [19].

For the optical region below 1.0 eV, we obtained optical conductivity spectra  $\tilde{\sigma}(\omega)$  [=  $\sigma_1(\omega) + i\sigma_2(\omega)$ ] of the SLs and SrTiO<sub>3</sub> substrate by measuring their reflectance at 20 K. Near-normal incidence reflectance spectra  $R(\omega)$  were measured in the energy region of 6 meV–1.0 eV using Fourier-transform infrared spectroscopy. A gold normalization technique was used to obtain the correct values of reflectance [27]. In this low-frequency region, we obtained  $\tilde{\sigma}(\omega)$  by fitting  $R(\omega)$  with a series of Lorentz oscillators and accounting for the effects of the sample geometry and substrate. The reflectance of the bare SrTiO<sub>3</sub> substrate was measured separately, and the complex optical conductivity of SrTiO<sub>3</sub> was extracted using Kramers–Kronig analysis. Because the wavelength of light was much longer than the characteristic lengths of the thin films, we assumed that each SL acted as a homogeneous medium and obtained its effective  $\tilde{\sigma}(\omega)$  accordingly. Figures 1(a)–1(c) show  $R(\omega)$  and the fitting results for the  $m = 1, 2,$  and  $\infty$  SLs. Below 20 meV, the  $R(\omega)$  of the SLs and SrTiO<sub>3</sub> substrate approached one another, due to the strong SrTiO<sub>3</sub> phonon, as shown in Fig. 1(d). When  $R(\omega)$  is close to 1, it is difficult to obtain accurate  $\tilde{\sigma}(\omega)$  from the Lorentz oscillator fitting. To avoid such complications, we will focus our discussion on  $\tilde{\sigma}(\omega)$  above 20 meV.

For the high-energy region above 0.74 eV, we performed ellipsometry measurements at 20 K using a V-VASE<sup>®</sup> ellipsometer (J. A. Woollam Co.). Figures 1(e)–1(g) show experimental  $\psi$  and  $\Delta$  values of SLs with  $m = 1, 2,$  and  $\infty$ . Using the film thickness of 32 nm and modeling the SrTiO<sub>3</sub> substrate below the thin film, we could obtain  $\tilde{\sigma}(\omega)$  of the thin films without relying on Kramers–Kronig analysis. The measured value of  $\tilde{\sigma}(\omega)$  was in good agreement with that from reflectance measurements in the overlapped energy region between 0.74 eV and 1.0 eV.

For  $m = 1, 2$  SLs and  $n = 1, 2$  Sr<sub>*n*+1</sub>Ir<sub>*n*</sub>O<sub>3*n*+1</sub> compounds, first-principles calculations were performed using density functional theory (DFT). We used projector augmented wave potentials with a PBEsol functional, which provides an improved description of structural parameters as implemented in VASP [28,29]. For structural relaxations, 1 meV/Å was used for the force convergence tolerance. For the SL calculations, the in-plane lattice constant was fixed as the lattice constant of SrTiO<sub>3</sub>, and the

out-of-plane lattice constant and internal coordinates were optimized. With the structure optimized by VASP, we used ELK code [30] to calculate the electronic band structure and  $\tilde{\sigma}(\omega)$  with high accuracy. The optical conductivity was calculated within the random phase approximation. To consider local Coulomb interactions  $U$ , we used different  $U$  values for each set, i.e.,  $U = 2$  eV for single-layer ( $m, n = 1$ ) and  $U = 1.8$  eV for double-layer ( $m, n = 2$ ) sets. The reduced  $U$  used for  $\text{Sr}_3\text{Ir}_2\text{O}_7$  accounts for more effective screening in the more itinerant bilayer compound, following a recent density functional plus dynamical mean field theory (DFT+DMFT) study [31]. For the magnetic structure of the ground states, canted  $ab$ -AF ordering was imposed for  $m = 1, 2$  SLs [19];  $\text{Sr}_2\text{IrO}_4$  [21] and collinear out-of-plane antiferromagnetic ordering was applied for  $\text{Sr}_3\text{Ir}_2\text{O}_7$  [22].

### III. EXPERIMENTAL RESULTS

In this study, we concentrated on the low-temperature optical properties and associated ground states of the SLs. We found that the optical spectra of all of our samples were strongly temperature-dependent. The RP series of iridates are known to be either semimetals or small-gap insulators [14,32,33]. For such small-gap materials, the thermal energy can be comparable to the gap energy value. As a result, the optical properties may acquire a strong temperature-dependence due to Fermi surface changes [34,35], indirect absorption [36], the thermal activation of carriers between bands near the Fermi energy ( $E_F$ ) [37] etc. Such temperature effects will obscure the signatures of the electronic ground state, which is the main interest of this study. In addition, our first-principles calculations can predict the electronic structures of the ground state only. For these reasons, we focused on  $\sigma_1(\omega)$  at 20 K to obtain insight into the electronic structure of artificial RP-like iridate SL systems.

