

Strain and High Temperature Superconductivity: Unexpected Results from Direct Electronic Structure Measurements in Thin Films

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(Received 10 July 2002; published 30 July 2003)

Angle-resolved photoemission spectroscopy reveals very surprising strain-induced effects on the electronic band dispersion of epitaxial $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ thin films. In strained films we measure a band that crosses the Fermi level (E_F) well before the Brillouin zone boundary. This is in contrast to the flat band reported in unstrained single crystals and in our unstrained films, as well as in contrast to the band flattening predicted by band structure calculations for in-plane compressive strain. In spite of the density of states reduction near E_F , the critical temperature increases in strained films with respect to unstrained samples. These results require a radical departure from commonly accepted notions about strain effects on high temperature superconductors, with possible general repercussions on superconductivity theory.

DOI: 10.1103/PhysRevLett.91.057002

PACS numbers: 74.78.Bz, 68.60.Bs, 79.60.-i

In-plane compressive strain is known to increase the critical temperature (T_C) of high temperature superconductors (HTSC). This phenomenon is quite dramatic [1,2] in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ (LSCO) thin epitaxial films: for $x = 0.1$, T_C doubles with respect to relaxed LSCO (and increases by a factor of 5 with respect to films with in-plane tensile strain [2]). The published theoretical studies [3,4] predict the in-plane compressive strain to flatten the bands. This could provide a simple explanation for the dramatic T_C increase, since band flattening implies an enhanced density of states near the Fermi energy E_F . Our angle-resolved photoemission spectroscopy (ARPES) studies on strained LSCO films flatly contradict this picture by revealing a dispersing band that crosses E_F . This experimental result thus directly impacts the models dealing with the influence of pressure on superconducting properties [3–7]. The justification of strain effects must be sought beyond the band flattening framework [8,9]. Strained (HTSC) films have been studied rather extensively because of the spectacular strain effects on T_C [1,2]. So far, however, the corresponding electronic structure changes had not been probed directly. We used ARPES to fill this gap by studying *in situ* grown LSCO films. This, incidentally, is the first direct ARPES study of as-grown (HTSC) films (as opposed to cleaved or scraped bulk samples [10] and/or cleaved thin films [11]).

Thin (8 unit cells 105 Å) LSCO films were epitaxially grown on polished (001)-oriented SrLaAlO_4 substrates by off-axis pulsed laser ablation of stoichiometric sintered underdoped (UD), optimally doped (OPT), and overdoped (OD) LSCO targets with $x = 0.10$, 0.15, and 0.20, respectively. Following > 20 min annealing in 1 atm of oxygen, the films were *in situ* transferred to the photoemission chamber. Before producing samples for photoemission experiments, a large number of epitax-

ial films was characterized in depth as described in Refs. [12,13], with microscopy, x-ray diffraction, susceptibility, and resistivity. This led us to identify the optimal parameters that were then used to grow films for ARPES studies. ARPES's data were taken on the 6 m Planar-Grating-Monochromator beamline at the Wisconsin Synchrotron Radiation Center—equipped with a SES200 Scienta analyzer—using photon energies ranging between 30 and 65 eV. The overall energy resolution was 40–50 meV and the angular acceptance $\pm 1^\circ$. Following ARPES measurements, x-ray diffraction (XRD) was performed on each sample to measure its strain. Upon refinement of the x-ray diffraction data along the (001) direction on maximally strained films, we consistently obtained for both OPT ($x = 0.15$) and OD ($x = 0.20$) samples $c = 13.29 \pm 0.02$ for the c axis and $d_{AP} = 2.50$ for the Cu-O apical distance, in agreement with Ref. [2]. In comparison with the relaxed bulk values ($c = 13.23$; $d_{AP} = 2.43$) this corresponds to a change of +0.60% for the c axis and +2.9% for d_{AP} .

Figure 1(a) shows photoemission spectra for an OPT strained film, plotted as momentum distribution curves (MDC), taken at 6.5 K along the reciprocal space Γ - X direction $[(0, 0) \rightarrow (\pi/a, 0)]$. The MDC representation provides a much clearer picture than the energy distribution curves (EDC) when a band approaches the Fermi edge cutoff [14]. The MDC in Fig. 1(a) clearly show a peak moving towards E_F and crossing it at $k_x = 0.82\pi/a$. A similar crossing was observed in strained UD ($x = 0.1$) samples. These experimental findings are very different from the previously obtained results [15] on scraped (unstrained) single crystals that show no E_F crossing except for highly overdoped samples ($x > 0.22$).

