**B_{1g}-Phonon Anomaly Driven by Fermi Surface Instability at Intermediate Temperature in YBa_{2}Cu_{3}O_{7-\delta}**

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We performed temperature- and doping-dependent high-resolution Raman spectroscopy experiments on YBa$_2$Cu$_3$O$_{7-\delta}$ to study $B_{1g}$ phonons. The temperature dependence of the real part of the phonon self-energy shows a distinct kink at $T = T_{B_{1g}}$ above $T_c$ due to softening, in addition to the one due to the onset of the superconductivity. $T_{B_{1g}}$ is clearly different from the pseudogap temperature with a maximum in the underdoped region and resembles charge density wave onset temperature, $T_{CDW}$. We attribute the $B_{1g}$-phonon softening to an energy gap on the Fermi surface induced by a charge density wave order, which is consistent with the results of a recent electronic Raman scattering study. Our work demonstrates a way to investigate Fermi surface instabilities above $T_c$ via phonon Raman studies.

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In strongly correlated electron systems, instabilities with complex order parameters are often accompanied by electronic orders that cause various broken symmetries and Fermi surface instabilities in the ground state. The instabilities generically lead to an energy gap at the Fermi surface to lower the energy of the system. The most representative cases are the Cooper pair and Peierls instabilities that are associated with superconductivity and charge density wave (CDW), respectively. In the former case, the superconducting ground state is created through the coherent superposition of electrons, and the superconducting gap is opened in the presence of weak attractive interaction between electrons. Similarly in the latter case, coherent electron-hole pairs create a CDW gap [1,2].

The gap opening driven by an electronic instability affects not only the electronic but also phononic excitation spectra. For example, it is well known that the $B_{1g}$ oxygen bond-buckling phonon in copper oxide high-$T_c$ superconductors shows a softening when the temperature is lowered below $T_c$ [3–6]. The origin of the phonon anomaly was understood to be from a phonon self-energy effect caused by the opening of the superconducting gap $2\Delta$ (see Fig. 1); the phonon peak in the Raman spectrum exhibits narrowing due to the reduced scattering rate upon gap opening. In contrast, phonons with $\omega > 2\Delta$ show broadening since, for such phonons, scattering channels are available and their scattering rate increases due to the increased quasiparticle density of states (DOS). In this way, we can indirectly infer the existence of a superconducting gap. In addition to the superconductivity, this explanation can be also applied to other electronic orders such as CDW which gives rise to an energy gap [7].

Among the various phonon modes in copper oxide superconductors, only the $B_{1g}$ phonon shows a noticeable renormalization in the Raman spectra as we mentioned above. This result drew much interest since it may reflect the intimate link between superconductivity and $B_{1g}$ phonon. Indeed, the coupling constant between electrons and $B_{1g}$ phonon at the Brillouin zone center ($q = 0$) possesses a $d$-wave nature, which is the symmetry of the superconductivity as well as CDW form factor in cuprates [8–12]. Such character allows the $B_{1g}$ phonon to strongly couple with the electrons near the antinode where the superconducting gap is the maximum. As a result, a strong renormalization in the electronic structure appears in the form of a kink or peak-dip-hump feature near the anti-nodal region [13,14]. A recent theoretical work pointed out that the $B_{1g}$ phonon may induce a charge order in underdoped copper oxide superconductors [15,16].

A possible way to address the issues described above is to investigate how the electronic structure in various phases of copper oxide superconductors affects the $B_{1g}$-phonon mode. In this Letter, we present results of comprehensive doping- and temperature-dependent high-resolution Raman
spectroscopy studies on YBa$_2$Cu$_3$O$_{7-\delta}$. Owing to the very high-statistics data, our results clearly show that phonon softening occurs not only in the superconducting state but also at a temperature higher than $T_c$ which has not yet been reported. The softening is robust in the underdoped region but is not observed for the most overdoped sample. The onset temperature of the phonon anomaly, $T_{B_{1g}}$, is distinguished from the pseudogap temperature $T^*$. It is rather close to the CDW temperature, $T_{CDW}$. Our experimental results can be interpreted that the Fermi surface instability induced by the charge density wave order causes the softening of the $B_{1g}$ phonon. Our results can serve as experimental evidence for the existence of a CDW gap in the copper oxide superconductors.

