Reduced effective spin-orbital degeneracy and spin-orbital ordering in paramagnetic transition metal oxides: Sr$_2$IrO$_4$ vs. Sr$_2$RhO$_4$

Cyril Martins, Markus Aichhorn, Loïg Vaugier, and Silke Biermann

1 Centre de Physique Théorique, Ecole Polytechnique, CNRS, 91128 Palaiseau Cedex, France
2 Japan Science and Technology Agency, CREST, Kawaguchi 332-0012, Japan
3 Institute of Theoretical and Computational Physics, TU Graz, Petersgasse 16, Graz, Austria

We discuss the notions of spin-orbit polarization and ordering in paramagnetic materials, and address their consequences in transition metal oxides. Extending the combined density functional and dynamical mean field theory scheme to the case of materials with large spin-orbit interactions, we investigate the electronic excitations of the paramagnetic phases of Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$. We show that the interplay of spin-orbit interactions, structural distortions and Coulomb interactions suppresses spin-orbital fluctuations. As a result, the room temperature phase of Sr$_2$IrO$_4$ is a paramagnetic spin-orbitally ordered Mott insulator. In Sr$_2$RhO$_4$, the effective spin-orbital degeneracy is reduced, but the material remains metallic, due to both, smaller spin-orbit and smaller Coulomb interactions. We find excellent agreement of our ab-initio calculations for Sr$_2$RhO$_4$ with angle-resolved photoemission, and make predictions for spectra of the paramagnetic phase of Sr$_2$IrO$_4$.

PACS numbers: 71.27.+a,71.15.-m,75.70.Tj,75.25.Dk

Probably the most important consequence of relativistic quantum mechanics in solids is the coupling of spin and orbital degrees of freedom. The concept of spin-orbit coupling (SOC) has been known for more than half a century, and its importance in magnetic materials has been recognized early on. Nevertheless, SOC in non-magnetic materials has only recently become a hot topic in condensed matter physics, in the context of topological insulators [1], within the search for systems for quantum computing applications. Still, the interplay of spin-orbit (SO) interactions with electronic Coulomb interactions in paramagnetic materials remains a largely unexplored field. This is at least partially due to the seemingly mutually exclusive regimes of their acting: SO interactions are strongest in heavy elements, that is in transition metal compounds with 5$d$ (and, to a lesser extent 4$d$) electrons. Coulomb interactions, on the other hand, are believed to be most efficient in 3$d$ compounds, due to the more localized 3$d$ orbitals. It is only recently that this separation has been questioned, e.g. in [2, 3].

In this Letter, we present a particularly striking example for the interplay of SOC and Coulomb interactions: in the room-temperature phase of the 5$d$ transition metal oxide (TMO) Sr$_2$IrO$_4$ the combined effect of SOC and distortions from the ideal K$_2$NiF$_4$-structure is strong enough to suppress the effective degeneracy of the coupled spin-orbital degrees of freedom. Even moderate Coulomb interactions then induce a Mott localized state. The resulting state – despite of being paramagnetic and paraorbital, i.e. in the absence of any magnetic or orbital order – displays a “spin-orbital order” in the sense that the only hole in the t$_{2g}$ manifold occupies a state of well-defined t$_{2g}$-projected total angular momentum $J^z$. This notion generalizes the concept of orbital order, well-known in QMOS, to the case where neither spin nor orbitals are good quantum numbers. We present – entirely from first-principle calculations – a scenario for the paramagnetic insulating state of Sr$_2$IrO$_4$, in comparison to the isostructural and isoelectronic 4$d$ compound Sr$_2$RhO$_4$. For the latter, we find that the smaller SOC and Coulomb interactions induce a partially spin-orbitally polarized metallic state. We calculate photoemission spectra for both materials and find excellent agreement with available experiments.

