

## Softening of Cu-O Bond Stretching Phonons in Tetragonal $\text{HgBa}_2\text{CuO}_{4+\delta}$

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Phonons in nearly optimally doped  $\text{HgBa}_2\text{CuO}_{4+\delta}$  were studied by inelastic x-ray scattering. The dispersion of the low-energy modes is well described by a shell model, while the Cu-O bond stretching mode at high energy shows strong softening towards the zone boundary, which deviates strongly from the model. This seems to be common in the hole-doped high- $T_c$  superconducting cuprates, and, based on this work, not related to a lattice distortion specific to each material.

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During the history of high- $T_c$  superconductivity research, there have been many pieces of evidence pointing to strong electron-phonon coupling in these systems. For example, electronic changes such as the superconducting transition or pseudogap opening definitely induce phonon renormalization effects [1]. Nevertheless, the phonon contribution to the electronic properties has been unclear or considered unimportant. Even though the Fermi surface shape favors the formation of a charge-density wave (CDW), no CDW gap has been observed. Instead, the parent compound is a Mott insulator. The carrier scattering mechanism responsible for the  $T$ -linear in-plane resistivity at the optimal doping is considered to be dominated by spin fluctuation rather than by phonons [2].

Recently the role of phonons in the electronic state has been reassessed. The isotope effect on the magnetic penetration depth suggests a tight connection of the oxygen vibrations to the superfluid density or the effective mass relevant to the pairing interaction [3]. Photoemission suggests that electron-phonon interaction causes a kink at 50–80 meV in the electronic dispersion for many cuprates [4].

While phonon dispersion in high- $T_c$  superconducting cuprates (HTSC) has been studied for a long time [5], recent interest has been stimulated by inelastic neutron scattering (INS) [6–10] and inelastic x-ray scattering (IXS) [11] studies that show anomalies in the copper-oxygen phonon branches. These anomalies were discussed in terms of spatial charge fluctuation [6,8,9] and connection to the mechanism of superconductivity [7,10]. However, the studies to date have been limited to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) and  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO), except for the recent work with electron doped  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  (NCCO). Thus, in order to really understand the physics of these phonon anomalies, it is strongly desirable to study phonons of different HTSCs.

$\text{HgBa}_2\text{CuO}_{4+\delta}$  (Hg1201) is, in principle, an excellent candidate for phonon studies. The crystal structure is

tetragonal, forming a completely square and flat  $\text{CuO}_2$  plane, as compared to the complexity of the chain structure in YBCO and the tetragonal to orthorhombic phase transitions in LSCO [12]. Moreover, the absence of a 1/8 anomaly suggests that static stripes play a small role in Hg1201 [13]. Hg1201 is also interesting because the structure is similar to LSCO while  $T_c$  ( $\sim 98$  K) is similar to YBCO, and, indeed, members of this (Hg based) family of HTSC also have the highest  $T_c$  demonstrated to date ( $T_c = \sim 135$  K). Despite these favorable properties, the Cu-O phonons in this material have not been studied, in large part because the material is not amenable to neutron scattering due to the very small size of the crystals.

We have performed IXS measurements on nearly optimally doped Hg1201, mapping the dispersion of the  $\Delta_1$  symmetry phonons, including the Cu-O bond stretching mode. It is the small beam size in IXS experiments that makes it even conceivable to measure samples of size  $< 0.1$  mm<sup>3</sup>. However, even so, this is a hard experiment since the sample contains heavy elements (Hg and Ba) which reduce the illuminated sample volume by a factor of about 3 compared to previously studied NCCO by IXS [11]. Thus, in a recent report of IXS from this material [14] the relevant mode was only barely visible at one momentum transfer and its dispersion was not measured. However, at BL35XU of SPring-8 [15] we obtained high quality data, allowing us to show that this mode softens similarly to optimally doped YBCO and LSCO [6,9]. Thus we can conclude the softening is a common feature in the hole-doped HTSCs, independent of lattice distortion and transition temperature.

