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Doping dependence of softening in the bond-stretching phonon mode of $La_{2-x}Sr_xCuO_4$ $(0 \leqslant x \leqslant 0.29)$

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The doping dependence of the softening in Cu-O bond-stretching optical phonons along [100] direction has been systematically studied on $La_{2-x}Sr_xCuO_4$ using inelastic x-ray scattering. The softening increases with x in the underdoped region and starts to saturate or makes local maximum around the optimum doping ($x \sim 0.15$). This behavior is discussed in terms of the coupling between the phonons and the low energy charge fluctuations on the doped CuO_2 planes.

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The driving mechanism for the Cooper-pair formation in the high critical-temperature (T_c) copper oxide superconductors (HTcS) remains an open question despite almost two decades of intense research. Investigations of HTcS, including $La_{2-x}Sr_xCuO_4$ (LSCO), have focused mainly on the interplay between superconductivity and antiferromagnetic fluctuations, since the two commonly coexist in HTcS.[1] However, recent studies of angle-resolved photoemission spectroscopy (ARPES) and inelastic neutron (x-ray) scattering [INS (IXS)] have triggered reexamination of the role of phonons for the Cooper-pair formation. A kink in the dispersion of electron quasiparticles is observed by ARPES in the hole-doped HTcS.[2] Interactions of electron quasiparticles with the highest energy longitudinal optical (LO) phonon are discussed as one of the possible origins of the kink. INS measurements, on the other hand, show a remarkable softening in the highest energy LO phonon branch in the hole-doped LSCO (Refs. 3–5) and $YBa_2Cu_3O_{7-\delta}$.[3,6] Softening for the same phonon mode is also observed by IXS studies on hole-doped $HgBa_2CuO_{4+\delta}$ (Ref. 7) and electron-doped $Nd_{2-x}Ce_xCuO_{4+\delta}$.[8] However, since such softening is observed among other nonsuperconducting oxides such as manganites[9] and nickelates,[10] the relation of the softening with the high-T_c superconductivity is not clear. Furthermore, even in the HTcS no systematic study has been performed on the doping dependence of the softening. Therefore, we undertook IXS studies on LSCO in a wide doping region to understand the relation of this phonon mode with the superconductivity, particularly in the highly overdoped region where superconductivity degrades and normal metallic conductivity dominates.

From a structural point of view $La_{2-x}Sr_xCuO_4$ is a simple hole-doped HTcS because it has a single CuO_2 layered structure. Furthermore, the doping concentration, x, can be easily controlled from the nondoped Mott insulator to the overdoped normal metal, so one can investigate the doping dependence of the phonon properties precisely with relation to superconductivity. The single crystals of LSCO used for this study were grown at Kyoto University and at Tohoku University using the traveling-solvent floating-zonetechnique without using any crucibles.[11] Samples (2–4-mm-thick plates) with a surface parallel to the *bc* plane were cut from cylindrical single crystal boules. We used two types of samples: one with a uniform Sr concentration in the crystal (uniform samples), and the other where the concentration varies smoothly along the cylindrical axis (gradient samples).[12] The gradient samples enable us to investigate the x dependence easily using the small beam size for IXS experiment. In the present study we used two uniform samples with $x=0.275$ and 0.29, and two gradient samples with x from 0 to 0.17 and from 0.21 to 0.24. It should be noted that the concentration variation inside the x-ray beam spot ($\sim 100\ \mu m$) on the gradient sample is expected to be less than 0.001 in x, comparable to that of the uniform sample. Typical mosaic spreads were $\sim 0.05°$ full width at half maximum (FWHM). The x of each sample was determined from lattice constant measurements which were compared with previously reported values from powder samples.[13] T_c of each sample was obtained by the measurements of magnetic susceptibility using a superconducting quantum interference device magnetometer. For the gradient samples T_c was measured for many small pieces cut perpendicular to the concentration gradient direction. The obtained doping dependence of T_c is reasonably consistent with the previous result from powder samples.[14] The superconducting transition was observed in a narrow temperature range ($|\Delta T_c| < 3$ K) except for specific concentration like $x \sim 0.12$ where T_c changes steeply as a function of x. At low temperatures down to 30 K samples with x above about 0.2 show a tetragonal structure, while those of x below about 0.2 show an orthorhombic structure and contain twinned domains. In this paper we use the tetragonal notation, in which a and b axes are parallel to Cu-O bonds in the CuO_2 plane.

