Anomalous Dispersion of LO Phonons in Oxygen-Doped La$_{2-x}$Sr$_x$CuO$_{4+\delta}$

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Inelastic neutron scattering has been used to study the in-plane Cu-O bond-stretching mode in oxygen doped La$_{2-x}$Sr$_x$CuO$_{4+\delta}$ (T$_c$ = 38 K) and La$_2$CuO$_{4+\delta}$ (T$_c$ = 43 K). Similar to results from optimally doped La$_{1.85}$Sr$_{0.15}$CuO$_4$ (T$_c$ = 35 K), we observe anomalous features in the dispersion of this half-breathing mode in the form of a softening halfway through the Brillouin Zone. Considering the differences in electronic structure and local environment between the oxygen- and strontium-doped compounds with similar T$_c$, we rule out a connection between the phonon anomaly and structural instabilities related to the specific dopant type. We interpret the phonon anomaly as a signature of correlated charge fluctuations possibly connected to stripes.

A widely accepted description of the low-temperature electronic state of underdoped cuprate superconductors is the ‘stripe’-picture, where, due to hole-doping, the anti-ferromagnetic (AFM) ground state of the parent compound is segregated by channels of charge resulting in magnetic anti-phase boundaries [1]. Experimentally, the magnetic part of the stripes shows up in neutron scattering experiments as a modulated AFM structure (static magnetic stripes) and excitations emerging with the magnetic part of the stripes shows up in neutron in magnetic anti-phase boundaries [1]. Experimentally, the relation of electronic structure and local environment between the oxygen- and strontium-doped compounds is segregated by channels of charge resulting in magnetic anti-phase boundaries [1]. Experimentally, the magnetic part of the stripes shows up in neutron scattering experiments as a modulated AFM structure (static magnetic stripes) and excitations emerging with similar wavevectors, in the low energy regime (dynamic magnetic stripes).

While experimental evidence of magnetic stripes have been extensively documented (see e.g. [2] for a review), the charge component of the stripes is more elusive. Static charge stripes only show up in superconducting (SC) samples close to the x = ½ anomaly [1, 3–6] and direct evidence of dynamic charge stripes has only been reported for isostructural, but insulating La$_{2-x}$Sr$_x$NiO$_4$ [7]. Understanding the relationship between these four signatures of stripe formation as a function of doping would be a crucial leap forward in our understanding of the cuprates.

Since direct, spectroscopic evidence of fluctuating charge stripes in SC cuprates is lacking, it may be possible to find an avenue of progress through indirect measurements. Recently, it was discovered that the dispersion of the Cu-O bond-stretching longitudinal-optical (LO) phonon in SC La$_{1.85}$Sr$_{0.15}$CuO$_4$ (LSCO15, T$_c$ = 38 K) and La$_{1.8}$Sr$_{0.2}$CuO$_4$ (T$_c$ = 35 K) displays a strong anomalous softening interpreted as a coupling to a novel charge collective mode [9]. Furthermore, merely a weak signature of the anomaly is visible in the phonon linewidth of La$_{0.93}$Sr$_{0.07}$CuO$_4$ (T$_c$ ≈ 15 K) and La$_{1.75}$Sr$_{0.25}$CuO$_4$ (T$_c$ ≈ 15 K), suggesting that the strength of the anomaly tracks the doping-dependence of T$_c$ [9].

Similar phonon anomalies have been observed in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [10], La$_{1.875}$Ba$_{0.125}$CuO$_4$ (LBCO) [11], La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$ (LNSCO) [8] and YBa$_2$Cu$_3$O$_{6.6}$ [12] hinting at a ubiquitous feature of cuprate superconductors.

In order to further investigate the robustness of the phonon anomaly in the 0.1 < x < 0.2 doping range, we examine two compounds derived from La$_2$CuO$_4$ with unique magnetic, structural and superconducting properties.

Hole-doping of the parent compound La$_2$CuO$_4$ can be performed by introducing two distinct dopant species. Replacing La$^{3+}$ for Sr$^{2+}$ yields La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) with ‘quenched doping’ [13], meaning that Sr has a fixed random distribution on La sites after crystal growth. On the other hand, an ‘annealed doping’ [13] can be obtained by introducing excess, mobile oxygen anions into the lattice by electrochemical methods [14], obtaining La$_2$CuO$_{4+\delta}$ (LCO+O). At low Sr concentrations (x ≤ 0.14) it is possible to combine Sr and O dopants, resulting in ‘co-doped’ La$_{2-x}$Sr$_x$Cu$_{4+\delta}$ (LSCO+O) [15]. Fig. 1A depicts the crystallographic sites of O/Sr dopant ions [16–18].

