# Theory of Fermi-surface pockets and correlation effects in underdoped YBa$_2$Cu$_3$O$_{6.5}$

I. S. Elfimov, G. A. Sawatzky, and A. Damascelli

*AMPEL, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z4*
*Department of Physics & Astronomy, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1*

The detection of quantum oscillations in the electrical resistivity of YBa$_2$Cu$_3$O$_{6.5}$ provides evidence for the existence of Fermi-surface pockets in an underdoped cuprate. We present a theoretical study of the electronic structure of YBa$_2$Cu$_3$O$_{7-\delta}$ aimed at establishing the nature of these pockets—i.e., CuO$_2$ plane vs CuO chain or BaO. We argue that electron correlation effects, such as orbital-dependent band distortions and anisotropic self-energy corrections, must be taken into account to interpret the quantum oscillation experiments.

The independent-particle picture fails miserably in the description of the undoped parent compound of the high-temperature superconductor (HTSCs), such as, for instance, La$_2$CuO$_4$ or YBa$_2$Cu$_3$O$_{6.0}$ (YBCO$_{6.0}$). These systems, as shown schematically in Fig. 1(a) for a single square CuO$_2$ plane or in Figs. 2(a) and 2(b) for YBCO$_{6.0}$, are predicted by band theory to be 1/2-filled metals; instead, due to strong electronic correlations, they are charge-transfer-gap antiferromagnetic insulators.[1,2] While on the overdoped side of the phase diagram a well-defined band-structure-like Fermi surface is recovered, as in the case of heavily overdoped Tl$_2$Ba$_2$CuO$_{6+\delta}$,[3–5] the underdoped regime is the most debated, with two alternative scenarios being proposed. The first originates from a wide variety of theoretical calculations,[6–8] which predict that the first few holes doped into the antiferromagnet would give rise to four "nodal Fermi pockets" with a volume, counting holes, proportional to the doping $x$ away from half filling [Fig. 1(b)]. The second consists of the truncation of the single-particle Fermi surface giving rise to four "nodal Fermi arcs" [Fig. 1(c)]; it is suggested based on experimental observations by angle-resolved photoemission spectroscopy[9,10] (ARPES) and is naturally connected to the existence of a $d$-wave-like pseudogap.[11–14]

The discrimination between the two scenarios of Figs. 1(b) and 1(c) has mainly relied on ARPES studies; one should realize, however, that this is a formidable and yet unsettled task.[15,16] It rests on the detection of an arc profile, or lack thereof, on the outer side of the pockets, where the electron-removal spectral weight is expected to be vanishingly small because of the strong drop in the quasiparticle coherence $Z_\mathbf{k}$ beyond the antiferromagnetic zone boundary [diamond in Fig. 1(b)].[17] The discovery of a closed Fermi-surface contour in quantum oscillation experiments on ortho-II YBCO$_{6.5}$ (Ref. 18) might lead to a resolution of this long-standing conundrum by providing direct support to the nodal Fermi-pocket scenario of Fig. 1(b). For this assignment to be conclusive, however, one must exclude the possibility that bands other than the Cu($3d_{x^2-y^2}$)−O($2p_{x,y}$) from the CuO$_2$ planes, such as, for instance, the BaO bands, are responsible for the detected signal. Note in this regard that the BiO and TlO pockets predicted, for instance, for Bi (Ref. 19) and Tl (Ref. 20) cuprates have never been detected experimentally; on the other hand, the situation for YBCO is much more complicated because of the presence of the CuO chains, which can potentially give rise to Fermi-surface sheets of purely chain character and provide an additional

channel for BaO hybridization. The presence of such BaO- and CuO-chain-based Fermi surface pockets in band theory calculations for optimally doped YBCO has been pointed out previously by Andersen *et al.*[21]

To illustrate the band structure effects on the Fermi surface of the YBCO family, we have carried out density functional theory (DFT) calculations of the electronic structure of YBCO$_{7-\delta}$, for $\delta=0$, 0.5, and 1 (Fig. 2 and Ref. 22). In agreement with previous density functional studies,[21,26] the Fermi surface of stoichiometric YBCO$_{6.0}$ and YBCO$_{7.0}$ consists of two large cylindrical sheets, originating from the CuO$_2$ bilayers, and small pockets of mainly BaO character (see below), all centered around the Brillouin zone corner [Figs. 2(a)–2(d)]. In addition, in YBCO$_{7.0}$ there is also the open one-dimensional Fermi surface of the "full" CuO chains running along the $b$ axis [Fig. 2(d)]. In oxygen-ordered ortho-II YBCO$_{6.5}$, the unit cell is doubled along the $a$ axis due to the alternation of full and empty CuO chains; correspondingly, the Brillouin zone is folded along the $(\pi/2,0)$-$(\pi/2,\pi)$ line [Figs. 2(g) and 2(h); momentum-space coordinates are here given modulo the lattice constants]. This affects both the shape and number of Fermi-surface sheets, but the small
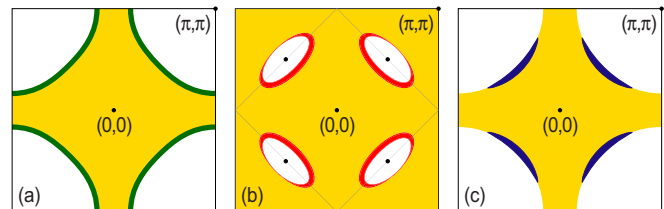


