Dynamics of low-frequency phonons in the $YBa_2Cu_3O_{7-x}$ superconductor studied by time- and frequency-domain spectroscopies

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We have investigated the temperature dependence of the optical reflectivity at femtosecond scale in $YBa_2Cu_3O_{7-x}$ superconductors. In both normal and superconducting states, we detect the oscillations associated with two A_{1g} metal-ion modes and compare the phonon dynamics to those obtained by frequency-domain (Raman) spectroscopy. Apart from the considerable increase of amplitude for low-frequency mode in the superconducting state, we observe that its initial phase in the time domain is approximately $\pi/4$ shifted by the superconductivity, whereas for the high-frequency mode the initial phase shift is almost two times larger. Even though similar lattice anomalies are observed in both time and frequency domains, the systematic analysis shows that the coherent lattice dynamics is different from the ordinary (thermal state) dynamics probed by frequency-domain spectroscopy.

I. INTRODUCTION

Raman scattering has been long one of the common techniques for studying the lattice dynamics of high-T_c superconductors.[1] Quite interesting aspects of the lattice dynamics are the anomalies of phonon frequency, linewidth, and intensity in the superconducting state, which might be important for understanding the nature of high-T_c superconductivity. The anomalies in frequency and linewidth, lavished with attention both theoretically[2] and experimentally,[3,4] have been understood as phonon self-energy effects to be successfully employed for estimating the superconducting gap in some of the high-T_c materials.[3] Much less attention has been paid to the intensity anomalies,[5–8] which have not yet found an adequate explanation. On the other hand, as ongoing advances in laser technology have led to the generation of laser pulses whose duration is shorter than the time of many motions in solids, the use of such short pulses makes possible a direct, time-resolved observation of the vibrations of crystal lattice (phonons). The phonons, created and monitored by the short laser pulses and referred to as coherent, have been observed in a great variety of solids ranging from insulators to superconductors.[9–13] For high-T_c superconductors, the first observation was reported for nonsuperconducting $YBa_2Cu_3O_{7-x}$ (Y123) and then for superconducting Y123 films in both normal and superconducting states.[11,12] The time-domain study by Kurz and co-workers[12] revealed the temperature dependence closely resembling the intensity anomaly observed by Raman scattering.[6,7] Just below the superconducting transition, the spectral weight at Ba-mode frequency is substantially enhanced, whereas the spectral weight of Cu-mode remains essentially unchanged. In this paper we concentrate on a detailed comparison of these two low-frequency phonons in Y123 studied over a wide temperature range by both time- and frequency-domain techniques. Preliminary results of the femtosecond pump-probe measurements of the Y123 film on MgO substrate have been published elsewhere.[14]

Our paper is organized as follows: The next section describes the sample characteristics and experimental setups. Section III provides basic information on the lattice dynamics of Y123 and a brief survey of time- and frequency-domain spectroscopies. The main experimental results obtained in this study are presented in Sec. IV, whereas Sec. V is devoted to discussion. We intentionally separate the results and discussion to open up the way to different interpretations. Finally, the conclusions are summarized in Sec. VI.

II. EXPERIMENTAL DETAILS

As samples we used *c*-axis oriented films of Y123 grown on different substrates ($SrTiO_3$ and MgO), as well as Y123 single crystals described in detail elsewhere.[7] The films grown on MgO were 300 and 440 nm thick and showed the superconducting transitions measured resistively at $T_c = 87$ and 89 K, respectively. The film on $SrTiO_3$ was 540 nm thick with $T_c = 88$ K. The Y123 untwinned single crystals had $T_c = 89$ K. All the samples measured by Raman spectroscopy exhibited some softening of the 340 cm^{-1} mode ($\approx$2–3 cm^{-1}) that testified to high quality and a doping close to the

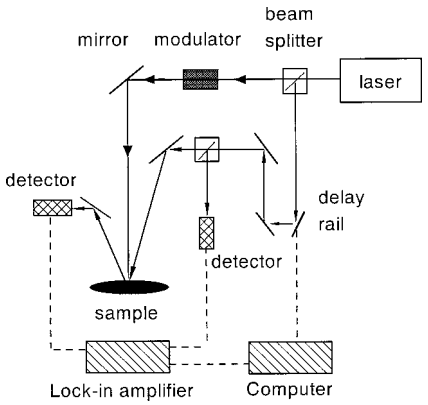

FIG. 1. A schematic diagram of the experimental pump-probe setup.

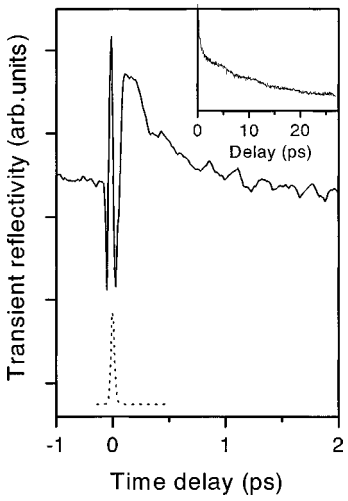

FIG. 2. Transient reflectivity change vs time delay obtained with chopped light. The dashed line depicts the laser pulse measured from the second harmonic generation in a nonlinear crystal. The inset shows the induced change at larger delays.