Quenched Sr$^{2+}$ doping creates a superconductor where T$_c$ varies continuously with doping, forming the so-called superconducting dome for 0.05 ≤ x ≤ 0.25. Meanwhile the mobile O dopants only seem to allow for certain superconducting phases to emerge (T$_c$ = 16.32, ≈ 40 K) due to oxygen content [19], pressure [20] or thermal treatment [21].

At sufficient O-doping, LSCO+O is superconducting at ambient pressure below T$_c$ ≈ 40 K, regardless of Sr-content [15]. While the underlying mechanism for the connection between annealed disorder and superconductivity is far from settled, the distribution of O dopants is clearly distinct from the distribution of Sr$^{2+}$ dopants. Contrary to the quenched Sr$^{2+}$ dopants, annealed O dopants in LSCO+O are responsible for a number of structural ordering phenomena such as staging [22, 23] and fractal-like distributions of ordered superstructure patches [21, 24].

Differences can also be observed in the magnetic struc-
The extracted dispersion from the zero-field data is shown in Fig. 3 along with a normal sinusoidal dispersion, \( h_\omega q = \alpha \cos(2\pi q) + \beta \), inferred from phonon calculations on LSCO using Density Functional Theory (See Fig. S5 in SM and [34]). We fit the cosine-function to points near the zone center \((q = (0, 0, 0))\) and edge \((q = (\frac{1}{2}, \frac{1}{2}, 0))\) to obtain the dashed curves of Fig. 3A. To quantify the magnitude of the anomaly, we define the

\[ S(q, \omega) = \frac{1}{\pi \omega q (\omega - \omega q) + \gamma} + I_{BG}, \]

where \( I_{ph} \) is the phonon intensity, \( \omega q \) the phonon energy at wave vector \( q \), \( \gamma \) the phonon linewidth and \( I_{BG} \) the background intensity.
 FIG. 2. Reduced data at selected wavevectors of the form \( Q = (h, h, 0) \) for both LSCO6+O and LCO+O at \( T = 5 \text{ K} \) and \( H = 0 \text{ T} \). Data at \( Q = (5, 5, 0) \) and \( Q = (4.85, 4.85, 0) \) was scaled by a factor of \( \frac{1}{2} \) for clarity due to an increase of intensity from the phonon form factor. Data at different \( h \) are offset for clarity. Solid lines are fits to a DHO lineshape (see text).

‘anomaly signal’ as the difference between the normal dispersion and the measured data (gray shaded area in Fig. 3A). Fig. 3B shows our anomaly signal for LCO+O and LSCO6+O along with previous results from optimally doped LSCO15 and insulating, stripe-ordered LNSCO [8]. We emphasize the presence of similar anomaly signals on an absolute scale across all studied samples. The linewidth broadening \( \gamma \) follows the softening of \( \omega_q \) similar to what was observed in LSCO15 and LNSCO [8] (see Fig. S2 in SM). Finally, our data can be qualitatively described by a linear combination of stripe ordered and optimally superconducting anomaly signals (See Fig. S7 in SM), consistent with the observation of phase separation in the (super)oxygenated compounds [15].

To begin the discussion of our results, we remark that softening and/or broadening of phonon modes is generally a signature of an incipient structural or electronic instability. Typical examples include structural phase transitions, \( q \)-dependence of the electron-phonon matrix element, Fermi surface nesting and electronic correlations [35]. In order to determine the origin of a given phonon anomaly, it is therefore important to carefully exhaust alternatives before making statements about the connection to novel phases such as dynamic charge stripes.

