Electron and hole doping in the relativistic Mott insulator Sr$_2$IrO$_4$: a first-principles study using band unfolding technique

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We study the effects of dilute La and Rh substitutional doping on the electronic structure of the relativistic Mott insulator Sr$_2$IrO$_4$ using fully relativistic and magnetically non-collinear density functional theory with the inclusion of an on-site Hubbard $U$ (DFT+$U$+SOC). To model doping effects, we have adopted the supercell approach, that allows for a realistic treatment of structural relaxations and electronic effects beyond a purely rigid band approach. By means of the band unfolding technique we have computed the spectral function and constructed the effective band structure and Fermi surface (FS) in the primitive cell, which are readily comparable with available experimental data. Our calculations clearly indicate that La and Rh doping can be interpreted as effective electron and (fractional) hole doping, respectively. We found that both electron and hole doping induce an insulating-to-metal transition (IMT) but with different characteristics. In Sr$_{2-x}$La$_x$IrO$_4$ the IMT is accompanied by a moderate renormalization of the electronic correlation substantiated by a reduction of the effective on-site Coulomb repulsion $U - J$ from 1.6 eV ($x = 0$) to 1.4 eV (metallic regime $x = 12.5\%$). The progressive closing of the relativistic Mott gap leads to the emergence of connected elliptical electron pockets at $(\pi/2, \pi/2)$ and less intense features at $X$ in the Fermi surface. The average ordered magnetic moment is slightly reduced upon doping but the canted antiferromagnetic state is perturbed in the Ir-O planes located near the La atoms. The substitution of Ir with the nominally isovalent Rh is accompanied by a substantial hole transfer from the Rh site to the nearest neighbor Ir sites. This shifts down the chemical potential, creates almost circular disconnected hole pockets in the FS and establishes the emergence of a two-dimensional metallic state formed by conducting Rh-planes intercalated by insulating Ir-planes. Finally, our data indicate that hole doping causes a flipping of the in-plane net ferromagnetic moment in the Rh plane and induces a magnetic transition from the AF-I to the AF-II ordering.

I. INTRODUCTION

The recently reported spin-orbital $J_{\text{eff}} = 1/2$ Mott insulating state in Sr$_2$IrO$_4$ [1, 2] has stimulated a lot of fundamental research aiming to clarify the underlying mechanism responsible for this novel state of matter which arises from the cooperative interplay of the crystal field, spin-orbit coupling (SOC), electron-electron interaction ($U$), and different types of simultaneously active spin-exchange interactions [3–7]. An important aspect of Sr$_2$IrO$_4$ that also has attracted considerable attention is its similarity with high-$T_c$ cuprate superconductors such as La$_2$CuO$_4$: these two compounds share the same quasi-two-dimensional layered perovskite structure, Ir and Cu have a nominal $d^5$ and $d^9$ configuration with one effective hole per site and both compounds are described by a $S(J_{\text{eff}}) = 1/2$ antiferromagnetic (AF) Heisenberg model [8–11]. Theoretical studies reporting the possible onset of superconductivity in electron-doped Sr$_2$IrO$_4$ [10, 11] have spurred an immediate experimental research that have reported the existence of unusual (pseudogap) metallic states in Sr$_{2-x}$La$_x$IrO$_4$, somehow similar to high-$T_c$ cuprates, but no sign of superconductivity has been found down to very low temperatures for supposedly optimal doping [12–15]. On whether the Fermi surface (FS) is formed by disconnected Fermi arcs or Fermi lenses is still experimentally uncertain. More generally, electron and hole doping in (relativistic) Mott insulators are one of the most studied and controversial issues in solid state theory due to the complex impact that excess carriers can have on the competing spin/charge/orbital interactions [16]. In Sr$_2$IrO$_4$ the study of doping effects can provide important insights on the robustness and tunability of the spin-orbital Mott state and of the canted in-plane antiferromagnetic ordering. This is associated with a controlled doping-induced modulation of the dominant interactions, in particular SOC and $U$, as well as with possible changes of the atomic positions (structural distortions), that can have a strong repercussion on the electronic and magnetic properties.