IXS experiments were performed at BL35XU of SPring-8.[15] A silicon (888) backscattering monochromator was used to provide a beam of about 3×10^{10} photons/s in a 4 meV bandwidth at 15.816 keV ($\sim 100\ \mu m$ spot size). The scattered radiation was analyzed using four independent spherical crystals in a horizontal scattering geometry. The spectrometer resolutions in momentum and energy were about 0.076 $Å^{-1}$ and 6.0–6.2 meV (FWHM), respectively. A notable advantage in IXS experiments, as compared with INS, is that the resolution function in energy and that in Q are decoupled, which makes data analysis simple. In addition, since energy resolution in IXS is independent of en-

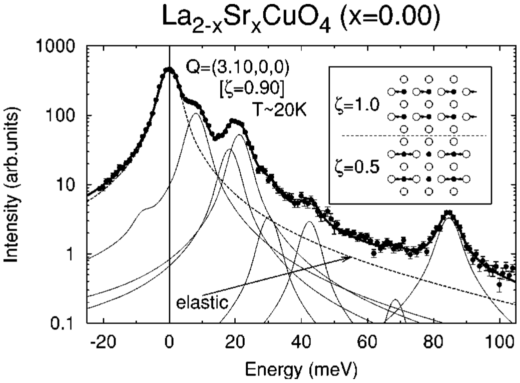

FIG. 1. Inelastic x-ray scattering spectrum of La_2CuO_4 at $Q=(3.10,0,0)$ $[\zeta=0.90]$ and $T\simeq 20$ K (filled circles). Solid lines are fits. The elastic response (resolution function) is also plotted with a dashed line. Inset: Polarization patterns of the highest energy LO bond-stretching phonon modes ($\simeq 80$ meV) within a CuO_2 plane for $\zeta=1.0$ and 0.5. The filled and open circles indicate the Cu and O atomic positions, and the arrows show the displacements of O atoms.

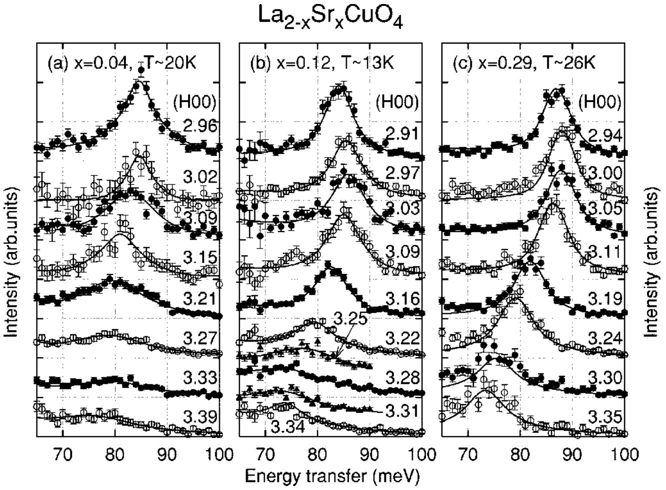

FIG. 2. Inelastic x-ray scattering spectra of the bond-stretching phonon branches in (a) $La_{1.96}Sr_{0.04}CuO_4$ at $T\simeq 20$ K, (b) $La_{1.88}Sr_{0.12}CuO_4$ at $T\simeq 13$ K, and (c) $La_{1.71}Sr_{0.29}CuO_4$ at $T\simeq 26$ K near the Brillouin zone boundary $[Q=(3,0,0)]$ along [100] crystal axis direction. Scans having different Q are shifted vertically.

ergy transfer, measurements with high energy-resolution at large energy transfer are relatively easy.

