Transfer of spectral weight across the gap of Sr$_2$IrO$_4$ induced by La doping

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We study with Angle Resolved PhotoElectron Spectroscopy (ARPES) the evolution of the electronic structure of Sr$_2$IrO$_4$, when holes or electrons are introduced, through Rh or La substitutions. At low dopings, the added carriers occupy the first available states, at bottom or top of the gap, revealing an anisotropic gap of 0.7eV in good agreement with STM measurements. At further doping, we observe a reduction of the gap and a transfer of spectral weight across the gap, although the quasiparticle weight remains very small. We discuss the origin of the in-gap spectral weight as a local distribution of gap values.

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The reaction of an insulator to doping can reveal many things on its underlying structure. For a band insulator, a simple shift of the chemical potential into bands that were previously completely filled or empty can be expected. If more complex electronic correlations are involved, the formation of in-gap states and/or large transfer of spectral weight across the gap could occur. If more complex electronic correlations are involved, the formation of in-gap states and/or large transfer of spectral weight across the gap could occur. If more complex electronic correlations are involved, the formation of in-gap states and/or large transfer of spectral weight across the gap could occur. If more complex electronic correlations are involved, the formation of in-gap states and/or large transfer of spectral weight across the gap could occur.

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Recently, a few Angle Resolved Photoemission (ARPES) studies of doped iridate phases were reported, but they lead to quite a confusing picture. For Rh substitutions, which results in effective hole doping, a metallic-like state was observed, albeit with residual pseudogaps instead of well defined quasiparticles (QP) peaks. Another kind of metallic state was observed by evaporating K on the surface of Sr$_2$IrO$_4$, which presumably dopes electrons into it. In this case, well defined QP were observed, with strong momentum and temperature dependences that resemble those found in the cuprates. In both cases, a large Fermi Surface (FS) containing $\sim 1\pm x$ electrons was apparently observed ($x$ is the number of added carriers), although the spectral weight along it could be strongly modulated. In contrast, La doping in Sr$_3$Ir$_2$O$_7$ produces a small FS containing only the added $x$ electrons, as if electrons were doped in the conduction band of a conventional semiconductor, without affecting the gap. As there is no equivalent study reported so far for La doped Sr$_2$IrO$_4$, it is not clear whether this behavior is particular to Sr$_3$Ir$_2$O$_7$ or to La doping. Clearly, the phenomenology of the metal-insulator transition in this system is still an intriguing and open problem.

To better understand this, we present here a study of both hole and electron doped Sr$_2$IrO$_4$, using respectively Rh and La substitutions. Upon doping, we observe a nearly rigid shift of the band structure, towards the Fermi level for Rh and to higher binding energies for La. This indicates an electronic gap of 0.7eV. The chemical potential of the pure compound is pinned well below the middle of gap. The spectral weight at the Fermi level follows a distribution in k-space that is surprisingly different for Rh (circular-like) and La (squarish-like). By examining the nature of the in-gap weight, we attribute this to a local distribution of gap values. This is in good agreement with STM measurements. At further dopings, the added carriers occupy the first available states, at bottom or top of the gap, revealing an anisotropic gap of 0.7eV in good agreement with STM measurements.

Figure 1. (a) In-plane resistivity in zero magnetic field and (b) magnetization at 1T, measured for the main samples studied in this paper: pure Sr$_2$IrO$_4$, La1 (1.5% La), La2 (4% La) and Rh1 (15% Rh).
agreement with observation by STM that the gap can be strongly reduced near defects\textsuperscript{17,18}. At the largest La doping that we could synthesize, we observe a small QP peak emerging.

The samples were prepared using a self-flux method, as reported in\textsuperscript{19}. Fig. 1 shows examples of the resistivity and magnetization measured for the main samples that will be used in this study. Their exact doping was estimated by Energy Dispersion X-ray analysis to be 1.5\% for La1, 4\% for La2 and 15\% for Rh1. Upon La and Rh dopings, the resistivity drops, as observed by other groups\textsuperscript{10–12}, with a slight upturn at low temperatures. The magnetic transition is suppressed by doping and it is not detectable anymore in the La2 and Rh1 samples. ARPES experiments were carried out at the CASSIOPEE beamline of SOLEIL synchrotron and the APE beamline of ELETTRA synchrotron, with a SIENTA R-4000 analyser and an overall resolution better than 15meV.