Figure 1(b) illustrates the MDC dispersion for the same OPT strained films along the Γ - M direction. The E_F

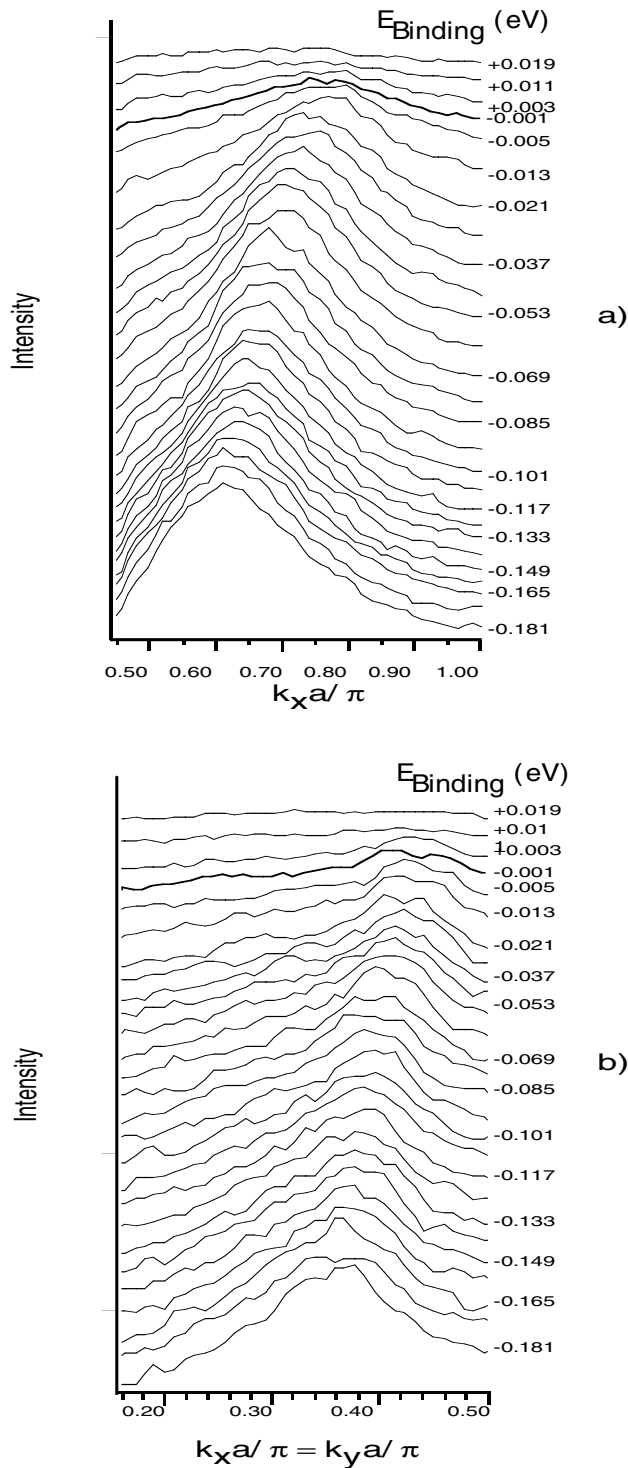


FIG. 1. (a) Angle-resolved MDC ARPES data along the Γ -X direction for an optimally doped ($x = 0.15$) LSCO film under in-plane compressive strain. (b) Angle-resolved MDC ARPES data along the Γ -M direction for the same sample as in (a).

crossing occurs at $k_x = k_y = 0.42\pi/a$ well beyond the crossing point ($0.37\pi/a$) reported in Ref. [15] for OPT single-crystal samples. This indicates that additional occupied states in strained films close to $(\pi/2a, \pi/2a)$ balance the disappearance of those related to the