Among the different forms of electron and hole doping tested in this system, the most studied ones are the substitution of Sr$^{2+}$ with La$^{3+}$ (electron doping) and the homovalent hetero-substitution of $5d^5$ Ir$^{4+}$ with $4d^5$ Rh$^{4+}$ (effective hole doping) [15, 17–26]. In one of the first studies, Lee and coworkers conducted a systematic investigation of La, Rh, and Ru doping in Sr$_2$IrO$_4$ by means of optical spectroscopy and found that the $J_{\text{eff}} = 1/2$ state remains spectroscopically robust upon doping and that in all cases doping induces an insulator-to-metal transition (IMT) for moderately low dopant concentrations ($\approx 5\%$) [19]. They have

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also suggested that the IMT is associated with subtle alterations of the strength of $U$ and SOC [19]. This hypothesis has been studied more recently in a combined angle-resolved photoelectron spectroscopy (ARPES) and tight-binding study of La-doped Sr$_2$IrO$_4$ where the authors have concluded that an optimal agreement between experiment and calculation can be achieved assuming a fast quenching of $U$ from 2 eV to 0 eV across the transition [15]. On the other hand, the idea that a reduction of the SOC should be responsible for the closing of the Mott gap in the Rh-doped sample has been revised by Cao and coworkers: they have shown that Rh doping effectively corresponds to hole doping and therefore also in this case the IMT can be explained by a band-filling mechanism [21]. In our study we reconcile these two apparently conflicting interpretations and will show that the effective hole doping mechanism is assisted by the different SOC strength in Rh and Ir.

Substitutional doping has also a significant influence on the magnetic order. Upon La doping, a complex phase diagram was proposed showing the weakening of the long-range antiferromagnetic (AF) order and the appearance of spin-glass-like phase beyond a critical La concentration [24]. Rh doping was found to induce a magnetic transition from the AF-I to the AF-II state involving the in-plane flipping of the net ferromagnetic (FM) moment [22, 23] as shown in Fig. 1(b).

Despite the relatively large amount of experimental studies on doped Sr$_2$IrO$_4$ first-principles calculations were not reported to date. In this work, we study the evolution of the spin canting Mott state in Sr$_2$IrO$_4$ as a function of La and Rh doping using relativistic density functional theory with the inclusion of an on-site Hubbard $U$, the same scheme that we have used for the description of the ground state electronic and magnetic interactions in the undoped compound [6]. Doped Mott insulators are generally studied using model Hamiltonian schemes as these methods are designed to describe the role of strong correlation across the IMT, in particular band renormalization and the transfer of spectral weight, which are not accessible by single-particle approaches. However, the combined ARPES and tight-binding study of La Torre et al. [15] indicates that the band structure of doped Sr$_2$IrO$_4$ is sufficiently well described using single-particle-like dispersions suggesting that a single-particle band theory like DFT+$U$ might be a suitable approximation in this case. We will carefully address this point in this work.

From an ab initio perspective the realistic treatment of doping requires the employment of large supercells (SC) and for a one-to-one comparison with available ARPES electronic structure it is necessary to map the band structure calculated in the supercell into an effective band structure (EBS) projected in the Brillouin zone of the primitive cell. To this aim we used the band structure unfolding method introduced few years ago by Popescu and Zunger [27, 28] and recently incorporated in the Vienna Ab initio Simulation Package (VASP) [29, 30]. With this approach we have computed the EBS and FS of La- and Rh-doped Sr$_2$IrO$_4$ at different concentrations across the IMT and the obtained results are in reasonable agreement with the available ARPES spectra. Our data suggest that La doping leads to a moderate reduction of the effective Coulomb interaction $U_{\text{eff}}=U-J$ from 1.6 eV, optimum value in the undoped system, to 1.4 eV at the electron doping concentration $x=12.5\%$. The upshift of the chemical potential upon electron doping and the renormalization of the electronic correlation result in a metallic state, however, we fail to predict the merging of the lower and upper Hubbard band at low electron doping concentrations at the optimum $U_{\text{eff}}$ values. The complete closing of the gap is achieved for smaller values of $U_{\text{eff}}$ ($\approx 0.8$ eV). As already mentioned, although Rh in Sr$_2$RhO$_4$ is isoelectric with Ir in Sr$_2$IrO$_4$, our DFT results confirm the experimental conclusions that Rh substitution in Sr$_2$IrO$_4$ acts as a hole donor shifting up the valence bands and creating a hole pocket around the $X$ point.

In the next section we will provide the technical details on the computational methods and setup. The results will be presented and discussed in Sec. III and summarized in Sec. IV.