In Fig. 2, we show the dispersion for Sr\textsubscript{2}IrO\textsubscript{4} along the direction corresponding to the Ir-O-Ir bond, named ΓX in the unit cell containing 2 Ir\textsuperscript{20}. In Sr\textsubscript{2}IrO\textsubscript{4}, the t\textsubscript{2g} manifold is filled with 5 electrons and split into a quartet of J\textsubscript{eff}=3/2 character and a doublet of J\textsubscript{eff}=1/2 character\textsuperscript{5,21–23}. In Density Functional Theory (DFT) calculations, both bands should cross the Fermi level, but they are pushed below E\textsubscript{F} in reality, as confirmed by previous ARPES studies in Sr\textsubscript{2}IrO\textsubscript{4}\textsuperscript{5,21} and Ba\textsubscript{2}IrO\textsubscript{4}\textsuperscript{22,23}. Along ΓX, a band of J=3/2 character is observed at Γ and a band of J=1/2 character at X\textsuperscript{5,21–23}. Their dispersions are highlighted by red and blue lines for clarity (these guides are modeled on the DFT dispersions with appropriate shifts). The line shapes at Γ and X are detailed by the Energy Distribution Curves (EDC) of Fig. 2(a2) and 2(a3). As the J=1/2 band is closer to the Fermi level than J=3/2, and closest at X, integration of the spectral weight at -20meV in a 50meV window gives rise to patches of high intensity near X [Fig. 2(a4)]. However, just the tail of the peak reaches E\textsubscript{F}, so that this map is not a Fermi Surface.

In Fig. 2b, we move to a sample Rh1, doped with 15\% Rh. The bands are shifted almost rigidly towards the Fermi level, by approximately 0.2eV. While the J=3/2 band is still well below E\textsubscript{F} and completely filled, the J=1/2 band now crosses the Fermi level. There is however no detectable quasiparticle at k\textsubscript{F}, as can be seen from the EDC in Fig. 2(b3). As the J=1/2 band is closer to the Fermi level than J=3/2, and closest at X, integration of the spectral weight at -20meV in a 50meV window gives rise to patches of high intensity near X [Fig. 2(a4)]. However, just the tail of the peak reaches E\textsubscript{F}, so that this map is not a Fermi Surface.

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The radius \( k \) calculations for the J=1/2 band of Sr blue dotted lines. This is the shape expected in DFT cal-
trical weight distribution map follows circles, sketched by
sent from the Rh case, although one could have expected similar shape from electron-hole symmetry.

For larger La doping, we attribute the change in binding energy positions to a reduction of the gap, up to 0.15eV (for Rh, the gap lies on the unoccupied side, so that we cannot easily comment with ARPES on its size). We sketch this reduced gap in Fig. 3, together with the transfer of weight from the lower band LB into in-gap states that we discussed with Fig. 2(d3). This transfer of weight is typical of correlated systems and favors a correlation driven picture of the insulating state. In the Dynamical Mean Field Theory picture of the metal-insulator transition, one would rather expect a small QP band emerging at the bottom of the UB band, as we discuss below, this feature is also probably present in our case, coexisting with the tail of the LB band.

To better understand the origin of the in-gap weight, it is instructive to focus on the \( \Gamma M \) dispersion of the La2 sample, presented in Fig. 3. In addition to the J=3/2 hole band centered at \( \Gamma \) (red line), there is a deep electron band formed by the J=1/2 band (blue line, given by the DFT dispersion shifted down by 0.48 eV). The bottom of the band near \( \approx -1.5eV \) is quite clear, but this band suddenly loses weight when reaching M. In Fig. 4b, its dispersion is extracted by fitting the Momentum Distribution Curves (MDCs) to Lorentzians. The peak positions are shown by blue markers and their amplitudes by the markers’ size. The J=1/2 dispersion follows the blue line, up to binding energy of -0.6 eV, where the correlation gap opens, as sketched by the dotted line. In the gapped region, we nevertheless observe reduced but non negligible intensity, as emphasized in Fig. 4c along MM direction. If fitted by MDC analysis, this in-gap weight gives rise to a nearly vertical line at M, from \( \approx -0.6eV \) up to \( E_F \). Such a “vertical dispersion” often occurs when the MDC analysis picks up the tail of a broad peak. It is particularly clear here due to the anomalously large weight in the tail of the J=1/2 EDC. Near the Fermi level, a small peak can be seen at M (Fig. 4h), which may be the sign of an emerging, very shallow, QP band. This band could form a small pocket around M, analogous to those observed more clearly in \( \text{Sr}_3\text{Ir}_2\text{O}_7 \).