optimum. In both time- and frequency-domain studies, the samples were mounted on the temperature-controlled stage of an optical cryostat. Excitation and detection of coherent phonons were carried out with a pump-probe setup schematically shown in Fig. 1. Our measurements used a Ti:sapphire pulse mode-locked laser operating at 800 nm, which produces 78 MHz train of 25 fs pulses. These pulses were divided into high-intensity pump and low-intensity probe pulses polarized perpendicular to each other to reduce the scattering of pump into the detector. The average power of the pulses was in the ratio 50:1, with the probe power not exceeding 1 mW. Both the pump and probe beams were kept close to normal incidence and focused to a spot diameter of 50 μm. By varying the time delay between the pump and probe, we were able to obtain transient reflectivity. We used two different detection schemes to provide phase-sensitive detection. In the first one, a shaker modulated the pump beam at 550 Hz, whereas in the second scheme the modulation at 2 KHz was achieved by a chopper. The first technique allowed increasing the signal-to-noise ratio for coherent oscillations. The Raman scattering measurements were made using the T64000 Jobin Yvon Raman spectrometer equipped with a nitrogen-cooled charge-coupled-device array detector. Raman spectra were recorded in a quasibackscattering configuration using radiation of an Ar^+/Kr^+ laser with the spectral resolution better than 2 cm^{-1}.

III. LATTICE DYNAMICS OF Y123

The crystal structure of Y123 is described by orthorhombic D_{2h} point group. However quite often instead of the orthorhombic group, the tetragonal D_{4h} group is employed for phonon classification, which will be used hereafter. A primitive unit cell of the Y123 contains 13 ions, and thus there are 36 optical modes at the Γ point of the Brillouin zone. Of these optical modes, $4A_{1g}+1B_{1g}+5E_g$ are Raman active.[15] The E_g phonons are substantially weaker than the A_{1g} and B_{1g}, phonons.[16] The latter phonons appear at 120, 150, 340, 435, 500 cm^{-1} for the in-plane polarizations of the crystals with doping level close to the optimum. All the phonons are generated by *c*-axis polarized displacements: the two low-frequency phonons coming from metal ions, while the other phonons from oxygen ions. The very early theoretical analysis of polarization properties of the Raman spectra pointed out that the oxygen modes could be significantly mixed, that is, each of the modes consists of the displacement of different oxygen ions.[17] This mixed nature of the high-frequency phonons was confirmed both experimentally and theoretically.[18,19] Although the detailed linear muffin-tin orbital calculations[19] predicted also the strong mixing of Ba and Cu ions for two low-frequency A_{1g} modes, the Raman experiments on isotope substituted samples failed to confirm such mixing.[20,21] Also it should be mentioned that two of the phonons, at 340 and at 120 cm^{-1}, exhibit asymmetric line shape.[22,23] This asymmetry, observed only for in-plane polarizations, is usually ascribed to a quantum interference between the phonon and electronic continuum which is quite strong in high-T_c superconductors.

The time- and frequency-domain studies provide the same information as long as energy splitting (phonon energy) is concerned. In spontaneous Raman we are dealing with thermal excitations. These excitations scatter light, and their spectrum is reflected in the spectrum of scattered light.[24] In a pump-probe technique, the ultrashort, intense pulse excites the sample causing a change in its properties monitored by the second, weaker pulse.[25,26] Here we encounter the excitations created by pump pulse. In such pump-probe experiments on a number of solids, the oscillations with frequencies that correspond to optical phonons (usually Raman active) of the samples are observed.[9,10] A few mechanisms have been proposed to explain these oscillations. Of these, light and displacive excitation of coherent phonons (hereafter LECP and DECP) are most frequently cited for opaque media.[9,10]

IV. EXPERIMENTAL RESULTS

Typical pump-probe reflectivity results obtained at room temperature are shown in Figs. 2 and 3. The runs performed in different regions of the samples to check the sample uniformity, and the runs for films on different substrate and/or of different thickness revealed no significant difference in the induced signal as demonstrated by Fig. 3. The films on

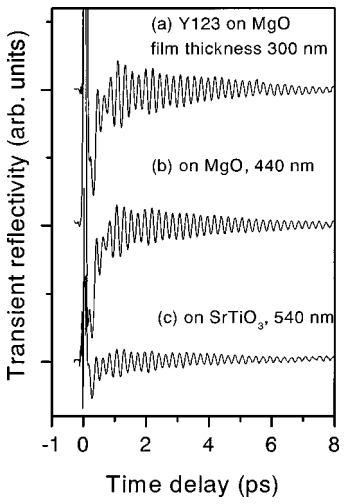

FIG. 3. Transient reflectivity change vs time delay obtained with a shaker for different Y123 films: (a) 300-nm-thick film on MgO, (b) 440-nm-thick film on MgO, (c) 540-nm-thick film on $SrTiO_3$. The transients have been offset for clarity.