II. COMPUTATIONAL DETAILS

Our first-principles calculations including $U$ and SOC were performed using the projector augmented wave method [31] as implemented in VASP [32, 33]. The Perdew-Burke-Ernzerhof (PBE) [34] approximation was employed for the exchange-correlation functional. Plane waves have been included up to an energy cut off of 400 eV. 4x4x2 $\bar{k}$-point grids were used to sample the Brillouin zone. For the undoped case, we used an effective $U_{\text{eff}} = U - J = 1.6$ eV on the Ir site, computed using the constrained random phase approximation.
FIG. 2. (color online) The relation between primitive cell (pc) and supercell (SC) in real space for (a) undistorted \( I4/mmm \) and (b) distorted \( I4_{1}/acd \) structure. (c) The corresponding primitive (pbz) and supercell (SBZ) Brillouin zones, and their associated wave vectors \( \mathbf{k} \) and \( \mathbf{\bar{k}} \) connected by the reciprocal lattice vector \( \mathbf{G} \) of the supercell, are illustrated. Note that in (c) the fractional coordinates of high-symmetry points are displayed using \( I4/mmm \) notation in units of \( 1/\alpha_0 \) with \( \alpha_0 \) being the ab-plane lattice constant of the undistorted structure.

(cRPA), which yields a very good account of the ground state electronic and magnetic properties [6]. The cRPA has also been employed to compute the \( U_{\text{eff}} \) in the high-doping regime \( (x = 12.5\%) \). For the Rh doping case, we have included an on-site \( U_{\text{eff}}=1.2 \) eV on the Rh sites, estimated by cRPA [35].

In order to fully account for the doping effects on the electronic structure of doped \( \text{Sr}_2\text{IrO}_4 \), we employed the supercell approach. The supercell \( (\sqrt{2} \times \sqrt{2} \times 1) \) with 112 ions, depicted in Fig. 1(a), was constructed based on the experimental unit cell with \( I4_{1}/acd \) symmetry [36], as shown in Fig. 2(b). For the La doping (La\(^{3+}\) for \( \text{Sr}^{2+}\) [18] the chemical formula becomes \( \text{Sr}_{32-2x}\text{La}_{x}\text{Ir}_{16}\text{O}_{64} \) with \( y \) being the number of La\(^{3+}\) ions in the supercell. Thus, substitution of one (two) \( \text{Sr}^{2+} \) by La\(^{3+}\) corresponds to a La doping concentration \( y \) of 3.125% (6.25%). It should be noted that the nominal electron doping counted per Ir site is doubled due to the stoichiometry of \( \text{Sr}_2\text{IrO}_4 \) [15], yielding electron doping concentrations of \( x=2y=6.25\% \) and 12.5%, respectively. With respect to the concentration \( x \), the general chemical formula for La doping reads \( \text{Sr}_{32-2x}\text{La}_{x}\text{Ir}_{16}\text{O}_{64} \). For the Rh doping (Rh\(^{3+}\) for \( \text{Ir}^{4+} \) in the supercell \( \text{Sr}_{22}\text{Ir}_{16-x}\text{Rh}_{x}\text{O}_{64} \) [21], substitution of one (two) \( \text{Ir}^{4+} \) by Rh\(^{3+}\) results in nominal hole doping on the Ir site of \( x=6.25\% \) (12.5%). To avoid confusion, we use \( x \) to label the electron (hole) doping concentration throughout the paper. Unless explicitly stated, all supercell calculations were performed by fully relaxing the atomic positions at fixed volume, corresponding to the experimental volume of the undoped compound, in order to preserve local structural effects of the dopant atoms.

To analyze the effects of doping on the band structure of the employed supercells, we have adopted the unfolding technique recently implemented in VASP [29, 30]. In fact, calculations based on the supercell approach, with a unit cell \( N \) times larger than the primitive cell, lead to a down folded Brillouin zone that, in most cases, makes it difficult to interpret directly the resulting band structures. An unfolding technique is required in order to obtain a clearer description of the band structure. The relation

\[ \mathbf{k} + \mathbf{\bar{g}} = \mathbf{\bar{k}} + \mathbf{G} \]

(1)
describes the folding of the reciprocal space, mapping a wave vector \( \mathbf{\bar{k}} \) of the supercell into \( N \) wave vectors \( \mathbf{\bar{k}} \) in the Brillouin zone of the primitive cell (pbz), by means of the reciprocal lattice vectors \( \mathbf{\bar{g}} \) and \( \mathbf{G} \) of the primitive and supercell, respectively [see Fig. 2(c)]. The projection \( P_{\bar{K}m}(\mathbf{\bar{k}}) \) of the eigenstates \( |\Psi_{\bar{K}m}\rangle \) of the supercell into eigenstates \( |\psi_{\bar{K}m}\rangle \) of the primitive cell, where \( m \) and \( n \) are energy band indexes, provides an effective band structure (EBS) in the pbz starting from eigenvalues calculated in the Brillouin zone of the supercell (SBZ). As proved by Popescu and Zunger [27, 28], the projection \( P_{\bar{K}m}(\mathbf{\bar{k}}) \), called Bloch character, can be written in terms of the plane wave coefficients of the supercell eigenstates only. In fact, given Eq. (1), the eigenstates of the supercell can be written as

