Coherent and incoherent bands in La and Rh doped \( \text{Sr}_3\text{Ir}_2\text{O}_7 \)

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In \( \text{Sr}_3\text{Ir}_2\text{O}_4 \) and \( \text{Sr}_3\text{Ir}_2\text{O}_7 \), correlations, magnetism and spin-orbit coupling compete on similar energy scales, creating a new context to study metal-insulator transitions (MIT). We use here Angle-Resolved photoemission to investigate the MIT as a function of hole and electron doping in \( \text{Sr}_3\text{Ir}_2\text{O}_7 \), obtained respectively by Ir/Rh and Sr/La substitutions. We show that there is a clear reduction as a function of doping of the gap between a lower and upper band on both sides of the Fermi level, from 0.2eV to 0.05eV. Although these two bands have a counterpart in band structure calculations, they are characterized by a very different degree of coherence. The upper band exhibits clear quasiparticle peaks, while the lower band is very broad and loses weight as a function of doping. Moreover, their ARPES spectral weights obey different periodicities, reinforcing the idea of their different nature. We argue that a very similar situation occurs in \( \text{Sr}_3\text{Ir}_2\text{O}_4 \) and conclude that the physics of the two families is essentially the same.

I. INTRODUCTION

Metal-insulator transitions are a central feature of correlated systems.⁴ They are often driven by doping, which is particularly well adapted to angle resolved photoemission (ARPES) studies, but still difficult to describe theoretically. Should the gap close progressively? Will all carriers contribute to the emerging Fermi Surface (FS) or just those added by the dopants? For a correlated system, coherent quasiparticles bands are expected to form within the gap, coexisting with incoherent Hubbard bands on both sides of the gap.⁵ These bands, as well as possible transfer of spectral weight between them, can be observed by ARPES. Consequently, this technique has been used extensively for the study of cuprates, where a particularly complicated situation takes place, as the FS emerges through a pseudogap phase, where parts of the FS are partially gapped.⁶ Deciding whether this is intrinsic to cuprates or more generic awaits the investigation of more types of Mott insulators.

Layered iridates offer a new test family, which is unusual as correlations take place in presence of strong spin-orbit coupling (SOC). In \( \text{Sr}_2\text{Ir}_2\text{O}_4 \), the SOC is necessary to remove the degeneracy of the ground state and form a narrow half-filled band at the Fermi level, where modest correlations open a Mott gap.⁷ Recent theoretical studies discuss whether, upon doping, the transition to the metallic state should occur through a pseudogapped phase.⁸ \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) shares many properties with \( \text{Sr}_2\text{Ir}_2\text{O}_4 \) but the role of correlations is not as obvious. Its bilayer structure creates a band gap of about 0.1eV in the doubled \( J=1/2 \) bands near the Fermi level, even without correlations.⁹¹². Fig. 7 sketches this gap opening, which results in a semi-metallic case in density functional theory (DFT) band structure calculations (full calculations are shown in appendix). Although correlations and/or magnetism are usually found necessary to enlarge this gap and reach the insulating state,¹¹¹² the two states are adiabatically connected, which is different from \( \text{Sr}_3\text{Ir}_2\text{O}_4 \).¹³ Indeed, one ARPES study of \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) doped with La concluded that it should be viewed as a doped semiconductor, very different from \( \text{Sr}_3\text{Ir}_2\text{O}_4 \) and with little traces of correlations.¹³ A subsequent ARPES study clarified that there is nevertheless a gap that closes as a function of doping and STM or optical studies also support a correlated behavior. As it would be quite interesting to have two examples of “spin-orbit Mott insulators”, with different strength of correlations and different symmetry of magnetic excitations, understanding how these two systems should be compared is crucial.

