Electronic structure and magnetic properties of iridate superlattice SrIrO$_3$/SrTiO$_3$

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Abstract
Motivated by an experimental report of iridate superlattices, we performed first-principle electronic structure calculations for SrIrO$_3$/SrTiO$_3$. Heterostructuring causes SrIrO$_3$ to become Sr$_2$IrO$_4$-like, and the system has the well-defined $j_{\text{eff}} = 1/2$ states near the Fermi level as well as a canted antiferromagnetic order within the quasi-two-dimensional IrO$_2$ plane. In response to a larger tensile strain, the band gap is increased due to the resulting increase in bond length and the bandwidth reduction. The ground state magnetic properties are discussed in comparison to the metastable collinear antiferromagnetic state. Our work sheds new light on understanding the recent experimental results on the iridate heterostructures.

Keywords: iridium oxide, density functional theory, superlattice, LDA+U, spin-orbit coupling

(Some figures may appear in colour only in the online journal)
of SL actually exhibits quite similar characteristics to Sr₂IrO₄ and is notably different from the other RP iridates, such as Sr₂IrO₃. It has an insulating ground state and canted antiferromagnetic (AF) ordering of \( j_{\text{eff}} = 1/2 \) moments. The electronic and magnetic properties are systematically changed by strain. Our results shed new light on understanding the novel correlated spin-orbital physics of iridate compounds.

2. Computational details

First-principles electronic structure calculations were performed by OPENMX code [15, 16], which is based on the linear combination of pseudoatomic orbitals method [17]. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [18] was adopted. The energy cutoff of 300 Ry and the Monkhorst–Pack \( k \)-meshes of \( 7 \times 7 \times 5 \) in the first Brillouin zone were used for the real and momentum space integrations, respectively. SOC was treated within a fully relativistic \( j \)-dependent pseudopotential scheme in the non-collinear methodology [16]. Electronic correlations were taken into account with the DFT+U formalism [19]. We used the effective on-site Coulomb interaction parameter of \( U_{\text{eff}} \equiv U - J = 2.0 \) eV for the Ir 5\( d \) orbitals [20, 21]. The energy criterion of \( 10^{-3} \) eV was adopted for the structural relaxation. The optimized \( c \)-axis lattice constant and the internal coordinates of the unit cell (space group \( P4/mmbn \)) with the various in-plane lattice constants of \( \sqrt{2} a \) are listed in table 1. The optimized structures were thoroughly compared with the results of the Vienna ab initio Simulation Package [22, 23].

### Table 1. Optimized structural parameters of the unit cell (space group \( P4/mmbn \)) for various in-plane lattice constants. The atomic positions are given as following: Sr, \((1/2, 0, z)\); Ti, \((1/2, 1/2, 0)\); Ir, \((0, 0, 1/2)\); O₁, \((0, 0, z)\); O₂, \((x_5, y_5, z)\); O₃, \((x_6, y_6, z)\).

| \( a (\text{Å}) \) | 3.80 | 3.85 | 3.90 | 3.95 | 4.00 |
|-----------------|------|------|------|------|------|
| \( c (\text{Å}) \) | 8.214 | 8.135 | 8.039 | 7.933 | 7.921 |
| \( z_1 \)      | 0.755 | 0.756 | 0.757 | 0.758 | 0.758 |
| \( z_4 \)      | 0.752 | 0.752 | 0.752 | 0.752 | 0.753 |
| \( x_5 \)      | 0.710 | 0.719 | 0.730 | 0.736 | 0.740 |
| \( y_5 \)      | 0.789 | 0.780 | 0.769 | 0.763 | 0.759 |
| \( x_6 \)      | 0.821 | 0.819 | 0.816 | 0.813 | 0.811 |
| \( y_6 \)      | 0.678 | 0.680 | 0.683 | 0.686 | 0.688 |

3. Results and discussion

3.1. Structural properties

Figure 1(a) shows the unit cell used in this study. As in Sr₂IrO₄, this SL has TiO₂ interlayers which are electronically inactive \((d^9\) configuration) and effectively suppress hopping between the neighboring IrO₂ layers. Therefore our system becomes quasi-two-dimensional, as is the case in Sr₂IrO₄. It was also found that the larger IrO₆ octahedra have rotational distortion along the \( c \)-axis in order to fit into the smaller SrO₆ cage (with the rotation angle \( \phi \)) as depicted in figure 1(b). This produces an environment for the electronic behavior similar to the Ir ions in Sr₂IrO₄.

