Fermi-surface pockets in magnetic underdoped cuprates from first principles

A. Filippetti(a), D. Puggioni and V. Fiorentini

CNR-INFM SLACS, and Dipartimento di Fisica di Università di Cagliari - I-09042 Monserrato (CA), Italy, EU

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Abstract – Using an innovative first-principles band theory enabling the exploration of Mott-insulating magnetic cuprates, we study the Fermi surface of underdoped \( \text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_6 \) in a selection of magnetically ordered and polaronic states. Inclusion of doping on the antiferromagnetically ordered \( \text{CuO}_2 \) planes causes the appearance of small, hole-like Fermi-surface pockets centered around the nodal points. The pocket properties (area, mass) depend on the underlying magnetic ordering (e.g. change with polaron formation), although the hole-like character is rather persistent for all the examined magnetic states.

Introduction. – The existence of a Fermi surface (FS) in underdoped high-\( T_c \) superconductors is attested [1] by angle-resolved photoemission (ARPES) [2,3] and by recent Shubnikov-de Haas (SdH) and de Haas-van Alphen (dHvA) quantum oscillation observed in mildly underdoped (~0.1 holes per \( \text{CuO}_2 \) unit) \( \text{YBa}_2\text{Cu}_3\text{O}_6.5 \) and \( \text{YBa}_2\text{Cu}_4\text{O}_8 \) [4,5]. However, the FS detailed shape and origin continue to escape an unambiguous identification. SdH/dHvA oscillations indicate the existence of a metallic phase with small Fermi pockets; ARPES observes large zone-corner-centered cylinders at optimal doping turning into disconnected arcs near nodal points upon underdoping. In addition, the SdH/dHvA Hall resistance sign is consistent with electron-like pockets, whereas all ARPES measurements consistently report hole-like arcs.

The microscopic nature of the pockets is currently under intense debate. Several hypotheses have been formulated under the general category of a symmetry-breaking FS reconstruction, as suggested for “1/8” compounds [6], among which \( d \)-density-wave order [1], field-induced long-range magnetic order [7], short-range magnetic order [8–10], and magnetic polarons [11,12], but none of them has yet gained a general consensus. Magnetic correlations are popular candidates as, according to various experimental probes [13,14], antiferromagnetic (AF) correlations coexist with, or survive into, the superconducting (SC) phase over a wide doping range.

A further problem is the discrepancy between SdH pockets and ARPES arcs, and their electron- vs.-hole nature. It is usually supposed in Ockham’s razor fashion that the same single normal (i.e. non superconducting) phase is observed by both techniques. Actually, this is far from obvious, because SdH/dHvA are done in high field at low \( T \), and ARPES in zero field and high \( T \). Field-induced magnetic fluctuations may well be incommensurate, hence not amenable to short-wavelength periodic models. On the other hand, ARPES measurements may be affected by surface contributions or lack of resolution. These issues complicate the interpretation of the experiments, and even more so the possibility of reconciling their results (see ref. [15] for a thorough discussion).

The very existence of a Fermi surface —hence of quasiparticles— and the hints about the role of magnetism suggest a considerable scope for \textit{ab initio} band-like quasiparticle calculations, accounting accurately for material-specific information and for coupling to the lattice. \textit{Ab initio} calculations so far mostly dealt with the non-magnetic-metal Fermi-liquid-like phase (the zeroth-order approximation to the normal state). In particular calculations for \( \text{YBa}_2\text{Cu}_3\text{O}_6.5 \) [16–18] and \( \text{YBa}_2\text{Cu}_4\text{O}_8 \) [5] indicate no solid evidence of FS pockets related to \( \text{CuO}_2 \) planes. Small \( \Gamma \)-centered pockets point with area comparable to that found in SdH are found in local-density calculations for non magnetic ortho-II \( \text{YBa}_2\text{Cu}_3\text{O}_6.5 \) [16,18], but they derive from doping oxygen and apical atom states. Thus they are planarly anisotropic by construction, a

\footnotesize{(a)}E-mail: alessio.filippetti@dsf.unica.it
property which seems to be negated by the isotropic SdH signal [4]. Furthermore, much experimental work suggests that a realistic description of high-Tc’s at low doping must involve magnetic correlations in some form, and hence must account for the underlying Mott-insulating behaviour, which is intimately connected to those magnetic correlations.