We performed Raman spectroscopy with backscattering geometry using 532 nm (2.3 eV) diode pumped solid-state (DPSS) laser (Cobolt). The incident light was focused on the surface of the sample by a ×40 (N.A. 0.6) objective lens (Olympus). The spot size of the focused light was approximately $2 \times 2 \mu m^2$ and laser power was set below 0.6 mW to avoid laser-induced local heating. To reject the stray light close to 10 cm$^{-1}$, BraggGrate notch filters (OptiGrate) were used. The superachromatic wave plate (Thorlabs) was used for polarization-resolved Raman spectroscopy. The polarization of the incident and scattered light was set to be perpendicular to each other and parallel to the diagonal direction of the Cu$_2$O plaquette [Fig. 2(a), inset] to probe the signal from the $B_{1g}$ channel. The direction of the Cu–O bonding was determined by the angle-resolved polarized Raman scattering measurement (see Sec. I of the Supplemental Material) [17]. The Raman scattered light was collected by the same objective lens and collimated before entering the focusing lens in front of the spectrometer. The collected light was dispersed by a Jobin-Yvon Horiba iHR320 spectrometer with 1800 grooves/mm grating and detected by a thermoelectric cooled CCD. Twinned YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals were mounted on an optical cryostat (Oxford) for temperature-dependent measurements. Optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals were annealed in a tube furnace with oxygen flow.
to control the oxygen content. The superconducting transition temperature was determined from the diamagnetic signal measured with a magnetic property measurement system (Quantum Design) (see Sec. II of the Supplemental Material) [17]. The typical size of the crystals is $2 \times 2 \times 0.5 \text{ mm}^3$. The measured Raman spectra were divided by Bose-Einstein factor to present Raman susceptibility $\chi^\prime$. 

We first briefly touch upon how the gap in the electronic phase can affect the phonon peaks in Raman spectra. Plotted in Fig. 1 is a schematic of the low energy single particle spectral function across the superconducting gap and its effect on a phonon peak in Raman spectra. In the superconducting state, the superconducting gap opens at the Fermi surface while quasiparticle DOS at $\omega = \pm \Delta$ is enhanced. It results in a singularity at $\omega = 2\Delta$ in the real and imaginary parts of the phonon self-energy [22,23]. At $T < T_c$, for a phonon with $\omega_{ph}$ smaller (larger) than $2\Delta$, softening (hardening) and narrowing (broadening) of the phonon is expected, in comparison to the $T > T_c$ case [Fig. 1(a)]. This phenomenon can be intuitively understood as follows. In the normal state, all phonons can be coupled by the electrons near the Fermi level [Fig. 1(b)]. In the superconducting state, however, phonons with $\omega_{ph} < 2\Delta$ cannot be scattered by electrons due to the lack of scattering channels. On the other hand, the scattering rate of $\omega_{ph} > 2\Delta$ phonons increases due to the enhanced quasiparticle DOS [Fig. 1(c)].