To simulate the epitaxial strain, the in-plane lattice constants were varied from 3.80 Å to 4.00 Å. Note that the equilibrium in-plane lattice constant of Sr₂IrO₄ is ~3.88 Å [11, 24]. If we assume the IrO₆ octahedra are rigid (i.e. no change in the Ir–O bond lengths), it is natural to expect the enhancement (reduction) of the octahedral rotation for the compressive (tensile) strain. In fact, our result qualitatively follows such a tendency in the rotation pattern. Simultaneously, however, we also found that the IrO₆ octahedra undergo significant tetragonal distortions, as summarized in figure 1(c). The in-plane Ir–O bond length is changed by \( \sim \pm 2.0\% \) as \( a \) is increased from 3.90 Å to 4.00 Å (tensile strain) or decreased down to 3.80 Å (compressive strain).

3.2. Electronic properties without \( U_{\text{eff}} \)

Figure 2 presents the calculated band structure with SOC (\( U_{\text{eff}} = 0 \)). The size and color of each band point represents the portions of \( t_{2g} \) and \( e_{g} \) states, respectively. As expected, the \( t_{2g} \) characters prevail around the Fermi energy. The three-fold degenerate \( t_{2g} \) states carry the effective orbital angular momentum \( l_{\text{eff}} = 1 \). Assuming that the SOC (~0.4 eV) of the Ir atom dominates over the other energy scales, such as intersite hoppings and tetragonal crystal fields (\( \lesssim 0.15 \) eV) [25–27], the \( l_{\text{eff}} = 1 \) states are split into an upper \( j_{\text{eff}} = 1/2 \) doublet and a lower \( j_{\text{eff}} = 3/2 \) quartet [4], where the \( j_{\text{eff}} = 1/2 \) states are split into an upper \( j_{\text{eff}} = 1/2 \) doublet and a lower \( j_{\text{eff}} = 3/2 \) quartet [4], where the \( j_{\text{eff}} = 1/2 \) and \( 3/2 \) states are defined as

\[
\begin{align*}
|l_{\text{eff}} = \frac{1}{2} \rangle \equiv & \frac{1}{\sqrt{3}} \left( |\uparrow \downarrow \rangle + i |\downarrow \uparrow \rangle \right) + \frac{2}{\sqrt{2}} \left( |\downarrow \uparrow \rangle + i |\uparrow \downarrow \rangle \right) |1, 1 \rangle, \\
|l_{\text{eff}} = \frac{3}{2} \rangle \equiv & \frac{1}{\sqrt{3}} \left( |0, \downarrow \rangle + |\uparrow 1 \rangle \right) + \frac{1}{\sqrt{3}} \left( |\uparrow \uparrow \rangle + |\downarrow \downarrow \rangle \right) |1, 1 \rangle, \\
|l_{\text{eff}} = \frac{5}{2} \rangle \equiv & \frac{1}{\sqrt{3}} \left( |0, \downarrow \rangle + |\uparrow 1 \rangle \right) + \frac{1}{\sqrt{3}} \left( |\uparrow \uparrow \rangle + |\downarrow \downarrow \rangle \right) |1, 1 \rangle,
\end{align*}
\]