Our optical data for the SLs revealed the characteristic spectral signatures of the spin-orbit-induced  $J_{\text{eff}} = 1/2$  system. The black lines in Figs. 2(a)–2(c) show the  $\sigma_1(\omega)$  of SL samples with  $m = 1, 2$ , and  $\infty$ , respectively;  $\sigma_1(\omega)$  of the corresponding RP series is overlaid as gray lines for comparison [14,32,33]. Similar to the RP iridates, the  $\sigma_1(\omega)$  of the SL samples showed two strong

peaks below 1.5 eV, labeled as  $\alpha$  and  $\beta$ . This two-peak structure has already been reported in the  $n = 1$  and  $n = 2$  of the RP series and is known to originate from the electronic structure of the spin-orbit-induced  $J_{\text{eff}} = 1/2$  Mott system [13,14,38]. For the insulating  $m = 1$  and  $m = 2$  SLs, the  $\alpha$ -peak arises from optical transitions from the lower to upper Hubbard bands of the  $J_{\text{eff}} = 1/2$  states, while the  $\beta$ -peak corresponds to excitations from the  $J_{\text{eff}} = 3/2$  states to the upper Hubbard band. The sharp peak around 76 meV is due to an infrared-active phonon mode.

The increase in dimensionality, i.e., the  $m$  value, induces an insulator-like to metal-like transition and yields important spectral changes in our SL samples. With increasing  $m$ , the  $\alpha$ - and  $\beta$ -peaks shifted to lower energies, as shown in Figs. 2(a)–2(c). In addition, the value of  $\sigma_1(\omega)$  at the lowest frequency increased, consistent with the increase in  $dc$  conductivity [19]. We calculated the low-energy  $SW$  by integrating  $\sigma_1(\omega)$  from 20 to 37 meV, which was the highest cutoff frequency lower than the interband transition for all three samples. The low-energy  $SW$  increased with  $m$ , as shown in Fig. 2(e). Similar spectral changes were observed in  $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$  compounds [13]; with increasing  $n$ , both the  $\alpha$ - and  $\beta$ -peaks moved to lower energies and the system experienced an insulator-to-metal transition. These spectral changes were attributed to an increase in bandwidth with the increase in dimensionality [14].

Although the overall spectral features are similar, the  $\sigma_1(\omega)$  spectra revealed three important differences between the SLs and their bulk RP counterparts. First, the  $\alpha$ - and  $\beta$ -peaks of the SLs are always located at lower frequencies than those of the RP series. The shift was particularly large for the  $\alpha$ -peaks, leading to a significant decrease in the optical gap. Second, while the  $\alpha$ -peak broadened as  $n$  increased from 1 to 2 in the RP series, it became sharper for  $m = 1$  to 2 in SLs [Fig. 2(f)]. Finally, the low-energy  $SW$  of the SLs is larger than that of the corresponding RP member. Here, one might argue that the finite low-energy  $SW$  in  $\sigma_1(\omega)$  of the SLs may be associated with sample quality issues, including oxygen vacancies [39] or the intergrowth of different  $m$  layers. However, the sharper  $\alpha$ -peak in the  $m = 2$  SL compared with  $\text{Sr}_3\text{Ir}_2\text{O}_7$  implies that this is not a simple matter of sample quality.

The  $\alpha$ -peak of  $\text{SrIrO}_3$  is not understood in detail. Given that  $\text{SrIrO}_3$  is metallic, this peak may not

be a transition between Hubbard bands; instead, it may correspond to an interband transition between low-lying  $J_{eff} = 1/2$  bands that can be seen from the DMFT band structure in Ref. [31]. The narrow width of this peak [Fig. 2(c)] is consistent with a recent angle-resolved photoemission spectroscopy (ARPES) experiment on SrIrO<sub>3</sub> films, which revealed strong bandwidth narrowing compared with Sr<sub>2</sub>IrO<sub>4</sub> [40]. This was attributed to band folding originating from octahedral rotation about the [110] direction in addition to [001] in SrIrO<sub>3</sub> [41]. Such a sharp peak was not captured in the previous optical spectrum of the SrIrO<sub>3</sub> film at room temperature [gray line in Fig. 2(c)]. This may be due to a large lattice mismatch between the SrIrO<sub>3</sub> thin film and MgO substrate used in Ref. [14]. Because the lattice constant of SrTiO<sub>3</sub> is much closer to that of SrIrO<sub>3</sub> than MgO, our SrIrO<sub>3</sub> thin film on SrTiO<sub>3</sub> substrate will be of better quality. Note that  $\sigma_1(\omega)$  enhancement of our SrIrO<sub>3</sub> thin film on the SrTiO<sub>3</sub> substrate may also come from the enhanced sample quality, as well as the lower measurement temperature (20 K).

