Soft phonons and structural phase transitions in La\textsubscript{1.875}Ba\textsubscript{0.125}CuO\textsubscript{4}

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Soft phonon behavior associated with a structural phase transition from the low-temperature-orthorhombic (LTO) phase (Bmnab symmetry) to the low-temperature-tetragonal (LTT) phase (P\textsubscript{4}2\textsubscript{1}/nmc symmetry) was investigated in La\textsubscript{1.875}Ba\textsubscript{0.125}CuO\textsubscript{4} using neutron scattering. As temperature decreases, the TO-mode at Z-point softens and approaches to zero energy around \(T_{\text{d1}} = 62\) K, where the LTO – LTT transition occurs. Below \(T_{\text{d2}}\), the phonon hardens quite rapidly and it’s energy almost saturates below 50 K. At \(T_{\text{d2}}\), the energy dispersion of the soft phonon along in-plane direction significantly changes while the dispersion along out-of-plane direction is almost temperature independent. Coexistence between the LTO phase and the LTT phase, seen in both the soft phonon spectra and the peak profiles of Bragg reflection, is discussed in context of the order of structural phase transitions.

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\section{I. INTRODUCTION}

It is well known that La-214 based high-\(T_c\) cuprates undergo successive structural phase transitions. On cooling temperature, the second-order phase transition from the high-temperature tetragonal (HTT; I\textsubscript{4}/mmm) to the low-temperature orthorhombic (LTO; Bmnab) occurs. In some cases, as seen in the La\textsubscript{2-x}Ba\textsubscript{x}CuO\textsubscript{4} (LBCO)\textsuperscript{4,8} or the La\textsubscript{2-x}Nd\textsubscript{x}Sr\textsubscript{2}CuO\textsubscript{4} (LNSCO)\textsuperscript{4} systems, further structural phase transitions from the LTO phase to the low-temperature-less orthorhombic (LTLO; Pccn) or to the low-temperature tetragonal (LTT; P\textsubscript{4}2\textsubscript{1}/nmc) follow the HTT-LTO transition with decreasing temperature. These structural phases can be categorized by the pattern of coherent tilting for CuO\textsubscript{6} octahedra. Extensive neutron scattering studies on La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4} (LSCO)\textsuperscript{15,16} have revealed that a condensation of zone-boundary soft phonons causes the HTT-LTO structural phase transition, resulting in a staggered tilting of CuO\textsubscript{6} octahedra.\textsuperscript{12,13} At the HTT-LTO transition, a degenerate pair of TO-phonon at X-point wave vectors \(\mathbf{q} = (1/2 \pm 1/2 0)_{\text{HTT}}\), associated with the tilting motion of CuO\textsubscript{6} octahedra, goes soft and split into two modes at \(\Gamma\)- and Z-points in the LTO phase. In LSCO system, Z-point phonon once hardens just below the transition temperature but softens again with decreasing temperature, indicating the structural instability toward the LTO-LTLO or LTO-LTT transitions. Keimer et al. have experimentally shown in La\textsubscript{1.65}Nd\textsubscript{0.35}CuO\textsubscript{4} that the LTO-LTLO transition is also understood as the ordinary displacive phase transition with the softening of Z-point phonons, which turns into zone-center phonon in the LTLO phase.\textsuperscript{2} (We call this phonon as \(\Gamma^\prime\)-point for the sake of convenience) The summary of the soft phonon behaviors at several structural phases and definitions of order parameter involving \{\(Q_1, Q_2\)\} or \{\(Q, \theta\)\} for the tilting of CuO\textsubscript{6} octahedra are schematically shown in Fig. 1.

The relevance between the structural instability and the high-\(T_c\) superconductivity has been also studied intensively in these systems. It has been reported that the evolution of the order parameter of the LTO phase suppressed below \(T_c\) in the LSCO of \(x = 0.13\). After that it has been discovered that the softening of Z-point phonons breaks at \(T_c\) in the LSCO of \(x = 0.15\) and \(0.18\). There facts indicate a competition between the LTO-LTLO (or LTO-LTT) structural instability and the high-\(T_c\) superconductivity. This competitive relation becomes more apparent in the LBCO and LNSCO systems around 1/8-doping, where the charge stripe order follows on the LTO-LTT phase transition, resulting in the suppression of superconductivity.\textsuperscript{12,13} The motivation of the phonon studies in LBCO system is to clarify the relevance among the low-energy lattice dynamics in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic diagram for the energy of soft phonons as a function of temperature. Inset depicts the definitions for the tilting of CuO\textsubscript{6} octahedra.}
\end{figure}
the LTT phase, the high-$T_c$ superconductivity, and the charge stripe order.

