Highly Anisotropic Anomaly in the Dispersion of the Copper-Oxygen Bond-Bending Phonon in Superconducting $YBa_2Cu_3O_7$ from Inelastic Neutron Scattering

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(Received 3 May 2011; published 19 October 2011)

Motivated by predictions of a substantial contribution of the ''buckling'' vibration of the CuO_2 layers to d-wave superconductivity in the cuprates, we have performed an inelastic neutron scattering study of this phonon in an array of untwinned crystals of $YBa_2Cu_3O_7$. The data reveal a pronounced softening of the phonon at the in-plane wave vector $\mathbf{q} = (0, 0.3)$ upon cooling below $\sim$105 K, but no corresponding anomaly at $\mathbf{q} = (0.3, 0)$. Based on the observed in-plane anisotropy, we argue that the electron-phonon interaction responsible for this anomaly supports an electronic instability associated with a uniaxial charge-density modulation and does not mediate d-wave superconductivity.

DOI: 10.1103/PhysRevLett.107.177004 PACS numbers: 74.25.Kc, 63.20.kd, 71.27.+a, 74.72.Gh

Research on the mechanism of high-temperature superconductivity in the cuprates has recently made substantial progress based on a quantitative analysis of possible Cooper pairing interactions, which include coupling to spin fluctuations and phonons. The spin-fluctuation-mediated pairing interaction favors the experimentally observed d-wave pairing state [1], but its strength relative to phonon-mediated pairing interactions remains a matter of intense debate [1–12]. Whereas density functional theory indicates a small [5,6] or negligible [10,11] contribution of the electron-phonon interaction (EPI) to d-wave superconductivity, it has been argued that electron correlations can greatly enhance the coupling strength [2,3] such that it yields a substantial [7] or even dominant [4] contribution to the pairing interaction. In this context, much attention has been focused on phonons that modulate the Cu-O bonds in the CuO_2 layers, which are generic to all cuprate superconductors. Most model calculations indicate that the EPI of high-energy stretching vibrations of these bonds is either detrimental [8,9] or indifferent [5–7] to d-wave pairing. However, several theories indicate that coupling to the lower-energy ''buckling'' vibration that modulates the Cu-O-Cu bond angle is attractive in the d-wave channel [5–9].

Two experimental strategies have been employed to test these theories and to quantify the strength of the different electron-boson coupling channels. The first approach has identified fingerprints of coupling to bosonic modes in the electronic spectral functions extracted from angle-resolved photoemission, optical, and tunneling data [1,2], but these data are not specific enough to unequivocally discriminate between contributions from spin excitations and phonons. A second, complementary approach therefore targets corresponding anomalies in the bosonic excitations. The prominent spectral-weight redistribution of spin excitations at the superconducting transition temperature determined by neutron scattering [13] indicates a positive contribution to the d-wave pairing susceptibility, in agreement with theoretical predictions [1]. The Cu-O bond-stretching vibration also exhibits anomalies indicative of a substantial EPI [14–20], but most model calculations agree that coupling to this mode does not support d-wave pairing. These, however, have not predicted or reproduced the above-mentioned anomalies [21] (with the exception of Ref. [12]).

Much less information is available on the buckling mode, which has been predicted to favor d-wave superconductivity [5–9]. Raman scattering experiments on optimally doped cuprates have shown that the mode exhibits a superconductivity-induced softening of $\sim$1.5% at wave vector $\mathbf{q} = 0$ [22,23]. However, $\mathbf{q}$-dependent data are required for a comprehensive assessment of the contribution of the buckling phonon to the experimentally observed electron self-energy anomalies and to the d-wave pairing state. Such data can be collected by inelastic neutron scattering. Since the lattice dynamics is further complicated by structural disorder, prior neutron scattering work has focused on stoichiometric $YBa_2Cu_3O_7$ [24,25]. The results confirmed a modest softening of the buckling mode upon cooling below the superconducting transition temperature T_c, which agrees with Raman scattering data [22,23] at $\mathbf{q} = 0$ and decreases rapidly with increasing $\mathbf{q}$,

in accord with model calculations [26,27]. However, a broadening of the neutron profiles with a maximum amplitude at nonzero $\mathbf{q}$ [25] was not explained by these calculations. Since these experiments were carried out on twinned specimens, the in-plane anisotropy of these features could not be resolved.

