Phonons and hole localization in La$_{1.475}$Nd$_{0.4}$Sr$_{0.125}$CuO$_4$

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(Received on August 28, 2019)

The phonon densities-of-states of La$_{1.475}$Nd$_{0.4}$Sr$_{0.125}$CuO$_4$ and La$_{1.9}$Sr$_{0.1}$CuO$_4$ were measured using inelastic neutron scattering. The ~70 meV phonon band which appears due to hole doping in La$_{1.9}$Sr$_{0.1}$CuO$_4$ is known to arise from strong electron-lattice coupling. This phonon band is strongly suppressed in the Nd-doped compound for which $T_c$ is also suppressed, establishing a link between in-plane oxygen optical phonons and superconductivity. This suppression is attributed to hole localization which becomes strong near the stripe ordering condition of certain cuprates near $x = 1/8$ and competes with superconductivity.

PACS numbers: 74.25.Kc, 63.20.Kr, 74.20.Mn, 74.72.Dn

The lattice dynamics of the high-temperature superconducting cuprates show evidence of very strong and unusual electron-lattice coupling. Early measurements of the phonon dispersion of La$_{2-x}$Sr$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_{6+y}$ by Pintschovius, Reichardt, et al. show evidence for large softening (15-20 % of the undoped phonon frequency) and broadening of high-frequency phonon modes (in the range from 50-90 meV) as holes are doped into these compounds. The softening appears to be directly proportional to the hole concentration, leading to the conclusion that the origin of these phenomena is the electron-lattice coupling. These modes are associated with the oxygen half-breathing vibrations which propagate along the (1,0,0)-direction (Cu-O bond direction) in the CuO$_2$ plane. It is puzzling that these modes should couple strongly to the holes because electronic structure calculations for La$_2$CuO$_4$ predict strong electron-phonon coupling along the (1,1,0)-direction (i.e. the oxygen breathing modes), consistent with the nesting vector of the Fermi surface within the local-density approximation.

Another testament to the size of the electron-lattice coupling, aside from the enormous frequency shifts, is the extent of the Brillouin zone which is affected. Single-crystal phonon dispersion measurements show that the suppression of phonon frequencies occurs primarily in the region $0.25 < q_z < 0.5$, $q_y < 0.15$ (in units of $2\pi/a$), and to some unknown degree along $q_z$ for La$_{1.85}$Sr$_{0.15}$CuO$_4$. However, more convincing evidence of the extent of these interactions in q-space is the fact that they are easily observed in phonon density-of-states (DOS) measurements as the formation of a softer subband of phonon modes from the main band of in-plane oxygen modes that accounts for perhaps 10% of the zone. An example of this subband is shown by Renker et al. as a peak at ~70 meV for La$_{1.85}$Sr$_{0.15}$CuO$_4$ which is known to grow at the expense of the 85 meV band as holes are added. A combination of all single-crystal phonon dispersion and polycrystalline phonon density-of-states measurements leads to a compendium of superconductors, with various crystal structures and methods of introducing holes, that display the similar phonon renormalizations, demonstrating the ubiquitous nature of the electron-lattice coupling.

The microscopic origin of these phonon anomalies has remained a mystery, and our collaboration has begun to look more carefully at these modes and also those of related systems such as the nickelates, La$_{2-x}$Sr$_x$NiO$_4$ is isostructural to the La$_2$CuO$_4$-based superconductors but remains an insulator up to very high doping $(x \sim 1)$. Measurements of the DOS of La$_{2-x}$Sr$_x$NiO$_4$ show no phonon softening from $x = 0$ to $x = 1/8$, in contrast to the large 70 meV subband formation for La$_{2-x}$Sr$_x$CuO$_4$. This leads to a hypothesis that the charge fluctuations present in the metallic cuprate are a necessary ingredient in the phonon anomalies. In this article, we compare the phonon DOS of La$_{1.8}$Sr$_{0.1}$CuO$_4$ and La$_{1.475}$Nd$_{0.4}$Sr$_{0.125}$CuO$_4$. The Nd-doped compound has a pronounced “1/8 anomaly” at $x = 1/8$, where the superconducting transition temperature $(T_c)$ and other transport properties are suppressed and static ordered charge/spin structures have been observed. We find that the 70 meV phonon band is suppressed in the Nd-doped cuprate, establishing a possible link between superconductivity and the oxygen optical phonons. Similarly to the nickelates, the suppression of the phonon subband in the Nd-doped compound can also be interpreted as arising from reduced charge fluctuations, in this case by a slowing down of the hole dynamics.