The measurements were done in a reflection (Bragg) geometry at low temperatures, <30 K, to reduce background from tails of low energy phonon peaks. Most scans were performed at above T_c, while the measurements for the samples of $x=0.12$ and 0.225 were carried out at below T_c. Though the measurements at both superconducting and normal states are mixed, the spectrum at room temperature $(T>T_c)$ is the same as that of low temperature $(T<T_c)$ within experimental error after the correction of Bose thermal factor at least for $x=0.12$ sample. The crystals were mounted in a ^{4}He closed-cycle refrigerator on a four circle diffractometer with the [100] crystal axis parallel to scattering vector. Energy scans were carried out at fixed $Q=(H,0,0)(2.9\leqslant H\leqslant 3.5)$ with typical scan ranges $-20\leqslant \Delta E\leqslant 100$ meV (see Fig. 1). Apart from a diffuse elastic component centered at 0 meV, clear distinct peaks are observed at low $(|\Delta E|\leqslant 30$ meV) and high $(\Delta E\sim 80$ meV) energy transfer. Though phonon peaks are not well separated in the intermediate energy region (30 to 70 meV), the whole spectrum can be fit using one elastic peak and 5-7 phonon peaks. Here, the energy widths of phonon peaks are fixed to the value of the instrumental resolution function, except for the highest energy bond-stretching LO phonon mode. The peak positions of phonons are consistent with both the previously reported neutron data[3] and a lattice dynamical calculation based on a shell model[16] at least near the zone boundary (zone center of two-dimensional CuO_2 plane) where the effect of the softening is small (see Fig. 1).

Figure 2 shows the energy spectra near the highest energy phonon mode.[17] In the figure, the elastic intensities were subtracted. The main peaks are the LO phonons propagating in the [100] direction (see inset of Fig. 1). For the $x=0.12$ and 0.29 samples [Figs. 2(b) and 2(c)], the peak energy changes from about 86 and 88 meV, respectively, at the zone boundary to about 69 meV at $\zeta=0.5$, where ζ is the momentum transfer in a reduced-zone scheme. In contrast, for the $x=0.04$ sample [Fig. 2(a)], the energy shift is much smaller, dispersing from about 83 meV at the zone boundary to about 78 meV at $\zeta=0.5$. In three cases the intensity decreases as one moves away from the zone boundary. However, for the $x=0.29$ sample [Fig. 2(c)] the peak intensity decreases more slowly than for $x=0.04$ and 0.12 ones [Figs. 2(a) and 2(b)].

The dispersion of the Cu-O bond stretching mode is plotted in Fig. 3(a) along with the previous neutron data from an optimally doped LSCO sample.[5] The amplitude of the softening increases with increasing x, however, the change becomes smaller in the overdoped region. The q dependence of peak width is plotted in Fig. 3(b). It is almost the same as the energy resolution of the spectrometer at $\zeta\sim 1.0$ and 0.5 after corrections of the twinned structure and the slope of the dispersion, though the error is large at $\zeta\sim 0.5$ due to the weak peak intensity. However, the peak width for the $x=0.12$ and 0.225 samples clearly show a broadening at around $\zeta\sim 0.75$. Interestingly, this broadening disappears for the highly overdoped samples. Similar effects have recently been observed using neutron scattering.[18]

Dispersion curves for the samples with $x\leqslant 0.225$ measured by IXS and 0.15 by INS show a flat region for $\zeta\leqslant 0.7$ (Fig. 3). On the other hand, the $x=0.29$ sample does not exhibit flat bottom feature, which is also consistent with a recent neutron data of $x=0.30$ sample.[18] To extract quantitative information on the amplitude of the softening, we fit the dispersion curves using a phenomenological function $0.5A\cos(2\pi\zeta)+B$, where A and B are constants. Fitted curves are shown in Fig. 3(a). Figure 4 shows the x dependence of the obtained parameter A, amplitude of softening. Some data derived from INS studies[3,5,18] and the result of calculation using a t-J model[19] are also shown in the figure. The softening amplitude increases with x in the underdoped region and starts to saturate or makes local maximum around the optimum doping.