Single crystals of Hg1201 were prepared with a solid-state reaction method [16] from HgO (99.9%), CuO (99.999%), and BaO purified from BaCO<sub>3</sub> (99.995%). The crystal with the size of  $0.3 \times 0.3 \times 0.2$  mm<sup>3</sup> was annealed at 340 °C in O<sub>2</sub> for 1 week. Magnetic susceptibility measurement shows a sharp superconductivity transition at 94 K, indicating that the sample is nearly

optimally doped [see Fig. 1(a)]. The crystallinity was examined by x-ray diffraction and there was no trace of a detectable impurity phase. The IXS spectrometer [15] employed backscattering at the silicon (888) reflection, providing  $\sim 3 \times 10^{10}$  photons/s (spot size  $\sim 150 \times 100 \mu\text{m}^2$ ) onto the sample in a 4 meV bandwidth at 15.816 keV. Four spherically curved analyzer crystals (each with an independent detector) were used on the 10 m horizontal arm to analyze the scattered radiation. The energy resolution (6.0–6.3 meV, depending on the analyzer crystal) was determined by measuring the elastic scattering of a standard polymethyl methacrylate sample near to its structure factor maximum at  $1 \text{ \AA}^{-1}$ , while the momentum resolution was set by the full (95 mm) diameter of the crystals, maximizing the count rate. The sample was mounted in a closed cycle He cryostat, with measurements performed at 55 K (well below  $T_c = 94$  K). Typically, about 20 h was needed to collect sufficient statistics in one spectrum [e.g., data in Fig. 1(b)].

IXS spectra were measured along the direction close to  $[\xi 00]$ , where  $\xi$  is varied from 3.11 to 3.48. The simultaneous use of four analyzers gives actual momenta slight deviation from  $(\xi 00)$  [exact values given in Fig. 1(b)]. In this arrangement, the  $\Delta_1$ -symmetry phonon modes, which includes eight branches in Hg1201, should have a strong

scattering cross section. Among the eight, one is the longitudinal acoustic mode, two are the  $c$ -polarized modes of apical oxygen and barium, which are Raman active with  $A_{1g}$  symmetry at  $\Gamma$ . The others are the  $a$ -polarized phonons that are  $E_u$  longitudinal optical modes at  $\Gamma$ . Figure 1(b) shows the phonon distribution curves taken along the direction close to  $[\xi 00]$  with experimental error bars. At each momentum, an elastic peak obtained from the standard material was subtracted. The peak positions indicated by short bars are determined by a Voigt fit function, and the results of the peak fitting are shown by red lines. Full components for fitting are indicated only for  $\xi = 3.11$  (blue lines). Some of the eight phonon branches are not detected, because of their weak intensity. Peaks at energies lower than 50 meV have FWHM (full width at half maximum)  $\sim 7$  meV, similar to that of the elastic peak. The highest energy peak over 50 meV has a wider FWHM,  $> 10$  meV. All presented data were collected at 55 K (some spectra at 110 K showed negligible changes relative to 55 K and are not shown).

The phonon dispersion (from our fits) is shown in Fig. 2 along with a simple shell model similar to that used previously to simulate cuprate phonon dispersion [6,11,17]. The parameters for this model were based on a common set for the cuprates [17], with slight modification for Hg1201 [18], and to fit the Raman  $A_{1g}$  data [19]. Calculations were done using the OPEN-PHONON code [20] with carrier screening included by a Thomas-Fermi potential,  $e^{-\kappa_s r}/r$  ( $\kappa_s \sim 0.41 \text{ \AA}^{-1}$ ). For low energies, this simple shell model provides a reasonable description of the phonon dispersion, as has also been the case for other cuprates including LSCO, YBCO, and NCCO [5,11,17]. However, in the region above 50 meV the agreement is not so good, in particular, for the highest energy  $c$ -polarized apical oxygen mode and the next highest  $a$ -polarized Cu-O bond stretching mode, and the Cu-O bond bending mode. Similar problems have been noted in calculations of YBCO [6], NCCO [11], and LSCO [9].