Polycrystalline samples of La$_{1.475}$Nd$_{0.4}$Sr$_{0.125}$CuO$_4$ (LNSCO) and La$_{1.9}$Sr$_{0.1}$CuO$_4$ (LSCO) were prepared by standard solid state reaction of stoichiometric ratios of La$_2$O$_3$, Nd$_2$O$_3$, SrCO$_3$ and CuO. Samples were subsequently annealed in flowing argon at 1100°C for 20 hours. Samples weighed 60 and 90 grams, respectively. The temperature-dependent resistivity of La$_{1.475}$Nd$_{0.4}$Sr$_{0.125}$CuO$_4$ was measured with a four-terminal low-frequency ac resistance bridge. Sample contacts were made with a conductive silver epoxy. The resistivity and its temperature derivative, shown in figure \[\square\], provide evidence for the LTO-LTT structural transition.
I extrapolating I I all scattering angles for each data set, giving a function M distribution I.I contribution is also assumed to be independent of I given by I φ, ω ranges. The intensity at the I scattering function factor and sample self-shielding. I k'/k phase space corrected for a time-independent intensity arising from I efficiency corrections, respectively. The data were also addition, empty aluminum can and white beam vanadium runs were performed for background and detector efficiency corrections, respectively. The data were also corrected for a time-independent intensity arising from the ambient neutron background, the k'/k phase space factor and sample self-shielding.

To a first approximation the experimental intensity, I(φ, ω), is proportional to the powder-averaged van Hove scattering function S(φ, ω) plus a multiple scattering contribution M(φ, ω), where hω is the energy transferred to the neutron. The reduced data I(φ, ω) were summed over all scattering angles for each data set, giving a function I(ω). The multiple scattering was accounted for by extrapolating I(φ, ω) to φ = 0 for several energy transfer ranges. The intensity at the φ = 0 intercept is assumed to arise from multiple scattering. The multiple scattering contribution is also assumed to be independent of φ (as warranted by the small self-shielding corrections) and is given by M(φ, ω) = M(ω).

In order to determine the multiphonon scattering, the nuclear neutron scattering intensity of undoped LSCO at 70 K and a broad superconducting transition with an onset at ~15 K and midpoint at ~7 K. The broadness of the superconducting transition is presumably due to inhomogeneity in the large sample.

Time-of-flight inelastic neutron scattering measurements were performed on the Low Resolution Medium Energy Chopper Spectrometer (LRMECS) at Argonne National Laboratory’s Intense Pulsed Neutron Source. Scattering angles (φ) from 1.95° – 120° are covered by LRMECS. For all measurements, an incident neutron energy of 120 meV was chosen. Powder samples were packed in flat-plate aluminum sample cans of dimensions 4”x3”x1/8” and oriented 45° to the incident beam direction. The sample can was mounted on a Displex closed-cycle He refrigerator for temperature dependence studies. Each sample was measured at 10 K and 100 K. In addition, empty aluminum can and white beam vanadium runs were performed for background and detector efficiency corrections, respectively. The data were also corrected for a time-independent intensity arising from the ambient neutron background, the k'/k phase space factor and sample self-shielding.

La2CuO4 was calculated in the incoherent approximation after replacing the cross-section of La with the average (La,Nd, Sr) cross-section. The partial phonon densities-of-states of La2CuO4 used in this calculation were obtained from a lattice dynamical shell model. From I(ω), we subtract the multiple and multiphonon scattering intensities and also subtract an elastic gaussian which was obtained by fits to each data set. Due to the encroachment of the elastic peak and the large error associated with its subtraction, only the portion of the DOS above 15 meV can be reliably extracted. The DOS is then obtained by multiplying by hω/(n(ω) + 1), where n(ω) is the Bose population factor.

