Anomalous Dispersion of Longitudinal Optical Phonons in Nd$_{1.86}$Ce$_{0.14}$CuO$_{4+\delta}$
Determined by Inelastic X-ray Scattering

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The phonon dispersions of Nd$_{1.86}$Ce$_{0.14}$CuO$_{4+\delta}$ along the [$\xi$,0,0] direction have been determined by inelastic x-ray scattering. Compared to the undoped parent compound, the two highest longitudinal phonon branches, associated with the Cu-O bond-stretching and out-of-plane oxygen vibration, are shifted to lower energies. Moreover, an anomalous softening of the bond-stretching band is observed around $q = (0.2, 0, 0)$. These signatures provide evidence for strong electron-phonon coupling in this electron-doped high-temperature superconductor.

While the coupling between electrons and phonons is known to be the driving mechanism for Cooper-pair formation in conventional superconductors, its role in the high-critical-temperature superconductors (HTcS) is the subject of intense research efforts. Recently, evidence for electron-phonon coupling has been invoked in the interpretation of inelastic neutron scattering (INS) and angle-resolved photoemission spectroscopy (ARPES) experiments. The INS studies, carried out on La$_{1.85}$Sr$_{0.15}$CuO$_{4+\delta}$,$^1, 2, 3$, oxygendoped La$_2$CuO$_{4+\delta}$,$^1, 2, 3$, and YBa$_2$Cu$_3$O$_{6+\delta}$,$^1, 2$, reveal an anomalous softening with doping of the highest longitudinal optical (LO) phonon branch, in particular along the $q = [\xi, 0, 0]$ direction. This branch is assigned to the Cu-O bond-stretching mode,$^2, 3$. The observed softening has been interpreted as a signature of a strong electron-phonon coupling,$^2, 3$, which has been discussed since the discovery of HTcS$^1, 2$. Furthermore, in an energy range similar to the LO bond-stretching phonon band, ARPES studies on three different families of hole-doped HTcS reveal a distinct “kink” anomaly in the quasiparticle dispersion$^3$. The scenario emerging from the above INS and ARPES works suggests a strong coupling between the charge carriers and the Cu-O bond-stretching phonon modes to be ubiquitous in HTcS materials, at least for hole-doped compounds. However, its role in the pairing mechanism remains completely unclear$^3$. At the moment, it may not even be excluded that the electron-phonon interaction is pair-breaking for the d-wave superconducting order parameter. Therefore, it appears very important to analyze the strength of the phonon anomalies in as many cuprate families as possible and to compare them with their superconducting properties. In this context, the electron-doped cuprates are of central importance due to the distinct character of the doped charges in this material: Cu $3d_{x^2−y^2}$ (O 2p) for n(p)-type cuprates$^1, 2$, leading to a very different electronic structure$^2$. Since the phonon anomalies are related to a coupling between charge fluctuations and phonons, charges with different character may induce quite different electron-phonon interactions.

In this Letter, we present an inelastic x-ray scattering (IXS) study of the phonon dispersion in the n-type cuprates Nd$_{1.86}$Ce$_{0.14}$CuO$_{4+\delta}$ (NCCO). Inelastic x-ray scattering can overcome the main limitation of inelastic neutron scattering, i.e., the need for sufficiently large single crystals of high chemical and structural quality$^2$. Lateral x-ray beam sizes of few tens of $\mu$m are routinely obtained. Moreover, at photon energies around 10-20 keV and $Z > 3$, the total cross section is dominated by photoelectric absorption, and therefore the typical x-ray penetration depths for high-Z materials is of the order of 10 - 100 $\mu$m. Consequently, very small samples (down to less than $10^{-4}$ mm$^3$) can be studied with signal rates comparable to typical INS experiments on cm$^3$-sized samples. Despite these advantages, little work has been done using IXS on the HTcS compounds$^1$. We choose Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ for our IXS study, since its crystallographic structure is one of the simplest among the HTcS, and because extensive INS studies exist for its undoped parent compound Nd$_2$CuO$_{4+\delta}$ (NCO)$^1, 2$. Our interest is focused on the [$\xi$,0,0] direction, where the LO branch displays its strongest anomaly for hole-doped HTcS$^1, 2$. The present results reveal that, near the zone center, the two highest longitudinal optical branches, assigned to the Cu-O bond-stretching and O(2) vibration modes, are shifted to lower frequencies with respect to the undoped parent compound. The interpretation of our data is supported by lattice dynamics calculations, taking into account a Thomas-Fermi screening mechanism. Furthermore, we observe an anomalous softening of the highest branch around $q = (0.2, 0, 0)$. Our results demonstrate that this anomalous behavior of the high-energy LO phonon branch is a universal property of both hole- and electron-doped HTcS compounds, therefore providing further evidence that electron-phonon in-
teractions may play an important role in high-Tc superconductivity. Furthermore, the present results are an important demonstration of IXS as a powerful tool for the study of the lattice dynamics in small, high-quality crystals of complex transition metal oxides.