$SrTiO_3$ exhibit a smaller oscillatory signal as compared to those on MgO, but the frequencies and dephasing times of oscillations are identical. The sample uniformity was also confirmed by the Raman study under a microscope. In time domain, all samples have similar dynamics in the normal state: The pulse width limited feature at $t=0$, stemming from a temporal overlapping of the pump and probe pulses, followed a resolvable turn-on and subsequent relaxation back to equilibrium. The pump-induced reflectivity changes at positive time-delay consist of two contributions—an oscillating signal, due to coherent phonons, superimposed on a slowly varying background of an electronic origin. For the chopped light the oscillatory part is less pronounced, compare Figs. 2 and 3. Even though in this study we will be primarily interested in the oscillatory part, we would like to mention that the sign of reflectivity change is reversed as well as the electronic relaxation time is modified in superconducting state.[27,28] These two feature can be seen in Fig. 4, where the femtosecond responses obtained for the normal and superconducting states are shown. The oscillatory signals approach the zero line shown in the figure from below (above) in the normal (superconducting) state, and the electronic relaxation time is longer in the superconducting state. The oscillations we are interested in are due to A_{1g}-phonon modes. This is confirmed by the comparison to the Raman spectra of Y123 crystal shown in Fig. 5. Above the transition temperature, the amplitude of oscillations in the Fourier transform (FT) shown in the inset to Fig. 4 is dominated by high-frequency (Cu) mode. Below the superconducting transition, the oscillation pattern in time-domain becomes more complicated signaling that the spectrum has been changed. In fact, the FT spectrum in the superconducting state, shown in the inset to lower panel of Fig. 4, is dominated by low-frequency (Ba) mode. This Ba mode is asymmetric in the FT spectrum, and its line shape resembles that for Raman spectra, see Fig. 5. Additionally, the oscillations in the superconducting state decay more slowly than in the normal state, and are observable at the time delays exceeding 20 ps.

The pump dependence of oscillations was studied by attenuating the pump beam. We estimated the pump dependence from both the amplitude of FT dominated by Cu mode at room temperature, and the amplitude of waveform at a fixed time delay (the maximum of fifth cycle). Figure 6 shows that the amplitude of oscillatory part depends linearly on the pump intensity. A least-square fit of the pump dependence is shown by a dashed line. Interestingly, that the extrapolation to zero pump power reveals a thresholdlike nature for the pump dependence. The pump effect is reversible in the sense that after the pump power is reduced the newly measured signal matches exactly that measured before at the same power. The oscillation decay and frequency do not significantly depend on pump intensity in the normal state. Fig-

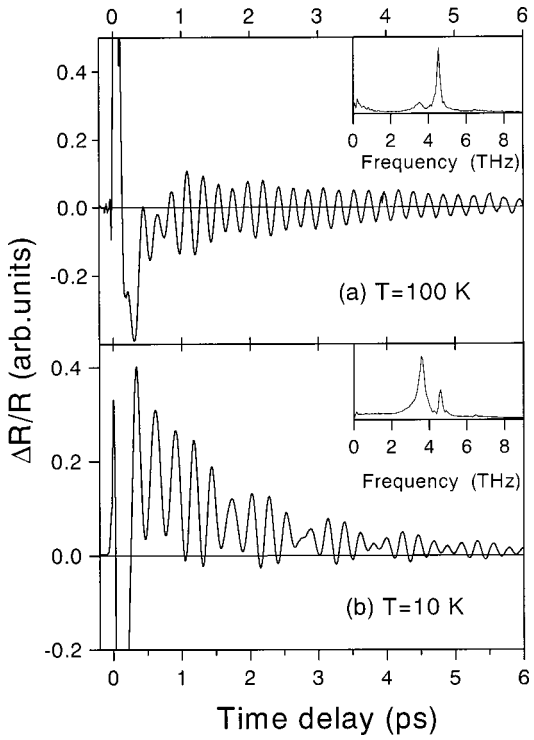

FIG. 4. The transient reflectivity in the normal and superconducting states. The insets show Fourier transformed signals.

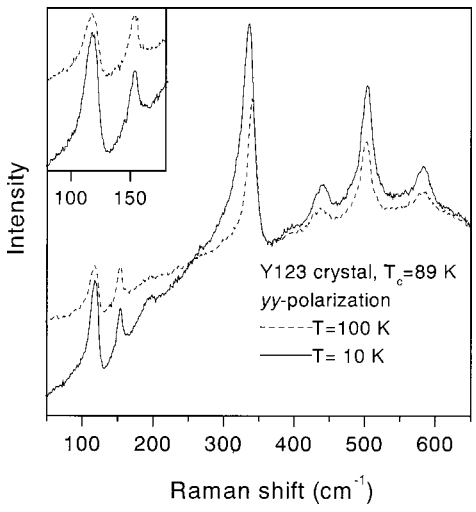

FIG. 5. Polarized Raman spectra of the Y123 crystal at two different temperatures.

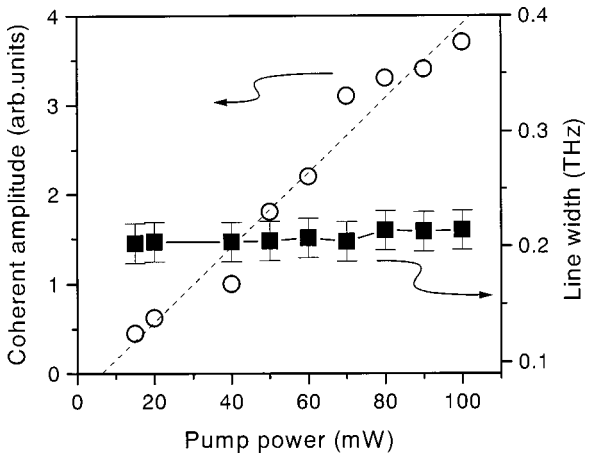

FIG. 6. Pump-power dependence for the 300-nm-thick Y123 film on MgO at room temperature shows (1) coherent amplitude (open circles) together with least-square fit (dashed line) and (2) the linewidth of the Cu-mode (filled squares) obtained from Fourier transformed spectra vs pump power.

ure 6 illustrates this for the decay time measured from the linewidth of Cu mode, which is almost independent of pump power.