#### IV. DISCUSSION

It is important to recognize that our SLs and the bulk RP series have different atomic arrangements. Schematic diagrams for single ( $m = 1$  and Sr<sub>2</sub>IrO<sub>4</sub>) and double ( $m = 2$  and Sr<sub>3</sub>Ir<sub>2</sub>O<sub>7</sub>) layer systems are shown in Figs. 3(a) and 4(a), respectively. The major difference is the atomic arrangements in the blocking layer between the quasi two-dimensional IrO<sub>2</sub> planes. In the RP series, the IrO<sub>2</sub> planes are separated by a SrO spacer. On the other hand, in the  $m = 1$  and 2 SLs, they are separated by a TiO<sub>2</sub> monolayer. This leads to different local environments for the apical oxygens, which are located at the boundary of the IrO<sub>2</sub> plane in SLs and near the blocking layer in the RP series. In the SLs, the apical oxygen can bond with the nearby transition metal ions to create Ir-O<sub>apical</sub>-Ti bonds. On the other hand, in RPs, the apical oxygen bonds only with the Ir ions at the center of an iridium–oxygen octahedron. As will be shown later, this difference induces significant changes in the electronic structure near the  $E_F$ , resulting in large changes at the low frequency  $\sigma_1(\omega)$  of our SLs.

To understand the experimental observations, we performed DFT+ $U$  calculations. Our calculations



captured the main spectral changes in  $\sigma_1(\omega)$  between the SLs and their RP counterparts. Figures 3(b) and 4(b) show DFT results of  $\sigma_1(\omega)$  for the  $m = 1$  and  $m = 2$  SL cases, respectively; these are compared to their RP counterpart  $\sigma_1(\omega)$ , displayed as dashed lines. The DFT+ $U$  calculation results revealed that the  $\sigma_1(\omega)$  of SLs have two peak structures, characteristic of the  $J_{\text{eff}} = 1/2$  state. As in experiments, the energy positions of the peaks are red-shifted compared with the RP series. Additionally, the calculations correctly reproduced the reduced optical gap with enhanced low-energy SW in both single- and double-layer SLs. In particular, the calculated positions of the  $\alpha$ -peak in the SLs were well-matched with those from the experimental data, as shown in Fig. 2(d). This agreement suggests that the electronic structure of the SLs can be properly explained by our DFT+ $U$  calculations.

To obtain insight into the different optical responses of RP and SLs shown in Figs. 2(a) and 2(b), let us look carefully at the DFT band structures. Figures 3(c) and 3(d) show the DFT bands for single-layer sets, i.e.,  $\text{Sr}_2\text{IrO}_4$  and  $m = 1$  SL, respectively. The different orbital components of the bands are plotted as colored circles. In both the RP and SL samples, the near- $E_F$  electronic structure is dominated by the Ir  $d$  bands, with the Ir-bonded O states located below  $-2$  eV. Due to the insertion of the  $\text{SrTiO}_3$  layer in the SLs, we found that several new bands emerged near  $E_F$ . Specifically, around 0.5 eV above  $E_F$ , Ti  $d$  states are visible. However, these states do not hybridize strongly with Ir  $d$  bands. Below  $-1.5$  eV, Ti-bonded O states were evident; these states appeared to originate from the in-plane oxygens of  $\text{TiO}_6$ , which hybridize with the Ir  $d$  states near the  $\Gamma$  and  $X$  points. Similar new bands near  $E_F$  emerged also for the double-layer sets, i.e.,  $\text{Sr}_3\text{Ir}_2\text{O}_7$  and  $m = 2$  SL, as shown in Figs. 4(c) and 4(d). The appearance of these new bands near  $E_F$  is an important characteristic of the iridate SLs.

