Fermi-surface pockets in YBa$_2$Cu$_3$O$_{6.5}$: A comparison of ab initio techniques

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(Dated:

We study the Fermi surface of metallic, non-magnetic ortho-II YBa$_2$Cu$_3$O$_{6.5}$ using three different density-functional-based band-structure techniques (GGA, GGA+U, PSIC). The calculated Fermi surface exhibits no pockets in GGA+U and PSIC, a minor one in GGA. Upon shifting the Fermi level in the vicinity of the calculated value, we instead observe several pocket structures. We calculate their cross-sectional areas and cyclotron masses. Overall, our calculations show no solid evidence of the existence of electron-like – nor, in fact, of any – Fermi surface pockets in this phase. This suggests that the origin of the pockets should be sought for in other, different phases.

PACS numbers: 71.18.+y, 74.72.-h, 74.25.Jb

I. INTRODUCTION

The Fermi surface of underdoped high-temperature cuprate superconductors is currently under intense investigation. Recently, Shubnikov-de Haas (SdH) and de Haas-van Alphen (dHvA) oscillations were observed in ortho-II YBa$_2$Cu$_3$O$_{6.5}$ (henceforth YBCO: ortho-II stands for the chain-aligned oxygen configuration with one Cu(1)-O chain per 2×1×1 cell). These oscillations correspond to closed sections (pockets) of the Fermi surface and they exhibit, as a function of the inverse of the magnetic field, characteristic frequencies related to the cross-sectional area of the pocket (or pockets: their number and location is undetermined).

The frequency measured by dHvA experiments (more accurate than SdH) is 540±4 T, corresponding to a small portion (2%) of the Brillouin zone being enclosed by the pockets. The cyclotron mass, deduced from a Lifshitz-Koslevic fit of the oscillation amplitude vs temperature, is $m=1.76\pm0.07$ free-electron masses. The oscillations were observed in high field and only at low (4 K) temperature; the sign of the Hall coefficient was seen to be negative from about 25 K downward, and this was interpreted as a signature of the pockets in question being electron-like in nature. A further recent measurement in YBa$_2$Cu$_3$O$_{6.51}$ reported, in addition to the same signal of Ref[4], an oscillation with frequency and mass in the vicinity of 1600 T and 3.4 $m_e$, respectively, allegedly (see Ref[4] p.201) associated with a hole-like pocket.

SdH and dHvA examine at low temperature a state obtained by applying a high magnetic field to the superconductor. To first an approximation this state is supposed to be the normal (possibly pseudo-gap) state. The simplest hypothesis is that once superconductivity is removed, YBCO is a metallic and non-magnetic Fermi-liquid like system (although more sophisticated options also exist, such as e.g. magnetic fluctuations and polaronic formations in stripe-like morphology and more). Since experiments are often interpreted based on this assumption, an issue to be settled is whether or not the Fermi surface of this specific non-magnetic metallic phase exhibits pockets as revealed in experiments. If no calculated pockets exist, or can be identified with those observed, then some other phase will have to be invoked as the state accessed in oscillation experiments. To address this issue, here we employ three distinct techniques based on density-functional theory (DFT): GGA (generalized gradient approximation), GGA+U, and PSIC (pseudo-Self-Interaction-Correction) method. Furthermore, we adopt the common practice (discussed below) of applying rigid-band shifts to explore the Fermi surface in a wide energy interval surrounding the calculated $E_F$. Our calculation widen the scope of recent calculations limited to the GGA approach.

Our study shows that overall there is no reliable indication that non-magnetic metallic YBCO possesses electron-Fermi surface pockets. Specifically, only one technique (the GGA+U) finds an electron-like pocket, appearing however at a ~60 meV shift away from calculated $E_F$. None of the other techniques find any such pocket in a ±100 meV interval around $E_F$. As we will argue, in fact, there is only scant evidence for hole-like pockets as well.