FIG. 1. (Color online) Different scenarios for the low-energy electronic structure of the single, square CuO$_2$ plane; Brillouin zone dimensions are expressed modulo the lattice constant. (a) Independent-particle Fermi surface for a metallic, 1/2-filled Cu-O band (green/gray); its volume is precisely 50% of the zone. When correlations are considered, the system becomes an antiferromagnetic insulator. (b) Light hole doping might result in four Fermi pockets (red/gray) with a volume that, counting holes, corresponds to the doping $x$ away from 1/2-filling (the enclosed diamond is the antiferromagnetic Brillouin zone). (c) Alternatively, the Fermi surface is truncated near the zone edges reducing to four disconnected arcs (blue/gray). In all panels, white and yellow (gray) areas identify hole and electron momentum-space regions, respectively; the thickness of the Fermi-surface lines represents the quasiparticle coherence $Z_\mathbf{k}$ (i.e., the spectral weight of the electron-removal quasiparticle peaks), which is strongly $k$ dependent in (b) and (c).
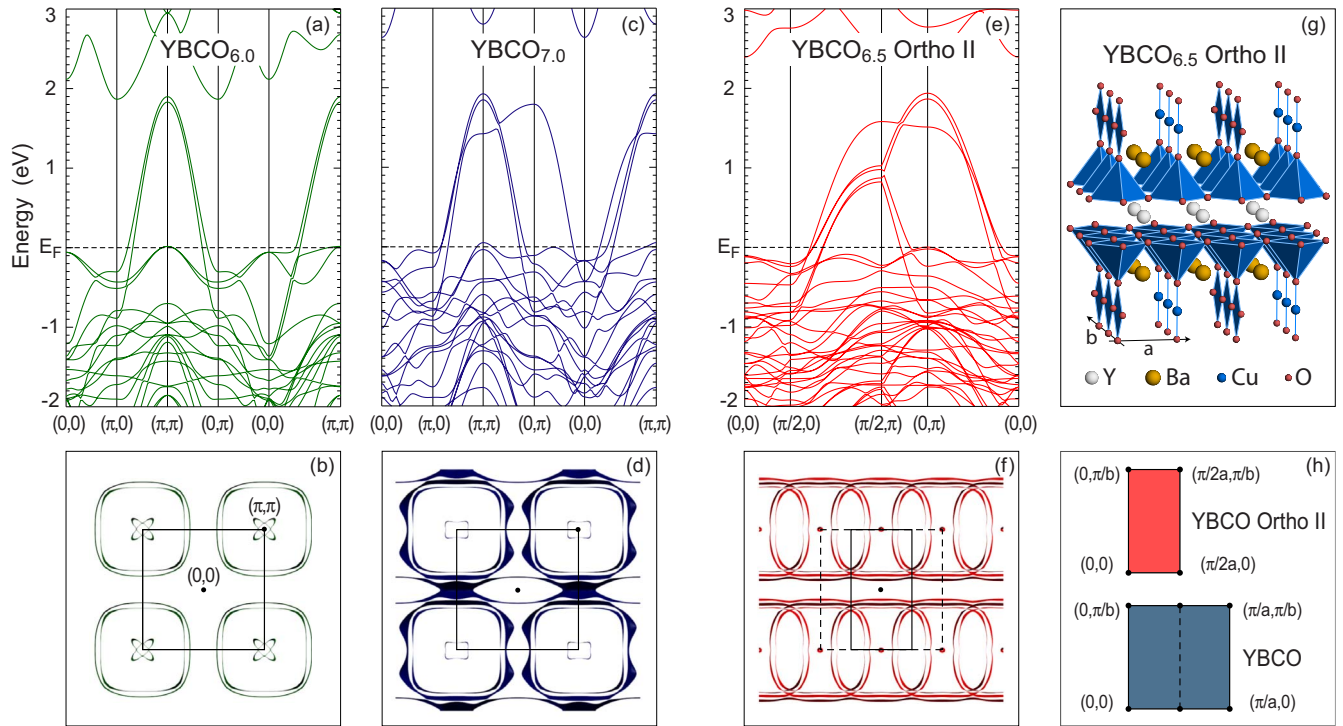
FIG. 2. (Color online) Local-density approximation (LDA) calculations of the in-plane electronic structure ($k_z=0$) and projected Fermi surface for (a),(b) YBCO$_{6.0}$, (c),(d) YBCO$_{7.0}$, and (e),(f) oxygen-ordered ortho-II YBCO$_{6.5}$ (the width of the Fermi surface lines is proportional to the amount of $k_z$ dispersion). (g) Ortho-II YBCO$_{6.5}$ crystal structure, with full and empty CuO chains alternating along the $a$ axis and running parallel to the $b$ axis (plane octahedra and chain plaquettes each contain one Cu atom). (h) Sketch of 1/4 Brillouin zone for YBCO and ortho-II YBCO$_{6.5}$; because of the folding to the reduced zone, $(\pi/a,0)$-$(0,0)$ and $(\pi/a,\pi/b)$-$(0,\pi/b)$ are sets of equivalent symmetry points in YBCO$_{6.5}$. In (a)–(f) momentum-space coordinates are given modulo the lattice parameters $a$ and $b$.

