PHYSICAL REVIEW B, VOLUME 64, 020507(R)

Role of electron-electron correlation in the valence states of $YBa_2Cu_3O_7$: Low-energy excitations and Fermi surface

S. Monastra and F. Manghi
Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Modena, Via Campi 213/a, I-41100 Modena, Italy

C. Ambrosch-Draxl
Institut fur Theoretische Physik, Universität Graz, Universitätsplatz 5, A-8010 Graz, Austria

(Received 2 February 2001; published 21 June 2001)

We have studied the role of on-site correlation in the low-energy excitations of $YBa_2Cu_3O_7$ in the normal state, calculating self-energies and spectral functions according to the three-body-scattering approach. The method allows to include all the details of realistic *ab initio* band-structure calculations and to augment them with the inclusion of electron-electron correlations, getting quasiparticle energies for one-particle removal. It is found that correlation effects modify the energy dispersion of hole quasiparticle states, both in the high and low binding energy region, and strongly modify the Fermi surface topology.

DOI: 10.1103/PhysRevB.64.020507 PACS number(s): 74.72.Bk, 74.25.Jb, 71.10.−w, 78.20.Bh

A detailed knowledge of low-energy electron excitations and Fermi surface topology is essential to understand the unusual properties of the normal state of high-T_c cuprates and to shed light on the superconducting mechanism.

The comparison between measured photoemission spectra and theoretical results, leading to a band mapping of electron states is a powerful tool to investigate energy dispersion and Fermi surfaces. Density-functional theory (DFT) in the Kohn-Sham (KS) scheme has been widely used as the starting point of most *ab initio* approaches. As is well known, according to the DFT-KS approach the ground-state total energy and the one-particle spatial density can be determined by solving an effective noninteracting problem. Many properties such as stable geometry,[1] phonon frequencies,[2] and electric-field gradients[3] have been calculated and successfully compared with the experimental findings, thus confirming the ability of the DFT-KS scheme to describe ground-state properties of quantum many-body systems.

Within the band theory based on the DFT-KS scheme the single-particle eigenvalues of the auxiliary noninteracting Hamiltonian are interpreted as physical quantities describing electron removal energies. This overinterpretation, even if very successful in many cases, fails when applied to solids such as cuprates where valence electrons are strongly localized and experience a strong electron-electron correlation; in these cases a true many-body solution of the problem is required in order to reproduce the observed band dispersion[4] and the occurrence in some cases of a metal-insulator transition.[5,6]

When dealing with highly correlated metals a question that has not been completely clarified yet is the role of electron correlation in the determination of Fermi surfaces. While the KS band gap in insulators is found to deviate considerably from experimental values, the KS Fermi surfaces usually agree well with experiments, even in the case of strongly correlated materials. On very general ground, systems that are both interacting *and* inhomogeneous should exhibit deviations from single-particle Fermi surface. This has been clearly demonstrated for model systems[7,8] and the question is to estimate the actual deviations in real materials. In the case of cuprates it has been shown that accurate approximations for the exchange and correlation functional can improve the agreement between calculated KS Fermi surfaces and experiments;[1,9] moreover recent calculation of quasiparticle energies[10] in a noncuprate layered superconductor have shown that the inclusion of Hubbard-type correlation according to second-order perturbation theory does modify the quasiparticle energy dispersions close to the Fermi energy but leaves the points where bands cross the Fermi energy totally unaffected, giving rise to a Fermi surface that coincides *exactly* with the noninteracting result. It is then clear that more systematic data on quasiparticle energies, obtained for different systems and with different approximations, are essential in order to draw general conclusions.

We have studied the influence of electron-electron correlation on the low-energy excitations of $YBa_2Cu_3O_7$ as a prototypical cuprate using the 3-body-scattering (3BS) approach.[11–15] 3BS is an approximate method that allows us to include many-body correlations (nonperturbatively and beyond mean field) in the calculation of one-electron removal energies; it provides self-energy corrections, spectral functions, and quasiparticle band structure including both long-lived coherent structures and incoherent short-lived ones. Within the 3BS approach, it is possible to combine an accurate treatment of many-body terms with a realistic description of the band structure. This is done starting from a multiband Hamiltonian, where the single-particle part contains all the details of an *ab initio* band-structure calculation and the electron-electron interaction is described by a Hubbard term.[14] The generalized Hubbard Hamiltonian in k space is