The experiment was carried out at the very-high-energy-resolution IXS beam-line ID16 at the European Synchrotron Radiation Facility (ESRF). X-rays from an undulator source were monochromated using a Si (111) double-crystal monochromator, followed by a high-energy-resolution backscattering monochromator [4], operating at 15816 eV (Si (888) reflection order). A toroidal gold-coated mirror refocused the x-ray beam onto the sample, where a beam size of 250 × 250 μm² full-width-half-maximum (FWHM) was obtained. The scattered photons were energy-analyzed by a spherical silicon crystal analyzer 3 m in radius, operating at the same Bragg reflection as the monochromator [15]. The silicon crystal analyzer 3 m in radius, operating at the same Bragg reflection as the monochromator [15]. The total energy resolution was 1.6 THz (6.6 meV) FWHM. The momentum transfer Q was selected by rotating the 3 m spectrometer arm in the scattering plane perpendicular to the linear x-ray polarization vector of the incident beam. The momentum resolution was set to ≈ 0.087 Å⁻¹ in both the horizontal and the vertical direction by an aperture of 20 × 20 mm² in front of the analyzer. Further experimental details are given elsewhere [13, 15 and references therein]. The sample is a single crystal grown by the traveling-solvent floating-zone method in 4 atm of O₂ at Stanford University. It has been reduced under pure Ar atmosphere at 920°C for 20 h, followed by a further 20 h of exposure at 500°C to a pure O₂ atmosphere. Such a procedure is necessary to produce a superconducting phase in Nd₁.₈₆Ce₀.₁₄CuO₄₊δ, although its exact effect is not understood. Following this treatment the sample had a narrow superconducting transition with an onset temperature of Tc = 24 K. The sample is of very good crystalline quality, with a rocking curve width of 0.02° (FWHM) around the [h, 0, 0] direction. It was mounted on the cold finger of a closed-loop helium cryostat, and cooled to 15 K. The experiment was performed in reflection geometry, and the probed scattering volume corresponded to about 1.5 × 10⁻³ mm³. IXS scans were performed in the -2< ν <24 THz range, in the τ = (6, 0, 0) and τ = (7, 1, 0) Brillouin zones [13]. The data were collected along the following three lines: I) Q = (6 + ξ, 0, 0), in longitudinal configuration (i.e. with q = (ξ, 0, 0) || Q), II) Q = (7 ± ξ, 1, 0) in almost longitudinal configuration (i.e. with q = (ξ, 0, 0) and (Q · q)/Q ≈ q), III) Q = (7, 1 − ξ, 0) in almost transverse configuration (q = (0, ξ, 0) and (Q · q)/Q ≈ 0).

The low temperature and high momentum transfer were chosen so as to optimize the count rate on the high-frequency optical mode while limiting the loss of contrast due to the contribution from the tails of the intense low frequency acoustic modes.

![Fig. 1](image.png)

FIG. 1: Experimental IXS phonon spectra of Nd₁.₈₆Ce₀.₁₄CuO₄₊δ at T = 15 K and corresponding harmonic oscillator model best fits (solid and dotted lines). Both scans were performed in the τ = (7, 1, 0) Brillouin zones with a propagation vector of ξ = 0.2 in an almost longitudinal geometry along the a* direction (diamonds) and in an almost transverse geometry along b* (open circles).
The experimental data (circles) are shown together with their corresponding harmonic oscillator model best fits (solid lines), as discussed in the text.

THz. At \( \mathbf{q} = (0.2, 0, 0) \) the highest mode is found at the much lower energy of 13.5 THz. Finally, for \( \mathbf{q} = (0.4, 0, 0) \), we again find a high-frequency mode around 15.5 THz.

The peak positions extracted from these and many other scans are summarized in Fig. 3. The highest branch exhibits a sharp dip around \( \mathbf{q} = (0.2, 0, 0) \) and recovers for larger \( q \)-values. This behavior is most likely due to an anti-crossing with the second highest branch which is mainly associated with vibrations of the O(2) position in the \( \xi \)-direction. Therefore, within a standard anti-crossing framework, one should interpret the highest longitudinal intensities for \( \mathbf{q} = (0.3, 0, 0) \) and above as being mainly due to O(2) vibration. Within that scenario, this second-highest branch increases its frequency in the middle of the zone as in the undoped compound, and, except for the fact that the Lyddane-Sachs-Teller (LO-TO) gap closes, seems to be insensitive to doping. The LO bond-stretching mode just above \( \mathbf{q} = (0.2, 0, 0) \) is then found at quite low energies, \( \sim 12 \) THz, but can not be unambiguously followed to larger \( q \)-values. Nevertheless, our data document that the LO bond-stretching branch in NCCO is strongly renormalized compared to undoped NCO, in particular it bends down anomalously from the zone center to \( \mathbf{q} = (0.2, 0, 0) \).