BaO pockets are still present although translated to $(0,\pm\pi)$.

As one can see in Fig. 2(f), if taken quantitatively the size of the $(0,\pm\pi)$ pockets is vanishingly small and is not nearly enough to explain the quantum oscillations in the electrical resistance observed by Doiron-Leyraud *et al.*[18] However, it is also evident that in such a multiband case the Fermi surface is quite susceptible to very small changes of the relative position of the bands and/or to a minimal rigid shift of the Fermi level itself, which can be induced by deviations in oxygen concentration or the presence of disorder. For instance (Fig. 3), for Fermi-level position $\Delta E_F=0$, $-13.6$, and $-19.1$ meV the area of the $(0,\pm\pi)$ BaO pocket is $A_k=0.3$, 3.01, and 5.22 nm$^{-2}$, respectively, to be compared to $A_k=5.1$ nm$^{-2}$ found in the quantum oscillation experiments on YBCO$_{6.5}$.[18] Also the BaO pocket average band mass $m_b=0.77m_0$, $1.68m_0$, and $1.56m_0$ for the three values of $\Delta E_F$ is in qualitative agreement with the observed cyclotron mass $m^\star=1.9m_0$, where $m_0$ is the free electron mass.[18]

Before elaborating on the deeper significance of these findings, we would like to discuss the anticipated BaO assignment of the small Fermi surface pockets. As shown in Fig. 4 for YBCO$_{6.5}$, a strong peak in the density of states (DOS) at energies just below the Fermi level belongs to Cu $3d_{xy}$ and $3d_{yz}$ orbitals, which are strongly mixed with the apex O $2p$ and Ba empty orbitals in a $pd\pi$ configuration.[21] Thus, BaO-Cu$_{chain}$ is primarily the character of the flat bands [Fig. 2(e)] and corresponding small pockets [Fig. 2(f)] about $(0,\pm\pi)$ in YBCO$_{6.5}$. A similar analysis for YBCO$_{6.0}$ con-

firms the same origin for the $(\pm\pi,\pm\pi)$ pockets; as for YBCO$_{7.0}$, which is somewhat different because the CuO chains are all full, oxygen from the BaO plane contributes the most to those bands defining the small hole pockets. Consistent with our assignment, all these pockets are rather isotropic in $k_x$ and $k_y$, contrary to what is expected for a purely one-dimensional chain electronic structure. Also, they are very sensitive to the Cu$_{chain}$−O$_{apex}$ and -Ba distances, which show a substantial variation with $\delta$ in YBCO$_{7-\delta}$.[27]

At this point the key question is, what is the relevance of

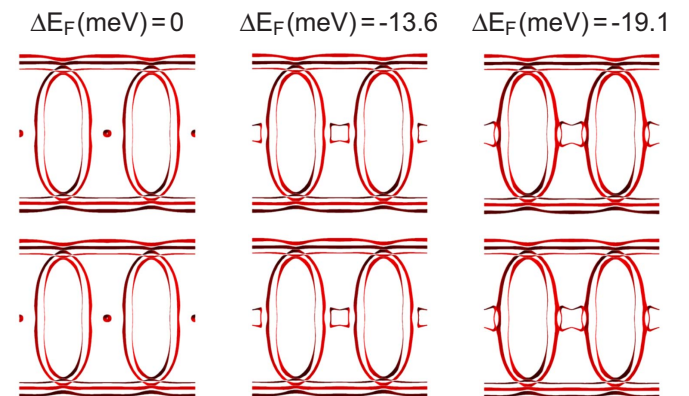$\Delta E_F(meV)=0$        $\Delta E_F(meV)=-13.6$        $\Delta E_F(meV)=-19.1$