$$\hat{H}=\sum_{\mathbf{k}n\sigma}\epsilon^{n}_{\mathbf{k}\sigma}\hat{a}^{n\dagger}_{\mathbf{k}\sigma}\hat{a}^{n}_{\mathbf{k}\sigma}+\sum_{\alpha\beta}\sum_{\mathbf{k}\mathbf{k}'\mathbf{p}}\sum_{nn'}\sum_{mm'}\frac{1}{N}U_{\alpha\beta}\times[C^{n}_{\alpha}(\mathbf{k})^{*}C^{\mathbf{n}'}_{\alpha}(\mathbf{k}+\mathbf{p})C^{\mathbf{m}}_{\beta}(\mathbf{k}')^{*}C^{\mathbf{m}'}_{\beta}(\mathbf{k}'-\mathbf{p})\times\hat{a}^{n\dagger}_{\mathbf{k}\uparrow}\hat{a}^{n'}_{\mathbf{k}+\mathbf{p}\uparrow}\hat{a}^{m\dagger}_{\mathbf{k}'\downarrow}\hat{a}^{m'}_{\mathbf{k}'-\mathbf{p}\downarrow}], \quad (1)$$

where $C^n_\alpha(\mathbf{k})$ are the expansion coefficients of single-particle Bloch states of wave vector k and band index n in terms of localized orbitals. α, β, are d orbital indices and $U_{\alpha\beta}$ describes the on-site Coulomb repulsion among d electrons on copper sites. Since a band-structure calculation based on the DFT-KS approach corresponds to the self-consistent mean-field solution of the interacting system, the matrix elements of the effective one-particle Hamiltonian $\epsilon^n_{\mathbf{k}\sigma}$ can be derived from DFT band eigenvalues according to

$$\epsilon^n_{\mathbf{k}\sigma} = \epsilon^{DFT}_{\mathbf{k}n\sigma} - Q^n_{\mathbf{k}\sigma} \tag{2}$$

with

$$Q^n_{\mathbf{k}\sigma} = \sum_{\alpha\beta} |C^n_{\alpha\sigma}(\mathbf{k})|^2 U_{\alpha\beta} \frac{1}{N} \sum_{\mathbf{k}'n'}^{occ} |C^{n'}_{\beta-\sigma}(\mathbf{k}')|^2. \tag{3}$$

This is the way DFT-KS band structure results are used in the present calculation: the on-site e-e interaction is removed as a mean-field term $Q^n_{\mathbf{k}\sigma}$ from the band eigenvalues—then avoiding any double counting of e-e correlation—and put back again in the Hamiltonian to be treated as a true many-body interaction (see Ref. 14 for a detailed discussion).

The band structure of $YBa_2Cu_3O_7$ has been calculated by the full-pontential linearized augmented plane-wave method utilizing the WIEN97 code.[16] Exchange and correlation effects are treated within a generalized gradient approximation (GGA).[17] Lattice parameters were taken from experiment, and all the atomic positions have been relaxed by atomic-force calculations. The computational details are described in Ref. 2. As far as the value of Hubbard U is concerned, we have chosen $U_{dd}=8$ eV in agreement with current estimates for cuprates.[18] This value optimizes also the agreement between the present theory and experiments concerning the position of satellite structures.[19]

According to the 3BS approach the interacting many-body state is expanded on the configurations obtained by adding one e-h pair to the Fermi sea, i.e., to the ground state of the single-particle Hamiltonian. The state with one removed electron ($N-1$ particle system) is expanded in terms of the basis set including 1-hole and 3-particle configurations (one hole plus one e-h pair). If the same level of approximation in the configuration expansion (just one e-h pair added) is consistently assumed for the N-particle system, including then zero- and two-particle configurations, it is easy to show that the ground state of the interacting N-particle system would coincide with the noninteracting one (rigid Fermi sea):[12–14] at this level of approximation electron correlation comes into play only when dealing with an $N-1$ or $N+1$ particle system, i.e., when calculating removal or addition energies. This point—that ground-state properties of the N-particle system are not affected within 3BS theory by correlation effects—must be kept in mind in the following discussion; in particular it explains why it is important to start from the *best* mean-field description of the N-particle system as the one provided by DFT with an accurate form of the exchange-correlation potential.

The response of the system to the removal of one electron is described by the hole spectral function

$$D^-_{\mathbf{k}n}(\omega) = -\frac{1}{\pi} \mathrm{Im} \frac{1}{\omega - \epsilon^n_{\mathbf{k}} - \Sigma_{n\mathbf{k}}(\omega)}. \tag{4}$$

The self energy $\Sigma_{n\mathbf{k}}(\omega)$ is determined identifying it with the hole self-energy $\Sigma^-_{n\mathbf{k}}(\omega)$ that enters the definition of the hole (retarded) Green function. This identification is justified in the limit of an almost filled valence band: although both one hole + one e-h pair and one electron + one e-h pair are in general required to describe time-ordered Green-function and self-energy corrections, the efficiency of scattering processes involving three-particle states depends strongly on the band occupation.[4] Whenever the number of empty states is very small, the most efficient scattering processes are those involving one hole plus one e-h pair. The occupation of d orbitals in $YBa_2Cu_3O_7$ ($n_d=9.8$ and $n_d=9.7$ for the two inequivalent Cu sites) makes this approximation quite appropriate in the present case. The interactions between three-body configurations are represented as in Ref. 14 by a set of t matrices describing h-h and e-h scattering and the Faddeev theory[20] is used to determine the total scattering matrix, the self-energy and the resolvent of the many-body system.