The crucial difference between the electronic structures of the SL and RP series can be explained in terms of the larger bandwidth ( $W$ ) of the Ir  $t_{2g}$  bands in the SLs. For our iridate systems, the Ir  $t_{2g}$  bands of the SLs [red circles in Fig. 3(d) and 4(d)] are more dispersive than those in the RP series compounds [red circles in Figs. 3(c) and 4(c)], especially along the  $MX$  line. As observed in the canonical Mott insulator  $\text{La}_x\text{Y}_{1-x}\text{TiO}_3$ , the Mott–Hubbard gap is expected to decrease systematically with an increase in  $W$  [42]. This can explain the optical spectral changes between the SL and RP series

in experiments [Figs. 2(a) and 2(b)] and in calculations [Figs. 3(b) and 4(b)]. The increase in  $W$  reduces the effective strength of the electron–electron correlation ( $U/W$ ), leading to an increase in low-energy  $SW$  and a shift in the correlation-induced  $\alpha$ -peak.

To understand the origin of the bandwidth increase, we used a tight-binding (TB) model on  $\text{Sr}_2\text{IrO}_4$ , following Ref. [43]. We looked for a parameter that affects  $W$  by changing the strength of various hopping. We found that  $t_1$ , which denotes the in-plane hopping integral between neighboring  $d_{xz}$  ( $d_{yz}$ ) and  $d_{xz}$  ( $d_{yz}$ ) orbitals along the  $x$  ( $y$ ) axis in Ir-O-Ir bonding [orange arrows in Fig. 5(a)], plays an important role. The Ir  $d$  bands become significantly more dispersive with an increase in  $t_1$ , as shown in Fig. 5(b). In particular, the dispersion along the  $MX$  line is increased, similar to the DFT results of the SLs shown in Figs. 3(d) and 4(d). This suggests that the large  $W$  in the SL is associated with an increase of Ir-Ir hopping in the  $\text{IrO}_2$  plane.

We speculate that the increased Ir-Ir hopping is due to the  $\text{SrTiO}_3$  layers in the SLs, which may allow additional hopping paths between Ir ions. As the Ir and Ti atomic positions are aligned along the same vertical lines, extra hopping paths become available in the SLs [colored arrows in Figs. 6(a)], which can make the  $d$  bands of Ir more dispersive. If this speculation is correct, the in-plane hopping will be affected by  $d$ , i.e., the distance between Ir and Ti ions [Fig. 6(b)]. In Fig. 6(c), the DFT+ $U$  band structures of  $m = 1$  SL, on which we intentionally increased  $d$ , are shown; the same parameters were imposed to obtain the band structure shown in Fig. 3(d), except for the elongation in  $\text{TiO}_6$  octahedra. Comparing Figs. 3(d) and 6(c), it is clear that increasing  $d$ , i.e., suppressing the extra hopping in SLs, reduced  $W$  while increasing the gap. This demonstrates the importance of local atomic arrangements near the interface in oxide heterostructures.

In principle, the physical properties of transition metal oxide thin films can also be affected significantly by epitaxial strain [44–48] and charge transfer [49]. For  $\text{Sr}_2\text{IrO}_4$  films, it has been reported that the application of tensile strain on  $\text{Sr}_2\text{IrO}_4$  shifts the  $\alpha$ - and  $\beta$ -peaks to higher energies and broadens them, making the system more insulating [31,50]. However, these systematic trends are in opposition to our observed peak shifts in both the  $m = 1$  and 2 SLs, which are tensile-strained due to

the SrTiO<sub>3</sub> substrate. Therefore, the tensile strain due to the substrate does not play an important role in the observed electronic structural changes in our SLs. Charge transfer from the SrTiO<sub>3</sub> layer to SrIrO<sub>3</sub> can lead to the emergence of mobile carriers with a contribution manifested in an increase in the low-energy spectral weight in the optical response. However, we verified experimentally that the valence of Ir and Ti in the SLs remains at 4+, showing that the SrTiO<sub>3</sub> layer acts as a good insulating barrier [19]. In addition, the observations of Ti  $t_{2g}$  bands far above Fermi level in our DFT result also support that the SrTiO<sub>3</sub> layer plays little role in the low energy optical transition.