The phonon anomaly appears in vicinity of the wave vector \( \mathbf{q}_\text{CP} = (\frac{2}{3}, \frac{2}{3}, 0) \), consistent with charge stripe ordering as illustrated in Fig. 1. Measurements of LNSCO [36], LSCO15 [8] and LBCO [8] have shown a suppression of the anomaly as one moves away from the bond-stretching direction [36], supporting a one dimensional stripe-like picture. Since static stripe order has, so far, not been observed in LSCO15 any connection between the phonon anomaly and stripes is likely dynamic. Additionally, the phonon anomaly in LSCO15 and LBCO has almost no temperature dependence apart from a slightly sharper peak shape when heating from 10 K to 300 K [8, 11]. These phenomena rule out anharmonicity and structural inhomogeneity as mechanisms for the phonon anomaly in these systems.

A combination of inelastic X-ray and ARPES measurements on overdoped LSCO (\( x = 0.2 \) and \( x = 0.3 \)) have shown that the phonon anomaly wavevector is inconsistent with Fermi surface nesting [9, 37], contradicting the idea of a phonon softening due to a Kohn anomaly. A different, possibly \( q \)-dependent, electron-phonon coupling could still be responsible for the phonon anomaly. Such

FIG. 3. (A): Dispersion of the LO phonon obtained from the peak positions of individual spectra of both LCO+O and LSCO6+O (offset by 5 meV for clarity). Error bars smaller than the markers are not shown. Dashed line is the normal sinusoidal dispersion as described in the text. All data was obtained at \( T = 5 \text{ K} \). (B): Difference between sinusoidal and measured dispersion in La\(_2\)CuO\(_{4+\delta}\) (LCO+O) La\(_{2-x}\)Sr\(_x\)CuO\(_{4+\delta}\) (LSCO+O), \( \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4\) (LSCO15) and \( \text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4\) (LNSCO). Data for LSCO15 and LNSCO adapted from [8].
an effect would renormalize the electronic quasiparticle dispersion (the so-called ‘ARPES kink’ [38]) at energies similar to the phonon softening. The ARPES kink has been observed in LSCO $x = 0.2$ and $x = 0.3$, but since only LSCO $x = 0.2$ shows anomalous phonons, the two phenomena appear to not be connected [9].

Thus, all previous studies are unable to explain the phonon anomaly through conventional means and any coupling to stripe order is likely dynamic. One possible scenario is a coupling of the Cu-O bond-stretching phonon with steeply dispersing charge fluctuations. Kaneshita et al. performed calculations based on the Hubbard model of this scenario, predicting anomalous phonon dispersions due to both transverse (meandering) and longitudinal (compression) coherent stripe fluctuations [25] (see Fig. 1 for a sketch of the transverse mode).

We emphasize that the observed phonon anomaly reported here (see Fig. 3) and in LBCO/LSCO [8, 11] is remarkably similar to the prediction of Kaneshita et al. (see Fig. 5 in [25]).

Despite differences in the magnetic excitation spectra as recorded by neutron scattering (including low and zero energy transfers), the three materials LCO+O, LSCO6+O and LSCO15 have remarkably similar in-plane Cu-O bond-stretching dispersions (Fig. 3). Furthermore, static charge order at zero field has been observed in a different sample of LCO+O [39] and in LNSCO [3] but so far not in LSCO6+O nor in LSCO15. These observations together rule out a unique, direct connection between static stripes (spin and charge) and the phonon anomaly. In order to further confirm this point, we performed scans of LSCO6+O at selected wave vectors in a $H = 10$ T magnetic field which is known to induce a considerable volume of stripe-like magnetic order in this particular sample [30]. While static charge order has not been observed in LSCO6+O, measurements on LSCO ($x = 0.12$) have shown that static charge and spin stripes respond identically to magnetic fields [4].

Figure 4 contains data at two wave vectors with and without an applied magnetic field of 10 T, clearly showing the absence of any detectable field effect on the in-plane Cu-O bond-stretching phonon at $q = (1/4, 1/2, 0)$. These measurements were performed simultaneously with measurements of the low-energy magnetic fluctuations [40], confirming a significant increase in the magnetic spectral weight towards lower energies consistent with the appearance of field-induced stripe-order [30]. Thus, the appearance of static magnetic stripe order does not affect the phonon anomaly in LSCO6+O. A similar insensitivity of the phonon anomaly to an applied magnetic field has been observed in underdoped ($T_c = 66$ K) YBa$_2$Cu$_{0.6}$O$_{6.6}$ [41].