\[ |\Psi_{\bar{K}m}(\mathbf{\bar{k}})\rangle = \sum_{\bar{c}} C_{\bar{k}+\bar{c},m} e^{i(\bar{k}+\bar{G})\cdot\bar{r}} |\psi_{\bar{K}m}\rangle \]

\[ = \sum_{\bar{c}} \sum_{\bar{f}} C_{\bar{k}+\bar{c},\bar{f}} e^{i(\bar{k}+\bar{G})\cdot\bar{r}} |\psi_{\bar{K}m}\rangle \]

(2)

Therefore, the Bloch character can be obtained from the supercell calculation alone and no primitive cell calculations are required, because of the relation:

\[ P_{\bar{K}m}(\mathbf{\bar{k}}) = \sum_{n} \langle |\Psi_{\bar{K}m}(\mathbf{\bar{k}})\rangle |\psi_{\bar{K}m}\rangle^{2} \]

\[ = \sum_{\bar{f}} |C_{\bar{k}+\bar{G},\bar{m}}|^{2} \]

(3)

The spectral function \( A(\mathbf{\bar{k}}, E) \) can be hence calculated as

\[ A(\mathbf{\bar{k}}, E) = \sum_{m} P_{\bar{K}m}(\mathbf{\bar{k}}) \delta(E_{m} - E) \]

(4)

providing a directly comparison of the calculated EBS with ARPES experiments in the reciprocal space of the primitive cell.
FIG. 3. (color online) Band structure of (a) primitive cell and (b) supercell. (c) EBS calculated from the unfolding method. Note that the color bar in (c) represents the Bloch character given by Eq. (3). The high-symmetry points here are consistent with the primitive $I4/mmm$ notation displayed in Fig. 2(c).

To validate and demonstrate the applicability of the unfolding scheme, we show in Fig. 3 a comparison between the ground state band structure of undoped Sr$_2$IrO$_4$ in the primitive $I4_1/acd$ cell [Fig. 3(a)] and in the $I4_1/acd$ supercell [Fig. 3(b)], together with the EBS of the supercell unfolded into the primitive cell [Fig. 3(c)]. The primitive cell band structure exhibits the well known relativistic Mott state formed by one filled and one empty band, usually referred to as lower and upper relativistic Mott-Hubbard bands (LHB and UHB, respectively), which are separated by a small band gap of about 0.3 eV [1]. The EBS of the undoped supercell shown in Fig. 3(c) reproduces well this behavior: the EBS are formed by sharp bands reflecting the fact that the eigenstates of the primitive cell can contribute either fully or not at all to a given supercell eigenstate. Dopant atoms will clearly disrupt this one-to-one correspondence between supercell and primitive cell eigenstates, introducing mixed contributions represented by intermediate values for the Bloch characters and, hence, broadened bands.

III. RESULTS AND DISCUSSION

A. La doping

We start this section by discussing the relation between doping and electron-electron correlation. The ARPES spectra clearly indicate a fast collapse of the relativistic Mott gap and the appearance of a large Fermi surface at relatively low doping levels [15]. As La doping effectively induces excess electrons in the system, one would expect that the strength of the electron-electron correlation measured in terms of $U_{\text{eff}}$ should decrease with increasing doping concentration as a consequence of the increased screening from the metallic states. Considering that the IMT occurs at rather low doping (few %) one would expect that the $U_{\text{eff}}$ would not change much across the transition. In contrast to this expectation, however, previous tight-binding calculations suggested that only a complete quenching of the Coulomb repulsion $U$ from an ideal value of 2.0 eV, assumed for the undoped case, to 0 eV at $x = 0.1$ reproduced the experimental ARPES data. To verify the reliability of this conjecture we have computed $U_{\text{eff}}$ fully ab initio using cRPA for the largest doping concentration considered in our study, $x = 12.5\%$, using the conventional cell containing 56 atoms. We found $U_{\text{eff}} = 1.4$ eV implying that $U_{\text{eff}}$ is only moderately affected by doping at these low concentrations. Assuming a linear decrease of $U_{\text{eff}}$ upon doping a full suppression of $U_{\text{eff}}$ would occur at very large doping, $x \approx 80\%$. A conceptually similar reduction of electronic correlation effects due to electron doping, analyzed in terms of the changes of the mass enhancement factor, was recently reported for La-doped Sr$_2$RhO$_4$ [37].