Other potentially important structural factors include the Ir-O-Ir bond angle and the tetragonality of the IrO<sub>6</sub> octahedra [2,40,50]. These parameters can affect electronic hopping, resulting in changes to the electronic properties of the SLs. In Table I, we summarize the DFT values for the SL and RP series; notably, the bond angle values are similar for SL and RP samples. All four systems were found to have IrO<sub>6</sub> octahedra rotated about the [001] direction by  $\sim 13^\circ$ , comparable to that observed experimentally for the bulk RP series [51–54]. Next, let us look at the tetragonality, which parameterizes the tetragonal distortion of the IrO<sub>6</sub> octahedron. It is defined as the ratio of the out-of-plane Ir-O bond length to the in-plane Ir-O bond length. Our DFT calculations suggest that the tetragonality was reduced slightly (almost identical) in the  $m = 1$  ( $m = 2$ ) SL, compared with Sr<sub>2</sub>IrO<sub>4</sub> (Sr<sub>3</sub>Ir<sub>2</sub>O<sub>7</sub>). This is related to the SrO spacers in the RP series, which provide relatively more space in the lattice; thus, IrO<sub>6</sub> octahedra may be more susceptible to elongation in the  $c$ -direction. The tetragonality value of the RP series from calculations is comparable to calculated values from parameters in the literature [51,53]. There exists a considerable change in tetragonality only in the single-layer set, but the  $\sigma_1(\omega)$  spectral changes between SLs and RP series show up for both single- and double-layer sets. Thus, we can conclude that the differences in the bond angle and tetragonal distortion of the SLs are not sufficiently strong to change the electronic structure significantly.

## V. SUMMARY

We examined the electronic structure of single and double IrO<sub>6</sub> layer systems of artificial SL

[(SrIrO<sub>3</sub>)<sub>m</sub>, SrTiO<sub>3</sub>] and the RP series Sr<sub>n+1</sub>Ir<sub>n</sub>O<sub>3n+1</sub> via optical spectroscopy and first-principles calculations. From the optical spectra of the SLs, we observed the formation of the spin-orbit-induced  $J_{eff} = 1/2$  state, in addition to an insulator-like semimetallic transition similar to the RP series with increasing  $m$ . A significant change was detected in the correlation-induced  $\alpha$ -peak of SLs, which was redshifted compared with their RP series counterparts. Finally, we observed an increase in low-energy SW in the SLs.

Our first-principles calculations revealed the possible origins of the difference between the optical properties of the SLs and RP series compounds. We identified that the replacement of the SrO blocking layer in RP iridates by SrTiO<sub>3</sub> in the SLs induces an increase in Ir  $d$ -band dispersion. This is attributed to additional hopping channels in the SLs, which may enhance the in-plane interaction between Ir ions. These observations indicate that SL samples have a larger bandwidth and weaker effective correlations than their bulk counterpart RP series. Our work demonstrates that the controlled synthesis of artificial oxide heterostructures provides a way to manipulate important parameters in the electronic structure of correlated electron systems, which could possibly lead to exotic metallic or even superconducting states in this class of materials.

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## VI. REFERENCE

- [1] D. Pesin and L. Balents, *Nat. Phys.* **6**, 376 (2010).
- [2] G. Jackeli and G. Khaliullin, *Phys. Rev. Lett.* **102**, 17205 (2009).
- [3] K. W. Plumb, J. P. Clancy, L. J. Sandilands, V. V. Shankar, Y. F. Hu, K. S. Burch, H. Y. Kee, and Y. J. Kim, *Phys. Rev. B* **90**, 041112(R) (2014).
- [4] L. J. Sandilands, Y. Tian, A. A. Reijnders, H. S. Kim, K. W. Plumb, Y. J. Kim, H. Y. Kee, and K. S. Burch, *Phys. Rev. B* **93**, 75144 (2016).
- [5] W. Witczak-Krempa, G. Chen, Y. B. Kim, and L. Balents, *Annu. Rev. Condens. Matter Phys.* **5**, 57 (2014).
- [6] B. J. Yang and Y. B. Kim, *Phys. Rev. B* **82**, 85111 (2010).
- [7] W. Witczak-Krempa and Y. B. Kim, *Phys. Rev. B* **85**, 45124 (2012).
- [8] Y. J. Yan, M. Q. Ren, H. C. Xu, B. P. Xie, R. Tao, H. Y. Choi, N. Lee, Y. J. Choi, T. Zhang, and D. L. Feng, *Phys. Rev. X* **5**, 41018 (2015).
- [9] F. A. Wang and T. Senthil, *Phys. Rev. Lett.* **106**, 136402 (2011).
- [10] J. Kim, D. Casa, M. H. Upton, T. Gog, Y. J. Kim, J. F. Mitchell, M. Van Veenendaal, M. Daghofer, J. Van Den Brink, G. Khaliullin, and B. J. Kim, *Phys. Rev. Lett.* **108**, 177003 (2012).
- [11] J. Matsuno, Y. Okimoto, M. Kawasaki, and Y. Tokura, *Phys. Rev. Lett.* **95**, 176404 (2005).
- [12] A. De La Torre, S. McKeown Walker, F. Y. Bruno, S. Ricco, Z. Wang, I. Gutierrez Lezama, G. Scheerer, G. Giriat, D. Jaccard, C. Berthod, T. K. Kim, M. Hoesch, E. C. Hunter, R. S. Perry, A. Tamai, and F. Baumberger, *Phys. Rev. Lett.* **115**, 176402 (2015).
- [13] B. J. Kim, H. Jin, S. J. Moon, J. Y. Kim, B. G. Park, C. S. Leem, J. Yu, T. W. Noh, C. Kim, S. J. Oh, J. H. Park, V. Durairaj, G. Cao, and E. Rotenberg, *Phys. Rev. Lett.* **101**, 76402 (2008).
- [14] S. J. Moon, H. Jin, K. W. Kim, W. S. Choi, Y. S. Lee, J. Yu, G. Cao, A. Sumi, H. Funakubo, C. Bernhard, and T. W. Noh, *Phys. Rev. Lett.* **101**, 226402 (2008).
- [15] H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, *Nat. Mater.* **11**, 103 (2012).
- [16] A. Ohtomo and H. Y. Hwang, *Nature* **427**, 423 (2004).
- [17] D. Xiao, W. Zhu, Y. Ran, N. Nagaosa, and S. Okamoto, *Nat. Commun.* **2**, 596 (2011).
- [18] T. J. Anderson, S. Ryu, H. Zhou, L. Xie, J. P. Podkaminer, Y. Ma, J. Irwin, X. Q. Pan, M. S. Rzchowski, and C. B. Eom, *Appl. Phys. Lett.* **108**, 6 (2016).
- [19] J. Matsuno, K. Ihara, S. Yamamura, H. Wadati, K. Ishii, V. V. Shankar, H. Y. Kee, and H. Takagi, *Phys. Rev. Lett.* **114**, 247209 (2015).
- [20] F. Ye, S. Chi, B. C. Chakoumakos, J. A. Fernandez-Baca, T. Qi, and G. Cao, *Phys. Rev. B* **87**, 140406 (2013).
- [21] B. J. Kim, H. Ohsumi, T. Komesu, S. Sakai, T. Morita, H. Takagi, and T. Arima, *Science* **323**, 1329 (2009).
- [22] J. Kim, A. H. Said, D. Casa, M. H. Upton, T. Gog, M. Daghofer, G. Jackeli, J. Van Den Brink, G. Khaliullin, and B. J. Kim, *Phys. Rev. Lett.* **109**, 157402 (2012).