In the light of recent reports of pronounced, strongly temperature- and doping-dependent in-plane anisotropies of the magnetic [13] and transport [28,29] properties of underdoped $YBa_2Cu_3O_{6+\delta}$, we have used inelastic nuclear neutron scattering to determine the in-plane anisotropy of the dispersion of the buckling mode in an untwinned specimen of $YBa_2Cu_3O_7$. Our sample consists of 185 individually detwinned single crystals with total mass 2.63 g, coaligned on an aluminum plate. Magnetization measurements on a representative set of crystals showed that $T_c = 90.0 \pm 0.5$ K. X-ray powder diffraction measurements yielded the room temperature lattice parameters $a = 3.8173$, $b = 3.8844$, and $c = 11.681$ Å. These data imply that the sample is nearly stoichiometric ($\delta \sim 1$) and slightly overdoped. This is important because even a small density of oxygen vacancies leads to the formation of superstructures that may affect the phonon dispersions [30]. The detwinning ratio of the array is 86%. The neutron measurements were performed on the PUMA spectrometer at the FRM-II reactor in Garching, Germany, and on the 1T spectrometer at the ORPHEE reactor at LLB, Saclay, France. The (2, 2, 0) reflection of Cu and the (0, 0, 2) reflection of pyrolytic graphite were used to monochromate and analyze the neutron beam, respectively. The final neutron energy was fixed at 8 meV, and the data were taken in the Brillouin zones adjacent to the (1, 0, 10), (0, 1, 10), and (0, 3, 1) reciprocal lattice vectors. [Wave vectors are quoted in units of $2\pi/(a, b, c)$.]

Figure 1 shows representative neutron scattering profiles in a scattering geometry that maximizes the structure factor of the buckling mode, at the in-plane wave vector $\mathbf{q} = (0, 0.3)$ where the broadening was observed in the early experiment [25]. In addition to the buckling mode at energy $E = 40$–42 meV, the data show a mode at 44.5 meV that is not strongly temperature-dependent and will not be discussed further. The profiles of the buckling mode, on the other hand, exhibit a highly unusual behavior. At temperature $T = 120$ K, the profile shows a single peak with a barely discernible shoulder on the low-energy side [Fig. 1(e)]. Upon cooling, however, the shoulder grows continuously and draws intensity from the main peak, resulting in a two-wing profile at low temperatures [Figs. 1(a)–1(d)]. In order to parameterize the temperature evolution of the line shape, we have fitted the data to a phenomenological form that comprises two Voigt functions with fixed energies 40.0 and 41.8 meV and widths 1.6 and 1.2 meV [black lines in Figs. 1(a)–1(e)]. The fits yield a good description of the experimental data over the