FIG. 4. (color online) Effective electron-electron interaction $U_{\text{eff}}$ as a function of electron doping concentrations $x$. The filled symbols correspond to the actual values computed by cRPA whereas the open symbol is the interpolated value of $U_{\text{eff}}$ for the lowest doping level, $x = 6.25\%$.

With this set of optimum values of $U_{\text{eff}}$ at hand, we have computed the EBS, FS and density of states (DOS) for increasing doping concentrations: $x = 0, 6.25\%$ and $12.5\%$. The results, shown in Fig. 5 clearly show that upon La-doping Sr$_2$IrO$_4$ undergoes an IMT associated with a progressive reduction of the separation between the LHB and the UHB, and the emergence of a structured FS. Already at the lowest doping

FIG. 5. (color online) Band structure of (a) primitive cell and (b) supercell. (c) EBS calculated from the unfolding method. Note that the color bar in (c) represents the Bloch character given by Eq. (3). The high-symmetry points here are consistent with the primitive $I4/mmm$ notation displayed in Fig. 2(c).
concentration, \( x = 6.25\% \), the bottom of the UHB crosses the Fermi energy at \((\pi/2, \pi/2)\) forming elliptical spots in the FS. By increasing doping the elliptical electron pockets become sharper and additional features appear in the FS around the X point arising from the doping-induced spectral weight broadening at the top/bottom of the lower/upper Hubbard bands. This is in modest agreement with the available ARPES experiments [12–15], specifically some differences are noticeable at the X point and at \((\pi/2, \pi/2)\). In the experiments, the distance between the upper and lower Hubbard band closes upon doping, and as the lower and upper Hubbard band merge, a Dirac cone develops at the \((\pi/2, \pi/2)\) point. In our simulations this only starts to happen at much larger concentrations beyond \( x = 12.5\% \) or for smaller values of \( U_{\text{eff}} \) (see Fig. 6). Furthermore in the experiments the valence band edge at the X point moves above the Fermi-level. If we keep the \( U_{\text{eff}} \) largely fixed, this feature is not observed in our theoretical calculations, though a doping-induced broadening of the lower/upper Hubbard bands is visible. We believe that the main reason for this erroneous result is the inadequacy of the LDA+U method. In the present case, the conduction band at the X point is non-localized, similar to conventional semiconductors. Likewise the top-most valence band state at the X point is itinerant. Using a simple local correction \( U \) can open the band gap between the lower and upper Hubbard band, but it is not able to deal properly with the intricate details of non-localized, itinerant states. The minimum complexity required to describe band gap narrowing upon doping is \( GW \), but \( GW \) for the system sizes considered here is yet very difficult, and we relegated this to future work.

To clarify how \( U_{\text{eff}} \) changes the band structure, we report in Fig. 6 the EBSs with projected spectral weight computed for different values of \( U_{\text{eff}} \) at \( x = 6.25\% \), and \( x = 12.5\% \). Specifically, we have considered \( U_{\text{eff}} = 1.5, 1.0, 0.75 \) and \( 0.5 \) eV for \( x = 6.25\% \), and \( U_{\text{eff}} = 1.4, 0.8, 0.5 \), and \( 0.0 \) eV for the largest concentration, \( x = 12.5\% \). Clearly, the value of \( U_{\text{eff}} \) affects the robustness of the \( J_{\text{eff}} = 1/2 \) state. Upon decreasing \( U_{\text{eff}} \) (from left to right in Fig. 6) the separation between the LHB and the UHB is progressively reduced as a result of the downward shift of the UHB, especially near the \((\pi/2, \pi/2)\) point and a upward shift of the LHB around the X point. Moreover, the reduction of \( U_{\text{eff}} \) strengthens the intensity of the Dirac cone at \((\pi/2, \pi/2)\) around \(-0.2 \) eV, and influences the intensity of the spectral weight at the X and \((\pi/2, \pi/2)\) points. Obviously reducing \( U \) would indeed reproduce the experimental results, for instance the emergence of the Dirac cone at \((\pi/2, \pi/2)\) and a shift of the valence band edge at X above the Fermi-level. However, from a first principles perspective this is certainly unsatisfactory, since we can not justify the rapid reduction of \( U \) with doping.