where \( |1, 1 \rangle \) and \( |0, \pm 1 \rangle \) denote the indices for the spin and the angular momentum eigenstates \( l = 1/2 \) and \( \pm 1/2 \), and \( l_{\text{eff}} = 1; 0, \pm 1 \), respectively, and the subscript \( z \) means that the momenta are quantized along the octahedral \( z \)-direction (perpendicular to the Ir plane). Although the splitting between the \( j_{\text{eff}} = 1/2 \) and \( 3/2 \) states is not perfect due to the sizeable effect from the bandwidth and the confinement in the SL, the \( j_{\text{eff}} = 1/2 \) characters in the low-energy states near the Fermi level are quite clearly noticed (blue colors in figure 2). It is found that the \( j_{\text{eff}} \)-characterization of the bands is valid in the whole range of strains we considered in this study. There are some minor differences between the band structure of SL in figure 2 and the bulk Sr₂IrO₄: In figure 2, the position of the valence band top at X point is lower by ~0.1 eV than that at \( \Gamma \), while they are nearly at the same energy in Sr₂IrO₄ [4, 27]. The same feature is also observed in the \( U > 0 \) calculations (figure 3(a)). The presence of the additional tetragonal crystal field, induced by the interface effect and the strain, yields some small changes in the relative position of the \( j_{\text{eff}} = 1/2 \) and \( 3/2 \) bands compared to the bulk Sr₂IrO₄.
The bandwidth $W$ of the low-energy $j_{\text{eff}} = 1/2$ states, which are located near the Fermi level, is of key importance in understanding the electronic property of RP iridates [28]. One way of defining $W$ is at the $\Gamma$ point as shown in figure 2. The inset of figure 2 presents the change of $W$ as a function of strain. It is clearly seen that the bandwidth $W$ is decreased as larger tensile strain is applied. This result can be surprising if one tries to understand the system based on the ‘rigid IrO$_6$ octahedron’ picture (see, for example, the discussion in Nichols et al [11]).

It is therefore important to note that the Ir–O bond lengths are increased (decreased) under tensile (compressive) strain as mentioned above. Since enlarged bond lengths generally reduce hopping, the reduction of the bandwidth by the tensile strain is attributed to the bond length changes.

3.3. Electronic and magnetic properties with $U_{\text{eff}}$

Figures 3(a)–(d) summarize the calculation results with SOC and $U_{\text{eff}} = 2$ eV. Two different magnetic configurations have been considered: the canted AF spin order (the ground state configuration of Sr$_2$IrO$_4$; see the inset of figure 3(a)) and the collinear AF order (the ground state of Sr$_3$Ir$_2$I$_7$; see the inset of figure 3(b)). In the canted AF state, the Ir moments lie within the $ab$-plane and their angles follow the tilting angles of IrO$_6$ octahedra. In the collinear AF state, the moments are parallel to the $c$-axis. It is found that, as in Sr$_2$IrO$_4$, the canted AF state is more stable than the collinear AF state by about 3 meV Ir$^{-1}$ over the strain range considered in this study.

In both magnetic configurations, the electronic correlation is found to play the key role in opening the gap and stabilizing the AF order as well as the dominant $j_{\text{eff}} = 1/2$ character in the upper Hubbard bands. Similar features were also observed in the previous study of Sr$_2$IrO$_4$ [29]. The calculated band gap of the canted and the collinear AF phase at $a = 3.90$ Å, 0.35 and 0.31 eV, respectively, is comparable to the optical gap of ~0.3 eV for Sr$_2$IrO$_4$ bulk and thin films [11, 28], considering a little ambiguity in the $U_{\text{eff}}$ parameter. Note that, when a larger (tensile) strain is applied, the band gap is markedly increased as shown in figure 3(c), which is consistent with the decreasing trend of $W$ (see figure 2). Importantly, this trend is in good agreement with recent optical spectroscopy data by Nichols et...
al for the Sr2IrO4 thin film under various strain conditions in which the enhancement of the optical gap upon tensile strain was observed [11]. This feature is hard to understand from the point of view of the conventional rigid IrO6 picture as discussed in Nichols et al [11], whereas our result based on the tetragonal distortion of the IrO6 octahedra provide a natural explanation.

Although the collinear AF phase is less stable than the canted AF, the data from this configuration also provides useful information. First, we note that the gap size in the collinear AF is smaller than that of the collinear AF state over the entire range of strain. It is interesting to note that the gap is closed at \( a = 3.80 \text{ Å} \) and the spin moment vanishes simultaneously. Since [SIO]/[STO], SL has considerable similarities in the electronic and magnetic properties with Sr2IrO4, this might provide clues for understanding the peculiar magnetoresistance behavior recently reported in Sr2IrO4 [30]. The experiment by Ge et al [30] seems to indicate a spin-flop-like transition upon application of the external fields parallel to the c-axis. This implies a possible switching of the magnetic configuration by external fields and a significant change of the electronic structure in Sr2IrO4. Our results also suggest a possible insulator-to-metal transition driven by an external magnetic field in the epitaxially strained SIO superlattices and ultrathin films.