FIG. 3. (Color online) LDA Fermi surface of ortho-II YBCO$_{6.5}$ for different positions of the Fermi level, so as to show the rigid-band-like doping dependence of Fermi surface and, in particular, of the BaO-Cu$_{chain}$ pockets at $(0,\pm\pi)$ and $(\pm\pi,\pm\pi)$.
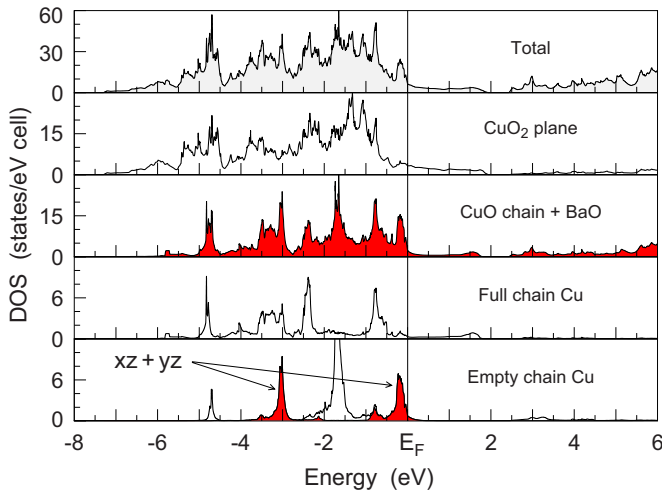
FIG. 4. (Color online) LDA density of states (DOS) for ortho-II YBCO$_{6.5}$. The high DOS at $E_F$ originates from BaO and (oxygen-empty) Cu$_{chain}$ orbitals; these are $pd\pi$ orbitals with Cu $d_{xz,yz}$ character, thus very different from the $pd\sigma$ orbitals typically found for the CuO$_2$ planes ($d_{x^2-y^2}$) or that one might expect for the empty CuO chains ($d_{3z^2-r^2}$) (see also Ref. 21).
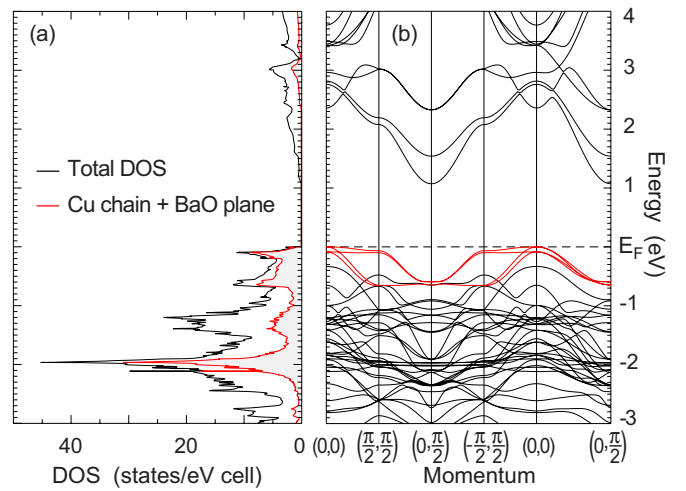


FIG. 5. (Color online) DOS and band dispersion calculated for YBCO$_{6.0}$ within the LDA+U approximation, with parameters $U$ =8 eV and $J_H$=1.34 eV (Refs. 22 and 31). The system is now a 1.08-eV-gap charge-transfer insulator, with a Fermi-level DOS dominated by the BaO-Cu$_{chain}$ bands; the CuO$_2$ plane band is split and pushed to high binding energies.