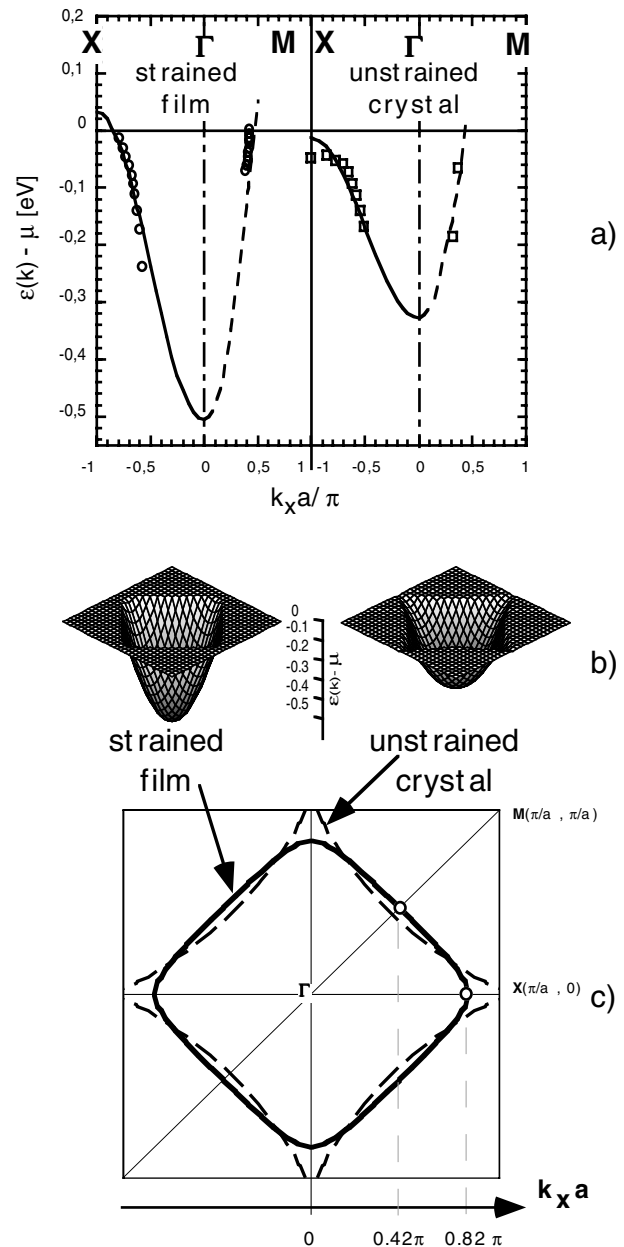


FIG. 2. (a) Fits of band dispersion for a strained film (circles, left panel) and for an unstrained single crystal (squares, right panel, data from Ref. [15]), along Γ -X (solid line) and Γ -M (dashed line). The fits are based on Eq. (1). (b) Visualization of the best-fit results: dispersion of the two-dimensional band for an optimally doped in-plane compressed film (left) and for an unstrained optimally doped single crystal (right). (c) Schematic illustration of changes in the Fermi surface topology.

flat band in unstrained samples consistent with equal doping ($x = 0.15$) in both cases. T_C of our strained films is 44 K, 6° higher than for relaxed films, consistent with the already known effects of compressive strain on T_C [2]. Specifically, this also rules out the possibility of accidental overdoping.

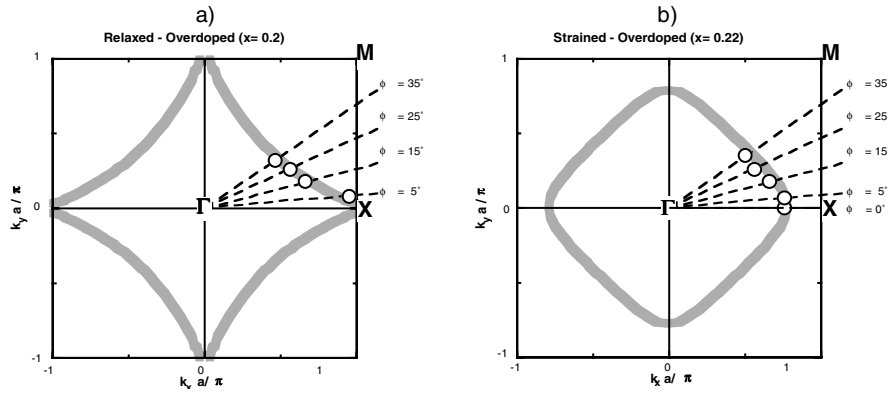


FIG. 3. Fermi surfaces of relaxed (a) and strained (b) overdoped films. White dots are located at the observed crossing points. Thick gray lines are calculated within the tight-binding approach [Eq. (1)], for $x = 0.20$.

In Fig. 2(a), we plot band dispersions of the OPT strained film (circles) and the bulk sample (squares, Ref. [15]), along Γ -X and Γ -M, the latter projected on the k_x axis. The points correspond to the intensity maxima in our thin-film MDC and in the EDC of Ref. [15]. Contrary to the E_F crossing in strained films, the unstrained data along Γ -X reveal a saddle point remaining at least 0.025 eV below E_F .