In order to further validate the correctness of our assignments, we performed a lattice dynamical calculation based on a shell model. We used a common potential model for cuprates, in which the interatomic potentials have been derived from a comparison of INS results for different HTcS compounds by Chaplot et al. [7], using a screened Coulomb potential, in order to simulate the effect of the free carriers introduced by doping. Following Ref. [7] for metallic \( \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4+\delta} \) and \( \text{YBa}_2\text{Cu}_3\text{O}_7 \), we replaced the long-range Coulomb potential \( V_c(q) \) by \( V_c(q)/\epsilon(q) \), and for the dielectric function we take the semi-classical Thomas-Fermi limit of \( \epsilon(q) = 1 + \kappa_s^2/q^2 \), where \( \kappa_s^2 \) indicates the screening vector. The results of the calculation (without screening: dot-dashed lines; with screening: solid lines) are shown as well in Fig. 3. The lattice dynamics calculations without screening have been included, since they reproduce very well the experimental dispersion of the undoped parent compound [6]. The shift at the zone center of the high-energy phonon branches of NCCO with respect to NCO is due to the closing of a large LO-TO splitting. Indeed, the corresponding \( \Delta_1 \) and \( \Delta_3 \) branches in \( \text{Nd}_2\text{CuO}_{4+\delta} \) are separated by almost 3 THz at the zone center, as observed by INS [6]. We point out that in our case a strong softening due to Thomas-Fermi screening does not imply a higher Thomas-Fermi parameter \( \kappa_s \): actually, we find a screening vector \( \kappa_s \) of about 0.39 Å\(^{-1}\), which is comparable to that for \( \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4+\delta} \) [7]. Though our modified calculation reproduces the closing of the LO-
in La1.5 THz, which is a shift comparable to the anomalous softening of the highest bond-stretching LO branch near \( q = (0.2, 0, 0) \), which is not reproduced by our calculations (see Fig. 4). This branch softens in frequency from \( q = (0.1, 0, 0) \) to \( q = (0.2, 0, 0) \) by about \( \Delta \nu \approx 1.5 \) THz, which is a shift comparable to the anomalous shift observed in La1.85Sr0.15CuO4+δ at slightly larger \( q \). Therefore, we believe that this anomalous softening is of the same nature as the one observed in p-type La1.85Sr0.15CuO4+δ.

A comparison between the experimental and calculated intensities for the two highest phonon branches is shown in Fig. 4. The good agreement of the observed integrated intensities with the calculated ones for the upper branches validates the correctness of our phonon branch assignment, at least for \( \xi \lesssim 0.2 \). For \( \xi > 0.2 \) we would have expected an intensity exchange between the two highest branches, which seems to be not observed.

The main difference between La1.85Sr0.15CuO4+δ and Nd1.86Ce0.14CuO4+δ is, besides the screening effect, that in NCCO the Cu-O bond-stretching branch is closer in energy to the out-of-plane oxygen vibration one, having almost the same energy at \( \xi = 0.2 \). These two branches belong to the same symmetry and therefore cannot cross, so that for \( \xi > 0.2 \) softening implies interaction with the out-of-plane oxygen vibration mode with the same symmetry. In the region between \( q = (0.25, 0, 0) \) and \( (0.3, 0, 0) \), the two modes are poorly defined in energy, which is consistent with what is observed in La1.85Sr0.15CuO4+δ by Pintschovius and Braden \[4\] and McQueeney et al. \[7\] for \( \xi \approx 0.25 - 0.3 \). The corresponding real space periodicity of 3 to 4 unit cells may therefore be linked to the proximity to some charge instability. We remark that a reduced vector \( \xi \sim 0.25 - 0.3 \) approximately corresponds to the nesting vector along [00] direction, as can be inferred from the ARPES data of Ref. \[2\].

In conclusion, the present results reveal that the anomalous softening previously observed in hole-doped compounds \[1, 2, 3, 4, 5, 6\], is also present in the electron-doped cuprates. This is evidenced by the comparison of the present results on doped NCCO with the previously reported ones on pure NCO \[1\]. This implies that: (i) the anomaly also exists in n-type cuprates, giving strength to the hypothesis \[1, 2, 3, 4, 5, 6\] of an electron-phonon coupling origin of this feature; (ii) this is a generic feature of the high-temperature superconductors, as expected, if phonons are relevant to high temperature superconductivity. Moreover, this Letter demonstrates that high-energy resolution inelastic x-ray scattering has developed into an invaluable tool for the study of the lattice dynamics of complex transition metal oxides, allowing measurements on small high-quality single crystals which are inaccessible to the traditional method of inelastic neutron scattering.

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