We have shown that the phonon anomaly is a robust feature in optimally doped as well as stripe-ordered cuprates which is independent of the structural details related to the doping process. Since it is equally well-formed in stripe-ordered and optimally doped systems, where the latter show no static magnetic order, the phonon anomaly is surprisingly insensitive to low-energy magnetic characteristics. This is further confirmed by the absence of a magnetic field effect in LSCO6+O which introduces static magnetic stripe-order.

The phonon anomaly is strongest in the doping region around optimal $T_c$ (0.125 $\leq n_h \leq 0.20$) (LSCO15, LNSCO [8], LBCO [11], LSCO6+O, LCO+O), regardless of the presence of static charge order (LNSCO [1], LBCO [42]), suppression of bulk superconductivity (LNSCO [3]) or dopant disorder (LCO+O, LSCO6+O). In addition, the phonon anomaly is unaffected by magnetic fields (LSCO6+O, YBa$_2$Cu$_{0.6}$O$_{6.6}$ [41]) and temperature (LBCO, LSCO15) [8]). Thus it appears to be an intrinsic, robust signature of doped cuprates near optimal doping.

In conclusion, we have measured the in-plane Cu-O bond-stretching phonon in LSCO6+O and LCO+O and provided evidence for significant anomalous behavior. Since one sample (LCO+O) exhibits charge order [39] while the other (LSCO6+O) does not [30], and since the samples also have distinct magnetic spectra with distinct field dependencies [30, 43] we conclude that the phonon anomaly has no direct, trivial relationship to either magnetic or charge static order. In addition, the unique structural characteristics of oxygen-doped samples rule out a connection between the specific dopant species and the phonon anomaly. We proceed to conclude that the phonon anomaly is a signature of transverse charge stripe fluctuations. If fluctuating stripes are the fundamental degrees of freedom relevant for the cuprates, it is appealing to draw a connection to Pair-Density-Wave superconductors [44]. In this system, the fundamental degrees of freedom are transverse charge fluctuations in an ‘electronic liquid crystal’ phase without long range order [45]. In this scenario, the phonon anomaly in materials without static stripe order is due to a matching of the
phonon wavevector with, otherwise undetectable, short-range transverse stripe correlations. The $x = \frac{1}{8}$ anomaly then corresponds to the special case where stripes exhibit long-range order.

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Supplemental Material for: Anomalous Dispersion of LO Phonons in Oxygen-Doped \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta} \)

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A. Sample characterization

The samples studied are high-quality single crystal La\(_2\text{CuO}_{4+\delta}\) (LCO+O) and La\(_{1.93}\text{Sr}_{0.06}\text{CuO}_{4.035}\) (LSCO6+O). Both have been characterized by magnetization measurements as shown in Fig. S1, showing \( T_{c,\text{onset}} \approx 43\,\text{K} \) (LCO+O) and \( T_{c,\text{onset}} \approx 37.5\,\text{K} \) (LSCO6+O).

B. Phonon measurement details

For the bond-stretching phonon, it is desirable to measure in the highest achievable odd-index Brillouin Zone (BZ) [2]. We thus performed measurements in the (5,5,0) BZ in steps of 0.05 r.l.u. with energies between 65 and 90 meV. To limit the spurious signal originating from the scattering plane (see SM), our sample was tilted by 12 degrees around the [1,1,0] axis, without affecting phonon measurements in the \((q,q,0)\) direction.

For measurements in magnetic fields, the sample could not be tilted and the PSD was replaced with a He\(^3\) single-detector setup in order to compensate for the decrease in intensity due to sample environment. While the spectral features of the phonon peak was partly obscured by spurious scattering, the increased counting statistics allowed us to better compare between \( H = 0\,\text{T} \) and \( H = 10\,\text{T} \).

The raw data and dispersion is reported in the main text, while the linewidths are reported in Figure S2. Similar to what has been observed in LNSCO and LSCO15 [3], the linewidths correlate with the phonon softening.

C. Identification/subtraction of spurious features

Spurious features in our neutron scattering experiments were initially observed as a high number of counts in a monitor placed before the analyser at certain combinations of energy and momentum. This, in turn, contributes to the measured signal as spurious scattering. We identified this scattering as accidental Bragg scattering (A-type)[4] from the \((8,4,0)\) Bragg reflection. Figure S3 outlines the scattering geometry responsible for accidental scattering along with a simulation of where to expect a spurious signal in our experiments. The simulation is performed with \( k_f = 2.662\,\text{Å}^{-1} \), \( a = 5.34\,\text{Å} \) and \( b = 5.36\,\text{Å} \).