As temperature is lowered the oscillation pattern in time domain changes gradually. We can trace the temperature effect by analyzing the ratio of Ba and Cu modes derived from the FT spectra. This ratio is shown in Fig. 7 together with the intensity ratio for the same modes obtained from Raman spectra. Clearly seen is that the drastic change in both, Raman and time-domain, ratios coincides with the transition temperature. For a comparison purpose, we show in the inset to Fig. 5 the Raman spectra for two different temperatures that illustrate the superconductivity-driven increase for the low-frequency mode. The temperature dependence of the Raman ratio obtained for the *xx* and *yy* polarizations is shown in

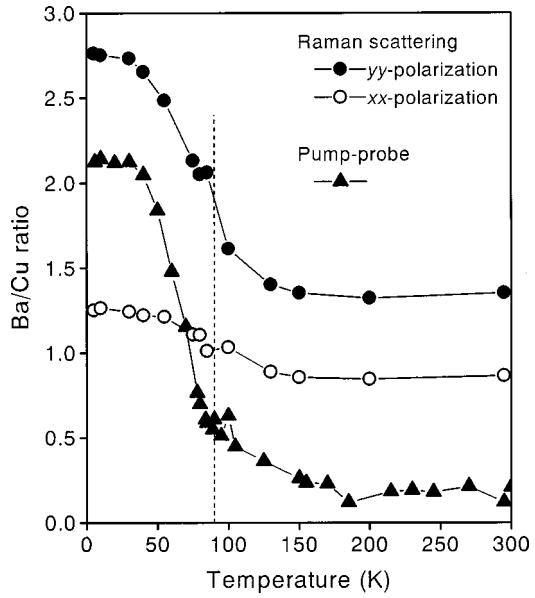

FIG. 7. Temperature dependence of the normalized Ba-mode intensity derived from Raman (solid circles, the *yy* polarization; open circles, the *xx* polarization) and pump-probe (closed triangles) experiments.

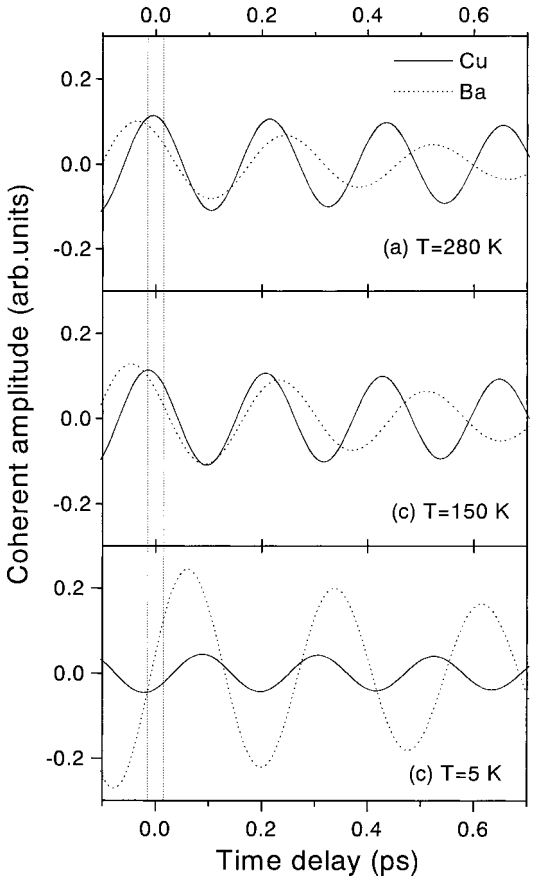

FIG. 8. The oscillatory signal decomposed for short delay times into Ba- and Cu-mode contributions.

Fig. 7 by open and closed symbols, respectively. The comparison of the time- and frequency-domain data reveals that even though overall temperature dependence is similar, the ratios from time- and frequency-domains are quantitatively different. We intentionally present the Raman ratio for two different polarizations since the superconductivity-induced change is polarization dependent in the Raman spectra.[7] Therefore we have to consider that in the pump-probe experiments we measure an uncontrolled mixture of the polarizations due to twinned nature of the films. However, neither single $\alpha\alpha$ polarization nor any combination of the *xx* and *yy* polarizations is able to reproduce the temperature dependence for the ratio derived from the pump-probe experiment. The ratio is always smaller for time-domain data, at least in the normal state. It should be noted, however, that the FT of oscillatory signal gives the amplitude averaged over time. The amplitudes at short delay times, as well as their ratio, are different. This is clearly seen from Fig. 8 where fits to the oscillatory part, described in detail below, are shown. At zero time delay the contribution of the two modes is almost equal at room temperature, whereas the low-frequency mode apparently dominates in the superconducting state. To obtain the independent contribution of the modes as a function of temperature we fit the oscillatory part shown in Fig. 9 for a few temperatures. The result obtained from such fits, which may be important, is that the 120- and 150-cm^{-1} modes are approximately $\pi/2$ shifted in the superconducting state.

