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Precise band structure and Fermi-surface calculation for $YBa_2Cu_3O_7$: Importance of three-dimensional dispersion

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With the appearance of angle-resolved photoemission data allowing the identification and measurement of the Fermi surface of the high-T_c cuprate superconductors, it is important to have precise local-density calculations with which to compare. We present well converged local-density predictions of the band structure and Fermi surface of $YBa_2Cu_3O_7$, giving special attention to the position of the flat Cu-O chain-derived bands and the effect of the buckling of the Cu-O chain that is predicted by total-energy calculations and has been inferred by an x-ray-scattering study. We emphasize the c-axis dispersion that will lead to apparent broadening of the Fermi surface in experiments interpreted in terms of a two-dimensional electronic structure.

INTRODUCTION

The electronic band structures of $YBa_2Cu_3O_7$ and other copper oxide superconductors have been calculated using a variety of methods (for a review see Ref. 1), with considerable variations occurring among the reported results. The differences arise either because of the approximations inherent in the various methods, because of the differing levels of convergence, or possibly due to the use of different structural parameters. Whereas for more common, structurally simpler compounds, the discrepancies are generally small, the large and complex unit cells of the copper oxides have resulted in comparably larger discrepancies. Indeed some calculations have been performed simply with the intention of elucidating the overall bonding characteristics, without a serious attempt to obtain an accurate prediction of precise band placements and, hence, the Fermi surface (FS).

The recent demonstration by several groups[2] that the Fermi surface of $YBa_2Cu_3O_7$ cannot only be detected but can, in fact, be mapped out by careful angle-resolved photoemission spectroscopy (ARPES) and angle-resolved inverse-photoemission spectroscopy (ARIPES) necessitates a more careful investigation of the precise predictions of the FS by local-density-functional (LDF) theory. The existence of a FS has ruled out those classes of models founded on a non-Fermi-liquid normal state of the cuprates, and the degree to which the measured Fermi surfaces agree with the LDF predictions will provide crucial insight into the electronic interactions which determine the properties of the quasiparticles.

The LDF prediction of the FS of $YBa_2Cu_3O_7$ has been provided by Yu, Massidda, Freeman, and Koelling[3] (YMFK) and by Krakauer, Pickett, and Cohen[4] (KPC), both using the linearized augmented plane wave (LAPW) method. Although the bands generally are in very good agreement, there are small differences near the Fermi level E_F which result in somewhat different predictions for the Fermi surfaces. We have recently used our codes to carry out extensive calculations of structural parameters, phonon frequencies, and electron-phonon coupling strengths for specific phonons, and in the course of these calculations performed extensive investigations of the various convergence cutoffs which must be chosen. Here we present converged results (to mRy level) for the band structures and the resulting FS. We find that these results differ slightly from our previous results and somewhat more from those presented by YMFK.

STRUCTURE

The structural parameters we have used within space group *Pmmm* are those referenced previously,[5] which differ only very slightly from those we used initially.[4] The orthorhombic lattice constants are $a=7.21309$, $b=7.33781$, and $c=22.05311$ a.u., corresponding to 3.817, 3.883, and 11.670 Å, respectively. The internal structural parameters, expressed as a fraction of c, are for Ba, 0.185; for the planar Cu(2), 0.3552; for the planar O(2) and O(3) atoms, 0.378 (for each); and for the bridging O(4) atom, 0.158.

CALCULATIONAL DETAILS

In the LAPW method nonoverlapping atomic spheres are used to define the basis set, which consists of plane waves in the interstitial region and a partial wave description inside each sphere; there are no shape approximations for the charge density or potential and the basis can be essentially fully converged. The sphere radii R were chosen as (in a.u.): Y and Ba, 2.2138; Cu(1) and Cu(2), 1.8438; and O(1), O(2), O(3), O(4), 1.5500. The level of

convergence is set by the maximum value of $|\mathbf{k}+\mathbf{G}| = K_{\max} = 3.87$ a.u., corresponding to values of $RK_{\max}$ of 6.0 for the oxygen spheres, 7.1 for the Cu spheres, and 8.6 for the Y and Ba spheres; this gives approximately 1150 LAPW basis functions. Lattice harmonic expansions of the nonspherical parts of the density and potential were carried out up to (spherical harmonic index) $L_{\max} = 8$. Using similar values of these parameters we have calculated[5] the frequencies of 15 zone-center phonons, obtaining excellent correspondence with experiment. Convergence was verified to be better than 1 mRy (0.01 eV) by increasing the basis-set size by 60% ($RK_{\max} = 7.0$ for O) and by increasing $L_{\max}$ to 12. Self-consistency was reached with a $6\times6\times2$ special k-point mesh with 5-mRy temperature broadening. The total energy changed by only 0.6 mRy when the mesh was increased from 9 to 16 k points ($8\times8\times2$), which implies convergence in the self-consistent potential with respect to k-point sampling. We computed eigenvalues for 165 k points in the irreducible wedge and used Fourier interpolation[6] to calculate the bands, find the Fermi level, and display the Fermi surface; the same number of k points and the same interpolating procedure was used as in KPC.