After discussing the origin of the doping-induced IMT we conclude this section by discussing the effect of La-doping on the structure and on the magnetic ordering. Due to the smaller ionic radius of La\(^{3+}\) compared with Sr\(^{2+}\), the inclusion of La\(^{3+}\) induces small local distortions (\( \approx 2\% \)) near the La site due to the stronger electrostatic La\(^{3+}\)-O attraction as compared to Sr\(^{2+}\)-O leading to a smaller La-O distance as compared to Sr-O in the undoped sample and to a small expansion of the Ir-O apical bond-length within the IrO\(_6\) octahedron, as schematically shown in Fig. 7. The structural modifications of 1-2 unit cells away from the La sites are found to be almost negligible (< 1%). We found that the effects of these structural rearrangements on the electronic structure (not shown) are minimal. Conversely doping and structural relaxation perturbed the ordered canted state characteristic of the undoped phase. Our data indicate that apart from a relatively small decrease of the average ordered moment, La-doping leads to a local disruption of the canted ordering in the Ir planes closer to the La impurity. This is in line with the experimental observation of a weakening of the long-range canted AF order [24] upon La-doping.

B. Rh doping

Following the same procedures adopted for the electron doping case we have studied the evolution of the electronic and magnetic state of Sr\(_2\)IrO\(_4\) upon hole doping. As mentioned in the introduction effective hole doping can be achieved by replacing 5d \( \text{Ir}^{4+} \) with the corresponding nominally isovalent 4d element \( \text{Rh}^{4+} \), situated directly above Ir in the periodic table. The parent Rh compound, Sr\(_2\)RhO\(_4\), is isoelectronic to Sr\(_2\)IrO\(_4\), but exhibits a smaller in-plane octahedral rotation angle of \( \approx 9.7\degree \) [38]. However, Sr\(_2\)RhO\(_4\) is a paramagnetic correlated metal [38–40], characterized by a weaker SOC strength combined with a more effectively screened Coulomb interaction between O-2p and Rh-4d electrons as compared to Sr\(_2\)IrO\(_4\) [35]. This is substantiated by a smaller \( U_{\text{eff}} \) for the Rh 4d states, 1.2 eV [35], as compared to 5d Ir, 1.6 eV [6]; we have used this value for our DFT+U analysis. The calcula-
tions for Sr$_2$Ir$_{1-x}$Rh$_x$O$_4$ were performed in large supercells of the same size as those used for the electron doping case, suitable to model the low doping regimes $x$=6.25% and 12.5%. The doping induced structural changes are generally small: we found a slight increase of the tetragonal distortion $c/a$ within the RhO$_6$ octahedron ($c$ and $a$ here refer to the apical and in-plane Rh-O bond length in the RhO$_6$ sublattice) and a decrease of octahedral rotation angle $\alpha$ compared to Sr$_2$RhO$_4$ (the structural data are listed in Table I).

It was proposed that Ir$\rightarrow$Rh chemical substitution leads to hole-transfer from Rh to Ir ideally leading to the formation of Ir$^{3+}$ and Rh$^{4+}$ ions [17, 21, 22]. While formally correct, this picture is rather simplified as it does not consider possible changes in the Ir-$d$-O-$p$ hybridization and does not account for the presence of the two inequivalent Ir$_{II}$ and Ir$_{III}$ sites in the compound (see Fig. 1). To clarify this issue, in Fig. 8 we show our calculated charge density difference between the doped and undoped sample within the plane containing the substitutional Rh ion. Here the intensity map offers a simple way to visualize the doping-induced changes in the charge density distribution in terms of charge transfer from the dark to the white regions: the electron transfer involves an accumulation of electronic charge around the Rh and (to a lesser extent) O sites and a substantial modification of the Ir$^{3+}$-O-Ir$^{3+}$ hybridization, in particular along the Rh-O-Ir-O-Rh direction. One can clearly identify the difference between the two kinds of iridium atoms: Ir$_{II}$ ions, nearest neighbor to Rh, are surrounded by a dark cloud indicating that these atoms donate electron charge to Rh and O, whereas the charge density around the Ir$_{III}$ ions (all other Ir sites in the supercell) remain essentially unaffected. This disproportionation between inequivalent Ir sites is also well captured by the DOS shown in Fig. 9 (middle panels): Ir$_{II}$ type atoms preserve a $t_{2g}$-projected DOS (shadow areas) almost identical to the Ir atoms in the undoped sample [Fig. 9(c)], with an essentially insulating character. In contrast, Ir$_{II}$-$t_{2g}$ states are pushed above the Fermi energy and the peak above the Fermi energy is progressively depleted by increasing doping concentration.