The first-principles description of the Mott phase, however, is challenging. Standard density functional theories (e.g., local spin density functional approximation (LSDA), generalized gradient approximation (GGA)) fail to describe the magnetic insulating Mott phase and predict a non-magnetic metallic behaviour at all dopings (see, e.g., ref. [19] for a review). To overcome this limitation, here we employ the parameter-free pseudo–self-interaction correction (pSIC) technique [20] (which is a simplified variant of the self-interaction pseudo–self-interaction correction (pSIC) technique [20,22] based on the removal of self-interaction from LSDA energy functional) previously applied satisfactorily to many correlated materials [23–25], and, in particular, proved to describe consistently the electronic properties of O-doped YBa$_2$Cu$_3$O$_{6+y}$ between the metallic (y = 1) and Mott limits (y = 0) [25].

Here we present results for the FS of Ca-doped Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_6$ at hole doping $h = x/2 = 0.125$ (thus hole injection only involves CuO$_2$ planes, without the complications due to oxygen doping). In particular we focus on the AF ordering and two other polaronic configurations (as well as the Pauli paramagnetic (PM) phase as a reference) as possible candidates of electronic ground state in an underdoped cuprate.

We anticipate that our results apparently do not solve the pockets-vs.-arcs contest, insofar as the calculated FS features partially agree, and partially disagree, with both the experiments. In fact, all the investigated magnetic states exhibit nodal pockets, with calculated areas not far from SdH experiments. However, the calculated pockets are hole-like, in contrast with oscillation results, but in agreement with the totality of ARPES measurements. This prevents an identification and leads us to conclude that the analyzed magnetic configurations are not those observed. We mention two possible solutions to this puzzle. First, as shown below, the FS properties are tied closely to the specific magnetic arrangement, so that different pocket areas and shapes, as well as, possibly, local curvature, will be associated with more complex magnetic correlations; e.g., Jahn-Teller bipolarons [11] or spin-bag-like ferromagnetic polarons [26] (these structures are currently beyond the computational limit of our method, although some of them may become feasible in the near future thanks to technical developments). Second, the high magnetic field in SdH may produce a state influencing the FS in ways beyond the scope of zero-field calculations [7] such as, e.g., inducing incommensurate magnetic correlations. On the other hand, ARPES results are easier to reconcile with our results, e.g., considering arcs as product of configurationally averaged PM and AF phases. Beside these speculations, we show that a first-principles theory can indeed describe the Mott phase of high-Tc compounds at low doping, and establish a relation, solidly grounded on realistic quantum-mechanical simulations, between magnetic ordering and the presence of small pockets at the FS of high-Tc superconductors.

**Method.** – Standard first-principles theories (e.g., LSDA, GGA, Hartree-Fock) demonstrated earlier on their inadequacy in treating of Mott insulators. Advanced methods improving the descriptions of underdoped cuprates have been developed, but only at the cost of a major increase in computing cost, so that in practice the Mott phase of underdoped cuprates has been rarely addressed. As a matter of fact, only one LSDA SIC calculation [27] and one pSIC calculation [25] exist for oxygen-doped YBa$_2$Cu$_3$O$_{6+y}$, and one LDA + U [28] calculation for undoped YBa$_2$Cu$_3$O$_6$ [29]. No study Ca-doped Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_6$ was yet attempted to our knowledge. LDA + U calculations are slightly more numerous for the simpler La$_{1−x}$Sr$_x$CuO$_4$ system [26,30] (in particular ref. [26] is a seminal first-principles study of polaronic configurations in high-Tc cuprates). Model calculations for polaronic configurations are more common (see, e.g., the Pearls-Hubbard Hartree-Fock Hamiltonian including electron-phonon coupling [31]).

Our pSIC calculations for Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_6$ are carried out with a plane-waves basis and ultrasoft [32] pseudopotentials (energy cutoff 30 Ryd, $12 \times 12 \times 12$ special k-point grids for density-of-states calculations, $11 \times 11 \times 11$ uniform grid for FS calculations). Cu doping is described by explicit Y-Ca substitutions in $2 \times 2 \times 1$ supercells, a choice which limits the magnetic patterns that can be simulated to PM and AF orderings, and two Zhang-Rice polaron configurations within AF background.

**Results.** – The pSIC approach successfully describes [25] the undoped precursor YBa$_2$Cu$_3$O$_6$ as an AF Mott insulator. The main features of the AF Mott phase can be recognized in the closely similar orbital-resolved density of states (OR-DOS) at $h = x/2 = 0.125$ (top panels of fig. 1): valence and conduction bands are a mix of spin-polarized Cu $d_{x^2−y^2}$ and unpolarized O $p_xp_y$ states, with the main optical transition (involving CuO$_2$-plane orbitals) starting at 1.2 eV, and higher transitions around 3.5 eV into apical O $p_z$ and Cu $d_z$ states. The Cu magnetic moments of 0.5 $\mu_B$ and in-plane AF coupling constant $J \simeq 0.15$ eV in YBa$_2$Cu$_3$O$_6$ agree well with experiment.