As shown in Figure S3, the spurious scattering coincides with the phonon dispersion and it can be difficult to separate the signals. Using a position-sensitive detector, it is possible to separate the contributions by integrating over certain areas of the detector to avoid the spurious signal. Figure S4 illustrates the definition of these areas along with the result of the data-reduction. During the
FIG. S2. Linewidths of dispersion presented in the main text (Fig. 3). The linewidths presented is only the Lorenzian (DHO) contribution. The instrumental (Gaussian) broadening was fixed to 5.4 meV (FWHM).

data-reduction, the final errorbars are normalized using the region-of-interest areas. While the spurious features are centered outside the field-of-view of the phonon, the tail of their scattering will contribute to the observed phonon intensity. For this reason, it is necessary to subtract the ‘background’-intensity.

**D. Phonon calculations**

Phonon calculations based on Density Functional Theory (DFT) in the fully relaxed high-temperature tetragonal (I4/mmm) crystal structure of La$_2$CuO$_4$ (LCO) were performed with the Vienna Ab-initio Simulation Package (VASP) [5–7]. Projected Augmented Wave (PAW) potentials [8] were used for all elements and the Perdew-Burke-Ernzerhof revised for solids (PBEsol) functional [9] was used for the exchange-correlation potential. Phonon calculations were performed in the finite displacement approach using the PhonoPy code [10]. We performed non-spin polarized calculations which incorrectly predict a metallic ground state of LCO. This prediction is, however, reasonably consistent with overdoped LSCO ($x = 0.23$) [11]. Phonon calculations on this metallic ground state are shown in Figure S5. We note that the metallic Cu-O bond-stretching mode is remarkably similar to our experiment in terms of absolute energies at the zone center and boundary. In addition, the sinuosoidal shape of the dispersion is apparent.

**E. Instrument Resolution**

Instrument resolution was estimated using the RESTAX software [12]. Figure S6 shows a colorplot of LSCO6+O data along with the calculated resolution ellipsoid. Since we are in the so-called focusing condition (the slope of the dispersion coincides with the slope of the resolution ellipsoid). We used the peak width at the zone center as our ‘baseline’ energy resolution in the data analysis. Our fitting is thus performed using a Voigt line-shape where the Gaussian width is fixed to $\sigma = 23$ meV (5.42 meV (FWHM)).

**F. Anomaly amplitude and phase separation**

Figure S7 shows our anomaly amplitudes from the main text (Figure 3) compared to a linear combination of the anomaly amplitude of LNSCO and LSCO15. While the numbers are chosen in an arbitrary way, the data is consistent with a picture where the oxygen-doped samples are phase separated into an insulating $x = \frac{1}{8}$ phase.
FIG. S4. Illustration of the data reduction performed using the PSD. **Top:** Summed raw data from an energy scan at \( q = (4.65, 4.65, 0) \). The dashed lines denote the regions of interest (ROI) used in the data reduction. The geometry of the instrument ensures that the desired phonon scattering will occur in the ‘Phonon’ ROI. **Bottom:** Corresponding raw (diamonds) and reduced/normalized (circles) data. The raw data is obtained by only considering the ‘Phonon’ ROI, while the reduced data is obtained by subtracting the intensity from the two ‘BG’ ROIs. The solid line is a fit to a DHO lineshape (see main text).

and a superconducting \( x \approx 0.15 \) phase.

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FIG. S5. Calculated phonon dispersion of La$_2$CuO$_4$ in the $(\pi, 0)$ direction of the tetragonal Brillouin Zone. The Cu-O bond-stretching mode is highlighted in red. Experimentally obtained dispersion of LSCO6+O is shown in green. Absolute energies at the boundary and center are accurate to $\approx 3$ meV.

FIG. S6. Colorplot of LSCO6+O data. The black ellipsoid represents the projected resolution FWHM contour and the white line is the 'normal' sinusoidal dispersion.

FIG. S7. Anomaly amplitude of LCO+O and LSCO6+O compared to a linear combination of stripe phase LNSCO (stripe) and optimally superconducting LSCO15 (sc). The numbers are chosen arbitrarily but correspond well to the known phase separation values from literature [13].