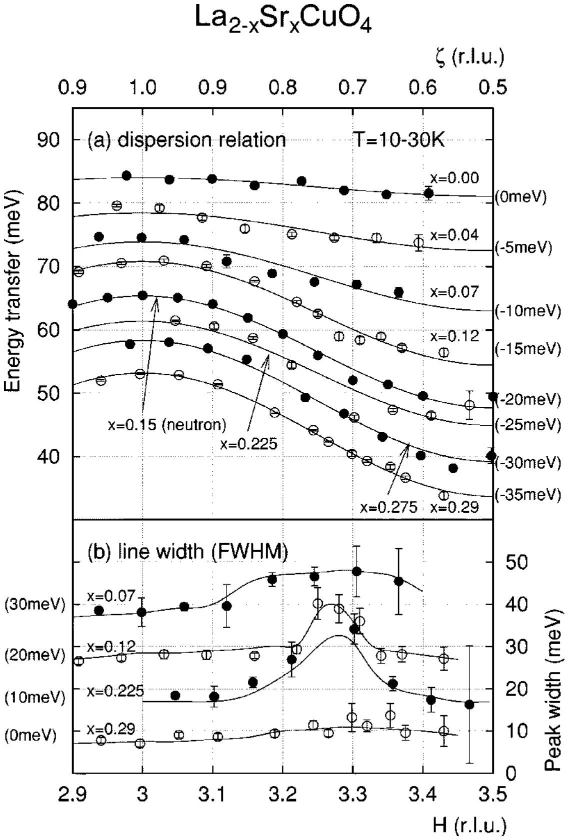

FIG. 3. (a) The dispersion relation of the highest energy longitudinal optic branches along [100] direction for $La_{2-x}Sr_xCuO_4$. Closed triangles are neutron data of the $x=0.15$ (optimally doped) sample reported by Pintschovius *et al.* (Ref. 5). Lines are fitted cosine curves. (b) The linewidth (FWHM) as a function of q for some selected x samples. Lines are a guide to the eye. The different x data are shifted vertically by the values in the parentheses for clarity in both (a) and (b).

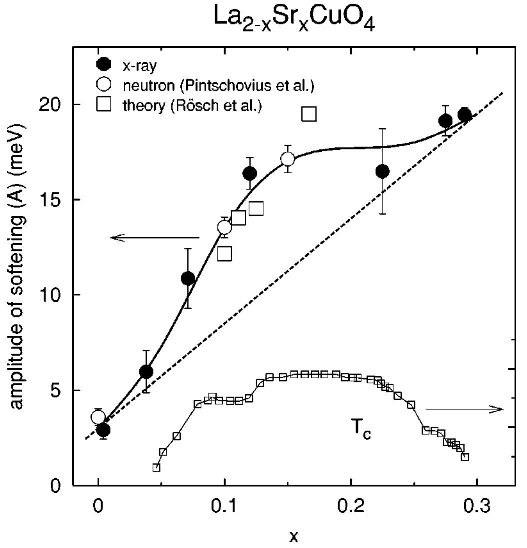

FIG. 4. Sr-doping (x) dependence of the amplitude of softening in the Cu-O bond-stretching vibration along [100] direction and the superconducting transition temperature in the $La_{2-x}Sr_xCuO_4$ system. Closed and open circles are the present x-ray data and the neutron data reported by Pintschovius *et al.* (Refs. 3, 5, and 18) respectively. Open squares are the calculation using a t-J model by Rösch *et al.* (Ref. 19) Solid line is a guide to the eye, and the dashed line shows an expected linear dependence on x when there is no enhancement by the charge collective mode from the calculations by Khaliullin *et al.* (Ref. 22) (see text).