Figure 2 report calculated band energies, hole density isosurfaces, and FS for both AF and metallic non-magnetic (i.e., Pauli-paramagnetic (PM)) phases at $h = 0.125$. The latter (right panels) shows doubly degenerate bands, and no Mott gap. The valence band is a 3.5 eV wide spin-unpolarized $d_{x^2−y^2}$ states, with Fermi level $E_F$ at $\sim 2$ eV below the valence band top (VBT). The corresponding hole density is an array of connected bonds
of self-evidently \( d_{x^2-y^2}-(p_x, p_y) \)-like shape; the FS is a large cylinder centered at the zone corner, as expected for the metallic Fermi-liquid-like state. Only in-plane atoms contribute to the FS, whereas apical-atom states start appearing \( \sim 0.2 \, \text{eV} \) below \( E_F \).

In the AF state (left panels) holes are homogeneously spread and evenly distributed through up- and down-polarized planar Cu. Despite the altered orbital filling and magnetic moments of, the AF ordering is weakened but remains substantially in charge. The Mott gap still splits the planar CuO\(_2\) band manifold into 2 eV wide empty upper and nearly filled lower Hubbard bands. The latter is sliced by \( E_F \) at 0.1 eV below its top, along the BZ diagonal near the nodal point, with off-plane states again far below \( E_F \). The reduced valence bandwidth with respect to the PM case follows from AF ordering, which hinders Cu-Cu nearest-neighbor hopping of spin polarized \( d_{x^2-y^2}-(p_x, p_y) \) holes. We see that the AF hole density is no longer an array of connected bonds, but disentangled in two spin-polarized sublattices in which hole carriers of same polarization are enclosed in a single CuO\(_2\) square. Because of this decoupling, the AF Fermi surface (plotted in the 1×1 reduced zone of edge 2\( \pi/a \)) is squeezed from a large cylinder to circlets enclosing small areas around nodal points. A closer inspection reveals four (double degenerate) concentric circles, one for each of the two up- and two down-polarized states per 2×2 CuO\(_2\) plane. An estimate of our calculated FS area \( A_k \) for a single pocket (averaged over the four circlets of each pocket) gives 1.9% of the 1×1 BZ area \( A = (2\pi/a)^2 \), which converts to a frequency of 600 T, close to the value obtained via Onsager relation from SdH measurements [4]. The calculated hole-like effective mass per pocket, however, is \(-0.5 \, m_e\), well below the experimental value reported in ref. [4]. According to Luttinger’s sum rule, an estimate of the carrier concentration can be derived from the pocket area in 2D as \( n = [2/(2\pi)^2] \, (A_k/A) \), which for the four pockets gives a carriers/holes ratio of \( n/h \sim 1.2 \) in the AF state at \( h = 0.125 \), thus suggesting a weak violation of Luttinger’s sum rule \( (n = h) \), or more likely that the FS differs slightly from the Luttinger surface to which the sum rule applies [33]. Experimentally [4] a similar value \( (n/h \sim 1.5) \) was deduced.

We emphasize that a reason to compare the FS of magnetic phases with experiment is the evidence [34] that magnetic order develops in high magnetic fields at low doping in the superconducting state (this was modeled in ref. [7]). The key difference between PM and AF Fermi surfaces is that in the former the electronic states are spin-degenerate, thus each FS point hosts two spin-compensating holes, while in the latter the injected holes are fully spin-polarized, i.e. each circlet visible in the AF FS plot can by only inhabited by fully spin-polarized carriers. Due to planar AF symmetry each up-polarized
The coupling may be driven or accompanied by local electron features of spinless polarons — embedded in the AF background, shape and size of these FS features surrounding nodal points is a general characteristic of ordinary AF. Indeed, while the presence of closed features is an indication of the AF background, shape and size of these FS features may be altered upon inclusion of polaronic states. Here we make a first attempt to model polarons and the ZRS contributions from injected and native antialigned holes shown for simplicity. Red (dotted) ellipses enclose the ZRS attendant FS.