Figure 3 (d) shows the change of spin moments with respect to strain. While the spin moment is reduced by increasing tensile strains in the canted AF phase, it is enhanced in the collinear AF state. This feature can be understood by considering the strain-induced tetragonal crystal fields and the low-energy states which have deviated from the ideal \( j_{\text{eff}} = 1/2 \) as follows. Let us consider the \( t_{2g} \) states with the dominating SOC, \( \lambda \), and the nonvanishing tetragonal fields, \( \Delta_t \). The effective atomic Hamiltonian is

\[
\mathcal{H}_{\text{eff}} = \lambda \mathbf{s} \cdot \mathbf{t} \mathcal{A} + \Delta_t \mathbf{l}_{\text{eff}} \mathcal{A},
\]

where \( \lambda < 0 \) for the \( t_{2g} \) states. Among the six eigenstates of equation (2), the upper twofold-degenerate states are given by [33]

\[
\pm \hat{s}_z = \pm \sin \theta \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \mp \cos \theta \begin{pmatrix} \pm 1 \\ 0 \\ -1 \end{pmatrix},
\]

or, when quantized along the in-plane (say, the octahedral \( x \)-direction),

\[
\pm \hat{s}_x = \pm 1/\sqrt{2} \begin{pmatrix} 1 \\ \mp 1 \end{pmatrix}.
\]

The orbital angle \( \theta \) is defined as \( \tan(2\theta) = 2\sqrt{2} \lambda / (\lambda - 2\Delta_t) \), and in the perfect cubic symmetry (\( \Delta_t = 0 \), \( \theta_{\text{cubic}} \approx 0.2 \pi \)) equation (3) reduces to the ideal \( j_{\text{eff}} = 1/2 \) states defined in equation (1). From equation (2) one can notice that the presence of the tensile strain or the confinement effect, which lowers the energy of the \( d_{xy} \) state (\( \Delta_t > 0 \)), corresponds to the larger \( \theta \). The strain dependence of the ordered spin moment in the collinear and the canted AF phases can be estimated from equations (3) and (4), respectively. For the collinear AF, \( \pm \hat{s}_z \) forms the lower/upper Hubbard bands to yield the local spin and orbital moments parallel to the \( z \)-axis on the Ir sites. The expectation value of \( s_z \) is

\[
\langle \pm | s_z | \pm \rangle = \pm 1/2 \cos(2\theta).
\]

In the canted AF phase, on the other hand, the moments are parallel to the octahedral \( x \)-axis, and the expectation value is

\[
\langle \pm | s_x | \pm \rangle = \mp 1/4 (1 - \cos(2\theta)).
\]

It is clear that \( |\langle \pm | s_x | \pm \rangle| \) and \( |\langle \pm | s_z | \pm \rangle| \) behave in different ways with respect to \( \Delta_t \); with larger tensile strains, \( |\langle \pm | s_x | \pm \rangle| \) is enhanced and \( |\langle \pm | s_z | \pm \rangle| \) is reduced. This is consistent with the results of figure 3(d) in the region \( \theta < \pi/4 \). Since the confinement effect in the SL introduces a significant amount of \( \Delta_t > 0 \), the \( \theta \) is smaller than \( \theta_{\text{cubic}} < \pi/4 \) over the entire range of strains.

4. Concluding remarks

We have investigated the structural, electronic, and magnetic properties of SIO/STO SL. The results clearly demonstrate...
the similarity between [SIO]/[STO] SL and bulk Sr2IrO4, as is to be expected from their structural similarities. By adding extra dimensions of controllability, the SL form of iridates can provide interesting new information for understanding the 5d transition metal oxides. This could be an important next step in the investigation of [SIO]2/[STO] SL in comparison with Sr3Ir2O7 [27, 31]. As the SIO-layer thickness is increased from the ultrathin limit to the bulk regime, the electronic structure can evolve from the insulating to the nodal semimetallic phase which also deserves intensive future study [14, 28, 32].