Sr$_2$IrO$_4$ is a 5$d$-TMO with a tetragonal crystal structure whose symmetry is lowered from the K$_2$NiF$_4$-type, well-known in Sr$_2$RuO$_4$ or La$_2$CuO$_4$, by 11$^\circ$ rotation of its IrO$_6$ octahedra around the c-axis as in its 4$d$-counterpart Sr$_2$RhO$_4$ [4, 5]. Although each Ir site accommodates 5 electrons, Sr$_2$IrO$_4$ exhibits an insulating behavior at all temperatures with an optical gap of about 0.26 eV at room temperature [8]. Below 240 K, canted-antiferromagnetic (AF) order sets in, with an effective paramagnetic moment of 0.5 $\mu_B$/Ir and a saturation moment of 0.14 $\mu_B$/Ir [9]. This phase has triggered much experimental and theoretical work recently [3, 4, 10, 11], highlighting in particular the importance of the SOC$\cdot$SOC was also shown to be relevant in Sr$_2$RhO$_4$, which is a paramagnetic metal down to 36 mK [12]: density functional calculations within the local density approximation (LDA), augmented by Coulomb interactions within the LDA+U method, reproduce the Fermi surface only if SO interactions are taken into account [13, 14].

Here, we focus on the paramagnetic insulating phase of Sr$_2$IrO$_4$ above 240 K, which has not been addressed by theory before. We analyze the electronic properties by a combination of the LDA with dynamical mean field theory (DMFT). Our method is a generalization of the LDA+DMFT scheme as implemented in [15] based on the Wien2k package [16], extended to include SO interactions [17]. The Coulomb interactions are calculated from the constrained random phase approximation (cRPA).
the structural distortions and a tetragonal crystal field

atomic states, yielding a diagonal density matrix of

were drawn for the AF phase in Ref. [11].

particularly obvious at the Γ point. Similar conclusions

formed by the

almost filled; we find

j

Fig. 2, we plot the

exceed half-filling with

n

j

half-filled

J

and

we estimate the Slater integrals as

Figure 1: LDA band structures of Sr

Sr

IrO

0

0

, taking matrix elements in the same set of local-

ized orbitals as used in the DMFT calculations [19]. For

Sr2IrO4 we estimate the Slater integrals as

F

0

=2.2 eV and

J

=0.3 eV, giving an intraorbital Hubbard U in the

half-filled

j

eff

=1/2 orbitals of

U

=2.25 eV [20].

Within an LDA band picture, Fig. 1 (d), a metallic

solution – at variance with experiments – is obtained for

Sr2IrO4. We construct Wannier functions for the

j

2g orbitals from the LDA bands within the energy window

[−3.0, 0.5] eV. The large SOC of about

ζ

SO

≈0.4 eV splits

these states into a quartet of states, commonly labeled as

j

eff

=3/2, and a higher lying doublet

j

eff

=1/2. Each state

is twice degenerate in

±m

j

. The four

j

eff

=3/2 states are almost filled; we find

n

j

=3/2,1/2=1.98 and

n

j

=3/2,−3/2=1.84

for the

j

eff

=3/2 orbitals. The

j

eff

=1/2 states thus slightly exceed half-filling with

m

1/2=1.16. In the left panel of

Fig. 2 we plot the

j

eff

character of the Wannier orbitals.

The four bands that cross the Fermi level are not purely

formed by the

j

eff

=1/2 orbitals, but there is a slight over-

lap of the

j

eff

=1/2 and

j

eff

=3/2

|m

j

|=3/2 characters, particularly obvious at the Γ point. Similar conclusions

were drawn for the AF phase in Ref. [11].

We now redefine the

j

eff

=1/2 and

j

eff

=3/2

|m

j

|=1/2 atomic states, yielding a diagonal density matrix of the

local problem. Thus, our definition takes into account

the structural distortions and a tetragonal crystal field

in each IrO6 octahedra. Our coefficients for the

j

eff

=1/2 state are similar to those obtained for the AF phase in Ref. [10].

We now turn to our LDA+DMFT results. In Fig. 2 we display the corresponding spectral functions. Within

LDA+DMFT, supplemented by the cRPA interactions, an insulating solution with a Mott gap of the size of the

optical gap measured at room temperature (about

0.26 eV [8]) is obtained. Despite the fact that the ARPES

measurements of Ref. [8] were performed in the AF phase, a comparison of the total spectral function to the experimental energy distribution curves shows qualitative and even quantitative agreement along the direction Γ-X and Γ-M (between -0.5 eV and -1.5 eV). Along the M-X direction a band around -1 eV is identified. From the orbitally-resolved spectral functions (Fig. 2 b and c), one can locate the lower

j

eff

=1/2 Hubbard band at about -0.5 eV, in agreement with the ARPES data.