RESULTS

The resulting band structure within the range from 1 eV below to 2 eV above E_F is shown in Fig. 1. Since the dispersion with k_z (perpendicular to the Cu-O planes) may become important in the interpretation of the data, we show bands both at $k_z = 0$ and at the top zone boundary $k_z = \pi/c$. The high-symmetry points in Fig. 1(a) are $X = (\pi/a, 0, 0)$, $Y = (0, \pi/b, 0)$, and $S = (\pi/a, \pi/b, 0)$. The bands in Fig. 1(b) are along parallel lines displaced upward by $(0, 0, \pi/c)$.

Since the specific characters of the bands have been discussed in detail previously,[1,3,4] we confine our comments to changes in bands which affect the FS relative to those presented earlier.[3,4] By comparing Fig. 1 with Fig. 5 of Ref. 4, we see that the higher level of convergence has resulted in only a single qualitative change from our previous results: The chain-derived band very near E_F along Y-Γ no longer crosses E_F, although it nearly touches it. Our resulting FS cross sections in the symmetry planes are shown in Fig. 2, laid out as was done in Ref. 3. The approach of the outer plane-derived FS to the Γ-Y line in this figure reflects how near the saddle point along Γ-Y is to E_F. The flatness of this band near E_F will make the experimental location of this piece of FS more difficult than for most other sections. This saddle point also shows k_z dispersion [compare the uppermost occupied bands along Γ-Y in Figs. 1(a) and 1(b)] which is an added complication.

With this change, our Cu-O *plane-derived* Fermi surfaces become topologically equivalent to those presented by YMFK, and the only noticeable difference is the above-mentioned bulge in the outer surface reflecting somewhat greater k_z dispersion of this band in the present calculation. There is one clear difference between the

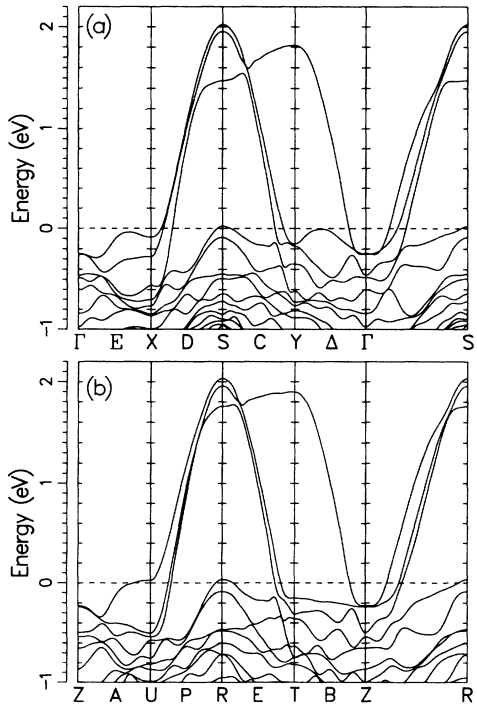

FIG. 1. Bands in the range -1–2 eV relative to E_F for (a) $k_z = 0$ and (b) $k_z = \pi/c$. Note the differences near E_F at X (U) and along Δ (B).

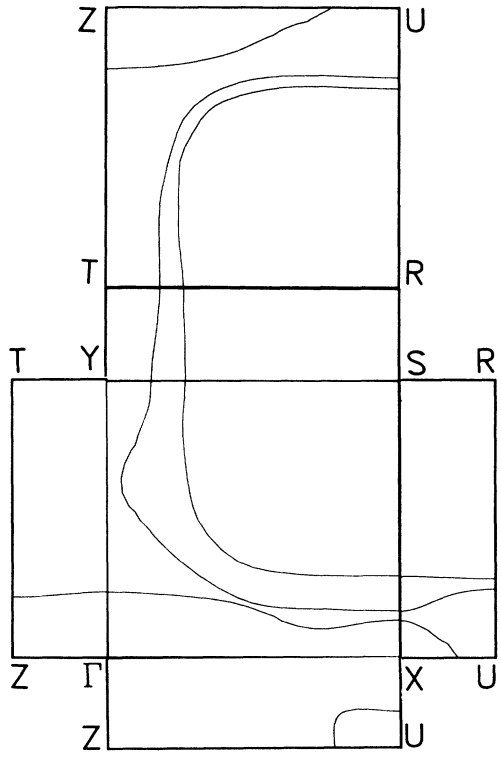

FIG. 2. Fermi-surface cross sections in all of the symmetry planes.

bands of Fig. 1 and those of YMFK, which rests with the *chain-derived* band near E_F at the Y point. YMFK find this band to lie above E_F (clearly so, but by less than 0.1 eV), while our previous results found it just below E_F and the present more converged results put it even lower, at -0.13 eV below E_F. The result is that the closed, irregularly shaped cylinder of the FS surface surrounding the Y-T line in Fig. 2 of Ref. 3 is missing in the present results. The other difference occurs at the U point, where k_z dispersion makes the band just below E_F at the X point end above E_F at U (Fig. 1), resulting in the pinching off of the planar FS around the U point. This does not occur in the YMFK calculation although it is very close to happening.