To get more insight into the dynamics of coherent phonons at different temperatures, we fit the time-resolved

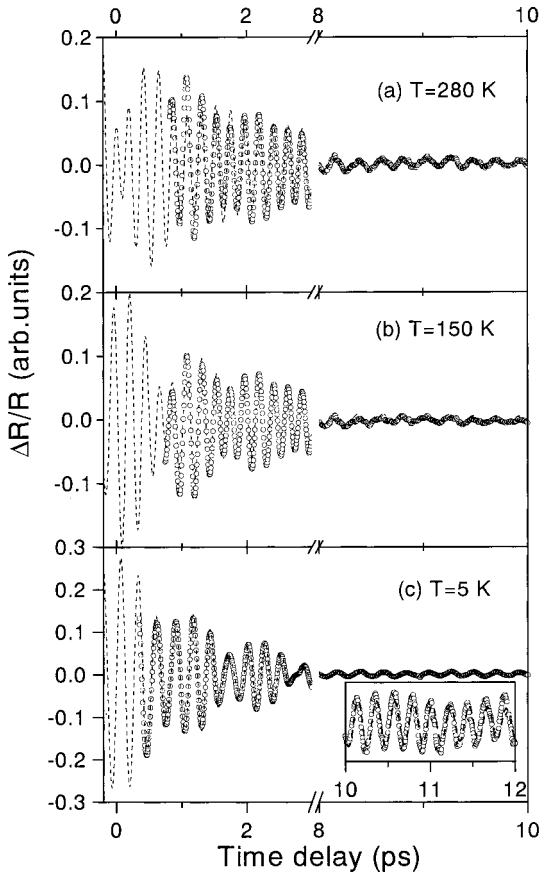

FIG. 9. The oscillatory part of reflectivity after the slow decaying background has been subtracted for three different temperatures ($T=280,150,5$ K) together with the fits described in the text and shown by dotted lines. The inset to lower panel shows the oscillations and fit at longer delay times.

reflectivity to the sum of two sine functions: $R=A\exp(-t/\tau_A)\sin[\Omega_A t+\varphi_A]+B\exp(-t/\tau_B)\sin[\Omega_B t+\varphi_B]$. The quality of the fits is demonstrated by Fig. 9. Alternatively, we performed FT of the oscillatory contribution. Before doing the fits or FT, we have removed the relaxational electronic response. Moreover, to minimize the influence of the waveform distortion by the removal of the relaxational component, we performed the fits starting from time delays unaffected by the removal. The phonon frequencies and decay times obtained in the two ways were essentially similar, and only those obtained in the second way are presented in Fig. 10. As the temperature is decreased the frequency becomes harder, and the dephasing time increases. Note that for the low-frequency mode at temperature higher than 200 K the error bars are large because of its low intensity. At temperatures near and below the superconducting transition the error bars are substantially lower. The temperature dependence observed in Raman experiments for frequency and linewidth is shown in the same figure. The temperature dependence of FT spectra is also illustrated by Fig. 11 for a limited set of temperatures. The figure shows that below the transition temperature the amplitude for low-frequency mode starts to grow. As we have mentioned, the amplitude ratio for the two modes is modified as the temperature is reduced, see also Fig. 7, and the temperature for this alteration appears to coincide with entering into the superconducting region. Additionally, through the detailed study of the temperature dependence in time domain we revealed that superconductivity affects not only amplitude but also initial phase of the coherent vibrations. Never being described by a pure cosine or sine function (within our experimental accuracy) the initial phase is almost $\pi/4$ shifted for Cu mode, whereas for the Ba mode, which exhibits the largest amplitude enhancement, the shift is $\pi/2$, see Fig. 8. The change of initial phase may be

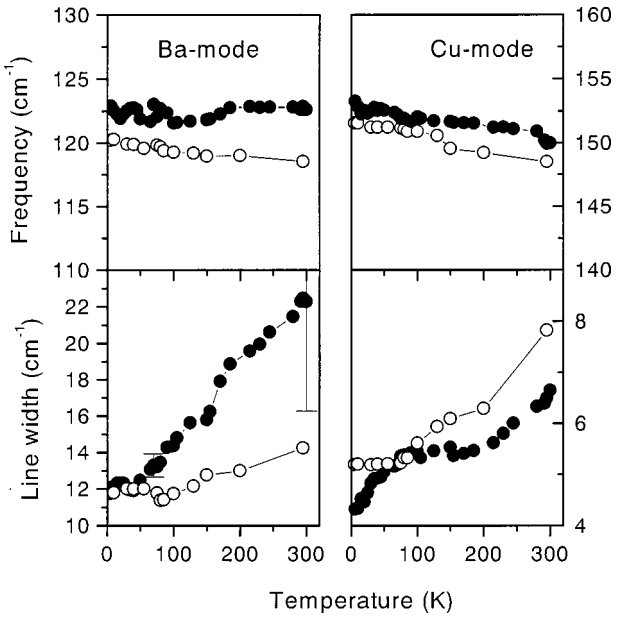

FIG. 10. The frequency and linewidth of two low-frequency modes obtained in time-probe (closed symbols) and Raman (open symbols) measurements.

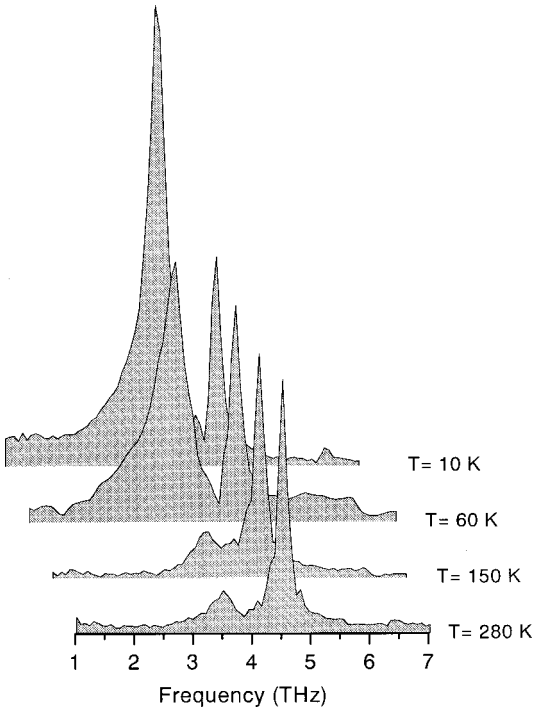

FIG. 11. Fourier transforms of the traces taken at different temperatures. Note that the Ba mode is very weak in the normal but dominant in the superconducting state. The spectra have been normalized to unity for the Cu-mode amplitude.