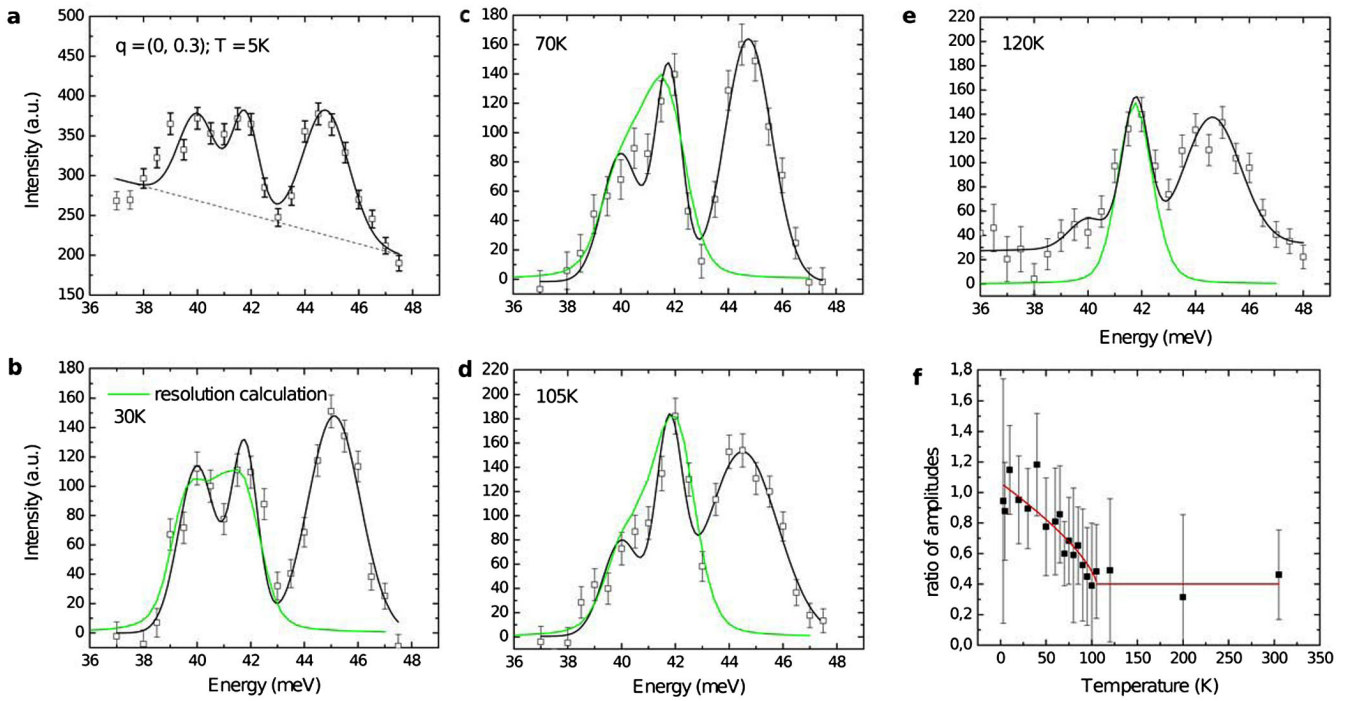

FIG. 1 (color online). (a)–(e) Constant-$\mathbf{Q}$ scans at $\mathbf{Q} = (0, 0.3, 10)$. The profile at energy 40–42 meV arises from the bucking mode. Panel (a) shows raw data. A sloping background (dotted line) was subtracted in the other profiles for clarity. The black and green lines are results of fits to a phenomenological expression comprising two Voigt functions and to a full resolution calculation, respectively, as described in the text. (f) Temperature dependence of the line shape parameterized by the intensity of the two peaks in the phenomenological expression.

entire temperature range (although they do not correctly capture the physics; see below). The T dependence of the resulting peak intensities [Fig. 1(f)] indicates a well-defined onset of the line shape anomaly at $T = 105 \pm 15$ K.

This unusual behavior is confined to in-plane wave vectors in the range $\mathbf{q} = (0, 0.2) \rightarrow (0, 0.4)$. The profiles for wave vectors outside this range along the same direction and for the entire range along the perpendicular direction, $\mathbf{q} = (0, 0) \rightarrow (0.5, 0)$, are well described by a single, undistorted peak. A representative scan at $\mathbf{q} = (0.3, 0)$ is shown in Fig. 2. The strong in-plane anisotropy of the anomalous dispersion of the buckling mode revealed by these data could not be recognized in previous work on twinned crystals [24,25].

Since the $E - \mathbf{q}$ range of the anomalous low-temperature dispersion of the buckling mode is comparable to the dimensions of the resolution ellipsoid of the neutron spectrometer, a careful resolution calculation is required to extract information from the observed line shape. We have performed such a calculation based on the dispersion relation shown in Fig. 3, which is flat along the a direction at all temperatures [Fig. 3(a)] and along b for $T \geq 120$ K [red line in Fig. 3(b)] but develops a sharp dispersion anomaly along b at lower temperatures [Fig. 3(b)]. Considering the simplicity of the model, the agreement between the calculated profiles [green lines in Figs. 1(b)–1(e)] and the data is satisfactory. In particular, the calculation provides an explanation of the two-wing profile discussed above. The low-energy wing results from the bottom of the dispersion anomaly at the nominal spectrometer setting. However, the instrumental resolution ellipsoid also encompasses a wide segment of the nearly flat dispersion surface away from the anomaly. This explains the high-energy wing of the profile.