While we do not question the reliability of the SdH/dHvA experiments, we note that one may envisage ways to generate a negative Hall coefficient other than the existence of electron-like pockets. For example, oscillations may be due to hole-like pockets, and the Hall coefficient positive-to-negative crossover may stem from the contribution of other electron-like Fermi surface structures, mixed up by differently temperature-dependent electron and hole mobilities. Other considerations that must be marked on the theoretical roadmap are that the pocket structure is partially at odds with the “Fermi arcs” observed in angle-resolved photo-emission spectroscopy; and that ordering phenomena, possibly related to magnetic structure or density waves, may be causing a reconstruction of the Fermi surface.
II. METHOD

We calculate the band structure of YBCO in the non-magnetic metallic state with three different DFT-based techniques. We assumed the crystal structure of YBa$_2$Cu$_3$O$_{6.5}$ determined by Grybos et al.\textsuperscript{13,14} We use the GGA (generalized gradient approximation), GGA+U, and the pseudo-self-interaction correction method (PSIC), a parameter-free, first-principles DFT-based method\textsuperscript{22} which correctly describes the physics of several correlated cuprates.\textsuperscript{16,17,18} The leftmost panel (Fig.1(a)) displays the bands within the GGA approach. Moving along the $(\pi/2,0)-(\pi/2,\pi)$ direction, the first band to cross $E_F$ is mainly due to states of the Cu(1)-O chain. This band is very close to being one dimensional. The next four bands crossings $E_F$ come from the CuO$_2$ planes. There is a splitting between the bonding and antibonding CuO$_2$ bands of $\sim 0.2$ eV along the $(\pi/2,0)-(\pi/2,\pi)$ line at $E_F$. Each of these two bands are further split up by the additional $2a$ periodicity (this is most evident close to the point $(\pi/2,\pi)$). We find that the splitting is $40$ meV at $E_F$ along the $(\pi/2,0)-(\pi/2,\pi)$ direction. In the GGA calculation a fairly flat Cu(1)O chain-apical band crosses $E_F$ close to the $(0,\pi)$ point and gives rise to a small tubular quasi-2D hole pocket. This band is $13$ meV above $E_F$ at $(0,\pi)$. In addition, a second band with a similar character lies just $20$ meV below $E_F$ at $(0,\pi)$. Our results are similar to calculations on YBCO reported previously.\textsuperscript{6,26}

Our GGA and GGA+U calculations are carried out using the VASP package\textsuperscript{19,20} with the projector-augmented wave method (PAW).\textsuperscript{21} The PSIC calculation are performed using a custom in-house code with ultrasoft pseudopotentials\textsuperscript{22} and a plane wave basis set. The cutoff energy was set at $420$ eV. A Monkhorst-Pack \textsuperscript{23} $9 \times 19 \times 6$ grid was used for the self-consistency cycle. We intentionally used the in-plane $2 \times 1$ periodicity appropriate to chain-ordered ortho-II YBCO at this specific doping, since experiments are claimed to be performed in this context. We tested non-spin-polarized calculations, spin-polarized calculations with small initial moments, and fixed-magnetic-moment calculations with zero imposed magnetization, consistently getting the same results, i.e. a non-magnetic metallic state. The Fermi surfaces are visualized with the Xcrysden package.\textsuperscript{24}

We used the Dudarev implementation\textsuperscript{25} of GGA+U, whereby the relevant parameter is the difference $U-J$ of the effective on-site Coulomb and exchange interactions. $U-J$ was set to $9$ eV for the $d$ states of planar Cu, the value reproduces the fundamental gap of Mott-insulating antiferromagnetic YBa$_2$Cu$_3$O$_6$ as obtained in PSIC\textsuperscript{17,18} or in experiment (no qualitative changes are observed down to $U-J=6$ eV for YBCO). We underline that the paramagnetic Fermi surface calculation is sensitive to $U-J$ via small orbital polarizations (i.e. deviations from exact half-filling) in the partially occupied Cu $d_{z^2-r^2}$ states, and this may affect the details of band morphology in the vicinity of $E_F$.

III. RESULTS AND DISCUSSION

A. Band structures

In Fig.1 we compare the band structures in the $k_z=0$ plane, as obtained by the three methods. The dispersion in $k_x$ is weak and not important in the present context. $k_x$ and $k_y$ are in units of the inverse $1/a$ and $1/b$ of the in-plane lattice constants. The leftmost panel (Fig.1(a)) displays the bands within the GGA approach. Moving along the $(\pi/2,0)-(\pi/2,\pi)$ direction, the first band to cross $E_F$ is mainly due to states of the Cu(1)-O chain. This band is very close to being one dimensional. The next four bands crossings $E_F$ come from the CuO$_2$ planes. There is a splitting between the bonding and antibonding CuO$_2$ bands of $\sim 0.2$ eV along the $(\pi/2,0)-(\pi/2,\pi)$ line at $E_F$. Each of these two bands are further split up by the additional $2a$ periodicity (this is most evident close to the point $(\pi/2,\pi)$). We find that the splitting is $40$ meV at $E_F$ along the $(\pi/2,0)-(\pi/2,\pi)$ direction. In the GGA calculation a fairly flat Cu(1)O chain-apical band crosses $E_F$ close to the $(0,\pi)$ point and gives rise to a small tubular quasi-2D hole pocket. This band is $13$ meV above $E_F$ at $(0,\pi)$. In addition, a second band with a similar character lies just $20$ meV below $E_F$ at $(0,\pi)$. Our results are similar to calculations on YBCO reported previously.\textsuperscript{6,26}