- [23] J. W. Kim, Y. Choi, J. Kim, J. F. Mitchell, G. Jackeli, M. Daghofer, J. Van Den Brink, G. Khaliullin, and B. J. Kim, *Phys. Rev. Lett.* **109**, 37204 (2012).
- [24] S. Boseggia, R. Springell, H. C. Walker, A. T. Boothroyd, D. Prabhakaran, S. P. Collins, and D. F. McMorrow, *J. Phys. Condens. Matter* **24**, 312202 (2012).
- [25] J. P. Clancy, K. W. Plumb, C. S. Nelson, Z. Islam, G. Cao, T. Qi, Y. Kim, and T. Iro, arXiv: 1207.0960v1 (2012).
- [26] S. Fujiyama, K. Ohashi, H. Ohsumi, K. Sugimoto, T. Takayama, T. Komesu, M. Takata, T. Arima, and H. Takagi, *Phys. Rev. B* **86**, 174414 (2012).
- [27] C. C. Homes, M. Reedyk, D. a Cradles, and T. Timusk, *Appl. Opt.* **32**, 2976 (1993).
- [28] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- [29] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [30] <http://elk.sourceforge.net/>
- [31] H. Zhang, K. Haule, and D. Vanderbilt, *Phys. Rev. Lett.* **111**, 246402 (2013).
- [32] C. H. Sohn, M. C. Lee, H. J. Park, K. J. Noh, H. K. Yoo, S. J. Moon, K. W. Kim, T. F. Qi, G. Cao, D. Y. Cho, and T. W. Noh, *Phys. Rev. B* **90**, 41105 (2014).
- [33] H. J. Park, C. H. Sohn, D. W. Jeong, G. Cao, K. W. Kim, S. J. Moon, H. Jin, D. Y. Cho, and T. W. Noh, *Phys. Rev. B* **89**, 155115 (2014).
- [34] F. P. Mena, D. Van Der Marel, and J. L. Sarrao, *Phys. Rev. B* **72**, 45119 (2005).
- [35] H. C. Choi, B. I. Min, J. H. Shim, K. Haule, and G. Kotliar, *Phys. Rev. Lett.* **108**, 16402 (2012).
- [36] H. J. Park, L. J. Sandilands, J. S. You, H. S. Ji, C. H. Sohn, J. W. Han, S. J. Moon, K. W. Kim, J. H. Shim, J. S. Kim, and T. W. Noh, *Phys. Rev. B* **93**, 205122 (2016).
- [37] B. I. Halperin and T. M. Rice, *Rev. Mod. Phys.* **40**, 755 (1968).
- [38] Y. S. Lee, S. J. Moon, S. C. Riggs, M. C. Shapiro, I. R. Fisher, B. W. Fulfer, J. Y. Chan, A. F. Kemper, and D. N. Basov, *Phys. Rev. B* **87**, 195143 (2013).
- [39] N. H. Sung, H. Gretarsson, D. Proepper, J. Porras, M. Le Tacon, A. V. Boris, B. Keimer, and B. J. Kim, *Philos. Mag.* **96**, 413 (2016).
- [40] Y. F. Nie, P. D. C. King, C. H. Kim, M. Uchida, H. I. Wei, B. D. Faeth, J. P. Ruf, J. P. C. Ruff, L. Xie, X. Pan, C. J. Fennie, D. G. Schlom, and K. M. Shen, *Phys. Rev. Lett.* **114**, 16401 (2015).
- [41] J. G. Zhao, L. X. Yang, Y. Yu, F. Y. Li, R. C. Yu, Z. Fang, L. C. Chen, and C. Q. Jin, *J. Appl. Phys.* **103**, 103706 (2008).
- [42] Y. Okimoto, T. Katsufuji, Y. Okada, T. Arima, and Y. Tokura, *Phys. Rev. B* **51**, 9581 (1995).
- [43] J. M. Carter, V. V. Shankar, and H. Y. Kee, *Phys. Rev. B* **88**, 35111 (2013).
- [44] J.-P. Locquet, J. Perret, J. Fompeyrine, E. Machler, J. W. Seo, and G. van Tendeloo, *Nature* **394**, 453 (1998).
- [45] Y. Tokura and N. Nagaosa, *Science* **288**, 462 (2000).
- [46] J. H. Gruenewald, J. Nichols, J. Terzic, G. Cao, J. W. Brill, and S. S. A. Seo, *J. Mater. Res.* **29**,