Absolute normalization of the DOS is made difficult by the presence of crystal-field excitations on the Nd-sites in La1.475Nd0.4Sr0.125CuO4. These excitations were observed by comparison of the LNSCO and LSCO data sets summed over the low angle range from 1.95° – 19.5°. Figure 3 shows the difference of the low-angle averaged LNSCO and LSCO data sets at 10 K and plotted as the dynamic magnetic susceptibility χ″(ω)/ω. Lorentzian fits to the excitations, shown as a solid line in the figure, give peak energies of 25.2 and 44.5 meV. These energy values are of the same order as the observed crystal-field splittings in Nd2CuO4. The inset to fig. 3 shows that the intensity of the 44.5 meV peak decreases with increasing momentum transfer, indicating a magnetic origin presumably arising from crystal-field excitations of the Nd3+ ion.

FIG. 1. The temperature dependence of the electrical resistance of La1.475Nd0.4Sr0.125CuO4. The inset figure shows the derivative of the resistance and indicates the ETO-LLT phase transition at TLT = 70 K.

FIG. 2. The difference of the inelastic neutron scattering spectra of La1.475Nd0.4Sr0.125CuO4 and La1.4Sr0.1CuO4 at low angles and low temperature plotted as the dynamic magnetic susceptibility χ″(ω)/ω. Lorentzian fits to the spectrum (solid lines) give peak positions at 25.2 meV and 44.5 meV. The inset shows that the intensity of the 44.5 meV excitation decreases with increasing momentum transfer, indicating a magnetic origin presumably arising from crystal-field excitations of the Nd3+ ion.
The feature of the data we wish to discuss is the \( \sim 70 \) meV phonon band which is not present in the cuprates. As discussed above, this band of modes softens out of the main 85 meV in-plane oxygen band with hole doping and is a signature of strong electron-lattice coupling in the cuprates. This band appears prominently in the LSCO compound possessing a high \( T_c \), but is surprisingly broadened and suppressed in LNSCO where \( T_c \) is reduced. By comparing these two materials, we can associate the presence of the 70 meV phonon band with superconductivity.

One may expect that the origin of the 70 meV band and its suppression could arise from local lattice vibrations and disorder associated with Sr\(^{2+}\) or Nd\(^{3+}\) dopants. This is very unlikely for several reasons. The 70 meV band does not form in La\(_{1.65}\)Sr\(_{0.15}\)NiO\(_4\) which has the same crystal structure as LSCO, and is therefore unrelated to local structural effects or Madelung terms associated with Sr\(^{2+}\) sites. In general, these particular phonon renormalizations depend only on hole concentration and similar softening is observed after the addition of holes by excess oxygen in La\(_2\)CuO\(_4\) and YBa\(_2\)Cu\(_3\)O\(_{6+y}\). The suppression in LNSCO does not originate from the increased disorder due to the Nd sites because such disorder would broaden many bands, especially (La,Nd,St)-O(2) vibrations at \( \sim 55 \) meV. With the exception of the 70 meV oxygen phonon band, all other phonon bands are unchanged upon the addition of Nd.