On the other hand, the weight picked up by the map in Fig. 2d is dominated by the in-gap states. The fact that it forms a square very clearly indicates that the gap
We describe here. Indeed, even in pure Sr$_2$O, on average a tail into the gap, quite similar to the one near a defect, for example an oxygen vacancy. A similar behavior was observed in Sr$_3$IrO$_7$. This creates a 2 Ir unit cell could produce such a gap. In Sr$_2$IrO$_4$, the unit cell always contains 2 inequivalent Ir, because of the rotation of the oxygen octahedra. However, such a rotation cannot lift the degeneracy between the two bands at X. Moreover, in Ba$_2$IrO$_4$, where there is no such rotation, a similar gap is observed. Interestingly, a distortion consisting of alternated elongation and squeezing along c of the oxygen octahedra has recently been proposed for Sr$_2$IrO$_4$. It could in principle produce such a behavior, although it is likely too small to produce such a large gap. The most likely candidate is of course the AF order that also produces a similar 2 Ir unit cell order. Even though the gap does not close at T$_N$ in Sr$_2$IrO$_4$, and though T$_N$ is strongly suppressed here by La doping, it is possible that AF fluctuations persisting above the transition are strong enough to maintain a pseudogap. In Ba$_2$IrO$_4$, a reduction of the gap above T$_N$ was suggested following similar reasoning.

The most natural way to explain the large tail of the peak would then be a local distribution of gap values. In fact, a rather similar picture emerges from STM studies. In ref. the authors observed in Sr$_2$IrO$_4$ a gap as large as 0.62eV away from defects, but as small as 0.2eV near a defect, for example an oxygen vacancy. A similar behavior was observed in Sr$_3$IrO$_7$. This creates on average a tail into the gap, quite similar to the one we describe here. Indeed, even in pure Sr$_2$IrO$_4$, we do see a small weight inside the gap behaving very similarly to that found in the La doped compounds. It is very likely that this is why the chemical potential is pinned at 0.2eV above the gap, which is the position expected for the J=1/2 band in the DFT calculation. Korneta et al. showed that at sufficient oxygen vacancies concentration (around 4%), a metallic state forms, suggesting that these “defect states” can be the precursor of a true metallic state.

In the case of surface doped Sr$_2$IrO$_4$ (which yields electron doping, like La), a good metallic state, with well defined QP and circular FS, seems to be realized. Interestingly, the position of the J=3/2 band in this study is back to its original position near -0.5eV (see Fig. S1 of ref. 15). From the trend presented in Fig. 3 this case would then find its place as an extrapolation to larger La dopings, when the gap completely closes. The circular FS is analogous to the case of Rh we report here, restoring the idea of electron-hole symmetry. Indeed, the Rh1 doping was larger than the La2 one. A difference is that there is no well defined QP in the case of Rh. They might develop at larger Rh dopings, but they could also be washed out by the disorder associated with the in-plane Ir/Rh substitutions.

Finally, our picture for La doping is the following. At low doping levels, the La impurities generate a small amount of free negative charges that shift the Fermi Level to the bottom of the unoccupied band. By further increasing the La concentration, the gap is slightly reduced, at most by ~150 meV for the dopings considered here. Locally, the La sites may further weaken the gap, creating a distribution of gap values responsible for large in-gap weight. Eventually, some percolation effect probably leads to the formation of conducting channels. The nature of correlation in this new state is one of the most interesting questions raised by the study of these iridates. The dispersive feature observed in all cases (pure, Rh and La doped) is well described by the unrenormalized DFT dispersion after appropriate shifts and should be viewed as an incoherent feature. In the Rh case, it is difficult to separate this incoherent weight from the possibly emerging QP band at its top. In the La case, it becomes easier as the QP band forms on the other side of the gap. The transfer of spectral weight we observe as a function of doping is characteristic of a correlated system. A study at higher La dopings would be highly desirable to further understand the nature of the metallic state and whether it depends on the way the carriers are introduced. Unfortunately, it has proved difficult so far to reach dopings larger than ~ 5% in this system.

1 A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996)
2 M. B. J. Meinders, H. Eskes, and G. A. Sawatzky, Phys. Rev. B 48, 3916 (1993)
3 A. Damascelli, Z. Hussain, and Z.-X. Shen, Rev. Mod. Phys. 75, 473 (2003)
4 K. M. Shen, F. Ronning, D. H. Lu, W. S. Lee, N. J. C. Ingle, W. Meevasana, F. Baumberger, A. Damascelli, N. P.