To guide the discussion on the band structure evolution, we use a simple tight-binding framework. Tight binding including the nearest neighbor (NN) and the next-nearest neighbor (NNN) hopping terms [16] is indeed quite successful in describing the experimental bands near E_F [17] for most HTSC. We use the energy dispersion

$$\xi_k = -2t[\cos(k_x a) + \cos(k_y a)] + 4t' \cos(k_x a) \cos(k_y a) - \mu, \quad (1)$$

where ξ_k is the momentum dependent energy relative to the chemical potential μ , k is the wave vector, and t and t' are the NN and NNN hopping terms. Equation (1) was used to fit the data of Fig. 2(a) with the constant-doping-level constraint $x = 0.15$. This constraint was implemented by noting that μ is related to the band filling n , and therefore to the hole doping level $x = 1 - n$. We choose μ so that the area enclosed by the Fermi surface (FS) is $n = 0.85$. The best-fitting parameters are $t = 0.135$ eV and $t' = 0.0284$ eV for the unstrained crystal (Ref. [15]) and $t = 0.145$ eV and $t' = 0.0052$ eV for the strained film. Thus, $r = t'/t$, the parameter characterizing the band shape, equals 0.21 for the unstrained crystal and 0.036 for the strained film. Main changes in the dispersion derived from the best fit are illustrated in Figs. 2(b) and 2(c). The strong reduction of r by a factor of 5 enhances the band dispersion and distorts the FS. The FS [Fig. 2(c)] is shifted inwards along Γ -X and outwards along Γ -M, changing its topology from holelike to electronlike. The vanishing of the saddle point is illustrated in Fig. 2(b). The NN hopping term t slightly increases in the

strained sample; this is reasonable since a small in-plane lattice contraction enhances the overlap integrals between the NN Cu $3d_{x^2-y^2}$ and O $2p_x$ orbitals. The same trend should be expected for the NNN hopping t' (overlap between the O $2p_x$ and O $2p_y$ orbitals). In fact, the increase should be much stronger for t' than for t since the NNN overlaps are much weaker [4]. Surprisingly, the observed trend is exactly the opposite: the NNN hopping t' is much lower for strained films than for the unstrained sample. This fact is not accounted for by published theoretical models [3,4]. Note that our x-ray diffraction data show that the strain-induced changes are much bigger for the Cu-O apical bond than for the other interatomic distances. This suggests a change in coordination and therefore in the hopping integrals that cannot be properly described by those theoretical models [3,4] that assume no coordination changes.

In substrate mismatched epitaxial films, when elastic energy is relaxed, it does so via misfit dislocations resulting in poor quality film surfaces. As a consequence, in relaxed optimally doped films, the significant incoherent background in ARPES prevented us from extracting the dispersion. This is a sensitive point, since the previous comparison between bulk and film samples was built on the assumption that film and bulk surfaces have no inherent differences (except for the strain). However, since band features become stronger with doping, in the OD regime ($x = 0.20$), we have measured the dispersions of both relaxed and strained films. The 2D FS in Fig. 3(a) is that of an OD relaxed film with a superconducting T_C of 24 K. Dashed lines indicate the scan directions in k space, and the white dots are located at the intersection of the band with E_F , observed on MDC plots. The thick gray line is calculated with Eq. (1), using the constraint $x = 0.2$ and the band parameters $t = 0.135$ eV and $t' = 0.036$ eV, very close (20%) to those found for the relaxed bulk. Similarly, in Fig. 3(b), we show the FS of an OD strained film with a superconducting T_C of 40 K. The band parameters used to draw the thick gray line are

$t = 0.145$ eV and $t' = 0.0052$ eV, the same as for the optimally doped strained film. The agreement is not surprising since the XRD analysis shows almost the same strain ($c = 13.30 \pm 0.02$) as for the OPT film. Thus the effect of strain on band structure, observed for OPT LSCO films is unambiguously confirmed, qualitatively and quantitatively, in the OD case. Moreover, the influence of inherent differences between bulk and film surfaces can be discarded. Indeed, the results obtained on the relaxed OD LSCO film are the same as for the bulk OD single-crystal reported in Ref. [15].

In summary, we have performed direct ARPES on UD, OPT, and OD strained LSCO films and have measured a dispersing electronic band that crosses E_F well before the Brillouin zone boundary, in contrast to a flat band observed in both unstrained films and single crystals [15]. Our results rule out a simple explanation of the strain-induced changes in T_C based on the increase in the density of states near E_F [18]. The fact remains that in-plane compressive strain does increase the critical temperature as confirmed by our measurements. Our findings, therefore, have a general impact on the evolving theories of high temperature superconductivity.

We acknowledge useful discussions with, among others, S. Barisic, H. Beck, A. Bianconi, J. Bok, I. Bozovic, L. Forro, M. Grioni, J.P. Locquet, I. Mrkonjic, L. Perfetti, and Z. X. Shen. This work was supported by the Swiss National Science Foundation and by the EPFL. The Synchrotron Radiation Center, University of Wisconsin–Madison, is supported by the NSF under Award No. DMR-0084402.

Note added.—Since the acceptance of this Letter, we have learned of the latest experimental and theoretical work that provide further important insights into the role of strain and electronic structure in high T_c cuprates [19].

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