To address these questions, we present an ARPES study of \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) doped with La or Rh. To our knowledge Rh doping, which substitutes for Ir, was never reported in \( \text{Sr}_3\text{Ir}_2\text{O}_7 \). We show it induces effective hole doping as it does in \( \text{Sr}_2\text{Ir}_2\text{O}_4 \).¹⁹–²² Previous ARPES studies have well documented the emerging FS under high La doping, characterized by small “lens-like” electron pockets around the M point.¹⁹–²² We focus on the bands below the Fermi level to determine more completely the evolution of the electronic structure. We confirm the reduction of the gap, not only at the X point of the Brillouin Zone (BZ) as previously reported,¹³ but also at the M point. At first sight, this brings the system back to the non-correlated case. Our key finding is however that, beyond the relative position of the bands, their nature is very different, as sketched in Fig. 1e. The band at the Fermi level exhibits well defined quasiparticle peaks, while the lower band has a much larger linewidth and loses weight as a function of doping, as expected for an incoherent band. This points to the presence of correlation effects, which go beyond predictions of simple band calculations. We also uncover different intensity modu-
Figure 1. (a) Sketch of the band structure expected for Sr$_3$Ir$_2$O$_7$ in DFT calculations (thick lines, see appendix for full calculation). Two bands cross the Fermi level that we call lower and upper band, forming respectively hole pockets at X and electron pockets at M. They can be viewed as originating from the thin lines with a gap (see arrow) opening at their crossings. The thin lines are similar to the J=1/2 band of Sr$_3$IrO$_4$ (see appendix), doubled because of the bilayer. The colors refer to the two bands of the bilayer and the solid/dotted lines to the direct/folded bands due to the 2 Ir in-plane (see appendix). (b) Simplified version of (a). (c) Same as (a) with a larger gap between lower and upper band. The two bands could be viewed as DFT bands split by a large magnetic gap, as obtained for example in a magnetic LDA+U calculation. They could also be viewed as incoherent Hubbard bands of a DMFT calculation. They are shown here shifted in k to recall the initial semi-metallic situation, but this is not an important point. The larger width of the lines is meant to symbolize the incoherent nature. (d) Scenario expected for electron doping of a Mott insulator: the Hubbard bands do not shift significantly, but transfer weight (their lower weight is symbolized by the grey color) to a QP band (solid lines) forming at the bottom of the upper Hubbard band. This QP band is typically strongly renormalized with respect to DFT bands. (e) What we observe in Sr$_3$Ir$_2$O$_7$ seems an intermediate situation, where the upper band behaves as a DFT or weakly renormalized QP band and the lower band as a shifted Hubbard band.

II. EXPERIMENTAL DETAILS

Single crystals of (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ with x=0, 0.016, 0.06 and Sr$_3$(Ir$_{1-x}$Rh$_x$)$_2$O$_7$ with x=0.03 were grown as follows. High purity powders of SrCO$_3$ (99.995%), IrO$_2$ (99%) (La$_2$O$_3$ (99.999%) or Rh$_2$O$_3$ (99.9%) were dried, weighed, mixed in a glove box under argon with SrCl$_2$ (99.5%) flux in the ratio 3:2:5. The mixture was loaded into a platinum crucible covered with a platinum tip, reacted in tubular furnace under oxygen flux (except for Rh, synthesized in air) at 1120°C for 6 hours and slowly cooled (10°C/h) to 600°C. Then deionized water was used to dissolve the SrCl$_2$ flux and extract the single crystals. The crystals are platelets with the smallest dimension along [001] direction and 0.3 to 1mm as side. The exact doping was estimated by Energy Dispersion X-ray analysis. Unit cell dimensions of pure Sr$_3$Ir$_2$O$_7$ have been determined by X-ray diffraction analysis of pure Sr$_3$Ir$_2$O$_7$ which was detected by X-ray diffraction measurements collected at 150 K on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo K\alpha radiation (\(\lambda = 0.71073 \text{\ Å}\) : a = b = 3.8951(2) Å and \(c = 20.8941(13) \text{\ Å}\) with tetragonal space group I4/mmm. No impurity phases were detected for the pure and La cases, but about 5% pure Sr$_2$IrO$_4$ was detected by SQUID measurements in the Rh case. However, ARPES signature of Sr$_3$IrO$_4$ is easy to distinguish from Sr$_3$Ir$_2$O$_7$ and none was observed on the cleaved surface for our measurements. Typical resistivity curves are shown in appendix. They are similar to those published in literature for the same La doping. For 3% Rh, the resistivity is in between the two La cases, on the insulating side of the transition. It increases weakly with decreasing temperatures.

ARPES experiments were carried out at the CASIOPEE beamline of SOLEIL synchrotron, with a SCIENTA R-4000 analyser and an overall resolution better than 15 meV. All data shown here were acquired at a photon energy of 100 eV, with linear polarization along ΓM. The temperature is 50 K, which is in the magnetic phase for all compounds, except for 6% La doping, where no magnetic transition is detected by SQUID measurements.