2491 (2014).

- [47] M. K. Stewart, C. H. Yee, J. Liu, M. Kareev, R. K. Smith, B. C. Chapler, M. Varela, P. J. Ryan, K. Haule, J. Chakhalian, and D. N. Basov, *Phys. Rev. B* **83**, 75125 (2011).
- [48] A. Lupascu, J. P. Clancy, H. Gretarsson, Z. Nie, J. Nichols, J. Terzic, G. Cao, S. S. A. Seo, Z. Islam, M. H. Upton, J. Kim, D. Casa, T. Gog, A. H. Said, V. M. Katukuri, H. Stoll, L. Hozoi, J. Van Den Brink, and Y. J. Kim, *Phys. Rev. Lett.* **112**, 147201 (2014).
- [49] P. Di Pietro, J. Hoffman, A. Bhattacharya, S. Lupi, and A. Perucchi, *Phys. Rev. Lett.* **114**, 156801 (2015).
- [50] J. Nichols, J. Terzic, and E. Bittle, *Appl. Phys. Lett.* **102**, 141908 (2013).
- [51] M. K. Crawford, M. A. Subramanian, R. L. Harlow, J. A. Fernandez-Baca, Z. R. Wang, and D. C. Johnston, *Phys. Rev. B* **49**, 9198 (1994).
- [52] For  $\text{Sr}_3\text{Ir}_2\text{O}_7$  additional rotation about [110] direction of  $\sim 0.5^\circ$  was reported in Ref. [54] but it is neglected in our calculations.
- [53] M. A. Subramanian, M. K. Crawford, and R. L. Harlow, *Mater. Res. Bull.* **29**, 645 (1994).
- [54] T. Hogan, L. Bjaalie, L. Zhao, C. Belvin, X. Wang, C. G. Van de Walle, D. Hsieh, and S. D. Wilson, *Phys. Rev. B* **93**, 134110 (2016).

## FIGURES AND CAPTIONS

FIG. 1. (a)–(c) Reflectance of the  $m = 1, 2$  superlattices (SLs) and  $m = \infty$  ( $\text{SrIrO}_3$ ) film at 20 K. The experimental data are plotted in symbols; calculated reflectance from the fitted model is shown as black lines. (d) The reflectance of all SLs and  $\text{SrTiO}_3$  substrate in the far-infrared range. (e)–(g) Ellipsometry data ( $\psi$  and  $\Delta$ ) of  $m = 1, 2$  SLs and the  $m = \infty$  film at 20 K. The experimental data are plotted in symbols, and the fitted models are shown as black lines.