We will now discuss the changes in the density of states in detail showing that the transition to the metallic state is caused by the reduced SOC at the Rh site as well as a downshift of

![Image](https://example.com/image1.png)  

**FIG. 6.** (color online) EBS of La-doped Sr$_2$IrO$_4$ as a function of the effective Hubbard interactions $U_{\text{eff}}$ (eV) for the electron doping concentration $x$=6.25% and 12.5%. The color coding indicates the spectral function calculated by Eq. (4).

![Image](https://example.com/image2.png)  

**TABLE I.** Rh doping ($x = 6.25\%$) effect on the structural distortions of the RhO$_6$ octahedra and its first nearest neighbor (1nn) Ir$_{II}$/O$_6$ octahedra. $c$ (a) (in Å) represents the apical (in-plane) M-O (M=Ir or Rh) bond length. $\alpha$ indicates the in-plane octahedral rotation angle (degree). For comparison, the calculated values for the bulk Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$ are also given. The Ir$_{II}$/O$_6$ octahedra remain almost unchanged (not listed). All data were obtained by DFT+$U$+SOC calculations. For Sr$_2$RhO$_4$ we used the experimental lattice parameters reported in Ref. [41].

| Species          | Sr$_2$IrO$_4$ | Sr$_2$RhO$_4$ | Sr$_2$Ir$_{1-x}$Rh$_x$O$_4$ |
|------------------|---------------|---------------|-----------------------------|
| $c$              | 2.071         | 2.087         | 2.062                       |
| $a$              | 1.992         | 1.969         | 1.977                       |
| $\alpha$         | 13.22$^\circ$ | 11.82$^\circ$ | 12.99$^\circ$               |

![Image](https://example.com/image3.png)  

**FIG. 7.** (color online) Side (a) and top (b) view of the structural relaxations around the La$^{3+}$ ion manifested by tilting and stretching of the IrO$_6$ octahedra (highlighted schematically by the arrows).
Rh 4d states compared to the Ir 5d states. Fig. 9(f) clearly shows that the shape of the DOS at the Rh atoms closely resembles that at the Ir atoms, however, the Rh t_{2g} states are located at more negative binding energies than the Ir t_{2g} states. This is well understood: as a result of relativistic effects, the Ir 6s states are closer to the nucleus, screening it and pushing the Ir 5d states upwards compared to the Rh 4d states; For isolated atoms the effect is typically 0.5 eV, here, the Rh 4d states are shifted downwards by about 0.2 eV compared to the Ir 5d states. The second important point is that spin-orbit coupling is much reduced in Rh compared to Ir. Thus the gap between the lower and upper Hubbard t_{2g} band closes: clearly the t_{2g} states that are located above the Fermi-level for Ir (peak around 0.5 eV) shift into gap shown by the prominent mid gap Rh t_{2g} peak at 0.1 eV. Since Rh has a very small spin orbit coupling these states even overlap with the lower Hubbard band, and become partially occupied. Hence the oxidation of the Rh is Rh^{4+} with \( \delta \) being the number of electrons per site transferred to Rh from the neighboring Ir ions. An oxidation state of Rh^{3+} is not quite reached in our calculations, as this would imply a larger occupation of the Rh upper Hubbard band. However, our DOS data and Bader charge analysis indicate that \( \delta \approx 0.7 \) e\(^{-}\). An additional important point is that the neighbouring in-plane Ir atoms strongly hybridize with the Rh atom [see Fig. 9(f) and (i)]. As already shown in Fig. 8, each Ir atom donates the charge \( \delta/2 \) to the Rh upper Hubbard band. Hence, Rh creates a fractional hole in the Ir lower Hubbard band, and the Fermi level is shifted into the lower Hubbard Ir band. This is in agreement with a recent DFT+U study reporting that Ir→Rh substitution is almost iso-electronic and introduces impurity states of predominantly Rh character in the gap region [42]. Finally, it is important to note that since Rh-substitution only affects the in-plane Ir atom, doping results in an essentially two-dimensional (2D) metallic; the planes containing only Ir atoms retain a predominantly insulating character, very similar to the undoped situation.

The hole doping induced IMT is described in Fig. 9 in terms of the EBS, FS, DOS and magnetic ordering. It can be seen that the insulating state is already perturbed at the lowest doping concentration, due to an upward shift of the LHB driven by the charge transfer process described above, involving electron transfer from the Ir\(_{22}\) sites to the Rh ions. The LHB crossing at the Fermi energy yields the emergence of hole pockets at \( X \) and \( \Gamma \) and the formation of a FS. These results, obtained for fixed (i.e., not doping concentration dependent) values of \( U_{\text{eff}} \) for Rh and Ir, are generally in good agreement with available ARPES data [21, 25]: the only exception is the position of the valence band maxima at \( \Gamma \) that is not well described by DFT+U (and \( GW \) [43]) as already mentioned previously. The UHB preserves its fundamental structure upon doping but it looses spectral intensity and becomes more disperse, suggestive of spectral weight across the gap [25]. This is also reflected in the weakening of the corresponding DOS with increasing doping [Fig. 9(f) and (i)] and compatible with the electron transfer process.