A highly anisotropic dispersion anomaly of the buckling mode that is strongly enhanced upon cooling below ~105 K thus provides an adequate explanation of all aspects of the experimental data. In view of the presence of several other phonon branches in the energy range 35–45 meV previously detected by Raman and infrared spectroscopies [31], one may wonder to what extent the T-dependent spectral-weight redistribution of the buckling mode results from mixing with other modes. We have calculated the neutron structure factors based on the eigenvectors provided by *ab initio* density functional theory calculations [32] and found that most of the modes in this energy range (mostly in-plane vibrations of the apical oxygen ions, with some admixture of chain and plane oxygens) exhibit substantial spectral weight in the Brillouin zone around the reciprocal lattice vector (0, 3, 1). Scans in this zone for $\mathbf{q} = (0, 0.3)$ show no evidence of temperature-dependent modifications of the phonon intensities or line shapes outside the statistical error. While a spectral-weight transfer to other modes analogous to the one discussed for the Cu-O stretching vibration [15,17] cannot be ruled out entirely, it therefore does not appear to play a major role for the buckling mode. This conclusion is also supported by the observation that the integrated intensity of the buckling mode profile shown in Fig. 1 is T-independent.

We now discuss the microscopic origin of the dispersion anomaly. Since wave vectors around $\mathbf{q} \sim (0, 0.3)$ connect nested segments of the Fermi surface of $YBa_2Cu_3O_7$ [33], an anomaly resulting from the EPI provides a natural explanation of our data. The strong temperature

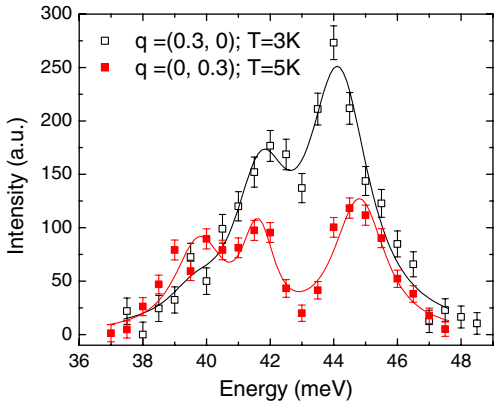

FIG. 2 (color online). Constant-$\mathbf{Q}$ scans of the buckling mode at $\mathbf{Q} = (0.3, 0, 10)$ and $(0, 0.3, 10)$. A sloping background [Fig. 1(a)] was subtracted.

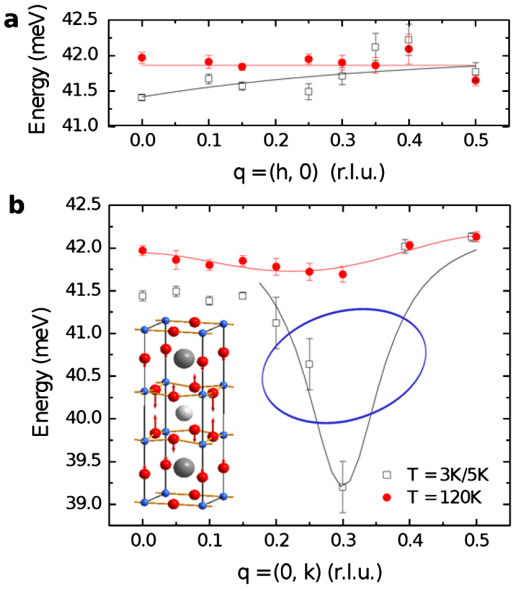

FIG. 3 (color online). Dispersion of the buckling mode along the a and b axes. The black line is the dispersion used for the resolution calculation. A projection of the four-dimensional resolution ellipsoid is shown for comparison. The data point at $\mathbf{q} = (0, 0.3)$ is the result of the resolution convolution described in the text; the remaining points were determined by fits to standard Voigt functions. The inset shows the eigenvector of the buckling mode at $\mathbf{q} = (0, 0.3)$. The elongations of the apical oxygen atoms and of the in-plane oxygen atoms along b were enlarged by a factor of 4 for clarity.

