Electronic and Magnetic Structure under Lattice Distortion in SrIrO$_3$/SrTiO$_3$ Superlattice: A First-Principles Study

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Abstract. Motivated by recent experiments on (001) [SrIrO$_3$]$_m$/[SrTiO$_3$]$_1$ superlattice (J. Matsuno, et al., arXiv:1401.1066), we perform first-principles calculations to study the electronic and magnetic structure of this superlattice under lattice distortion. We consider two different magnetic structures, a non-collinear in-plane canted antiferromagnetic (AFM) order and a collinear AFM order along $c$ direction, and find that these two AFM states exhibit different strain dependence. The canted AFM order is enhanced with compressive strain while the collinear AFM order is enhanced with tensile strain. Moreover, the local magnetic moments of these magnetic structures show different linear dependence with respect to compressive or tensile epitaxial strain. We also find that the electronic band structure is sensitive to strain, local rotation, and $ab$-plane Ir-O bond length. Under a certain condition of lattice distortion, the band gap is even closed to induce an effective total angular momentum $J_{\text{eff}} = 1/2$ metal. These unexpected behaviors deserve more careful investigation on the microscopic mechanism played by a strong spin-orbit coupling, electron correlations, and lattice distortion.

1. Introduction

The discovery of novel effective total angular momentum $J_{\text{eff}} = 1/2$ states in Sr$_2$IrO$_4$ by Kim et al. [1] is like a knocking stone dropped into a peaceful pond. The inherently large spin-orbit coupling (SOC) of 5$d$ orbitals in Ir ion reorganizes the $t_{2g}$ states into so called $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$ states, provided that the local crystal field separates unoccupied $e_g$ states and partially occupied $t_{2g}$ states (five electrons per Ir ion) in a much larger energy scale. Soon after the discovery of the $J_{\text{eff}}$ states, Moon et al. [2] have established a general picture of the electronic states for Ruddlesden-Popper series Sr$_{n+1}$Ir$_n$O$_{3n+1}$ ($n = 1, 2, \infty$) based on the interplay among SOC, electron correlations ($U$), and band width ($W$). As $W$ becomes larger with increasing the number $n$ of perovskite layers, the series turns from insulating ($n = 1, 2$) to metallic ($n = \infty$) state. Although the insulating Ir oxides, Sr$_2$IrO$_4$ (hereafter 214) and Sr$_3$Ir$_2$O$_7$ (hereafter 327), have promoted a large amount of research, the metallic compound, SrIrO$_3$ (hereafter 113), has not received much attention. This is presumably because on the experimental side, it requires high pressure and high temperature to synthesize 113 [3], and on the theoretical side, 113 has...
three-dimensional (3D) perovskite structure while the other 214 and 327 compounds are in two-dimensional (2D) perovskite structures. The available experimental results suggest that 113 is a bad metal close to the metal-insulator transition boundary [4], as manifested by the low-temperature upturn in resistivity [5].

Recently, Matsuno and coworkers [6] have fabricated the (001) \([\text{SrIrO}_3]_m/[\text{SrTiO}_3]_1\) (hereafter SIO/STO) superlattice (SL) and found a signature of metal-insulator transition as the number \(m\) of SrIrO\(_3\) layers decreases below 4. Thus building superstructures such as SL is another effective way to tip the metallic state in 113 bulk to an insulating state. It has been suggested that the magnetic structure is a canted in-plane antiferromagnetic (AFM) order with a weak ferromagnetic moment (see Fig.1(b)) for a single 113 layer \((m=1)\) [6]. This in-plane canted AFM structure is the same ground state as the one for 214 bulk [1]. Thus it is interesting to make a comparable study between SIO/STO SL and 214 bulk. Indeed, both experimental [6] and theoretical [7] studies suggest that SIO/STO SL with a single 113 layer \((n=1)\) is similar to 214 bulk in the electronic and magnetic structure. By the same token, it is also natural to expect that SL with \(m > 1\) would be comparable to \(\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}\) \((n > 1)\), following Moon’s picture [2]. The story would come to the end if SIO/STO SL were simply an artificial duplicate material of the corresponding bulk. As will be shown below, the detailed analysis reveals distinct properties between the SL and bulk compounds due to the intrinsic structural difference.