We conclude by reporting the impact of Rh doping on the stability of the AF-I magnetic ordering. Our DFT+U+SOC calculations confirm that Rh doping drives a magnetic transition from the AF-I to AF-II canted ordering in the doping range 0.05 < \( x < 0.15 \) [22, 23]. The AF-II state is found to be more stable by 4 meV per formula unit. The obtained magnetic state is shown in Fig. 9(j).

IV. CONCLUSIONS

We have investigated the effects of dilute La (electron) and Rh (hole) doping on the electronic, structural and magnetic properties of Sr\(_2\)IrO\(_4\) by means of magnetically non-collinear DFT+U+SOC based supercell calculations combined with the unfolding band-structure technique. We have shown the effective band structure, Fermi surfaces, density of states, and evolution of the magnetic ordering.

For La doping, our data provide only a partly satisfactory interpretation of the IMT. Electron doping causes an increase of the chemical potential and drives a moderate renormalization of the electron-electron interaction quantified by a reduction of the on-site Coulomb interaction \( U_{\text{eff}} \) with doping, from 1.6 eV at \( x = 0 \) to 1.4 eV at \( x = 12.5\% \). Upon doping, a metallic state emerges in our simulations, however, the vanishing of the gap between the lower and upper Hubbard band can not be reproduced satisfactorily. Therefore, some features are not captured in our simulations, for instance, we fail to observe Dirac like states at \( (\pi/2,\pi/2) \). Only if \( U \) is reduced significantly (\( \approx 0.5 \) eV), the Dirac cone emerges as the lower
and upper Hubbard bands approach and the gap closes, in accordance with previous model studies done at $U = 0$ [15].

From a first principles perspective this is certainly not satisfactory, implying that the one-electron methods used here are not sufficient to reproduce the experiments satisfactorily. As for the magnetic properties, although the magnitude of the local moment is only marginally affected by doping, the characteristic canted AF-I state is locally perturbed in the vicinity of the La site and for doping concentrations $x > 12.5\%$ a regular long-range canted AF-I pattern is lost.

For the Rh doping case our data demonstrate that Rh doping is responsible for a charge redistribution involving predominantly a fractional electron transfer to the Rh sites from the nearest neighbor Ir sites (Ir$_{II}$). This in turn leads to the formation of two dimensional metallic Rh-Ir$_{Z_2}$ planes intercalated by unperturbed insulating Ir$_I$ planes. The emergence of this metallic state is assisted by the smaller SOC strength on the Rh site: the DOS indicates that the Rh $t_{2g}$ states are located at more negative binding energies than the corresponding Ir states mostly due to smaller relativistic effects. As a consequence, since the upper Hubbard Rh-Ir-$t_{2g}$ states are located below the Fermi-level, the lower Hubbard band loses electrons and becomes partially occupied. Upon Rh doping the canted AF-I state undergoes a substantial modification, manifested by a flipping of the net in-plane FM moment in the Rh-Ir$_{II}$ planes and lifts the magnetic ordering from AF-I to AF-II type. All our results are in generally good agreement with available ARPES and neutron measurements.

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FIG. 9. (color online) Electronic and magnetic properties of Rh-doped Sr$_2$IrO$_4$. First column: EBS of (a) undoped and Rh-doped Sr$_2$IrO$_4$ with the nominal hole concentration (d) $x=6.25\%$ and (g) $x=12.5\%$. The color code represents the intensity of the spectral function. Second column: (b) constant energy contour of undoped Sr$_2$IrO$_4$ at the binding energy $E_b=100$ meV, and Fermi surfaces for (e) $x=6.25\%$ and (h) $x=12.5\%$. Third column: $t_{2g}$ DOS (states/eV-atom) projected on the Rh, Ir$_I$ and Ir$_{II}$ sites for (c) $x=0$, (f) 6.25\%, and (i) 12.5\%. Fourth column: schematic plot of the AF-II-like magnetic ordering emerging upon doping very similar to the ideal AF-II ordering shown in Fig. 1 (given for $x=12.5\%$, a similar ordering is obtained at the lower doping concentration). The magnitude and direction of the resulting planar magnetic moment obtained by DFT+$U$+SOC is also given.