In the central panel, Fig.1(b), we show the GGA+U bands. Overall, the GGA+U rendition appears quite close to those of GGA. This is expectable as U only affects magnetic and/or orbital-polarized states, thus the paramagnetic configuration is mildly affected. The main difference with respect to the GGA case is that the flat chain-apical bands crossing $E_F$ near $(0,\pi)$ are now about $80$ meV above $E_F$ and $140$ meV below $E_F$ at $(0,\pi)$, i.e. they are split by more than $200$ meV, compared to about $30$ meV in GGA. This difference is due to the indirect (i.e. self-consistent) effect of the orbital polarization of in-plane Cu $d$ states on the band manifold.\textsuperscript{25}

The right panel, Fig.1(c), shows our calculation with the PSIC technique. Here we see more radical differences with respect to the other two methods, mainly due to the fact that PSIC corrects for self-interaction Cu $d$ as well as O $p$ state occupations, so that the corrections can be equally sizable for non magnetic and/or non orbitally-polarized states. This description results in generally less dispersed band structure; chain bands are now far from $E_F$, and the net result is that there are no small pockets in the Fermi surface.

B. Fermi surfaces

Strictly speaking, the theoretical prediction of the Fermi surface is based on the calculated electronic struc-
ature and Fermi level. Here, however, we also consider
how the Fermi surface changes upon an upward or down-
ward shift of the Fermi level compared to the calculated
value. This is a fairly common practice in band theory
studies of superconductors. The first motivation is that,
while DFT calculations usually describe well the general
features of the band structure of metals, small discrep-
ancies in the relative positions of the bands are common
when comparison with experiment is involved. (Gener-
ally, this relates to structural details and of course to the
DFT description of the electron correlation.) For exam-
ple, in Sr$_2$RuO$_4$, studied in detail with the dHvA tech-
nique, the Fermi energy needs to be shifted by 40 meV in
either direction to improve the calculated-bands agree-
ment with experiment. Even in MgB$_2$, shifts of the order
of 100 meV are needed.

A further motivation pertaining to doped cuprates is
that Fermi level shifts roughly simulate doping fluctu-
ations. Of course the shift-doping relation depends on
which specific band or bands are or get occupied upon
shifting. In our case the maximum shifts applied (~50–60
meV) correspond to rather substantial doping fluctu-
ations (~±0.04, i.e. a 30% of the nominal doping).

In Fig.2 we collect the Fermi surface for the three tech-
niques (top to bottom), and upward to downward (left to
right) shifts of the Fermi level. The top panel (Fig.2(a))
reports GGA results. For $\Delta E_F = +50$ meV the Fermi
surface consists of just two large hole-like CuO$_2$ sheets
centered on $(\pi/2, \pi)$, plus three quasi-one-dimensional sheets
(one from the chains, and two from the planes). As $E_F$
shifts down, a small hole-like pocket develops near the
$(0, \pi)$ point, originating from the flat CuO-O$_{apical}$ band
discussed earlier. A further lowering of $E_F$ causes this
pocket to grow in size and then merge with the anti-
 bonding CuO$_2$ plane sheet. As $E_F$ is further reduced,
the second CuO-BaO band crosses the Fermi level, giv-
ning rise to another pocket. Eventually, this merges with
the bonding CuO$_2$ plane sheet. Similar results were re-
cently reported in Refs. 6 and 30.