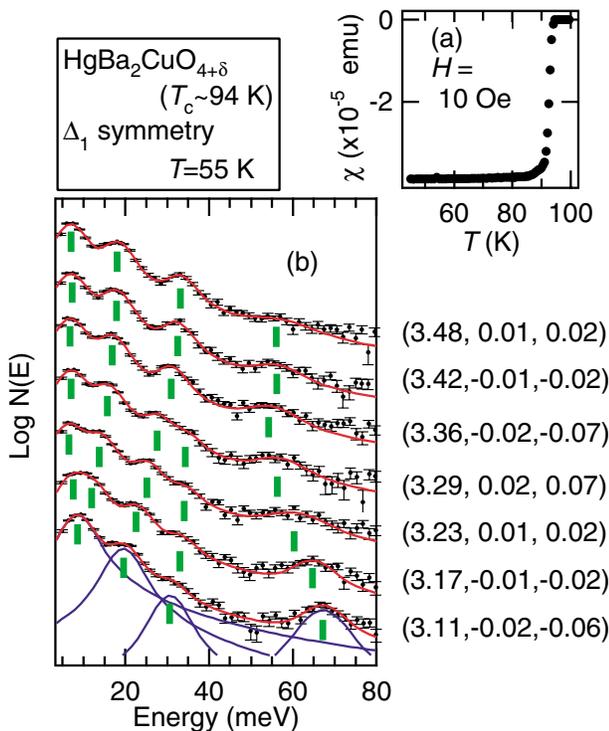


FIG. 1 (color). (a) Magnetic susceptibility of the studied crystal  $\text{HgBa}_2\text{CuO}_{4+\delta}$ . (b) IXS data taken along the direction close to  $[\xi 00]$  with experimental error bars (black), and the fitting curves (red) with several peaks (blue curves as an example for  $\xi = 3.11$ ). The phonon branches (peak positions) are indicated by the vertical bars (green).

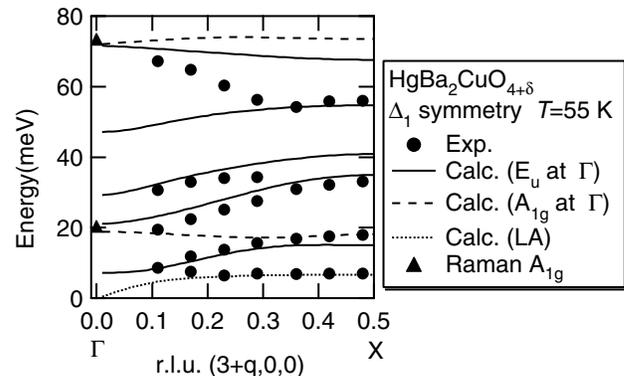


FIG. 2. Comparison of the experimental data (circles) with the calculation (lines). The Raman data in Ref. [19] are indicated by triangles.

Modification of the shell model by including a next-nearest neighbor oxygen interaction, similar to Ref. [21], was attempted. Such an interaction phenomenologically explains a Jahn-Teller-type electron-phonon coupling that results in a rhombic distortion of the  $\text{CuO}_2$  square [22]. This interaction changes only the high-energy mode dispersion. Figure 3(b) shows the results from this modified shell model: the apical oxygen mode softens slightly while the bond stretching mode softens more; in fact the strength of the coupling was chosen to match the experimental energy at  $q = 3.48$ . However, this still does not provide an adequate model of the high-energy phonon dispersion, failing to reproduce the sharp minimum in dispersion at  $q \sim 0.3$ .

The assignment of the measured dispersion to the bond stretching mode deserves some additional consideration, given the presence, in calculation, of the other two modes in this energy region. The grounds for this assignment are the intensities and broadened FWHM of the observed peaks [shown by the bars in Fig. 3(b)]. In regards to intensity, our modified shell model shows that apical oxygen mode intensity is so weak as to be unobservable in our experiment, and, while stronger than the apical oxygen mode, the bond bending mode is also much weaker than the bond stretching mode. Furthermore, the calculation also shows that the bond stretching mode, like the data, falls off with intensity as the zone boundary is approached ( $q = 0.5$ ), similar to the data (a structure factor effect). As to the FWHM, it was reported for YBCO and LSCO that the bond bending mode shows a narrow FWHM close to the resolution limit [23,24],

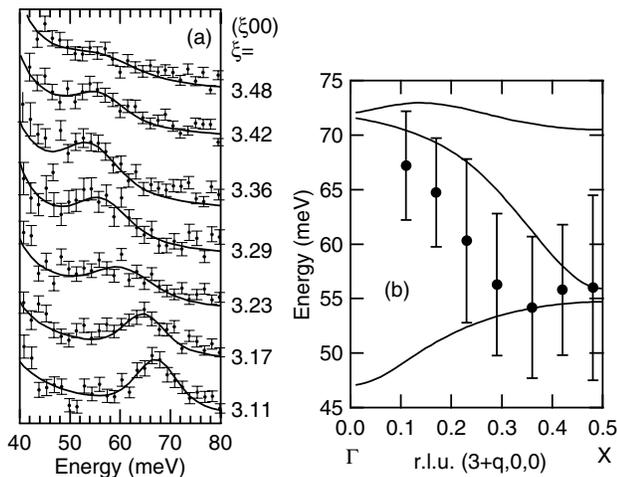


FIG. 3. (a) Enlarged spectra taken close to the bond stretching mode in a linear scale [see also Fig. 1(b)]. (b) The lines show the shell model calculation in which the interaction between the next-nearest neighbor oxygens in the  $\text{CuO}_2$  plane is added. The lines indicate (top to bottom) the  $c$ -polarized apical oxygen mode, the  $a$ -polarized Cu-O bond stretching mode, and the  $a$ -polarized in-plane Cu-O bending mode, respectively. The vertical bars indicate the FWHM of the peaks determined in fitting in Fig. 1(b).