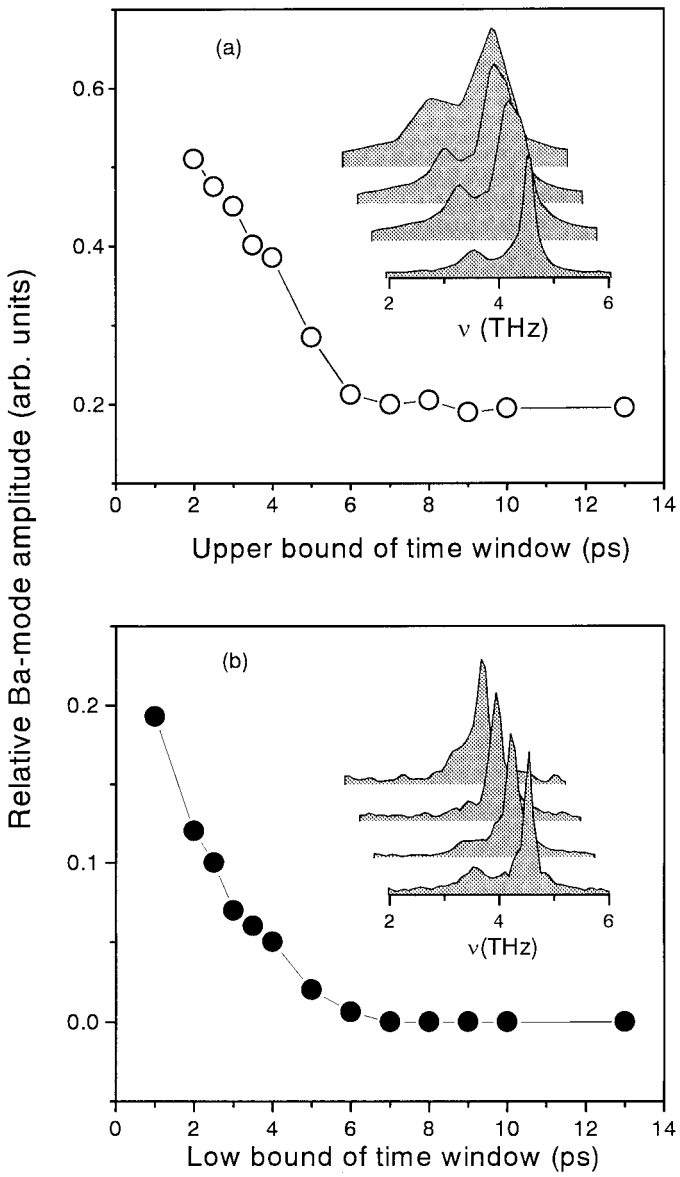

FIG. 12. The ratio of Ba and Cu amplitudes is shown by open (closed) circles as a function of the upper (lower) bound of the Fourier transform. The time-resolved spectra shown in each panel illustrate the ''fast'' and ''slow'' dynamics.

somehow related to the change of polarity for electronic response in the superconducting state.[27–29]

In addition to the FT performed over the whole time range (usually equal to 15 ps), we attempted to analyze time-resolved spectra. For this purpose we made FT varying the low (upper) bound for the time frame of the oscillatory trace and analyzed the ratio of Ba and Cu amplitudes. The results obtained from such Fourier transforms in terms of the relative amplitude are shown in the two panels of Fig. 12. The upper panel shows how the spectral content varies when we increase the time window. The front spectrum in the inset shows the spectrum over the whole time window equal to 15 ps, and the next spectra are for progressively shorter time window being representative of ''fast'' dynamics. The low panel presents the results for various low bounds of time window. The front spectrum is identical to the front spectrum of the upper panel, whereas the next spectra are representative of ''slow'' lattice dynamics that occur at later times. We can see that at early time the spectral content is different from that obtained over longer time. This is primarily caused by the fact that dephasing times are different for the two modes, thus after some time the mode dephasing faster ceases contributing to the spectrum. In this context we would like to point out that a straightforward comparison of the spectra obtained in time-domain to those obtained by frequency-domain spectroscopy could be misleading. Indeed, the relative amplitudes for a multimode spectrum are a function of time window and depend on a relation between the time window and the dephasing time of the modes.

V. DISCUSSION

Below we present one possible interpretation of the results obtained concentrating on the differences for time- and frequency-domain data. We first address the pump dependence. The fact that coherent amplitude decay is independent from pump-power indicates that the lifetime for the phonons created by ultrashort pulse is independent from excitation level. This is a consequence of coherence since for the coherent state the ratio of coherent amplitude to its uncertainty is independent of the coherent amplitude. This pump independence has to be contrasted with Raman data that show a stronger temperature dependence of the linewidth caused by anharmonic decay [that is the lifetime of thermal phonons is a strong function of excitation (temperature)]. This discrepancy implies that the density fluctuations are somehow modified for the phonons generated in pump-probe experiments, and their statistical properties are different from those of natural thermal excitations.