Fig.2(b) shows the Fermi surface evolution according
to GGA+U calculations. In this case for $\Delta E_F = +50$ meV
the Fermi surface is similar to the GGA calculation, but
shows a hole-like pocket near the $(0, \pi)$ point, whose ori-
gin is the chain-apical band. This pocket merges with the
CuO$_2$ sheets at zero shift. This trend is again expected
given the larger splitting of the chain-apical band at $(0, \pi)$
discussed in connection with Fig.1. For $\Delta E_F = -55$ meV,
an electron-like pocket appears near $(\pi/2, \pi)$, surrounded
by a hole-like sheet. Going back to Fig.1, one immedi-
ately realizes that this is also due to the enhanced splitting
in GGA+U: a similar pocket would appear in GGA
for a much larger negative shift of over 200 meV.

Fig.2(c) shows the PSIC results. The only structures
in the Fermi surface are two large hole-like CuO$_2$ sheets
centered on $(\pi/2, \pi)$. The Fermi level shift only moder-
ately affect their area. No small pockets appear in this
shift interval.

Overall Fig.2 shows a marked sensitivity of the GGA
and GGA+U Fermi surface to the relative positions of
the bands. This suggests that subtle changes in dop-
ing could result in the formation of small Fermi sur-
face pockets. On the other hand, the PSIC Fermi surface is
quite independent of doping, and would lead to predict
or expect no small pockets at all.

C. Fermi surface pockets: frequencies and masses

To make contact with the quantum oscillations mea-
sured in SdH and dHvA experiments, we calculate the
quantum oscillation frequencies $F = (h A / 2 \pi e)$ from
the cross-sectional area $A$ of the orbits (i.e. the pockets),
and the attendant cyclotron masses $m = h^2 (\partial A / \partial E) / 2\pi$
for the various structures found by the different tech-
niques. They are reported in Figs. 3, 4, and 5 for GGA,
GGA+U, and PSIC, respectively.

For all techniques we report the high-frequency oscil-
lations related to large cylinders; for GGA and GGA+U
only, low-frequency oscillations related to small pockets
are reported in a second panel. Thus, the frequencies
shown in Fig 3(a), Fig 4(a) and Fig 5 (F_1 and F_2) are from the main CuO_2 sheet surfaces, whereas those in Fig 3(b) and Fig 4 (b) (F_3 and F_4) are from the small pockets. We note, first of all, that the frequencies calculated for the main CuO_2 sheets (F_1 and F_2) are similar for GGA and GGA+U with frequencies between 3000 T and 5500 T, whereas the frequencies calculated with the PSIC approach are between 1000 T and 2000 T. The reason of this difference is the lesser dispersion of the band structure as calculated with the PSIC technique. All values are way larger than the experimental one; the masses are typically a factor of two (or more) smaller than in experiment, and always negative. These Fermi surface sheets can therefore be ruled out as the origin of the experimental oscillations reported so far.

Next we analyze the small-pocket signals in the frequency range 0 to 900 T. In the GGA calculation, the hole-like pocket F_3 has a frequency between 100 and 600 T depending on the E_F shift; the experimental value would be attained at a shift of about –65 meV. The calculated mass of this pocket is shift-independent, and equal to ∼–1.4 m_e. The F_4 pocket has a fairly low frequency of 100 to 300 T and a negative mass similar to F_3. With the GGA+U approach we find the hole-like pocket F_4, with a roughly shift-independent mass of ∼1.25 m_e and frequency in the 400 to 600 T range, and the electron-like pocket F_3 with frequency between 400 and 800 T and a
 sharply varying mass, between 1.5 \( m_e \) and 2.3 \( m_e \).

Comparing with experiments, several of our calculated pockets may seem good candidates. Frequencies and masses (in absolute value) are more or less in the ballpark. If we accept the assumption that the change of sign of the Hall resistance is purely due to the electron-like nature of the pockets, we implicitly fix the experimental sign of the mass to a positive value. The frequency and mass deduced from observation would then be compatible only with the \( F_3 \) GGA+U pocket.

A very recent measurement in YBa\(_2\)Cu\(_3\)O\(_{6.51}\) has revealed, in addition to the same signal of Ref. 1, an oscillation with frequency and mass in the vicinity of 1600 T and 3.4 \( m_e \), respectively. In Ref. 4 (p. 210) the signal is attributed tentatively to a hole-like pocket. In all our calculations, including shifts, there is only one case (GGA+U at large negative shift) that both pockets exist: one is the electron pocket \( F_3 \) discussed above; the other a larger hole-like pocket surrounding \( F_3 \) itself. Their simultaneous presence is due to a change in curvature of the same band, most notably between \( (\pi/2,\pi) \) and \( (\pi/2,0) \). The character of this band is, like that of \( F_3 \), strongly chain-apical. The corresponding calculated frequency is about 2200 T and a mass of ~1.4 \( m_e \). The frequency is very roughly similar to the 1600 T measured in Ref. 4, while the mass is over a factor two smaller.