Here, based on first principles calculations, we report the electronic and magnetic properties under various lattice distortion for the SL with \(m=1\) \([\text{SrIrO}_3]_1/[\text{SrTiO}_3]_1\). Considering two different magnetic structures, we show that in both cases the magnetic moment depends differently on the compressive or tensile strain. The band structure is also found to be sensitive to local distortion. We demonstrate that the band gap in the \(J_{\text{eff}}=1/2\) based bands can be closed in certain condition to induce an insulator-metal transition.

2. Computational Method

Our calculations are performed by using density functional theory (DFT) with local (spin) density approximation (L(S)DA) implemented in the Vienna Ab Initio Simulation Package (VASP) [8], adopting the projector augmented wave (PAW) method [9]. The valence electrons are described by a plane-wave basis set with an energy cutoff of 400 eV, and the convergence criterion on the total energy is \(1 \times 10^{-6}\) eV. At least, \(6 \times 6 \times 2\) \(k\)-point grids are employed. To take into account the correlation effects and strong SOC effect of Ir 5\(d\) orbitals, the L(S)DA+U+SOC method is adopted, where the on-site Coulomb energy \(U\) and the exchange interaction \(J\) are treated using the rotationally invariant method introduced by Liechtenstein et al [10]. The \(U\) and \(J\) values are chosen to be 2.3 eV and 0.16 eV, respectively [11]. For optimization of the SIO/STO superlattice, we compared LDA, LDA+U, LDA+SOC, and LDA+SOC+U methods. The optimized structure parameters (see Fig. 1(c)) are quite similar among these methods. Therefore, to save the computational time, we can safely relax the structure with LDA and use this relaxed structure for other methods. To mimic the epitaxial strain, the structure relaxation is performed as follows: (1) We first optimize the lattice constants and the atomic positions of \([\text{SrIrO}_3]_1/[\text{SrTiO}_3]_1\) under the tetragonal crystalline symmetry, (2) we then fix the in-plane lattice constant at a certain value \(a\) around the optimized one \(a^{\text{opt}}\) obtained in (1), and optimize the out-of-plane lattice constant \(c\) and the atomic positions so as to minimize the total energy, and (3) we repeat the calculation (2) for different values of \(a\) and the epitaxial strain (\%) is defined as \(100 \times (a - a^{\text{opt}})/a\).

3. Results

3.1. Ground state

The structure crystallizes to a tetragonal lattice, as shown in Fig. 1(a). The lattice constants obtained are \(a=3.83\) Å and \(c=7.76\) Å, which are in consistent with the experimental value [6]. To
determine the ground state magnetic structure, we calculate the total energy of two different magnetic structures, the canted in-plane AFM and along-c collinear AFM structures, as shown in Fig. 1(b). The ground state turns out to be canted AFM with a weak ferromagnetic moment along either \(a\) or \(b\) axis, which is in good agreement with experiments [6] and previous calculations [7]. Due to the correlation \(U\), a band gap opens between the \(J_{\text{eff}}=1/2\) based states (see Fig. 3(a)). In the following subsections, we examine in detail how the magnetic and electronic structure changes under strain or local octahedron distortions.

### 3.2. Magnetic structure

To study strain effects, we systematically change the lattice constant in \(ab\)-plane from 3.75Å to 3.95Å, and relax \(c\)-axis lattice constant as well as the internal atomic coordinates for a given in-plane lattice constant until the optimized structure is obtained. The optimized \(c\)-axis lattice constant decreases under tensile strain and increases under compressive strain, which is in consistent with expectation. The IrO\(_6\) (TiO\(_6\)) octahedron is distorted locally in an antiferroelectric way, i.e., rotating along the \(c\)-axis in phase (out of phase), instead of simply altering the Ir-O (Ti-O) bond length, as shown in Fig. 1(a).

