

Sharp optical-phonon softening near optimal doping in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4+\delta}$ observed via inelastic x-ray scattering

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We report a direct observation of a sharp Kohn-type anomaly in the doubly degenerate copper-oxygen bond-stretching phonon mode occurring at $\mathbf{q}=(0.3,0,0)$ in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4+\delta}$ with $x=0.14\pm 0.01$, thanks to the high \mathbf{Q} resolution of inelastic x-ray scattering. This anomaly is clearly seen when the inelastic signal is analyzed using a single mode but is also consistent with a two-mode hypothesis, possibly due to a splitting of the degenerate modes due to symmetry-breaking stripes. Our observation shows that the effect persists at the stripe-propagation vector in a superconducting system close to optimal doping.

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I. INTRODUCTION

Copper-oxygen bond-stretching (BS) modes in high-temperature superconducting cuprate (HTCS) have long been known to show anomalies related to doping.¹ The origin of the anomalies is still an open issue. Along with electron-phonon coupling effects, a mechanism involving the formation of an inhomogeneous charge state, also known as *stripes*,²⁻⁶ has been discussed.^{7,8} At the outset let us clarify the anomalies seen in this phonon mode. Earlier works¹ focused on the gradual softening of this mode with doping, a phenomenon seen quite universally in HTCS and now relatively well understood, even theoretically,⁹ on the basis of electron-phonon coupling and screening mechanisms which come into play on doping. This softening can be well described by a cosinelike behavior of the mode with its minimum at the zone boundary. Even in the earliest works, however, there were indications that the dispersion might be more complicated, with deviations from the cosinelike shape.⁷ The possibility that these deviations are caused by stripes has been invoked and adopted in a recent paper¹⁰ in which previous data on HTCS are compared to newer ones, in particular for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4+\delta}$ with $x=1/8$. In this system, for $x\sim 1/8$, an anomalous suppression of the superconductivity reported in Ref. 11 was later shown to be associated with charge and spin stripe orders.¹²⁻¹⁴ Signatures of stripes in superconducting samples remain elusive although it was proposed that stripes are difficult to detect in these samples because they are no longer static.^{15,16} Using phonons to probe charge fluctuations can potentially lead to a reliable signature of static and dynamic stripes in HTCS. Reznik *et al.*,¹⁰ in describing their high-resolution inelastic neutron-scattering data of the copper-oxygen bond-stretching mode, showed how one of its two normally degenerate components follows the expected cosinelike dispersion while the other deviates presenting a much sharper dip. They interpret this

behavior as a Kohn-type anomaly due to stripes which lift the degeneracy.¹⁷ Although this scenario is intriguing, the dip is not directly visible in the data of Ref. 10, and the authors deduced its existence from a broad shoulder on the low-energy side of the Cu-O bond-stretching phonon mode. It is then desirable to have a direct measurement of the dip¹⁸ since without it other reasons could be invoked to explain the observed signal. To clarify this point we have carried out a high (\mathbf{Q}, ω) resolution measurement in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4+\delta}$ using inelastic x-ray scattering (IXS) with a comparable energy resolution but with a higher resolution in reciprocal space compared to previous inelastic neutron-scattering experiments.

This allowed us not only to confirm the presence of a dip around $\mathbf{q}=(0.3,0,0)$ in the dispersion of the copper-oxygen bond-stretching mode but also to extend this observation to a doping value ($x=0.14$). This near optimal doping level leads to a stripe-propagation vector $\mathbf{q}\approx(0.3,0,0)$,⁶ in striking agreement with our findings, and supports a picture based on the interaction with stripes.^{7,10}

II. EXPERIMENT

We studied a single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4+\delta}$ grown from melting in an image furnace by the traveling solvent zone method under a pressure of 3 bar oxygen. The measured $T_c=18.1$ K, with $\Delta T_c=7$ K defined as the temperature range from 90% to 10% of the maximum Meissner signal, is consistent with microprobe results indicating a content of $x=0.14\pm 0.01$.¹⁹ The experiment was carried out at the IXS beamline II (ID28) at the European Synchrotron Radiation Facility in Grenoble. The sample was mounted in reflection geometry, on the cold finger of a closed-loop helium cryostat, in order to keep it at constant temperature $T=(17.8\pm 0.5)$ K during the experiment. The low temperature was chosen so as to optimize the signal of the high-energy