dependence of the anomaly (Fig. 1) can then be attributed to the opening of a gap (or pseudogap) on the Fermi surface. Although the data of Fig. 1(f) are consistent with a sharp onset or enhancement at T_c, the momentum-space structure of the anomaly speaks against a direct relation to the superconducting gap [23,34,35]. Raman scattering experiments have shown that the pair-breaking energy $2\Delta \approx 60$ meV, with a $\sim$10% anisotropy between the a and b directions [23,34]. Since 2Δ significantly exceeds the phonon energy along both a and b axes, the onset of superconductivity is expected to affect the phonon line shapes similarly in both directions. Specifically, a softening of the phonon is expected as the gap sweeps through the phonon energy upon cooling [36,37]. This is indeed the case for the superconductivity-induced softening centered at $\mathbf{q} = 0$ (Fig. 3) [22,23] but not for the anomaly at $\mathbf{q} \neq 0$, which is present only along the b axis. The strong anisotropy in phonon softening is indicative of a uniaxial EPI, which cannot be responsible for the superconducting gap whose magnitude is similar along a and b, as further explained below.

Based on these considerations, a (real or incipient) instability other than superconductivity must be responsible for the T-dependent anomaly of the buckling mode. The strong in-plane anisotropy of the anomaly indicates that it has a one-dimensional structure, which may arise from a uniaxial charge-density wave (CDW) instability. There is independent evidence for a CDW originating in the CuO chains in the $YBa_2Cu_3O_7$ crystal structure [38–40], and the wave vector of the phonon anomaly is similar to the one of the CDW recently reported by x-ray diffraction [40]. The temperature onset of the phonon anomaly [Fig. 1(f)] is also near the onset of a pronounced in-plane anisotropy of the Nernst effect in $YBa_2Cu_3O_7$ [29], which has been interpreted as evidence of a stripe or Pomeranchuk instability originating in the CuO_2 planes. We note, however, that the wave vector of the instability indicated by the phonon anomaly is perpendicular to the one characterizing the uniaxial spin density wave state recently observed in strongly underdoped $YBa_2Cu_3O_{6+\delta}$ [41]. This may imply that spin (charge) driven instabilities with propagation vectors along a (b) dominate the interplay with d-wave superconductivity in the low (high) doping regimes of the $YBa_2Cu_3O_{6+\delta}$ phase diagram. Such a multiphase competition may be influenced by the hybridization between the chain-derived energy bands with those arising from the CuO_2 layers [33].

We finally address the magnitude of the dispersion anomaly. If we assume that the phonon softens due to an opening of a gap on the Fermi surface (see Ref. [36] for the case of the superconducting gap, although our argument would work for a gap of any origin) the phonon renormalization magnitude should be proportional to the $\mathbf{q}$-dependent EPI strength. The observed $\sim$6% softening of the buckling phonon at $\mathbf{q} \sim (0, 0.3)$ upon cooling indicates that the EPI of the buckling mode may be strong enough to contribute significantly to the electronic self-energy along the antinodal direction of the d-wave gap function, as hypothesized based on angle-resolved photoemission measurements [2,7]. Our data provide an improved basis for a quantitative assessment of this contribution relative to the one generated by spin fluctuations [1,13]. Despite its strength, we have shown that the highly anisotropic EPI responsible for the anomaly at $\mathbf{q} \sim (0, 0.3)$ does not support d-wave superconductivity. We conclude that the buckling mode does not contribute to d-wave pairing beyond $\mathbf{q} = 0$, where the phonon softening below T_c translates into a small dimensionless coupling constant $\lambda_d \sim 0.02$, in agreement with density functional theory calculations [11]. It is possible, however, that it contributes to the observed subdominant s-wave admixture to the pairing state [23,34,35].

In any case, the sharp phonon anomaly indicates that overdoped $YBa_2Cu_3O_7$ is close to an instability associated with a uniaxial CDW. Further work is required to assess the contribution of the electron-phonon coupling driving this instability to the anomalous band dispersions revealed by angle-resolved photoemission.

We thank O. K. Andersen, C. Bernhard, P. Bourges, M. Cardona, V. Damljanovic, O. Gunnarsson, T. Keller, G. Khaliullin, D. Manske, L. Pintschovius, Y. Sidis, and R. Zeyher for discussions and R. E. Dinnebier and D. Haug for help with the x-ray measurements.

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