Figure 2(a) shows the $B_{1g}$ Raman response of optimally doped ($T_c = 94$ K) YBa$_2$Cu$_3$O$_{7-\delta}$. As the temperature decreases below $T_c$, a broad electronic Raman continuum appears near 550 cm$^{-1}$. It is a signature of superconducting pair breaking peak, $2\Delta_{AN}$, representing the superconducting gap near the antinodal region in the Brillouin zone [Fig. 2(a), inset] [24,25]. The strongest peak at 340 cm$^{-1}$ corresponds to the $B_{1g}$ phonon. Consistent with previous results, our results also show hardening in the normal state [Fig. 2(b)] and strong softening below $T_c$ [Fig. 2(d)] [3–6]. However, an additional weak phonon softening was observed for a temperature range just above $T_c$ [Fig. 2(c)]. To quantify the phonon softening, we extracted the frequency and line width of the $B_{1g}$ phonon by fitting the peak with a Fano line shape [3,6,26]. Figures 2(e) and 2(f) show the frequency and linewidth of the $B_{1g}$ phonon, respectively, as a function of temperature. The black dashed curves represent the simulated frequency and linewidth behavior using a phonon anharmonicity model [27]. Above 150 K, phonon hardening was well described by the phonon anharmonicity. The frequency of the $B_{1g}$ phonon begins to deviate from the anharmonic behavior around 150 K. The frequency decreases slowly until the temperature reaches $T_c$, then decreases rapidly below $T_c$. In Fig. 2(f), the linewidth of the $B_{1g}$ phonon also appears to deviate from the black dashed curve above $T_c$. However, if higher order terms are added to the phonon anharmonicity model, the linewidth data can be fitted well from $T_c$ to 300 K (see Sec. IV of the Supplemental Material) [17]. Hence, we define the onset temperature of the phonon anomaly, dubbed as $T_{B1g}$, from the temperature versus frequency data.

To verify the doping dependence of $T_{B1g}$, we performed the same experiment and analysis on samples with various dopings. We find that not only the optimally doped sample but also underdoped samples (UD62, UD68, and UD85) [Figs. 3(a)–3(c), respectively] clearly show the $B_{1g}$-phonon anomaly between $T_c$ and $T_{B1g}$. On the other hand, the phonon anomaly significantly weakens for a slightly overdoped sample [Fig. 3(d)] and vanishes for the most overdoped sample [Fig. 3(e)]. This indicates the fact that the instability that causes the $B_{1g}$-phonon anomaly disappears in the overdoped region. An interesting observation is that the magnitude of $B_{1g}$-phonon softening is proportional to the $T_c$ ($T_{B1g}$) in the superconducting (normal) phase (refer to Sec. VI of the Supplemental Material for more details) [17].

Plotted in Fig. 4 are the measured $T_{B1g}$ (filled red circles) with the onset temperatures of various phases. The value of

![FIG. 3. Temperature-dependent $B_{1g}$-phonon frequency from YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals with different dopings. Results for UD62 (a), UD68 (b), UD85 (c), OD91 (d), OD89 (e). The hole doping concentration was determined using the method in Ref. [28]. $T_c$ and $T_{B1g}$ are indicated by blue and red vertical dashed lines, respectively.](277001-3)
The phonon softening above $T_c$ represents the $1_g$ phonon. It is more natural to interpret that phonon softening at $q_g$ is quite different from that of $1_g$ phonons. While our results demonstrated definite coupling between $1_g$ phonon and the possible CDW phase in the intermediate temperature range, they may not provide direct evidence for an active role of the $1_g$ phonon in the formation of the CDW or other phases as has been argued previously [15,16]. To investigate the active role of the $1_g$ phonon for various electronic orders in copper oxide superconductors, systematic doping- and temperature-dependent studies on the $1_g$ phonon around phase boundary via diverse experiments are required. For example, pump-probe spectroscopic techniques that can perform a “coherent electron-phonon lock-in” measurement [37,38] on $1_g$ phonons may be a way.

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[17] See Supplemental Material http://link.aps.org/supplemental/10.1103/PhysRevLett.127.277001 for additional information on (I) experimental geometry and angle-resolved polarization dependent Raman spectra, (II) magnetization measurement, (III) electronic Raman spectra from $B_{1g}$ channel, (IV) anharmonicity fitting with the higher-order terms, (V) doping- and temperature-dependent linewidth and asymmetric parameter $q$ of $B_{1g}$ phonon, (VI) numerical calculation of charge susceptibility with CDW ordering, and (VII) temperature-dependent intensity of pair breaking peak in optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$. The Supplemental Material includes Refs. [3,15,18–22].

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