III. ARPES IN Sr$_3$Ir$_2$O$_7$

We start with a discussion of the band structure of Sr$_3$Ir$_2$O$_7$ to set clear the context of our measurements. In Fig 2 we show the energy-momentum plots of ARPES intensity obtained in Sr$_3$Ir$_2$O$_7$ along ΓM (a) and ΓX (b). Similar results were published previously at Γ, the characteristic double peak structure of the J=3/2 band can be recognized. The two J=3/2 doublets are completely filled with 4 electrons. The two peaks at -0.35 and -0.5eV are noted A and B and are also shown in the EDC at Γ in Fig 2d. There is a clear alternation of weak bands at Γ and strong bands at Γ for this double peak. These two points are equivalent in a 2 Ir BZ (do-
The J=1/2 band is also clear at X, with a maximum located at E, near -0.2eV (Fig. 2d and 2e for the corresponding EDC). We note that there seems to be a small splitting of the band at X, of about 0.1eV (see marks on the EDC), which may either be an intrinsic structure of the band due to correlations or may reveal a further lowering of symmetry.

IV. ARPES IN DOPED Sr$_2$IrO$_7$

Fig. 3 displays the evolution of the electronic structure for Rh (a) and La (b-c) dopings. At first sight, they look very similar to the pure case, except for 6% La, where small pockets appear at the Fermi level. There are nevertheless significant shifts of the structures for the low dopings. As a reference, we show by black dotted line the position of the first J=3/2 band in Sr$_3$Ir$_2$O$_7$ (-0.35eV). For 3% Rh doping (Fig. 3a), all bands move up by 0.13eV, which is confirmed by the nearly perfect overlap of the dispersions when this shift is applied, as done in Fig. 3d. Although the bands at X are very close to E$_F$, the leading edge is still at -20meV (see Fig. 3a), in agreement with the non-metallic character. Also, the double peak structure that existed in the pure case at X has weakened or disappeared. This rigid shift up towards the Fermi level is analogous to the one observed in Sr$_2$IrO$_4$ and can be attributed to effective hole doping.

For 1.6% La (Fig. 3b), there is also a rigid shift, except it is of -0.08eV, to higher binding energies, consistent with electron doping. The bands also tend to broaden, which may be due to inhomogeneities introduced by doping. As can be seen on the EDC spectra in Fig. 3b, there are no in-gapped states around -0.1 eV, neither at M nor X, contrary to what was reported in Ref. 30. Such states then probably comes from some type of disorder and/or inhomogeneities. We also do not observe any significant change of the effective mass for the main bands, as can be seen from the good overlap of all dispersions, contrary to what was reported based on these in-gapped states.

Fig. 3c displays the evolution of the electronic structure for 1.6% La (Fig. 3c) and (f), the shift is not rigid anymore. The J=3/2 band is near the position of the pure case, but, remarkably, the J=1/2 bands at X have moved up by 0.15eV (see arrows). This explains the anomalous “stopping” at C and D, also observed in Sr$_2$IrO$_4$ (see appendix).

On the contrary, in 6% La [Fig. 3c and (f)], the shift is not rigid anymore. The J=3/2 band is near the position of the pure case, but, remarkably, the J=1/2 bands at X have moved up by 0.15eV (see arrows). This evidences a true reduction of the gap within the lower and upper J=1/2 bands. As we estimated the gap in the pure case to 0.2eV, this reduction is very sizable. The remaining gap of about 50meV is even smaller than the “structural gap” obtained in band structure calculations (about 100meV, see appendix and ref. 31), so that it seems the magnetic/correlated part of the gap has totally collapsed. We do not know if this smaller gap should be assigned
Figure 3. (a-c) Energy-momentum plots of the dispersion along ΓM and around X in Sr$_3$Ir$_2$O$_7$ doped with 3% Rh (a), 1.6% La (b) and 6% La (c). The black dotted line indicates the position of the J=3/2 band in Sr$_3$Ir$_2$O$_7$. (d-f) Extracted dispersion, compared with that of the pure (Fig. 2), shifted as indicated. (g) EDC at Γ compared between selected samples. (h) EDC at M, X and X’ (X’ is defined in panel c).