Despite a great body of investigation on the lattice dynamics of high-T_c superconductors, experiments aimed at clarification of the phonon eigenvectors are still rare. This stems from the fact that though symmetry properties can readily be deduced from the polarization dependence, to determine the relative weight of different ion displacements for the phonons of the same symmetry requires usually more sophisticated experiments. The mixed nature of high-frequency phonons is well established, however, the case of low-frequency phonons appears to be more complicated. The detailed experimental study accompanied with a thorough theoretical analysis put the limit of Ba (Cu) admixture to upper (lower) mode at less than 15%.[21] However, the lattice dynamics calculations[19] predicted the strong mixing (50%) of the Ba and Cu in the two low-frequency modes, and the strong mixing was used to interpret the results of the time-domain study in Y123.[29] Although the coherent phonons in Y123 have been reported in two independent experimental studies, the mechanism for coherent phonon generation in Y123 is at present not fully understood in either the normal or superconducting state. The DECP mechanism suggested by Kurz and co-workers[12] is supported by the observation of only fully symmetric modes excited on both sides of the superconducting transition. Furthermore, it has been shown that DECP is capable to explain not only oscillatory part but also the sign change of electronic response in the superconducting state.[29] It should be noted, however, that the intensity of E_g phonons is too low even in Raman experiments and,

for *c*-axis oriented films it is not possible to observe the E_g phonons. The study by Kurz and co-workers also reported a strict sinelike oscillation.[12] Such initial phase for the oscillations is difficult to reconcile with DECP mechanism. Indeed, one of the features that distinguishes DECP from LECP is the initial phase of oscillations: the first mechanism favoring cosinelike, whereas the second sinelike oscillations.[9] Note, however, that our study did not confirm such strict sine dependence in either normal or superconducting state. Nevertheless, with all the discrepancies in mind we cannot at the moment rule out the LECP mechanism, which allows coherent oscillations to be driven by a Raman-like process.[9] We would like to point out on two features supporting the Raman-like mechanism. The first one is a striking similarity of the intensity anomaly for Ba mode, observed by both time- and frequency-domain studies.[3,7,12,14] The second feature is the asymmetric line shape for Ba mode, observed in both spontaneous Raman[23] and time-resolved spectra.[14] This asymmetry can arise from Fano-type interference between the phonon and electronic background, and is quite natural for a Raman-like process.[30] However, Raman-like mechanism cannot explain why there is a large discrepancy between the time-domain amplitudes and Raman intensities for fully symmetric modes, which is apparent at least in the normal state,[12,14] and why the high-frequency modes are not observed. Recall that our pulse width allowed us to see the spectrum bounded from above by 600 cm^{-1} and with similar pulse duration the coherent phonon at 480 cm^{-1} has been detected in metal-doped C60.[13] The intensity of other modes in the Raman spectrum of Y123 is either larger or comparable to that of the modes observed in time-domain experiment. Below we will try to show how the inclusion of a competition between the modes can, in principle, remove the first (ratio) disparity and to find a plausible explanation for the second inconsistency (the lack of high-frequency modes).

We will start with the consideration of the disparity in ratio. Consider a thermal (stationary) state comprising two, different in frequency, phonons, and assume that the state is probed by spontaneous Raman scattering. In the thermal state the phase is arbitrary and both modes can oscillate in the absence of the other. In contrast, in the coherent state with a well-defined phase relation, one of the modes might not be able to oscillate in the other's presence. Such mode competition can arise from the fact that both mode eigenvectors share the same ions. Thus, a build-up of one of the modes prohibits excitation of the other. It should be noted that the eigenvectors suggested by Rodrigiez *et al.*[19] are compatible with such a picture since the in-phase admixture of Cu to Ba in the low-frequency and the out-phase admixture of Ba to Cu in the high-frequency modes make impossible their coexistence in coherent state. As a result, in the normal state the build-up of 150-cm^{-1} mode almost excludes the excitation of the 120-cm^{-1} mode, whereas in the superconducting state the situation is almost reversed. It is plausible to suggest that only initial conditions, different for the normal and superconducting states, determine which mode will oscillate. However, at early time the amplitudes for the two modes are almost equal at room temperature, as it is evident from the fit in real time, see Fig. 8. Moreover, in the superconducting state, the amplitude of high-frequency mode is slightly smaller than in the normal state. Note that the similar temperature dependence was reported for the Cu-mode intensity in an early Raman study.[31]

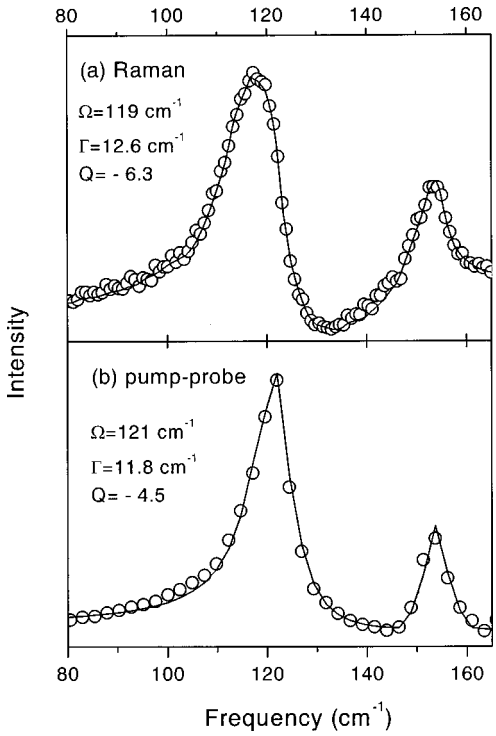

FIG. 13. Low-frequency part of Raman (a) and Fourier transformed (b) spectra together with Fano+Lorentzian fitting showed by a solid line. The Fano parameters for low-frequency mode are shown in each panel.