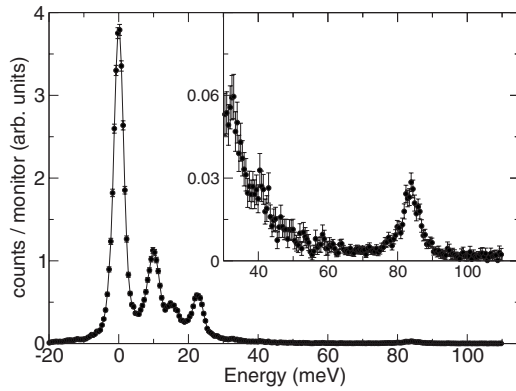


FIG. 1. Inelastic x-ray scattering example spectrum of $\text{La}_{1.86}\text{Ba}_{0.14}\text{CuO}_{4+\delta}$ at $\mathbf{Q}=(3.11,0.04,0)$. At zero energy one observes the elastic line, while at positive energy, several phonon modes are observed corresponding to Stokes processes. In the inset we zoom on to the high-energy optical Cu-O bond-stretching mode. Anti-Stokes modes are not visible because of the unfavorable detailed balance at low temperature.

modes over the tails of the low-energy ones. The sample c crystal axis was perpendicular to the scattering plane. We consider the tetragonal unit cell with $\alpha=\beta=\gamma=90^\circ$ and the axes a and b along the Cu-O bond. The sample was aligned along $(H,0,0)$, and we refined the parameter $a=3.792\pm 0.001$ Å according to the $\theta-2\theta$ scan on the $(4,0,0)$ reflection and adopted the value of $c=13.235$ Å. The rocking curve at the $(4,0,0)$ reflection had a full width at half maximum (FWHM) $\sim 0.06^\circ$ indicating a very low mosaic spread in the small volume probed. The IXS multianalyzer spectrometer^{20,21} configurations chosen were of type $\mathbf{Q}=\mathbf{G}+\mathbf{q}=(3,0,0)+(q_x,q_y,0)$, with simultaneous measurements from seven analyzers. We collected data from the first five analyzers closer to the beam direction, which are at fixed angular spacing of $\sim 0.75^\circ$ ($q_x \sim \pm 0.07$), with the third one in longitudinal condition $q_y=0$ while for the others $q_y \leq \pm 0.045$. This setup corresponds to the third extended Brillouin zone (BZ) where the zone center Γ is at $(4,0,0)$ and the extended zone boundary at $(3,0,0)$. The standard or folded zone boundary is at point $M=(3.5,0,0)$. The scattering vector resolution was set using a slit opening in front of the analyzers of $h \times v = 20 \times 60$ mm corresponding to a solid angle of $\delta\theta \times \delta\xi = 0.19^\circ \times 0.57^\circ$. The resolution in the reciprocal space for 0.6968 Å wavelength was $(\pm \delta q_x, 0, 0)$, with $\delta q_x \approx 0.009$. The high-energy resolution is obtained using the backscattering silicon monochromator aligned along the (111) direction.^{22,23} In the present experiment we choose to work with the Si $(9,9,9)$ reflection order, with a wavelength of 0.6968 Å ($17\,794$ eV) and an energy resolution $\Delta E = 3.0 \pm 0.2$ meV. An example of a raw IXS spectrum is given in Fig. 1. The energy scans were fitted using a sum of pseudo-Voigt for elastic and resolution-limited inelastic contributions, with parameters fixed to match the instrumental function, while a Lorentzian line shape was used to fit modes with an intrinsic width larger than the instrumental resolution. In order to assign the measured phonon modes, we performed a lattice-dynamical calculation using a computer code²⁴ based on a shell model.²⁵ More details on analysis and simulation are described elsewhere.¹⁸