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References

[1] Datta S and Das B 1990 Appl. Phys. Lett. 56 665
[2] Qi X-L, Li R, Zang J and Zhang S-C 2009 Science 323 1184
[3] Mattheiss L F 1976 Phys. Rev. B 13 2433
[4] Kim B J et al 2008 Phys. Rev. Lett. 101 076402
[5] Kim B J, Ohsumi H, Komesu T, Sakai S, Morita T, Takagi H and Arima T 2009 Science 323 1329
[6] Witzak-Krempa W, Chen G, Kim Y B and Balents L 2014 Ann. Rev. Condens. Matter Phys. 5 57–82
[7] Kane C L and Mele E J 2005 Phys. Rev. Lett. 95 226801
[8] Chang C-Z et al 2013 Science 340 167
[9] Shitade A, Katsura H, Kuneš J, Qi X-L, Zhang S-C and Nagaosa N 2009 Phys. Rev. Lett. 102 256403
[10] Rayan Serrao C et al 2013 Phys. Rev. B 87 085121
[11] Nichols J, Terzic J, Bittle E G, Korneta O B, De Long L E, Brill J W, Cao G and Seo S S A 2013 Appl. Phys. Lett. 102 141908
[12] Nichols J, Korneta O B, Terzic J, De Long L E, Cao G, Brill J W and Seo S S A 2013 Appl. Phys. Lett. 103 131910
[13] Jenderka M, Barzola-Quiquiu J, Zhang Z, Frenzel H, Grundmann M and Lorenz M 2013 Phys. Rev. B 88 045111
[14] Jobu M, Kota I, Shugen Y, Hiroki W, Kenji I, Shankar Vijay V, Hae-Young K and Hidenori T 2014 arXiv:1401.1066
[15] Han M, Ozaki T and Yu J 2006 Phys. Rev. B 73 045110
[16] Ozaki et al 2013 Open MX Technical notes (www.openmx-square.org)
[17] Ozaki T 2003 Phys. Rev. B 67 155108
[18] Perdew J P, Burke K and Emzerhof M 1996 Phys. Rev. Lett. 77 3865
[19] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Phys. Rev. B 57 1505
[20] Arita R, Kuneš J, Kozhevnikov A V, Eguiluz A G and Imada M 2012 Phys. Rev. Lett. 108 086403
[21] Foyevtsova K, Jeschke H O, Mazin I I, Khomskii D I and Valenti R 2013 Phys. Rev. B 88 035107
[22] Kresse G and Hafner J 1993 Phys. Rev. B 47 558
[23] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[24] Crawford M K, Subramanian M A and Harlow R L 1994 Phys. Rev. B 49 9198
[25] Haskel D, Fabbri G, Zhernenkov M, Kongs P P, Jin C Q, Cao G and van Veenendaal M 2012 Phys. Rev. Lett. 109 027204
[26] Hyun K B, Khalilullin G and Min B I 2012 Phys. Rev. Lett. 109 167205
[27] Zhang H, Haule K and Vanderbilt D 2013 Phys. Rev. Lett. 111 246402
[28] Moon S J, Jin H, Choi W S, Lee J S, Seo S S A, Yu J, Cao G, Noh T W and Lee Y S 2009 Phys. Rev. B 80 195110
[29] Jin H, Jeong H, Ozaki T and Yu J 2009 Phys. Rev. B 80 075112
[30] Ge M, Qi X F, Korneta O B, De Long D E, Schlottmann P, Crummett W P and Cao G 2011 Phys. Rev. B 84 100402
[31] Kim J W, Choi Y, Kim J, Mitchell J F, Jackeli G, Daghofer M, van den Brink J, Khalilullin G and Kim B J 2012 Phys. Rev. Lett. 109 037204
[32] Carter J-M, Vijay Shankar V, Ahsan Zeb M and Kee H-Y 2012 Phys. Rev. B 85 115105
[33] Jackeli G and Khalilullin G 2009 Phys. Rev. Lett. 102 017205