V. INTENSITY MODULATIONS

Another difference between the lower and upper bands is detailed in Fig. 4. While the pockets at $E_F$ are rather symmetric, it is never the case for the lower tail. Only the part of the dispersion going up from Γ to M is clear, its "folded" side (dotted line in Fig. 4) is simply missing. The connection with the lower J=1/2 band questions its nature (this connection was noted in ref. 13). The connection with the lower J=1/2 band questions its nature (this connection was noted in ref. 13). An EDC spectrum at M in Fig. 3(h) shows that these lower bands form a hump of full width ~160meV, below the QP peak of full width ~40meV. Similarly, the peak due to the lower J=1/2 at X’ has evolved into a hump in the 6% La case. It is much broader and has smaller weight than in the pure and Rh-doped cases. The much larger width is not simply due to the higher binding energy, as the peak in J=3/2 remains relatively narrow despite its higher binding energy (full width ~80meV, see Fig. 3b). The difference of behavior in width and weight between the two bands is surprising because they have similar orbital character. In a band view, there should be no difference between the upper and lower band of J=1/2, contrary to what we see in Fig. 3(h). The change in spectral weight rather reminds a correlated case. Evidently these two bands have a different “status”, which will be discussed further in conclusion.
Figure 4. (a,d,g) Energy-momentum plots of the dispersion along Γ′M in sample with 6% La, at photon energies of (a) 80, (d) 54 and (g) 36eV, corresponding respectively to k_z = 1, 0, 0.5. (b,e,h) Zoom on the dispersion around M (k = 0.707) of the image above. Thick lines: Sketch of the J = 1/2 bands expected around M. The different colors correspond to bilayer splitting and the solid (dotted) line to the direct (folded) character. (c,f,i) MDC spectra at E_F (top) and -250meV (bottom), showing the oscillation of weight between the different bands. The vertical markers indicate the positions expected for the four different bands.

at 54eV, it is in the one at -0.3eV and at 36eV, it is similar in both. The J=1/2 bands near M follow exactly the same trend, both for the small pocket at E_F and the tail. The left one is strong for 80eV, the right one for 54eV and they have similar weight at 36eV. This can also be seen by the momentum distribution curves of Fig. 4. The vertical lines indicate where the peaks are expected for the 4 different bands and it is easy to check that it is almost entirely on the green ones at 80 eV, the blue ones at 54 eV and is more evenly distributed for 36eV, both for the upper and lower bands.

The dephasing between the 2 Ir in the plane gives rise to a very similar modulation of intensity, but this time it is in-plane, between the direct and folded bands (solid and dotted lines). This is very obvious between Γ and Γ′ for J = 3/2, as we discussed before with Fig. 2a. As for the J = 1/2 band, the same modulation is observed for the lower band (the part from Γ to M is strong, but the part from M to Γ′ is not visible), but not for the upper band forming quite a symmetric pocket. This can be appreciated more quantitatively on the MDC spectra of Fig. 4. Two peaks can be distinguished on solid and dotted lines at E_F, while the spectra are mostly peaked on the solid lines at 250meV. Although it was shown[22] that, in some conditions, one can also obtain an asymmetric pocket (which changes the appearance of the FS from a pocket to a Fermi arc), it remains that the modulation of intensity is much more ubiquitous for the lower band.

As the intensity of the folded bands is related to the strength of the potential at the origin of the symmetry breaking, this suggests that the upper band probes a larger difference between the two Ir than the lower one. Following our previous observations, we could suggest that the lower/incoherent band is essentially sensitive to on-site properties (hence obeying a 1Ir BZ periodicity), while the upper/coherent band delocalizes over many sites and therefore respects the true 2Ir BZ periodicity of the unit cell.

Interestingly, a very similar behavior was observed for Sr_2IrO_4 at high La doping.[24] A clear and symmetric pocket is observed at M near E_F, followed by a tail, which rapidly loses weight and is not the symmetric part of the Dirac cone expected in the calculation. On the other hand, when the lower J = 1/2 band is clear, for smaller dopings, only the direct part is observed, as shown in appendix.

VI. CONCLUSION

Our study points to a large role of correlations in Sr_3Ir_2O_7. Even though it has a structure that already breaks the J = 1/2 doublet into lower and upper bands, the size of the gap between them changes as a function of doping, from 200meV to 50meV, demonstrating the impact of correlations and/or magnetism. Furthermore, Sr_3Ir_2O_7 presents a peculiar type of insulator to metal transition, where the bands have intermediate character between “Hubbard” and “coherent” bands. On the one hand, we observe for the lower band spectral weight transfer and large linewidth that are typical of Hubbard bands. On the other hand, this band exists in a DFT calculation, suggesting a coherent nature. This situation may be closer to that of an antiferromagnetic insulator, where DMFT predicts “Slater” bands to appear within the Mott gap, which may have such an intermediate status.

The bands we observe in Sr_3Ir_2O_7 are not renor-
ized compared with DFT calculations, which is usually taken as a sign of small correlations. However, correlations are patent in the width and loss of weight behaviors of the lower band. The absence of renormalization should rather be viewed here as a sign of the incoherent nature of the bands away from $E_F$. The coherent region in the vicinity of the Fermi level is very narrow, of the order of 50 meV. If this is the energy scale for coherence in this system, it is indeed a rather strongly correlated metal.