Previous to the present IXS study there were two conflicting INS studies on LSCO ($x=0.15$) which should be compared with our results: McQueeney *et al.*[4] suggests the dispersion in this region involves two (discontinuous) branches or a phase separation at low temperatures, while Pintschovius and Braden[5] (PB) suggest a single branch. Our results for the $x=0.12$ and 0.225 samples resemble that of PB. However, we note that the absolute value of the peak width at around $\zeta \simeq 0.75$ for $x=0.12$ sample is much wider than that obtained by PB (1.8 THz $\simeq$ 7.4 meV before resolution correction, which is compared to 17 meV after corrections of the present experiment). This difference cannot be explained by resolution effect, but might be caused by the different scattering mechanism of IXS and INS, and/or the use of gradient samples. More systematic experiments are required to understand fully the origin of the difference. On the other hand, this anomalous broadening at $\zeta \simeq 0.75$ resembles the results of McQueeney *et al.*, though no clear double branch is observed in our study. According to their explanation, dynamical charge ordering like charge stripes accompanied with dynamical magnetic stripes could be the origin of the discontinuous dispersion, that is, the energy-lowering of the bond-stretching phonon mode at $\zeta=0.75$. However, if charge stripes induce the softening, it is difficult to explain the similar softening observed in the nonmagnetic $Ba_{1-x}K_xBiO_3$.[20]

Falter *et al.* calculated the softening of the highest energy LO phonon in HTcS to be a result of long-ranged, nonlocal electron-phonon interaction effects of an ionic charge-fluctuation type.[21] Their model does not need charge stripes and, in principle, it can describe the phonon softening in many perovskites. However, they only consider the range $x \leq 0.15$, so to test this model the calculated doping dependence up to x in the highly overdoped region should be compared with our experimental result.

Recently Rösch and Gunnarsson calculated the doping dependence of the softening by a t-J model with electron-phonon coupling.[19] Their calculation explains the observed softening of the bond-stretching phonon mode as well as the weaker effect on other phonons. However, their calculation is only for the x between 0.1 and 0.167 (open squares in Fig. 4), thus again the calculation for the highly overdoped region is required to compare with our result.

Khaliullin and Horsch also calculated the x dependence of the softening over the full range of doping ($0 \leq x < 0.37$) based on the interaction between low energy charge fluctuation (polaron) and the phonon mode by using a t-J model in a slave boson $1/N$ representation.[22,23] According to their calculation, hole doping induces a low energy charge collective mode in the dynamical density response not along [110] but along [100] direction, and the phonon-softening is enhanced when the phonon and the collective mode coincides each other. As a result, the softening along [100] shows a highly nonlinear dependence on x, while along [110] the softening depends only linearly on x. This means that if there is no anomalous enhancement by the charge collective mode, the normal linear dependence on x is also expected along [100] direction like the calculated result along [110]. Surprisingly, our experimental result in Fig. 4 is quite similar to the calculated nonlinear x dependence along [100] direction. A dashed line is added as a guide with no enhancement mentioned above, and the x dependence of T_c measured on the studied single crystals are also shown in Fig. 4. What should be noticed is that the enhanced softening occurs near the superconducting region, and the maximum deviation is seen at around the optimum doping $x \simeq 0.15$. Therefore, we speculate that the enhancement of phonon softening along [100] relates to the superconductivity.

In conclusion, we systematically observed the doping dependence of softening in the Cu-O bond-stretching LO phonon of LSCO using inelastic x-ray scattering, and found an anomalous behavior of this vibration mode in the superconducting phase. We emphasize that to get a clear picture of the doping dependence it is important to measure many concentrations, not just two or three values. In terms of future work, investigations on the doping dependence of the phonons along [110] and of nonsuperconducting oxides are highly required in order to establish the relation between the anomalous phonon softening and the superconductivity. The present observation of precise x dependence of the phonon softening in the normal metallic phase will evoke further discussions and studies to elucidate the reason for the anomalous phonon softening in the high temperature superconducting cuprates.

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[17] Our first, early, measurement of the $x=0.29$ sample suggested there was little softening of this mode. However, two subsequent measurements showed the softening as presented here. We believe the present results to be correct. The previous (nonsoftening) result might have been due to beam motion on the sample. While this, of course, does not affect the phonon structure, it can have strong impact on the elastic intensity, which, due to the long Lorentzian tail of the resolution function, impacts the measured spectrum even at high energy.

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