It is worthwhile to discuss the suppression of the phonon anomaly in the Nd-doped cuprates in the context of electron-lattice coupling and the \( x = 1/8 \) anomaly. It is well-known that superconductivity is destroyed for La\(_2\)CuO\(_4\)-based superconductors which have the low-temperature tetragonal (LTT) structure near hole concentrations \( x = 1/8 \), as first detected in La\(_{2−x}\)Ba\(_x\)CuO\(_4\). The La\(_{2−x}\)Sr\(_y\)CuO\(_4\) superconductors exist in the low-temperature orthorhombic (LTO) structure. The substitution of Nd\(^{3+}\) or other rare earth ions for La\(^{3+}\) in LSCO stabilizes the LTT phase without changing the hole concentration. In addition to the suppression of superconductivity, the LTT distortion strongly affects other transport properties, such as electrical resistivity, thermopower, thermal conductivity, and the Hall effect, and is a testament to the importance of the electron-lattice coupling in the cuprates. In particular, the electrical resistivity has a semiconductor-like upturn below the LTO-LTT transition temperature \( T_{LT} \) (see fig. 1) which signifies reduced mobility or a localization of the holes in the LTT phase. Büchner et al. have shown that the upturn in resistivity and destruction of superconductivity in the LTT phase occur when the CuO\(_6\) octahedral tilts responsible for the LTT phase (tilting around the [100] axis in tetragonal notation) exceed a critical angle. Tranquada et al. have used neutron diffraction to detect the presence of magnetic and charge superlattice peaks in the LTT phase of La\(_{1.6−y}\)Nd\(_{0.4}\)Sr\(_y\)CuO\(_4\) which infer a static ordering of holes and Cu spins into a striped structure oriented along [100]. The octahedral tilts of the LTT phase correlate with the stripe direction and hole spacing for \( x = 1/8 \) and commensurability effects between the two are hypothesized to pin the stripe structure. In LSCO in the LTO phase, the LTO tilt pattern (tilt axis around [110]) is not commensurate with the stripe structure and the frustrated stripes are no longer pinned. In superconducting LSCO however, dynamic stripe correlations persist. The spatial correlations determined by the peak positions in LSCO are the same as in LNSCO, but become purely dynamic rather than elastic and signify a fluctuating stripe state. Tranquada et al. have asserted that superconductivity favors the presence of a dynamic stripe state and is in competition with the order created by the pinning of stripe fluctuations by the LTT distortion. The phonon behavior mimics this competition because the 70 meV phonon band is most prominent in the superconducting compounds where purely dynamic stripe states are thought to exist.

It is possible that reduced charge fluctuations in LNSCO near the stripe ordering temperature suppress the 70 meV phonon band. Evidence for reduced charge fluctuations in LNSCO comes mainly from the aforementioned electrical resistivity measurements, neutron scattering, and also from far infra-red reflectivity measurements. Obviously, the static stripe structures observed by neutron scattering imply reduced charge and spin fluctuations. The downward shift of the magnetic spectral weight to the elastic region upon stripe ordering indicates a gradual freezing out of the holes and Cu spins. The infra-red results show that the optical conductivity
is reduced in La$_{1.475}$Nd$_{0.4}$Sr$_{0.125}$CuO$_4$, as compared to La$_{1.9}$Sr$_{0.1}$CuO$_4$, over a wide energy range from $\sim$50 - 500 meV with a corresponding decrease in spectral weight of $\sim$10%. How does this hole localization affect the phonon spectrum? In an exaggerated manner, we can compare the lattice dynamics of LSCO to La$_{2-x}$Sr$_x$NiO$_4$, which is isostructural to LSCO but remains an insulator up to $x \sim 1$. We see no renormalizations of the oxygen phonons in La$_{2-x}$Sr$_x$NiO$_4$ at $x = 1/8$. In reference to the insulating nickelates, the metallic nature of the cuprates and the presence of charge fluctuations appears to be a necessary ingredient in the phonon anomaly observed in high-$T_c$ compounds. It seems reasonable to associate the suppression of the 70 meV phonon band in LNSCO with slower hole dynamics.

One inconsistency in this interpretation is the temperature independence of the phonon band in LNSCO above and below either the stripe ordering transition at $\sim$50 K or the LTO-LTT transition at 70 K. The phonon DOS extracted for LSCO and LNSCO at 10 K and 100 K are unchanged. Of course, this does not imply that more subtle changes in the phonon dispersion, related to the stripe structure or the LTT distortion, cannot be observed in single-crystal measurements. For example, the measured dispersion of the oxygen half-breathing branch in single-crystals of La$_{1.85}$Sr$_{0.15}$CuO$_4$ displays subtle temperature dependent changes (discussed below), which are not apparent in polycrystalline measurements. However, it is evident that the differences in the phonon DOS of LNSCO and LSCO do not depend on the static stripe order of LNSCO or the long-range LTO/LTT crystal structures.