Overall, however, we conclude that there is not enough evidence to actually associate our calculated results to the experimental findings of Refs. 1, 3, 4. The reasons will be discussed in the next Section.

### D. Discussion and summary

The calculations just reported have detected several small pockets (mainly hole-like) roughly compatible with the observed oscillation. However, all these small pockets have essentially chain or chain-apical character, and not in-plane character. GGA+U does seemingly find the “right” pattern of coexisting electron and hole pockets, but (aside from the need for an artificial ~60-meV Fermi level shift, corresponding to a 30% overdoping) both pockets have a chain-apical nature even stronger than the corresponding GGA-calculated band due to the remarkable (perhaps exaggerated) \( U \)-induced lowering of in-plane Cu bonding states.

On the other hand, there appears to be experimental evidence that the negative and oscillating Hall resistance at low temperature resulting from electron-like pockets (i.e. a positive mass) be related to states residing in the CuO\(_2\) planes. This is supported by the suppression of \( ab \)-plane conductivity anisotropy below 100 K, implying that chains do not conduct at low temperatures (and high field).

Further supporting the fact that Fermi surface pockets are a plane-related feature, quantum oscillations were observed in YBa\(_2\)Cu\(_3\)O\(_{6.5}\) [22,32,33]. Calculations for that compound have shown that the GGA-calculated band related to the \( F_4 \) hole pocket in YBa\(_2\)Cu\(_3\)O\(_{6.5}\) is now as far as ~400 meV below \( E_F \), hence cannot otherwise be invoked to explain the observations. Consistently, we found (unpublished calculations) that no pockets appear in a non-magnetic phase of chainless \( Y_{0.75}Ca_{0.25}Ba_2Cu_3O_6 \).

We further recall that pockets appear only upon appreciably shifting the Fermi energy: the proper calculated Fermi surfaces, i.e. those at zero shift, show no small pockets, except for the GGA \( F_4 \) hole pocket of Fig. 2(a), related to the backfolding in the \( 2\times1 \) cell of a pocket found by GGA itself in YBa\(_2\)Cu\(_3\)O\(_7\) (not seen by ARPES).

Were we forced to embrace one of the methods applied here and the pertaining conclusions as the most reliable in this context, we would by means pick PSIC, and conclude that in non-magnetic YBCO simply there are no small pockets, electron-like or otherwise. Indeed, among those used here, PSIC has shown to be by far the most dependable technique in the context of cuprates. For instance, the energy balance of various magnetic phases of YBa\(_2\)Cu\(_3\)O\(_{6+\delta}\) is correctly described, and so are the general properties of a number of cuprates. Furthermore, in the context of Fermi surface determination, PSIC matches ARPES perfectly for YBa\(_2\)Cu\(_3\)O\(_7\) (unpublished calculations) whereas GGA finds, as mentioned, a zone-corner pocket which ARPES does not observe.
In summary, we presented calculations of the electronic structure of YBCO in the non-magnetic state with three different DFT-based approaches: GGA, GGA+U and PSIC. Upon substantial shifts of the Fermi energy, GGA and GGA+U do produce small Fermi surface pockets, mostly originating from chain or chain-apical bands, with frequencies and band masses similar to those experimentally observed (one GGA+U pocket has a positive cyclotron mass, i.e. is electron-like), while PSIC shows no small pocket at all. As discussed, our conclusion is that there is no unambiguous evidence for the existence of electron-like pockets –nor, indeed, of any pockets– in that state. This is a conclusion coherently obtained by three different \textit{ab initio} techniques. We suggest that the experimentally observed pockets are a property of another state of YBCO, possibly characterized by some form of ordering (probably magnetic, given its coexistence with superconductivity up to high doping revealed by many experiments) causing a Fermi surface reconstruction. We will present elsewhere further first-principles work in this direction.

\section*{Acknowledgments}

Work supported in part by MiUR through PRIN 2005 and PON-CyberSer projects, and by Fondazione Banco di Sardegna. Calculations performed on the Cyber-ser@UNICA and SLACS-HPC@CASPUR clusters.

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