the results we have just presented to the physics of the underdoped cuprates? After all, these are strongly correlated electron systems and it is well known that standard LDA for the exchange correlation potential fails to treat strong correlations properly. In order to gain more direct insight into this fundamental methodological shortcoming, we further our analysis within the so-called LDA+U method[22] which, by adding the on-site Coulomb repulsion $U$ to the LDA in a mean-field-like way, can reproduce the correct magnetic ground state and forbidden gap in correlated antiferromagnetic insulators such as La$_2$CuO$_4$.[1,28] However, the LDA +U approach works fairly well only in the case of integer orbital occupation and well-established long-range order (e.g., spin, charge, or orbital order).[29] This constrains our DFT analysis of YBCO in the presence of strong correlations to the single case of YBCO$_{6.0}$ (Fig. 5), which is truly an antiferromagnetic insulator with $3d^9$ and $3d^{10}$ configurations for plane-Cu$^{2+}$ and chain-Cu$^{1+}$, respectively. It is important to realize that in such a framework, as shown in Fig. 5, the CuO$_2$ in-plane states are almost completely removed from the Fermi energy and the first electron-removal state has nearly 100% BaO-Cu$_{chain}$ character. This is partly due to the inadequacy of LDA+U in fully accounting for the many-body physics of the CuO$_2$ planes; while the LDA in-plane states are about 0.5 eV below the Fermi level, we do know that in the undoped cuprates there are Zhang-Rice singlet (ZRS) states[30] pushed ~0.5 eV closer to $E_F$, thus back into the first ionization energy range, but these two-particle states are completely missed by the single-particle LDA description.[1] In the scope of this paper, we can make one very important observation: independently of the exact energy of the ZRS states, in YBCO$_{6.0}$ a rigid-band-like hole doping would give rise also to pockets originating from the BaO-Cu$_{chain}$ bands and, in direct contrast to materials like La$_2$CuO$_4$, not just the in-plane Cu($3d_{x^2-y^2}$)-O($2p_{x,y}$) states. Furthermore, the folding of the Brillouin zone, in this case

due to antiferromagnetic spin order and not a CuO chain superstructure, would translate the BaO-Cu$_{chain}$ pocket from $(\pi,\pi)$ to the $\Gamma$ point [Figs. 1(a) and 5(b)].

Let us now attempt a critical summary of experimental and theoretical findings. In light of our understanding of the underdoped cuprates, it is definitely very tempting to interpret the recent quantum oscillations results[18] as direct evidence for nodal Fermi pockets originating from the CuO$_2$ planes electronic states. Our analysis shows, however, that the details of the band structure cannot be neglected in the case of YBCO$_{6.5}$, since BaO-Cu$_{chain}$ states might give rise to additional Fermi pockets consistent with the recent experimental observations both as far as volume and especially small effective mass are concerned. As a matter of fact, their role might become even more significant when correlation effects are also included, as they should for these very low doping values. Although not as extreme as in the case of YBCO$_{6.0}$, the Coulomb repulsion $U$ associated with the Cu $3d$ orbitals would strongly affect the in-plane CuO$_2$ bands but much less so the BaO-Cu$_{chain}$ bands. This would lead to an orbital-dependent band distortion (as opposed to a rigid shift) and trigger a hole transfer from the more to the less correlated electronic states, conspiring to generate qualitatively different Fermi features: "highly correlated" CuO$_2$ pockets playing a primary role in the emergence of high-temperature superconductivity and "more conventional" BaO-Cu$_{chain}$ pockets behaving as mere spectators. In the event of such a coexistence, the latter would be more likely observed in quantum oscillation experiments, while the CuO$_2$ pockets might escape detection because of the highly momentum-dependent self-energy effects, which could even result in vanishing quasiparticle residues and/or diverging effective masses at some momenta along the Fermi pocket contour [e.g., beyond the antiferromagnetic zone boundary as in Fig. 1(b)]. If this were indeed the case, it would also suggest that the detection of quantum oscillations might be

limited to those cuprates containing CuO chains.[32]

Due to the complex multiband and correlated character of the electronic structure of YBCO$_{6.5}$, the precise determination of the nature of the Fermi-surface pockets revealed by quantum oscillation experiments[18] will require further study of this underdoped system by a variety of techniques. One serious issue, which has not been addressed here, concerns the negative sign of the Hall coefficient observed by Doiron-Leyraud *et al.*[18] In a simple one-particle picture, this negative sign would point to an electron rather than holelike character for the Fermi-surface pockets detected in quantum oscillations. As in Ref. 18, we also concentrated on the oscillatory part of the Hall resistivity above and beyond the rather smooth "background" contribution from which the negative sign is derived. We note that this Hall resistivity background is expected to be rather complicated because of contributions from the strongly correlated CuO$_2$ planes and the presence of localized magnetic moments; a net negative sign for the Hall coefficient need not be inconsistent with the presence of holelike Fermi-surface pockets.

*Note added.* After completion of this work, we became aware of a recent DFT study of YBCO by Carrington and Yelland.[36] The LDA band structure results are very similar, with minor exceptions due to the difference in the treatment of the exchange correlation potential.[36]

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