We found stable ZRS solutions provided that an O distortion was frozen-in (the four oxygens of one ZRS-to-be CuO$_4$ unit were equally displaced by 1% of lattice parameter towards the Cu at the center of one ZRS-to-be CuO$_4$ unit). The condensation of one ZRS occurs within each breathing-distorted CuO$_4$. We remark that the breathing displacement is not obtained by structural relaxation, although the qualitative description of the ZRS state would not change by structural optimization in 2×2 symmetry. The nature of this state is apparent from the hole spin densities: in fig. 3(a2) we have one ZRS per cell (dashed circle), in fig. 3(b2) two ZRS per cell aligned into [110]-oriented stripes. (Those two are the only configurations which can be considered in 2×2 in-plane symmetry). We observe that the ZRS “condenses” on the distorted CuO$_4$ plaquette: holes localize on oxygens, and the induced magnetization is indeed anti-aligned to that of Cu, producing a vanishing total magnetization on the distorted CuO$_4$ unit. The exchange splitting between Cu and O antipaired holes is ∼2 eV. Notice that the other non ZRS-populated CuO$_4$ units (i.e. belonging to the AF background) remain substantially unaffected by the presence of ZRS on the adjacent unit. This arrangement is different from that described by LDA+U in ref. [26] where spin-bag (i.e. non spin-compensated) polarons were obtained on the CuO$_2$ planes of La$_{1−x}$Sr$_x$Cu$_2$O$_4$.

The ZRS signature in fig. 3(a1) is a single CuO$_2$ band being depleted (i.e. hole-filled) and lifted by about 0.7 eV over the valence bands related to the AF-ordered units. In the stripe configuration of fig. 3(b1), two ZRS bands are now raised by roughly the same amount above the valence AF background. All other bands related to non-ZRS CuO$_2$ units are well below E$_F$ and unaffected by hole injection. Thus, in both cases, only the ZRS bands contribute to the FS. The OR-DOS in fig. 3(c), left panel, shows that each ZRS band involves all the four in-plane oxygens first-neighbors to the central Cu of the ZRS unit. This up-polarized hole couples to the native Cu down-polarized hole (the two are enclosed in dashed ellipses) to form the singlet. The DOS from non-ZRS CuO$_2$ units in (fig. 3(c), right panel, is close to that of the AF phase in fig. 1, with hardly any magnetic moment reduction on Cu. Table 1 reports moments and energies for the three orderings. For the single ZRS, the moments on the four oxygens of the CuO$_4$ plaquette compensate that of Cu. For two ZRS the cancellation is incomplete. The two ZRS states are energetically disfavored over ZRS-free doped AF. This is because the displacements are not obtained by structural relaxation; more
Fermi-surface pockets in underdoped cuprates

Table 1: Magnetic moments ($\mu_B$) and energies (eV/polaron) for AF, AF plus one ZRS, AF plus two ZRS, Cu and O are non-ZRS atoms; Cu$^*$ and O$^*$ sit in ZRS-occupied CuO$_2$ units. $M_{O^*}$ is the total moment on all O’s of a ZRS unit.

|        | $M_{Cu}$ | $M_{Cu^*}$ | $M_{O}$ | $M_{O^*}$ | $E$  |
|--------|----------|------------|---------|-----------|------|
| AF     | 0.45     | 0          | 0       | 0         | 0    |
| 1 ZRS  | 0.47     | 0.29       | 0       | -0.28     | 0.19 |
| 2 ZRS  | 0.44     | 0.38       | -0.24   | 0.20      |      |

![AF, AF plus one ZRS, AF plus two ZRS configurations](image)

![AF, 1 zrs](image)

![AF, 2 zrs](image)

![h=0.2, h=0.125, h=0.015](image)

Fig. 4: (Color online) Evolution of the FS vs. rigid Fermi-level shift $\Delta E_F$ for AF (top panels), AF plus one-ZRS (middle panels), AF plus two-ZRS (bottom panels) configurations. From left to right, $\Delta E_F = -0.2$ eV ($h \sim 0.2$), 0 ($h = 0.125$), and +0.1 eV (for AF), +0.5 eV for the two ZRS configurations ($h \sim 0.02$).

complicated polaronic structures will form at this doping, as mentioned above.