In the present study, we examined the soft phonon behavior in 1/8-hole doped LBCO for a wide temperature range including the HTT-LTO and the LTO-LTT structural phase transition. Our measurement is a first case which observes the soft phonons associated with the first-order LTO-LTT transition in La-214 system.

II. EXPERIMENTAL DETAILS

The single crystal of La$_{1.875}$Ba$_{0.125}$CuO$_4$ was grown by traveling-solvent floating-zone method. Details in growing the single crystal are described elsewhere. The crystal has a cylindrical shape of which dimension is $\sim$ 8 mm in diameter with 20 mm height. Note that the crystal in the present study is the very same as used in the measurements of spin dynamics related with the charge stripe order. Diamagnetic susceptibility was measured with SQUID magnetometer, showing no bulk superconductivity down to $T = 2$ K. We determined the structural phase transition temperatures for the HTT-LTO (defined as $T_{d1}$) and for the LTO-LTT (defined as $T_{d2}$) transitions, which is quite sensitive to the Ba concentration in the crystal. Figures a) and (b) are the temperature variations of peak intensities for (0 1 4) and (1 1 0) Bragg reflections measured with neutron diffraction, which corresponds to the order parameters for the LTO and the LTT phase, respectively. As a result, $T_{d1}$ and $T_{d2}$ were obtained as 250 K and 62 K, respectively, which is almost consistent with the previous result. Note that all the Bragg reflections measured at the lowest temperature ($\sim$ 15 K) had well defined single peak profiles, showing that the crystal structure in the lowest temperature phase is not an orthorhombic but a tetragonal. The lattice parameters obtained at $T = 16$ K are $a = b = 5.351$ Å and $c = 13.239$ Å.

Inelastic neutron scattering measurements of soft phonons were performed at triple-axis spectrometer TOPAN of Tohoku University installed at JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI). The final energy of neutrons was fixed at $E_f = 13.5$ meV using PG(002) analyzer. The sequences of the horizontal collimations were 40'-30'-30'-60' and 30'-30'-30'-60', which yields the energy resolutions of 0.9 meV and 0.8 meV, respectively. A pyrolytic graphite filter and a sapphire cut-off filter were inserted for scattered and incident beam to reduce the higher-order contamination of neutrons. The sample was mounted in the ($h 0 l$) zone. Since the single crystal has twinned domains at the LTO phase, both the ($h 0 l$) and ($0 k l$) zones are superposed. Throughout this paper, if no specification is given, the reciprocal space is described by the reciprocal lattice unit in the LTO ($Bmab$) coordination, of which definitions are consistent with that in the LTT ($P4_2/nmc$) one. Temperature of the sample is controlled between 16 K and 450 K using $^4$He-closed-cycle cryostat with high-power heater.

III. RESULTS AND DISCUSSION

A. Soft phonon behavior in wide temperature range

We measured the energy spectra of phonons around $Q = (3 0 2)$, which corresponds to TO-mode at $Z$-point in the LTO phase, as a function of temperature and as a function of $Q$. All the scans were performed in a constant-$Q$ mode. Since soft phonons become overdamped in the vicinity of the structural phase transition temperature, we could not obtain a well-defined phonon spectra just at $Q = (3 0 2)$ (=$Z$-point). Therefore we measured $(3 + q 0 2)$ mode and determined the phonon dispersion as a function of temperature.

Typical energy spectra of the phonons at $Q = (3.075 0 2)$ are shown in Fig. taken at several temperatures. The phonon energy $\omega_{ph}$ was extracted by fitting the observed spectra with the functions of a damped harmonic oscillator form and a Gaussian central peak, which convolved with the instrumental resolution. In these fittings, we assumed $\omega_{ph}$ to be constant within the energy resolution, meaning that the dispersion of phonons was not considered. The solid lines in Fig. are the results of fittings, which well reproduce the observed spectra. The arrows in the figures point to the peak positions determined by the fittings. Above $T_{d1}$ (= 250 K), a single phonon peak is clearly seen, which corresponds to the phonon branch from the degenerate X-point in the HTT phase. $\omega_{ph}$ decreases as temperature decreases, indicates that the X-point phonon goes soft toward the HTT-LTO phase transition. Below $T_{d1}$, in the LTO phase, two phonon peaks appear, showing that the degenerate X-point phonon split into a lower energy phonon at $Z$-
FIG. 3: Energy spectra of (3.075 0 2) phonons at several temperatures.

FIG. 4: Energy of the four phonon modes as a function of temperature. Lines in the figure are guides to the eye.

FIG. 5: Energy of the four phonon modes as a function of temperature. Lines in the figure are guides to the eye.