FIG. 2. (Color online) (a)–(c) The real part of the optical conductivity  $\sigma_1(\omega)$  of the SL with  $m = 1, 2, \infty$  at 20 K and their Ruddlesden–Popper (RP) series counterparts at 25 K for  $\text{Sr}_2\text{IrO}_4$  single crystal from Ref. [32] and at 10 K for  $\text{Sr}_3\text{Ir}_2\text{O}_7$  single crystal from Ref. [33]). (d) The energy position of the  $\alpha$ -peaks. The experimental data are shown as black squares, and the calculation data are plotted as red circles. (e) Spectral weight obtained by integrating  $\sigma_1(\omega)$  from 20–37 meV. (f) The widths of the  $\alpha$ -

peaks of the SLs.

FIG. 3. (Color online) (a) Schematic diagrams of the crystal structures for the  $m = 1$  SL and  $\text{Sr}_2\text{IrO}_4$ . Sr atoms are shown in green, O atoms in white, Ir atoms in red, and Ti atoms in blue. (b) Calculated optical conductivity of the  $m = 1$  SL and  $\text{Sr}_2\text{IrO}_4$ . Density functional theory (DFT)+ $U$  band structure of (c) the  $m = 1$  SL and (d)  $\text{Sr}_2\text{IrO}_4$ . The colored circle indicates the intensity for projection of Ti, Ir,  $\text{O}_{\text{Ti}}$  (in-plane oxygens of  $\text{TiO}_6$ ), and O (apical oxygens of  $\text{IrO}_6$  and  $\text{TiO}_6$ , in addition to in-plane oxygens of  $\text{IrO}_6$ ). The larger radius indicates a larger portion of corresponding ions in each state.

FIG. 4. (Color online) (a) Schematic diagrams of crystal structures for  $m = 2$  SL and  $\text{Sr}_3\text{Ir}_2\text{O}_7$ . Sr atoms are drawn in green, O atoms in white, Ir atoms in red, and Ti atoms in blue. (b) The calculated optical conductivity of  $m = 2$  SL and  $\text{Sr}_3\text{Ir}_2\text{O}_7$ . DFT+ $U$  band structure of (c) the  $m = 2$  SL and (d)  $\text{Sr}_2\text{IrO}_4$ . The colored circle indicates the intensity for projection of Ti, Ir,  $\text{O}_{\text{Ti}}$  (in-plane oxygens of  $\text{TiO}_6$ ), and O (apical oxygens of  $\text{IrO}_6$  and  $\text{TiO}_6$ , in addition to in-plane oxygen of  $\text{IrO}_6$ ). The larger radius indicates a larger portion of corresponding ions in each state.

FIG. 5. (Color online) (a) Orbital arrangements of Ir and Ti orbitals ( $d_{zx}$  or  $d_{yz}$ ) of  $\text{Sr}_2\text{IrO}_4$ . The hopping paths from Ir  $d_{zx}$  ( $d_{yz}$ ) to Ir  $d_{zx}$  ( $d_{yx}$ ) states are drawn in orange arrows, where  $t_1$  is integral strength of corresponding hopping. (b) Tight binding band structure of  $\text{Sr}_2\text{IrO}_4$  with changed weight on  $t_1$ .

FIG. 6. (Color online) (a) Orbital arrangements of Ir and Ti orbitals ( $d_{zx}$  or  $d_{yz}$ ) near interfaces of  $\text{SrIrO}_3$  and  $\text{SrTiO}_3$  in the SLs. Extra in-plane hopping paths from Ir  $d_{zx}$  ( $d_{yz}$ ) to Ir  $d_{zx}$  ( $d_{yx}$ ) states in SLs are drawn as colored arrows (purple, yellow, and green). (b) Schematic diagrams of SLs showing  $d$ , i.e., the distance between Ir and Ti ions. (c) DFT+ $U$  calculations on  $m = 1$  SL with increased  $d$  by 2% and 6%.



Table I. Rotation angle of  $\text{IrO}_6$  octahedron and tetragonality from our first-principles calculations, and those from the literature [51,53].

		$m = 1$ SL	$\text{Sr}_2\text{IrO}_4$	$m = 1$ SL	$\text{Sr}_3\text{Ir}_2\text{O}_7$
[001] rotation	This work (cal.)	$13^\circ$	$13^\circ$	$13^\circ$	$13^\circ$
	Reference (exp.)	-	$11.5^\circ$	-	$11.8^\circ$
Tetragonality	This work (cal.)	0.998	1.036	1.007	1.010
	Reference (exp.)	-	1.039	-	1.012, 1.002