The spin-orbital polarization is enhanced when taking into account Coulomb correlations: the Wannier orbital

j

eff

=1/2 is now exactly half-filled, and the upper Hubbard band is of

j

eff

=1/2 type only. We are thus dealing with a state exhibiting a “spin-orbital order” in the sense of a well-defined

j

eff

quantum number. In contrast to the AF phase, where it is also the

j

eff

=1/2 state that carries

the hole, we do not have an ordering of the corresponding

m

j

eff

=±1/2 quantum number. Also, the orbital

occupations of the original

j

2g orbitals to the

j

eff

=1/2 spin-orbital are roughly equal. We are thus facing the remarkable situation of “spin-orbital order”, with neither orbital nor magnetic order.

As it is well-known from studies of multi-orbital Hub-
Figure 3: Momentum-resolved spectral functions $A(k,\omega)$ of the paramagnetic phase of $\text{Sr}_2\text{IrO}_4$ from LDA+DMFT at $T=300$ K.

In Fig. (b), the SOC is neglected but the structural distortions are included. This lowers the symmetry of $\text{Sr}_2\text{IrO}_4$ and results in a four-times larger unit cell and four-folded bands. Similarly as in $\text{Sr}_2\text{RhO}_4$ [19], a $d_{xy}$-$d_{xz/yz}$ hybridization gap opens between the $e_g$ and the $t_{2g}$ bands (between 0.4 and 1.3 eV), and the $d_{xy}$ band becomes almost filled. The orbital polarization is thus enhanced compared to the undistorted case, and the Mott transition occurs for smaller values of $F^0$. Indeed, LDA+DMFT gives the insulating state for $F^0=3.0$ eV with $J=0.3$ eV.

In Fig. (c), we show the band structure of “undistorted” $\text{Sr}_2\text{IrO}_4$ but with SOC. Three $j_{\text{eff}}$ bands can be identified: the $j_{\text{eff}}=1/2$ one with an occupation of $n_{1/2}=1.20$ lies above the two $j_{\text{eff}}=3/2$ ones, with fillings $n_{3/2}/|3/2|=1.92$ and $n_{3/2}/|1/2|=1.96$. We find this three band system to be insulating at $F^0=3.0$ eV with $J=0.3$ eV. Although the problem is effectively reduced to an almost half-filled one-band model, the large bandwidth of the $j_{\text{eff}}=1/2$ band prevents a smaller value for the critical $F^0$.

Finally, panel Fig. (d) depicts the band structure of the true compound. In this case, the Mott transition occurs between $F^0=2.1$ and 2.2 eV for $J=0.3$ eV, the values that have been estimated by our cRPA calculations. The combination of both the structural distortions and the SOC is thus necessary for $\text{Sr}_2\text{IrO}_4$ to be insulating.

In particular, we would expect $\text{Sr}_2\text{IrO}_4$ to be metallic, if either the distortions or the SOC were smaller. Such a situation may be realized if the material is strained, or grown on a substrate [20]. It also occurs in $\text{Sr}_2\text{RhO}_4$, the isostructural and isoelectronic $4d$ counterpart of $\text{Sr}_2\text{IrO}_4$. As expected for $4d$-orbitals, the bandwidth is smaller. As before, we construct Wannier $j_{\text{eff}}$ orbitals from the bands within the energy window $[-2.67, 0.37]$ eV; the Wannier $j_{\text{eff}}$ character along the bands of $\text{Sr}_2\text{RhO}_4$ is shown on the right hand side of Fig. 2. Again, there is a mixture of the $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2$ $|m_j|=3/2$ orbital character along the four bands crossing the Fermi level. However, since the SOC is weaker in this compound ($\zeta_{SO}=0.161$ eV) than in its $5d$-counterpart, the effective splitting between the bands $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2$ $|m_j|=3/2$ is smaller and these two states have similar filling ($n_{1/2}=1.42, n_{3/2}/|3/2|=1.64$), whereas the $j_{\text{eff}}=3/2$ $|m_j|=1/2$ state is filled ($n_{3/2}/|1/2|=1.96$). The system is thus close to a $3/4$-filled two-band model, which favours a metallic state.