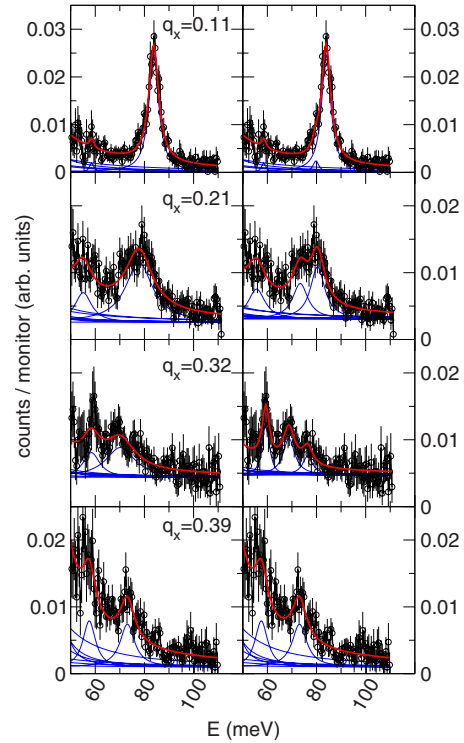


FIG. 2. (Color online) Inelastic x-ray scattering example spectra from $\text{La}_{1.86}\text{Ba}_{0.14}\text{CuO}_{4+\delta}$ at different wave vectors $\mathbf{Q}=(3+q_x, q_y, 0)$ (see text). In the left column the data are fitted using the degenerate Cu-O bond-stretching mode hypothesis. In the right column the data are fitted supposing two Cu-O bond-stretching mode.

III. RESULTS AND DISCUSSION

The high-energy portion of some typical measurements is shown in Fig. 2. In this spectral window, at least two modes could be identified: a mode at about 60 meV, corresponding to the fifth longitudinal optic mode (in order from the lowest energy), and a second dispersing from about 90 meV down to about 70 meV, the highest-energy (sixth) longitudinal Cu-O bond-stretching (or half-breathing) optic mode. The fast downward dispersion is accompanied by a rapid broadening from 5 meV to about 15 meV FWHM. This mode is doubly degenerate and could eventually split if the local symmetry is lowered by some anisotropy. Such splitting has been suggested¹⁰ for a $q_x \sim 0.2-0.3$, corresponding to the propagation vector of a charge modulation (stripe). Other possible origins of the double modes have been previously reported,^{7,26} always in connection with microscopic phase-separation. The doubling of the modes can contribute to the observed broadening if the energy resolution is not enough to distinguish the two modes as in our case. In most of the measured spectra it is then not possible to have independent fitted parameters for frequency, intensity, and width of each mode. We have used the error estimation of the fitted widths as a goodness of fit criterion, and only in the case of $q_x=0.32$ (see Fig. 2), the two-mode fit appears to be better than the single mode fit for our data.

In Fig. 3 we show the results of our fitting for the frequencies (left panel) and width (right panel) for the single mode (blue squares). A minimum at $q_x=0.32 \pm 0.04$ is clearly ob-

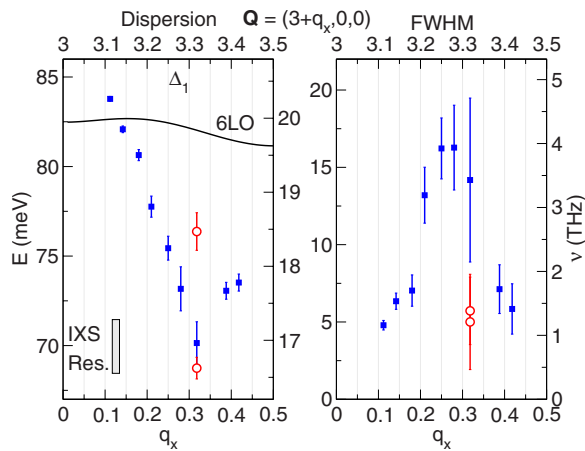


FIG. 3. (Color online) Left panel: $\text{La}_{1.86}\text{Ba}_{0.14}\text{CuO}_{4+\delta}$ Cu-O BS dispersion. Blue squares represent frequencies from the model fit with one mode, while red hollow circles represent a fit with two modes. The line corresponds to a shell-model lattice dynamics calculation. Right panel: $\text{La}_{1.86}\text{Ba}_{0.14}\text{CuO}_{4+\delta}$ Cu-O BS width, symbols as above.

served. In the same figure, we also show the results for the fit in a double mode hypothesis (red circles) for $q_x=0.32$.