Note that the two phonons are observable simultaneously because of the twinning of (h 0 l) and (0 k l) zones in the LTO phase. As seen in the figures, $\omega_{ph}$ for Z-point at $T = 60$ K increases at $T = 16$ K. This indicates that the LTO-LTT structural phase transitions occurs and the Z-point phonons turn into $\Gamma'$-point around $T = 60$ K, which is consistent with the temperature dependence of (1 1 0) super lattice shown in Fig. 2 (b). Figure 4 shows the representative phonon spectra just at $Q = (3 0 2)$, taken below $T_{d2}$. At $T = 62$ K, we cannot see clear phonon peak because of the overdamping of phonons in the vicinity of the structural phase transition. However at $T = 52$ K, below $T_{d2}$, the phonon peak becomes well defined around $\sim 5$ meV and its phonon energy is almost temperature independent down to 16 K.

Figure 5 shows the summary of soft phonon behaviors as a function of temperature. The phonon energy at $q = 0$, defined as $\omega_0$, was extrapolated from the dispersion relations of $(3 + q 0 2)$ phonons. Note that $\omega_0$ for $(3 0 2)$ $\Gamma'$-point below 60 K (denoted by filled squares in Fig. 5) was directly derived from the $(3 0 2)$ phonon spectra. The phonon at degenerate $X$-point (open circles) in the HTT phase goes soft with decreasing temperature and splits into two modes below $T_{d1}$, which is due to the reduction of crystal symmetry into orthorhombic with $Bnab$ space group. Thus these two modes correspond to zone-boundary phonon at $(3 0 2)$ $Z$-point and zone-center one at $(0 3 2)$ $\Gamma$-point. On further cooling temperature, the $Z$-point phonon (open squares) remains soft and start decreases again in energy while the $\Gamma$-point phonon (filled triangles) keeps on hardening with decreasing temperature, indicating that the LTO phase evolves and the lat-
tice instability toward the further structural phase transition increases. These behaviors are qualitatively consistent with that of La$_2$CuO$_4$. Below $T \sim 60$ K, $Z$-point phonon discontinuously hardens and its energy becomes almost temperature independent (filled squares), showing that the LTO-LTT phase transition occurs and the LTT phase becomes robust rapidly. The phonons at ($0 \ 3 \ 2$) $\Gamma$-point (denoted by filled triangles) show small anomaly around the transition temperature $T_d2$, which indicates that the fluctuation for the tilt amplitude of CuO$_6$ octahedra was also affected by the LTO-LTT transition. Below $T_d2$, $Z$-point becomes zone-center $\Gamma'$-point and Raman active, because the structural transition from $B$-base centered lattice to primitive lattice occurs. It should be noted that the overall behaviors of soft phonons in the present LBCO is qualitatively consistent with the results for La$_{1.65}$Nd$_{0.35}$CuO$_4$, which shows the second order HTT-LTO-LTLO phase transitions.

We systematically measured the phonon spectra of ($3 + q \ 0 \ 2$) and ($3 \ 0 \ 2-q$) modes as a function of $q$ in whole temperature range below 450 K to determine the dispersion relation of the soft phonons. We show the dispersion relation as $\omega^2_{ph}$ versus $q^2$ plot because the soft phonon dispersion near a structural phase transition can be expressed as

$$\omega_{ph}^2 = A(T - T_{d1(d2)}) + b_1 q_1^2 + b_2 q_2^2 + b_3 q_3^2$$

where $b_1$, $b_2$, and $b_3$ are coefficients for $a$-, $b$-, and $c$-axis, respectively. Figures 5(a) and (b) show the dispersion of ($3 + q \ 0 \ 2$) mode and Fig. 5(c) shows the dispersion of ($3 \ 0 \ 2-q$) mode taken at several temperatures. Solid lines are guides to the eye.

| $T$ (K) | $b_1$ || a (meV$^2\text{Å}^2$) | $b_2$ || c |
|---------|----------|------------------|----------|----------|
| 60      | 1100     | 1080             |
| 16      | 290      | 1370             |

TABLE I: The slope of the phonon dispersion parallel to $a$- and $c$-axis at $T = 60$ K and 15 K.

B. Coexistence between the LTO and the LTT phases

We focus on the detailed transition scheme from the LTO to the LTT phase. Figure 6 is an enlarged figure of Fig. 5 to emphasize the phonon behaviors around $T_d2$. It is clearly seen that the phonon at $Z$-point (open squares) coexists with that at $\Gamma'$-point (filled squares) between 60 K and 50 K, which is seen in a region with a gray hatching in the figure. The figure also shows that the $\Gamma'$-point phonon discontinuously appears, and the $\omega_0$ of $Z$-point phonon gets close to zero quite rapidly but remains at finite energy below $T_d2$, indicating the incomplete softening due to a first-order LTO-LTT transition. Note that the energy of the $\Gamma'$-point phonon (filled triangle) gradually decreases with decreasing temperature where the LTO and the LTT phases coexist.