In interpreting ARPES and ARIPES data, often advantage is taken of the expectation that dispersion along the k_z direction is negligible. In Fig. 3 we illustrate the regions in the zone where dispersion is not negligible by plotting both FS's at $k_z=0$ and $k_z=\pi/a$ in the same plane, and shading the regions in between, in essence collapsing the FS along the k_z direction. It is seen that the chain-derived band at S and the inner layer-derived surface, also centered around S, give rise to "projected Fermi lines" which are relatively well defined. The outer layer-derived projected surface, which corresponds to the antisymmetric mixture of the layer $pd\sigma^*$ antibonding bands, is well defined except where the bulge occurs near the Γ-Y line. The other chain-derived projected FS, which in the simplest approximation would be simply a pair of flat surfaces perpendicular to the b axis, is well defined in the region nearest the Γ point, but k_z dispersion along the X-U line makes it ill defined around X. Also, this one-dimensional (1D) FS intersects and hybridizes with the outer plane-derived FS. Experimental assignments of FS crossings in regions of broad projected FS (broad hatched regions) may be confusing unless the dispersion is accounted for. Nevertheless, we predict that in most regions of the zone the two-dimensional (2D) approximation is tenable.

Further care should be taken in the comparison of the photoemission data with these results because of peculiarities of $YBa_2Cu_3O_{7-\delta}$ samples. The oxygen content of $YBa_2Cu_3O_{7-\delta}$ samples is rarely as high as 7.0 and is often quoted as 6.9, reflecting missing oxygen atoms in the Cu-O chains. Missing oxygen atoms will strongly affect the chain-derived bands, particularly since there is a strong degree of one dimensionality in the chain bands and one-dimensional systems are especially sensitive to defects. Changes in the band structure are not likely to follow a rigid-band picture,[7] because the absence of an oxygen atom (or ion) changes the local potential drastically as well as the electron count. The change in potential may well introduce local distortions as well, which will give additional non-rigid-band behavior.

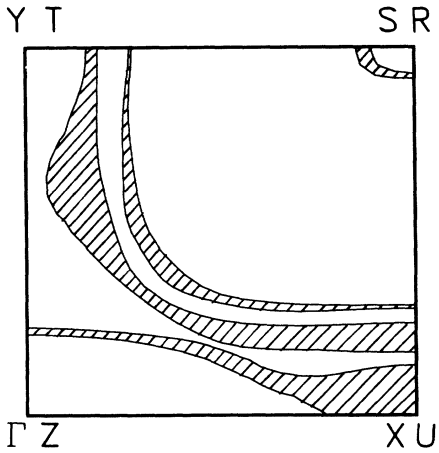

FIG. 3. Fermi surface for all k_z projected onto the $k_z=0$ plane. The shaded regions indicate values of (k_x,k_y) for which there is a Fermi surface for some value of k_z.

Even if there are no oxygen vacancies in the chains, there may be deviations from the calculated band structure because only the *average* crystal structure has been taken into account. Structural refinements and measurements of pair-distribution functions (see references in Ref. 1) indicate substantial deviations of the atoms from their ideal sites. In addition, we have shown[5] that the Cu-O chain is unstable towards buckling, with a small energy decrease of 1 mRy per primitive cell for displacements of 0.3 Å. X-ray studies[8] on detwinned crystals have verified that the chain oxygen atoms indeed lie off their ideal positions, with a buckled chain being suggested as the likely structure. In spite of the large atomic displacements that are involved, we find that band shifts due to chain buckling are small. The flat $pd\pi$ band that lies near E_F is only displaced by about 0.02 eV at the double-well minima so even though the band is flat the position of the FS will not be very sensitive to the bending of the Cu—O—Cu bond along the chain. For the $pd\sigma^*$ chain band, the eigenvalue shift is 0.08 eV, but since the dispersion is steep, this FS position is also weakly affected by chain buckling.

We have presented here LAPW calculations of the band structure and Fermi surfaces of $YBa_2Cu_3O_7$ which are more highly converged than those published previously. Work by Massidda[9] presents his more recent LAPW bands in the basal plane which are in quite good agreement with the results of Fig. 1(a), especially with respect to Fermi-surface topology and dimensions. Our results should be preferred to previously published bands for comparison to measured Fermi surfaces in detwinned crystals.

Most importantly, we wish to emphasize the three-dimensional character of the electronic structure. The planes and chain electronic states hybridize through the out-of-plane O(4) atom, and there is significant c-axis dispersion for some bands. This leads to effective broadening of parts of the Fermi surface when projected onto the x-y plane, as is done in photoemission experiments. Broadening in the Fermi surface has been interpreted in terms of "marginal" Fermi-liquid behavior,[10] but may simply reflect three-dimensional dispersion. Furthermore, the three-dimensional nature of the electronic structure in $YBa_2Cu_3O_7$ suggests that models for high-T_c superconductivity that require two-dimensionality may not be applicable to $YBa_2Cu_3O_7$. Finally, recent experimental studies of $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ superlattices suggest that three dimensionality is required to reach high T_c in $YBa_2Cu_3O_7$.[11]

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