Moreover, the Hubbard interactions are smaller than in $\text{Sr}_2\text{IrO}_4$: a cRPA calculation as above gives $F^0=1.6$ eV and $J=0.3$ eV for $\text{Sr}_2\text{RhO}_4$. Indeed, the weaker hybridization of the Rh-4d states with the O-2p locates the latter about 1 eV higher in energy than in $\text{Sr}_2\text{IrO}_4$. As a
result, the Coulomb interactions are screened more efficiently in Sr$_2$RhO$_4$ compared to Sr$_2$IrO$_4$. By computing the interaction within cRPA for an artificial Sr$_2$RhO$_4$ system in which we shift the O-p-states down by 1 eV we verify that $F^0$ is indeed increased.

Our LDA+DMFT calculations, Fig. 4[1], are in good agreement with energy distribution curves obtained by ARPES at 10 K[27, 28]. We observe a large electron-like pocket of radius 0.65 – 0.69 Å$^{-1}$ and a smaller hole pocket of radius 0.19 – 0.18 Å$^{-1}$ in the undistorted Brillouin zone. Further structures are found between -0.1 and -0.2 eV along Γ-Ω and around -0.1 eV along Γ-M. The orbitally-resolved spectral functions allow to attribute both of these structures to the $j_{\text{eff}}=3/2$ $|m_j|=1/2$ (b), $j_{\text{eff}}=3/2$ $|m_j|=3/2$ (c) and $j_{\text{eff}}=1/2$ (d) at $T=300$K.

In conclusion, we have shown that only the cooperative effect of SOC, lattice distortions and Coulomb correlations drives the 5d compound Sr$_2$IrO$_4$ insulating, due to a complete spin-orbital polarization resulting in an effective half-filled one-orbital (more precisely, two-spin-orbital) system. The isostructural and isoelectronic 4d compound Sr$_2$RhO$_4$ has smaller SOC and Coulomb interactions, leading to a less dramatic reduction of spin-orbital fluctuations and, as a result, a two-orbital (or four spin-orbital) metal. The structural and electronic similarities between Sr$_2$IrO$_4$ and La$_2$CuO$_4$ – both are Mott insulators with one hole in an effective one-orbital system – together with the pronounced difference in their magnetic structure, suggest that the transport properties of doped Sr$_2$IrO$_4$ may give valuable information about the role of magnetic fluctuations in high-$T_c$ superconductivity. Oxygen-deficient Sr$_2$IrO$_4$ is not superconducting[29]. Our electronic structure calculations show, however, that doping by impurities with extremely weak SOC should act as giant perturbations to the spin-orbital structure, in analogy to introducing a magnetic impurity into a system with weak SOC. It would be most interesting to introduce carriers into the system while conserving as much as possible the very specific electronic structure, e.g. by doping with heavy atoms such as Os or Re.

This work was supported by the French Agence Nationale de la Recherche under project CorrelMat and GENCI/IDRIS under project 20111393. We acknowledge useful discussions with R. Arita, J.-S. Bernier, M. Ferrero, M. Imada, J. Kunes, J. Mravlje, O. Parcollet, and H. Takagi.
rameters were calculated for the undistorted phases without SOC. Screening with $e_g$ states is excluded in the range of the hybridisation gap in order to mimic the band structure of the distorted material. We then transform to the basis of $t_{2g}$-projected total angular momentum eigenstates, keeping density-density interaction terms only.

[21] A. Georges, S. Florens, and T. A. Costi, Journal de Physique IV 114, 165 (2004).

[22] N. Manini et al., Phys. Rev. B 66, 115107 (2002).

[23] A. I. Poteryaev et al., Phys. Rev. B 78, 045115 (2008).

[24] E. Pavarini et al., Phys. Rev. Lett. 92, 176403 (2004).

[25] J. J. Randall, L. Katz, and R. Ward, Journal of the American Chemical Society 79, 266 (1957).

[26] Due to the similarity of the lattice constant of SrTiO$_3$, Sr$_2$IrO$_4$ on SrTiO$_3$, e.g. should be nearly undistorted.

[27] F. Baumberger et al., Phys. Rev. Lett. 96, 246402 (2006).

[28] R. S. Perry et al., New Journal of Physics 8, 175 (2006).

[29] O. B. Korneta et al., Phys. Rev. B 82, 115117 (2010).