The lack of temperature dependence of the phonon anomaly is in strong contrast to static properties which change drastically at $T_{LT}$. The bulk transport properties of LSCO and LNSCO are similar above $T_{LT}$ and diverge below. It would seem that the suppression of the 70 meV band could not originate from reduced charge fluctuations, since holes are seemingly “unpinned” above $T_{LT}$. However, there are several reasons to expect only small changes of the phonons at $T_{LT}$. Hole pinning in the static stripe phase is certainly not complete since the upturn in resistivity in the stripe phase is rather modest and slow, incommensurate spin fluctuations exist both above and below the stripe ordering temperature in LNSCO. This implies that Nd-doping slows the dynamic stripe fluctuations and shifts spin and charge spectral weight down to low energies. Bulk properties would only be sensitive to the static component below $T_{LT}$. For the purposes of determining the effect of hole localization on the phonons, it is crucial to understand how the electronic susceptibility changes in an energy range closer to the oxygen phonon frequencies, rather than $\omega = 0$. We expect the electron-lattice interaction to be stronger when the electronic susceptibility has increasing weight at the phonon energy. It would therefore prove quite useful to determine the spin fluctuation spectrum of LNSCO up to $\sim$100 meV and compare this to LSCO. While one can only infer the underlying charge dynamics from the spin fluctuation spectrum, slower stripe fluctuations would look more static to the phonon either above or below $T_{LT}$ and could suppress the phonon anomaly. This may help to explain why the optical conductivity and the reduced spectral weight of LNSCO between 50 meV and 500 meV is also unchanged through $T_{LT}$. The finite energy spectroscopic results of both the phonon and charge system change very little through $T_{LT}$.

Another factor contributing to the insensitivity of the phonon anomaly to stripe order is its local behavior. Previous inelastic neutron scattering work on single-crystals of La$_{1.85}$Sr$_{0.15}$CuO$_4$ has demonstrated that the phonon anomaly is related to, but different than, stripe order. The discontinuity of the Cu-O half-breathing phonon branch at $q=(0.25,0,0)$ is interpreted as an incipient doubling of the unit-cell ($\lambda = 2a$), rather than a reflection of the stripe spacing of 4a along [100]. The phonon branch is flat between (0.25,0,0) and (0.5,0,0) indicating that these vibrations are more properly discussed in terms of localized oxygen modes near to localized holes and the electron-lattice coupling induces charge transfer between neighboring oxygens. The phonon anomaly does not reflect the superlattice of the stripe structure unlike infra-red and Raman phonon signatures of stripe order in the nickelates. Rather, the phonon anomaly depends on local charge fluctuations in the vicinity of the stripe and is independent of stripe order. In the Nd-doped compounds above $T_{LT}$, such stripe correlations still remain dynamically. There is also evidence that, at least in La$_{2-x}$Ba$_x$CuO$_4$, LTT type octahedral tilts still exist above $T_{LT}$ and are correlated over $\sim$10 Å.

The phonon anomaly in high-$T_c$ cuprates seems to depend on charge fluctuations and their energy spectrum. In order to completely characterize the electron-lattice interaction much more work is required. Systematic studies of the single-crystal phonon dispersion of various compounds as a function of hole concentration seem necessary. Given the relatively high energies and short wavelengths of these phonons, only inelastic neutron experiments requiring large single-crystals are sufficient at this time. However, the phonons may prove to be as important as the spin fluctuations in probing the charge dynamics of the cuprates. A large investment into their study may be worthwhile.

In summary, La$_{2-x}$Sr$_x$CuO$_4$ displays a large phonon anomaly attributed to strong electron-lattice coupling and is indicated by the presence of a soft $\sim$70 meV oxygen phonon band in polycrystalline inelastic neutron scattering measurements. The 70 meV phonon band is suppressed in La$_{1.475}$Nd$_{0.4}$Sr$_{0.125}$CuO$_4$, a cuprate with reduced $T_c$ due to hole order, demonstrating a link between superconductivity and the oxygen optical phonons. By comparison of phonon densities-of-states in the cuprates to La$_{1.85}$Sr$_{0.15}$NiO$_4$, an insulator which has no phonon anomaly, we suggest that charge fluctuations are necessary in order to explain the phonon renormalizations.
ACKNOWLEDGMENTS

RJM would like to thank T. Egami, A. R. Bishop, P. C. Hammel and J. M. Tranquada for useful discussions. This work is supported (in part) by the U. S. Department of Energy under contract No. W-7405-Eng-36 with the University of California. This work has benefited from the use of the Intense Pulsed Neutron Source at Argonne National Laboratory. This facility is funded by the U. S. Department of Energy, BES-Materials Science, under contract W-31-109-Eng-38.

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