A crucial issue in the comparison between theory and photoemission data is the definition of Fermi energy $E_f = E_0(N) - E_0(N-1)$ where $E_0(N)$, $E_0(N-1)$ are the ground-state energies of the interacting system of N and $N-1$ particles. In general we expect the interacting E_f to be different from the noninteracting one. This is true also in the 3BS approach where correlation effects do not enter $E_0(N)$ (see the above discussion) but do affect the $N-1$ particle system.

The noninteracting Fermi energy E^0_f is the highest occupied energy defined by the sum-rule involving the single-particle (band) density of states $n(\epsilon)$,

$$\int_{-\infty}^{E^0_f} n(\epsilon) d\epsilon = N, \tag{5}$$

N being the number of occupied states. The interacting Fermi energy E_f in turn is generally assumed to be related to E^0_f by self-energy renormalization

$$E_f = E^0_f + \Sigma(E_f) \tag{6}$$

in the same way as quasiparticle energies are related to single-particle ones. While expression (6) is clearly applicable to the interacting homogeneous electron gas, it cannot be used for inhomogeneous systems where self-energy is intrinsically k dependent: the chemical potential is a property of the system as a whole and a k-dependent renormalization is meaningless.

An alternative definition of the interacting E_f is obtained extending sum rule (5) to the quasiparticle density of states

$$-\frac{1}{\pi} \mathrm{Im} \int_{-\infty}^{E_f} \frac{1}{\omega - \epsilon^n_{\mathbf{k}} - \Sigma_{n\mathbf{k}}(\omega - \Delta)} = N. \tag{7}$$

$\Delta = E_f - E^0_f$ makes the imaginary part of the self-energy—equal to zero by construction at E^0_f—vanish correctly at

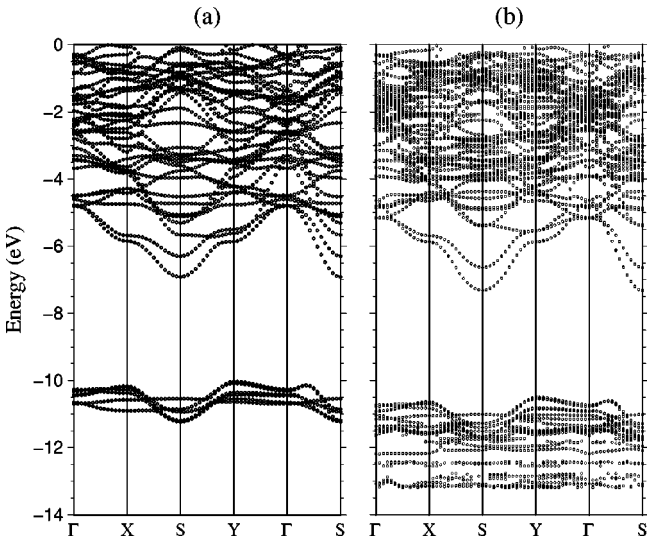

FIG. 1. (a) Single-particle band structure of $YBa_2Cu_3O_7$ obtained in the DFT-GGA approach; energies are referred to E_f^0. (b) Quasiparticle band structure obtained in the 3BS scheme with $U_{dd}=8$ eV with energies referred to the interacting E_f.

E_f.[21–23] This definition of E_f guarantees the correct occupation of the band, adjusting at the same time the origin of the energy scale of self-energy to provide quasiparticle states of infinite lifetime at the interacting E_f. This is the expression we have used to calculate Fermi energy and Fermi surfaces of $YBa_2Cu_3O_7$.