The difficulty of the analysis (the impossibility of reliably fitting two closely placed peaks) is inherent to the experimental strategy chosen: in order to follow in detail the dispersion we chose a higher \mathbf{Q} resolution with comparable energy resolution to Ref. 10. This also results in a significantly different line shape. In Ref. 10, using inelastic neutron scattering, the highest mode appears more intense because it is weakly dispersing and thus benefits from a large \mathbf{Q} integration, while the low-energy one appears broader because the supposed Kohn-type dip in the dispersion is only as large as the experimental \mathbf{Q} resolution. Assuming that the two-mode hypothesis is valid, let us examine the consequences for our data. A \mathbf{Q} resolution narrower than the dip width results in a sharper low-energy mode. We have already seen that the intensity of the high-energy mode decreases due to better \mathbf{Q} resolution. This results in two modes of similar intensity and width, more difficult to separate with this energy resolution. Returning to the results shown in Fig. 3, in a one mode hypothesis, we obtain a maximum of the width around $q_x \sim 0.3$, coinciding with the dispersion minimum. Indeed, even a one-peak fit gives a well pronounced anomalous dip that is inconsistent with a cosinelike dispersion. The dip is observed even with a one-peak fit because the dispersion of the concerned mode and its intensity are strong enough and dominate even after averaging with the less dispersing higher-energy mode. The maximum in the width is, in fact, a measure of the energy distance between the modes which is associated with the dip, as already pointed out (see Fig. 4 in Ref. 10). Note that we extended the observation of this anomaly to a doping range which is well beyond the singular 1/8th level and crucially in a superconducting range

where the stripes should be dynamic. Consistent with this higher doping level we observe that the dip is more spread out over the BZ, already starting at $q_x \approx 0.1$ with a FWHM of 4.7 ± 0.3 meV, and that the softening is reduced even in the two-mode hypothesis. These observations are thus consistent with a persisting anomaly at the stripe-propagation wave vector in a more metallic system where both the doubling and the shift of the low-energy mode appear to be reduced. Previous results obtained by IXS (Ref. 27) on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ for different doping level are interpreted in the standard cosinelike dispersion picture but corresponds to a setup with only ≈ 6 meV resolution, about twice the present one. A review of this anomaly in other HTCS is reported in Ref. 10. Finally, we note here that a possible link has recently been suggested in single layer $\text{Bi}_2\text{Sr}_{1.6}\text{La}_{0.4}\text{Cu}_2\text{O}_{6+\delta}$ (Ref. 28) between the maximum of the Cu-O bond-stretching softening and width and a Fermi-surface nesting vector at $q_x \approx 0.22$, with a clear kink in the electron dispersion at the energy of the phonon mode. The vector is close to the stripe-propagation vector in double layer $\text{Bi}_{2-x}\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ reported by scanning tunnel microscope in Ref. 29 and very recently in single layer $\text{Bi}_{2-y}\text{Pb}_y\text{Sr}_{2-z}\text{La}_z\text{Cu}_2\text{O}_{6+x}$.³⁰ This correlation suggests that stripes are closer to the classical charge-density wave, which in fact fully develops in other systems as bismuthates, with similar effects on the Bi-O bond-stretching modes.³¹ In order to confirm this hypothesis, however, further investigations, similar to the one in Ref. 28, on other systems and dopings are required.³²

IV. CONCLUSIONS

We directly observe a sharp dip in the dispersion of the Cu-O bond-stretching or half-breathing mode at the wave vector $q_x \sim 0.3$ associated with the stripe-propagation vector, as previously suggested in Ref. 10. Our data are consistent with the two-mode hypothesis, which would describe this softening as associated with a doubling of the mode possibly due to a splitting of the doubly degenerate Cu-O bond-stretching mode.¹⁰ Our observation shows that the effect persists in a superconducting system close to optimal doping.

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