while the broad FWHM was observed for the stretching mode in LSCO [9]. The broad FWHM plotted in Fig. 3 is thus another support for the bond stretching mode. Since the observed peak approaches the calculated branch for the bending mode near the zone boundary, we cannot completely exclude the possibility of mixing of the bending modes above  $q \sim 0.3$ . However, judging from the broad FWHM, we expect a dominant contribution of the bond stretching mode also to the peaks at  $q > 0.3$ .

The softening of the Cu-O stretching mode is also observed in LSCO [5,9,10] and YBCO [5–7]. Here, we focus on the hole-doped HTSC (LSCO, YBCO, Hg1201), as the limited data available for the electron doped materials [11] apparently show a different behavior [25]. Figure 4 shows a comparison of the bond stretching branches for Hg1201 (present results), LSCO [9], and YBCO [6]. All three materials show similar softening of the Cu-O bond stretching mode, irrespective of the difference in crystal structure, band dispersions, and  $T_c$ . This implies that the similar type of electron-phonon coupling affects the  $\text{CuO}_2$  plane in the hole-doped HTSC.

It should be noted that the bond stretching phonon softening in the [100] direction is also observed in doped  $\text{La}_2\text{NiO}_4$  [21,26],  $\text{LaMnO}_3$  [27,28], and  $\text{BaBiO}_3$  [29]. Therefore, the softening of the bond stretching phonon is a common property in the perovskite related materials. However, the cuprates show softening only in the [100] direction while for the other materials the softening is observed both in the [100] and [110] directions. Although the softening along the [110] direction is possibly induced by the Fermi surface nesting [30], the softening in the [100] direction cannot be understood in the nesting scenario.

Various theoretical models have been used to explain the softening of the bond stretching phonon in the cuprates [22,31–39]. One is a shell model, as demonstrated in Fig. 3(b), while another is to treat band effects explicitly in a calculation such as the LAPW (linearized augmented plane-wave) method. This model gives a gradual softening of the bond stretching phonon towards the zone

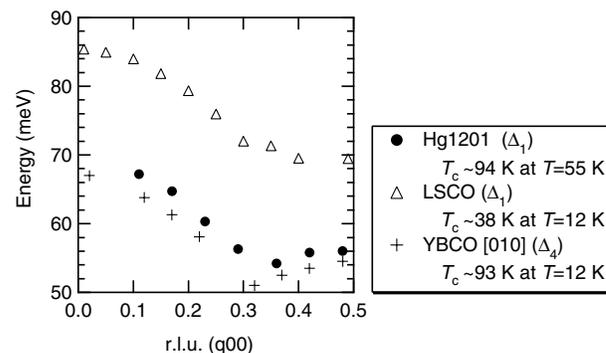


FIG. 4. Comparison of peak position in hole-doped cuprates (YBCO [6], LSCO [9], and Hg1201). For the YBCO, the equivalent  $\Delta_4$  symmetry modes are shown for simplicity [6].

boundary [31,32]. However, a rapid drop of the phonon branch at an intermediate  $q$  is not explained by this model.

The abrupt phonon softening we observe suggests introduction of some kind of charge modulation [33–39]. The mechanisms of charge inhomogeneity are different in different models. For example, the spin stripe order accompanied by the charge stripes is considered as a source of the additional feature in Refs. [33,34], while the Jahn-Teller instability is a driving force in Refs. [35,36]. In order to clarify the mechanism, further studies of various materials, and comparison between theory and experiment, are needed.

In summary, we have studied the phonon dispersion of Hg1201 by IXS. While the low-energy branches are well described by the poorly screened shell model, the Cu-O bond stretching branch is found to be radically softened towards  $q \sim 0.3$  along the [100] direction. This softening is quite similar to LSCO and YBCO, and thus we consider it a common property of the hole-doped HTSC, and independent of lattice distortion such as the orthorhombicity and the buckling of CuO<sub>2</sub> plane. The weak minimum with  $q$  hints at some kind of inhomogeneous charge distribution.

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