The maxima of spectral functions for k points along high-symmetry directions in the Brillouin zone give rise to the *quasiparticle band structure* reported in Fig. 1(b). Energies are referred to the interacting Fermi energy E_f, which turned out to be shifted with respect to E_f^0 of $\Delta=0.46$ eV. By comparing these data with single particle results [Fig. 1(a)] the most evident effect of e-e correlation is the appearance of a bunch of satellite structures around 12 eV partially overlapping Ba states. The shape of spectral functions in a small energy window close to the Fermi energy are shown in Fig. 2 with and without self-energy corrections. Along X-S the quasiparticle band structure exhibits much less structures than the single-particle one in agreement with recent photoemission data[24] where structures are absent in this energy region in most of the direction. Modifications are even more drastic along $\Gamma-X$ and $\Gamma-Y$ where the energy dispersion of the highest band is strongly affected by correlation: while according to single-particle theory this band crosses the Fermi level, after the full renormalization it does not. This is the band exhibiting the saddle point behavior resulting in the well-known van Hove singularity, which is believed to have an important role in the explanation of high-T_c superconductivity in cuprates.[25]

These features are going to affect the Fermi surface as well. The results obtained for $YBa_2Cu_3O_7$ in the plane $k_z=0$ for two different values of U_{dd} are shown in Fig. 3. It appears that modifications do occur and that they scale with the strength of the interaction. This point is important *per se*, independently of the quantitative corrections, since it allows us to draw general conclusions concerning the role of

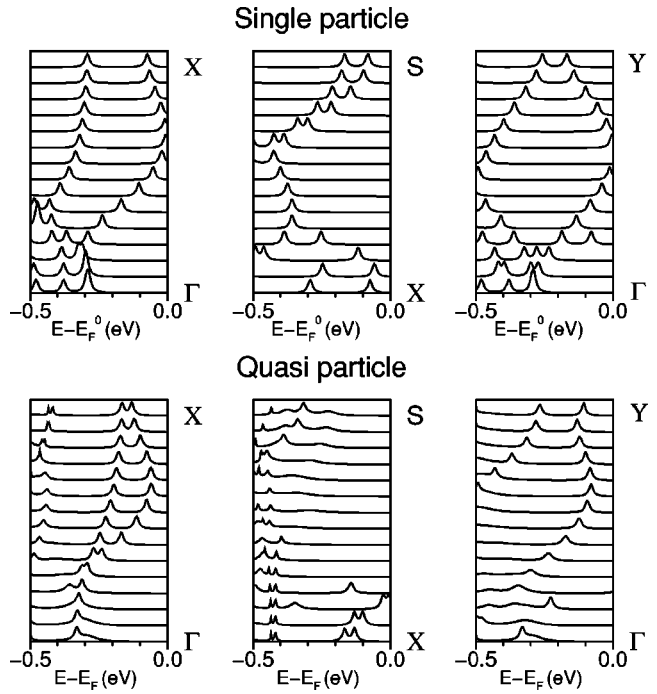

FIG. 2. Spectral functions (arbitrary units) along high symmetry directions. (a) Single-particle and (b) quasiparticle results with $U_{dd}=8$ eV. Energies are referred to E_f.

Hubbard-type interactions in the determination of Fermi surfaces of realistic systems: the Fermi surface calculated from band theory does not coincide with the quasiparticle Fermi surface inclusive of self-energy renormalization, and this is true not only in model systems[8,26] but also in a real material. Quantitatively the differences between quasiparticle and single-particle Fermi surfaces are not too large—and perhaps below the experimental accuracy.[24,27,28] The effect of e-e correlation on the topology of the Fermi surface is, however, rather impressive: the Fermi surface is deformed just near X and Y k points where single-particle bands exhibit the saddle-point van Hove singularity, which is now shifted below E_f converting the external sheet from electronlike to holelike. Moreover for $U_{dd}=8$ eV the external sheet turns out to be parallel to the internal one giving rise to an almost perfect nesting. The presence of two Fermi surface sheets running parallel over a considerable distance can give rise to anomalously strong scattering that may be extremely relevant in the interpretation of transport properties.

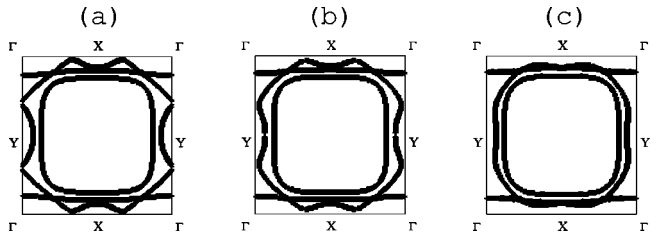

FIG. 3. Fermi surface at $k_z=0$ obtained from the DFT-GGA band structure (a), and according to 3BS theory with $U_{dd}=4$ eV (b) and $U_{dd}=8$ eV (c), respectively.

This research was supported by the University of Modena e Reggio Emilia, by Murst-COFIN99, by INFM-BACH beamline project, and has benefited from the collaboration within the ESF Program on ''Electronic Structure Calculations for Elucidating the Complex Atomistic Behavior of Solids and Surfaces.'' C.A.D. appreciates support from the Austrian Science Fund FWF for Projects Nos. P11893-PHY and P13430-PHY.

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