Figure 4 shows the FS of the three examined magnetic states (AF, one-ZRS, two-ZRS) at different values of $h$. The calculated FS at $h = 0.125$ is in the central-column panels (the others are discussed below). Closed FS structures near nodal points appear to be a general feature of spin-polarized states. The one-ZRS FS shows a large nodal-point centered pocket due to the ZRS band (plus a minor AF-background pocket). In the two-ZRS configuration we find intersecting pockets from the two ZRS bands. The pocket shape is circular for the single ZRS, while for the stripe it is the intersection of two 90°-rotated ellipses. From the calculated FS areas of the ZRS bands, we obtain $n/h \sim 1.2$ and $\sim 1$, respectively, again mildly deviating from the Luttinger sum rule. (Notice that for PM and AF orderings, as previously discussed, holes were evenly distributed on all CuO$_2$ units. In the one- and two-ZRS configurations, they concentrate on one and two CuO$_2$ units respectively, so the effective doping is in fact $h = 0.5$ and $h = 0.25$.) The frequency and mass for the one- and two-ZRS cases are 2500 T and 1600 T, respectively, with masses of -0.4 and -1. These do not match the SdH experimental values reported for YBa$_2$Cu$_3$O$_{6.5}$ at $h \approx 0.1$ [4]. The numerical discrepancy may be attributed in part to the different doping mechanism and different effective doping $h$; however, the difference in mass sign (hole-like for our calculations, electron-like for the experiments) suggests that this polaron configuration is not what it is actually observed in SdH and dHvA experiments.

Discussion. – A definite conclusion we can draw is that different magnetic configurations in zero field and 2 × 2 periodicity will produce FS differing in the details, but sharing the character of nodal hole-like pockets. This is broadly consistent with ARPES, but not with SdH/dHvA. To verify if electron-like branches may appear in the vicinity of $E_F$ as calculated for $h = 0.125$, in fig. 4 we also plot the FS obtained rigidly shifting $E_F$, which very roughly simulates doping fluctuations [16]. The FS remains hole-like and the pocket area falls sharply for an upwards shift (“decreasing doping”, right panel column in fig. 4). Electron pockets at the anti-nodes do instead appear (while hole pockets open up) for $E_F$ shifting down (left panel column in fig. 4). The shift, however, would correspond to optimal doping, i.e. to a unrealistic 50% doping fluctuation. There is no obvious way to reconcile the Hall resistance sign with the present results. If one accepts the notion that the low-$T$ high-field Hall resistance (i.e. mass sign) change is a genuine electron current signature in the normal state, the present configurations should be ruled out. This does not imply that magnetism is not involved (we in fact think it is). A series of different polaronic patterns (e.g., as in refs. [11] and [26]) have been proposed as possible stable electronic configurations at low doping, but the present approach cannot yet tackle computationally the supercells needed.

We finally touch upon attempts to reconcile SdH pockets —whose shape, number, and location is undetermined— with ARPES arcs near nodes (see, e.g., [9,10,36] for a summary). Recently, a photoemission pattern switching from large-doping Fermi cylinders to low-doping arcs was observed [3] upon tuning the self-doping of YBa$_2$Cu$_3$O$_6$ via surface treatment. Cylinders and arcs appear to coexist in different sample portions depending on the local self-doping, and arcs were hypothesized [3,10] to be residual pockets (the estimated “virtual” areas would be, as our own are, in fair agreement with SdH data). From total energies, we find the PM phase slightly lower than, but still quite close to AF. Coexistence may be expected, as suggested by $\mu$SR experiments [14]. One may then speculate that the observed FS results from a configuration-averaged superposition of pockets and cylinder portions whose shape and spectral intensity depends on extension and
shape of coexisting AF and PM regions. Indeed, short-range AF order \[9,10\] has been shown to cause a similar “unfocusing” of the pocket shape into an apparent arc shape. Finally, of course, oscillations may turn out to be a token of the high-field conditions in SdH/dHvA, but this is outside our present scope.

**Conclusions.** – In summary, we studied in detail the electronic structure of underdoped \(\mathrm{Y}_{1-x}\mathrm{Ca}_x\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_y\) by the first-principles pSIC band-theory approach. We found that AF phases (with or without embedded polarons) produce closed hole-like FS branches centered at nodal points, whose area depends on the doping concentration and for \(h = 0.125\) is comparable to the pocket area observed by SdH for \(\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{6.5}\) at \(h = 0.1\). On the other hand, Fermi-liquid cylinders are related to spin-compensated (i.e. non-magnetic) states. These results support the viewpoint that pocket/arc dichotomy may be due as a superposition of pockets and cylinder portions related to competing AF and PM regions. We remark that some features of the pockets (specifically the effective mass and its sign) are inconsistent with oscillation experiments on \(\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{6.5}\), thus barring an unambiguous identification of the AF and high-density ZRS polaron configurations explored here with the states observed by oscillation experiments. Candidate alternatives may be either exotic field-induced states, which are beyond the scope of our method; or more complex polaronic structures \[11,26\] (plus coexisting orderings separated at nanoscopic range \[14\]) which are conceptually describable by our method, but for the moment computationally unapproachable.

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