As shown in Fig. 2, the magnetic moments for the two different magnetic structures exhibit different dependence of compressive or tensile strain. Because the canted AFM structure has a weak ferromagnetic moment, we decompose the local magnetic moment to \(m_y\) (along the AFM direction) and \(m_x\) (along the canted ferromagnetic direction). We also plot in Fig. 2 the
Figure 2. Local magnetic moment with varying strain for the in-plane canted AFM structure ($m_x$ and $m_y$) and the along-c collinear AFM structure ($m_z$). Solid lines are linear fitting of the moments. The epitaxial strain corresponding to the SrTiO$_3$ substrate is indicated by an arrow.

magnetic moment ($m_z$) for the collinear AFM structure along c direction. We find that both $m_y$ and $m_z$ increase with increasing the compressive strain while $m_z$ enhances with increasing the tensile strain. The different dependence is due to the resulting tetragonal distortion by either compressive or tensile strain. The compressive strain shifts the $d_{xy}$ orbital level ($E_{d_{xy}}$) higher in energy than the $d_{yz}$ and $d_{xz}$ levels ($E_{d_{yz/xz}}$), and thus $\Delta = E_{d_{xy}} - E_{d_{yz/xz}}$ is positive. On the other hand, the tensile strain shifts $E_{d_{xy}}$ lower than $E_{d_{yz/xz}}$, and thus $\Delta$ is negative. A positive $\Delta$ favors the canted AFM structure while a negative $\Delta$ favors the collinear AFM structure [7, 12].

An unexpected behavior is found in the strain dependence of the magnetic moments. As shown in Fig. 2, $m_x$ for the canted AFM structure seems to vary smoothly under compressive or tensile strain. However, $m_y$ for the canted AFM structure and $m_z$ for the collinear AFM structure exhibit different strain dependence for the compressive and tensile cases. We have also examined the strain dependence of $\alpha_{Ir}$ and $\alpha_{Ti}$ and found that $\alpha_{Ti}$ is correlated to the unexpected behavior of the magnetic moments $m_y$ and $m_z$. The reason why $\alpha_{Ti}$ is relevant to the magnetic moments can be understood in the electronic band structures. In Fig. 3(b), we show the electronic band structure for SL ($m = 1$) under compressive strain. The bands with the $j_{eff} = 1/2$ character and the bands with the Ti-3$d$ character already mix with each other above Fermi level at around 6 eV at the $\Gamma$ point. This indicates that the electron hopping between Ti-3$d$ and $j_{eff} = 1/2$ states should play a role to influence Ir magnetic moment via the effective exchange interaction.
3.3. Electronic band structure

The local lattice distortion affects the electronic band structure and sometimes induces novel electronic phases. Fig. 3(a) shows the electronic band structure for SL \((m = 1)\) with the optimized structure. The band gap opens between the upper and lower \(J_{\text{eff}} = 1/2\) based bands, which is in good agreement with the previous reports \([7]\). The bands immediately above the upper \(J_{\text{eff}} = 1/2\) based bands (around 0.5 eV at the \(\Gamma\) point) have Ti-3\(d\) character, indicating that the Ti-3\(d\) bands are close to the upper \(J_{\text{eff}} = 1/2\) based bands. This behavior is more pronounced when the compressive strain is applied, as shown in Fig. 3(b), where the upper \(J_{\text{eff}} = 1/2\) based bands are mixed with the bands originated from Ti-3\(d\) at the \(\Gamma\) point around 0.5 eV above the Fermi energy \((E_F)\).