This coexistence is apparently seen not only in the phonon spectra but also in the peak profiles of Bragg reflections. Figure 7 shows (3 0 2) phonon spectra and $h$-scan profiles of (1 1 0)$_{HTT}$ Bragg reflection taken at three different temperatures between 60 K and 50 K. Mirror index of (1 1 0) for Bragg reflection is coordinated as used in the HTT phase, which corresponds to...
FIG. 7: Enlarged view of the energy of the phonon modes as a function of temperature. Coexistence between the $Z$-point phonon and the $\Gamma'$-point one is seen in the gray hatched region. Several lines are guides to the eye.

(2 0 0) in the LTO coordination. Three peaks are seen in the phonon spectra as shown in Figs. 7(a)-(c). The peaks located at the lowest, medium, and the highest energy correspond to (3 0 2) $Z$, (3 0 2) $\Gamma'$, and (0 3 2) $\Gamma$-points, respectively. As temperature decreases, the intensity of the phonon for $Z$-point decreases whereas that for $\Gamma'$-point increases, and the $\Gamma'$-point phonon finally robust at $T = 50$ K. The present crystal has four domain in the LTO phase, resulting in the peak splitting into four (1 1 0)$_{\text{HTT}}$ Bragg points. The geometry of the splitting is illustrated in the inset of Fig. 7(d). At 60 K, as shown in Fig. 7(d), the peak profiles has components of two main peaks from the LTO domains and a minor peak at (1 1 0)$_{\text{HTT}}$ position which comes from the LTT structure. With decreasing temperature, the central peak increases but two sideward peaks decreases, and finally, the peak at (1 1 0)$_{\text{HTT}}$ becomes almost dominant at $T = 50$ K, of which behaviors has been also reported previously and consistent with the present results for soft phonons. Therefore, we conclude that the LTO phase and the LTT phase competitively coexist and the volume fraction of each phase changes with decreasing temperature.

We finally introduce a simple discussion by the framework of Landau phenomenological theory to understand the nature of the LTO-LTT transition in this system. Axe et al. proposed a free energy near the structural phase transition from the LTO to the LTT (LTLO) phase with the expression of

$$F(Q, \theta) = f(Q) + \alpha \cos 4\theta + \beta[\cos 8\theta - 4 \cos 4\theta]$$ (2)

where $\alpha \sim T_{d2} - T$ near $T_{d2}$. $Q$ and $\theta$ represent the amplitude of displacement and the rotation angle from $a$-axis for CuO$_6$ octahedra, which is defined in the inset of Fig. 7(d). In this model, $\theta = 0^\circ$ and $45^\circ$ correspond to the LTO and the LTT phase, respectively, and, in the case of $0^\circ < \theta < 45^\circ$, the LTLO phase appears. Since the order parameter $Q$, which corresponds to the tilt amplitude of CuO$_6$ octahedra, is almost temperature independent in the vicinity of $T_{d2}$, the free energy $F$ can be regarded as a function of only $\theta$. When $\beta > 0$, Eq. 2 has one local minimum at $0^\circ < \theta < 45^\circ$ below $T_{d2}$ and the second-order phase transition from the LTO to LTLO phase occurs. On the other hand, for $\beta < 0$, two local minimums at $\theta = 0^\circ$ and $45^\circ$ appear in Eq. 2 and the first order LTO-LTT transition occurs, suggesting that the two phases can be coexist near $T_{d2}$. Our present results and the previous study of La$_{1.65}$Nd$_{0.35}$CuO$_4$ show the validity of this simple model.

IV. CONCLUSION

The present study has confirmed the soft phonon behavior of La$_{1.875}$Ba$_{0.125}$CuO$_4$ in the wide temperature range including the HTT-LTO and the LTO-LTT structural phase transitions, which can be totally understood by soft-mode transitions. The dispersion relation of phonons along $a$-axis suddenly changes below $T_{d2}$ while that along $c$-axis is independent of temperature, which might be characteristic in the LTT structure. The coexistence of the LTO and the LTT phase observed in both the phonon spectra and the Bragg peak profiles can be understood as the consequence of the first order structural phase transition in the frame work of Landau theory. The relevance between the change of the phonon velocity along $a$-axis in the LTT phase and the forma-
tion of charge stripe order should be clarified in the near future.

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