Our study of $\text{Sr}_3\text{Ir}_2\text{O}_7$ also gives a fresh view on the situation in $\text{Sr}_2\text{IrO}_4$. As a gap is always present in $\text{Sr}_3\text{Ir}_2\text{O}_7$, it is possible to study independently the distance between the lower and upper bands and their respective widths. This makes the separation of coherent and incoherent bands on the two sides of the gap easier. In $\text{Sr}_2\text{IrO}_4$, a clear and symmetric pocket can be observed at the Fermi level, followed by an incoherent tail. It is difficult to determine whether the gap is closed or not, as the incoherent tail of the lower band extends to the upper band, yielding a very asymmetric shape. This asymmetry is precisely the one we have described between the lower and upper bands of $\text{Sr}_3\text{Ir}_2\text{O}_7$, suggesting a unified picture. This has important consequences to discuss the presence/absence of a pseudogap. In $\text{Sr}_3\text{Ir}_2\text{O}_7$, the meaning of these pockets is not straightforward. On the one hand, the different width of the lower and upper bands emerges clearly from the comparison of the two systems as an intrinsic fingerprint of their correlations. Interestingly, these different widths are in very good agreement with predictions of cluster DMFT calculations in $\text{Sr}_2\text{IrO}_4$, where they also lead to a pseudogap behavior\cite{14}. We conclude that both $\text{Sr}_2\text{IrO}_4$ and $\text{Sr}_3\text{Ir}_2\text{O}_7$ are suitable systems to study this physics in more details.

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FIG. 5. We show typical resistivity for samples used in this study. They were measured via standard four-wire measurements within a Quantum Design PPMS.

FIG. 6. We show for reference a sketch of the band structure in Sr$_2$IrO$_4$.
blue lines. The size of the line is proportional to the expected ARPES spectral weight. By contrast, in Sr$_3$Ir$_2$O$_7$, this crossing is already gapped by interaction within the bilayer (see Fig. 1 and below), so that the effect of the AF order/correlations is only to enlarge this gap.

Very similarly to Sr$_3$Ir$_2$O$_7$, ARPES along ΓM (Fig. 6c) shows a band going up from Γ to M, but the folded side form M to Γ' is missing.

C. Band structure calculations for Sr$_3$Ir$_2$O$_7$

Band structure calculations were done using the WIEN2k package and including spin-orbit coupling. Due to the complexity of the structure of Sr$_3$Ir$_2$O$_7$ and to a systematic underestimation of the strength of SOC in LDA calculations, calculations for Sr$_3$Ir$_2$O$_7$ have often been done using tight-binding models. Our results will be in qualitative agreements with these previous findings, but we use the actual experimental structure with space group #68 (Ccca) to avoid using adjustable parameters.

In Fig. 7(a), we highlight bands of J=1/2 and J=3/2 characters by blue and red colors. It is easy to see that the bands of Sr$_2$IrO$_4$ have split, by about 0.3eV at Γ. The J=3/2 band will be pushed lower in energy by a stronger SOC (below -0.2eV, see ref. 27 and Fig. 2), so that we can focus on the J=1/2 band alone. We see that the J=1/2 bands interact with each other, opening a gap of structural origin in the black circles (100meV near X, 200meV near M). In this calculation, the small electron pockets at M are compensated by the J=3/2 hole pocket at Γ. If this band was pushed lower in energy, it would be compensated by narrow hole pockets at X, forming a semi-metallic structure presented in Fig. 1(a-b).

In Fig. 7(b), we stabilize the magnetic state by adding an orbital potential U=2.7eV. This yields a magnetic moment M=0.28μ$_B$, somewhat larger than in experiment. The structure of J=1/2 into lower and upper band remains the same, but the gap between them (defined as in Fig. 1a) is enlarged to about 0.4eV.
Figure 6. (a) Sketch of the Fermi Surface expected for the J=1/2 band of Sr$_2$IrO$_4$. The black square is the 1Ir BZ and the dotted square the 2Ir BZ. We call “direct” the bands of the 1Ir BZ (solid lines) and “folded” those obtained by folding in the 2Ir BZ (dotted lines). (b) Dispersion along XΓM of the J=1/2 band (thin blue line) and its folded band (dotted blue line). Bold curves simulate the opening of a gap for an interaction at q=(π,π), such as the AF order. The top of the J=3/2 band at Γ is shown by red lines. (c) ARPES Energy-momentum plots of the band structure along ΓM in Sr$_2$IrO$_4$.

Figure 7. (a) Black lines : band structure calculation for Sr$_3$Ir$_2$O$_7$. The bands of dominant J=1/2 (J=3/2) character are emphasized by blue (red) lines. The folded bands are shown as dotted lines. (b) Calculation for the same compound, but with magnetism stabilized by U=2.7eV.