Next, we increase the rotation of local IrO\(_6\) and TiO\(_6\) octahedra both in-phase (IrO\(_6\)) and out-of-phase (TiO\(_6\)) and examine how the electronic band structure evolves. The electronic band structure obtained is shown in Fig. 3(c), corresponding to \(\alpha_{\text{Ir}} = \alpha_{\text{Ti}} = 16^\circ\), which is larger than the optimized values \(\alpha_{\text{Ir}} = 14.5^\circ\) and \(\alpha_{\text{Ti}} = 3.5^\circ\). Due to the enhanced rotational distortion, the band mixing between the upper \(J_{\text{eff}} = 1/2\) based bands and the Ti-3\(d\) based bands disappears. Now if we adjust the local \(ab\)-plane Ir-O (Ti-O) bond length to be inequivalent between the nearest neighbor octahedrons, the band structure changes dramatically, especially in the \(J_{\text{eff}} = 1/2\) based bands, as shown in Fig. 3(d). The almost doubly degenerate upper \(J_{\text{eff}} = 1/2\) bands along the X-M line are lifted and one of these bands is pushed downward to cross the Fermi energy. This unexpected insulator-metal transition demonstrates that the \(J_{\text{eff}} = 1/2\) based bands of the SIO/STO SL with \(m = 1\) are very sensitive to local distortion.

Figure 3. Electronic band structure of SL with \(m = 1\) along high symmetry momentum directions for various distortions: (a) optimized structure, (b) with compressive strain, (c) with enhanced rotation of local IrO\(_6\) and TiO\(_6\) octahedra, (d) with additional distortion for Ir-O (Ti-O) bond length. The Fermi energy is denoted as \(E_F\) at zero energy (dashed lines).
4. Summary
We have performed first principles calculations on the SIO/STO superlattice with several approximate schemes including LDA, LDA+U, LDA+SOC, and LDA+SOC+U. We have demonstrated that the magnetic and electronic structure is very sensitive to the lattice distortion. We have found that the magnetic moments follow the different linear dependence under the compressive or tensile strain. The electronic band structure indicates that the magnetic structure is influenced by the band mixing between $J_{\text{eff}} = 1/2$ based bands and the Ti-3$d$ based bands above $E_F$. The degree of this mixing can be tuned by the strain. Indeed, we have found that the band mixing increases (decreases) by the compressive strain (by the tensile strain or by increasing the local rotation of IrO$_6$ and TiO$_6$ octahedron). We have also shown that in certain conditions, the band gap can be closed between the $J_{\text{eff}} = 1/2$ based bands, e.g., by increasing the local rotation with an inequivalent in-plane Ir-O (Ti-O) bond length. These unusually sensitive electronic and magnetic properties to the lattice distortion urgently require more careful and intensive research in $5d$ materials with the strong SOC.

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References
[1] Kim B J, Jin H, Moon S J, Kim J Y, Park B G, Leem C S, Yu J, Noh T W, Kim C, Oh S J, Park J H, Durairaj V, Cao G and Rotenberg E 2008 Phys. Rev. Lett. 101 076402.
[2] Moon S J, Jin H, Kim K W, Choi W S, Lee Y S, Yu J, Cao G, Sumu A, Funakubo H, Bernhard C and Noh T W 2008 Phys. Rev. Lett. 101 226402.
[3] Longo J M, Kafalas J A, Arnott R J 1971 J. Solid State Chem. 3 174.
[4] Cheng J, Zhou J, Goodenough J B, Matsubayashi K, Uwatoko Y 2014 JPS Conf. Proc. 3 013014.
[5] Zhao J G, Yang L X, Yu Y, Li F Y, Yu R C, Fang Z, Chen L C. Jin C Q 2008 J. Appl. Phys. 103 103706.
[6] Matsuno J, Ihara K, Yamamura S, Wadati H, Ishii K, Vijay Shankar V, Kee H Y, Takagi H 2014 arXiv:1401.1066.
[7] Kim K, Kim H, Han M J 2014 J. Phys.: Condens. Matter 26 185501.
[8] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169.
[9] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758.
[10] Liechtenstein A I, Anisimov V I, Zaanen J 1995 Phys. Rev. B 52 R5467.
[11] Arita R, Kunes J, Kozhevnikov A V, Eguíluz A G and Imada M 2012 Phys. Rev. Lett. 108 086403.
[12] Jackeli G and Khaliullin G 2009 Phys. Rev. Lett. 102 017205.