In the FT spectra, the line shape of low-frequency mode is strongly asymmetric being significantly steeper at high-frequency shifts. The asymmetry is changed as the temperature is lowered, however, it is difficult to trace a detailed temperature dependence since the mode intensity is low at the temperature higher than T_c. To examine the line shape more quantitatively we fitted the mode at low temperature to the Fano profile. We also fit the same mode, obtained by Raman spectroscopy in the Y123 crystal. The two fits give similar line-shape parameters presented in Fig. 13.

More information about phonon dynamics can be obtained through the comparison of the phonon line shape in Raman and FT spectra. By making such a comparison, we revealed that besides the already mentioned discrepancy in relative intensity, the linewidth of the phonons excited thermally and coherently could be different. The discrepancy in linewidth for Cu mode was mentioned in the study of Kurz and co-workers, however, this was ascribed to Landau damping which, by these authors' opinion,[12] was present for most Raman experiments and absent for time-domain study. The Landau damping in high-T_c superconductors, even being extensively treated theoretically,[32–34] was reported only by one research group[32] and not reproduced ever since.[35] However, our results in time domain show that the situation with line width seems to be more complicated and can hardly be ascribed to Landau damping only. Indeed, we observe that for normal state the linewidth of high-frequency mode is always larger in frequency domain, whereas the situation is reversed for low-frequency mode. We note that given the small-

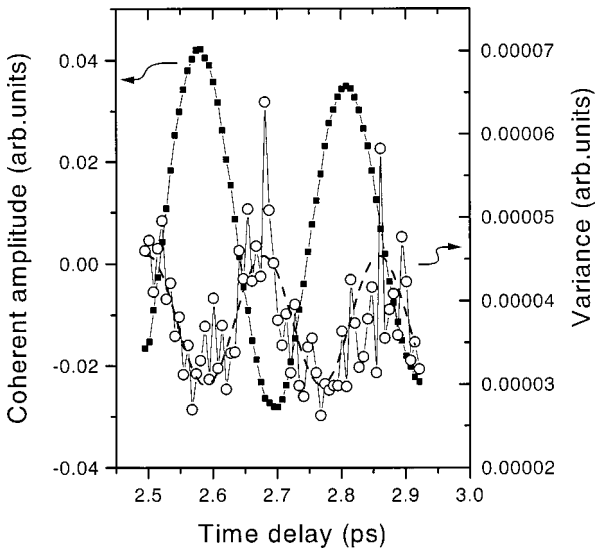

FIG. 14. Coherent amplitude and its variance for different phase angles (time delays) obtained from the pump-probe experiment explained in the text.

frequency spitting between the modes, if the low-frequency mode is Landau damped the high-frequency mode is most probably also within the damping region. The situation for high-frequency mode with dephasing time being longer than time required for damping is interesting and not well understood. Numerous time-domain studies tacitly assume that the dephasing rate, $1/T_2$, is a sum of two contributions: a phase-destroying part $1/T_{\text{phase}}$ and a population-related part $1/T_1$. This point of view, explicitly stated in a recent review,[10] suggests that $1/T_2 = 1/2(1/T_1 + 1/T_{\text{phase}})$. In such a picture, the dephasing rate cannot be smaller than damping. However, the experimental results tell otherwise implying that the processes contributing to damping and dephasing can be distinctly different.

We would like also to point out that the fact that the two modes are phase-shifted can provide a unique possibility to check as to whether the phonons are squeezed in pump-probe experiments. Indeed, if one quadrature is squeezed, the other should be stretched, and with the two phase-shifted modes we measure different contributions of the two quadratures. Assuming the same squeezing angle for both modes and taking Raman data at the lowest temperature as a measure of zero-point fluctuations, the situation with the linewidth in time- and frequency-domain data is suggestive that the high-frequency mode is squeezed, whereas the low-frequency mode is stretched at least in the normal state. To test the hypothesis of squeezing we have investigated in a separate series of measurements *fluctuation properties* of the state created by femtosecond pulse. To do this, we measured 100 times a part of the oscillatory waveform from 2.5 to 3 ps to calculate the amplitude variations at different phase angles (time delays). The variance of coherent amplitude as a function of phase (delay time) is shown in Fig. 14. There is a very weak modulation of the variance suggestive that the coherent amplitude fluctuates more strongly at certain phase angles. However, to claim with certainty the phase-dependent fluctuations, which will be a signature of the phonon squeezing, definitely requires a better signal-to-noise ratio. Note that for $KTaO_3$ and $SrTiO_3$ crystals irradiated with femtosecond laser pulses the phonon squeezing has been reported.[36]

Now we would like to dwell on the observation that only two of the five Raman active phonons are detected in pump-probe experiments. This fact speaks strongly against Raman-like mechanism for the coherent phonon generation in high-T_c superconductors. Our pulse width allows to excite the whole spectrum of optical phonons in Y123, however, except the two discussed above modes we are only confident that there is a very weak feature at 200 cm^{-1}, which may be related to Van Hove singularity recently observed by the Raman in a number of high-T_c materials.[37] One of the possible reasons for the lack of oxygen phonons can be our using the shaker to modulate the pump beam. In such a technique we integrate over time, and the high-frequency modes can be effectively washed out of the spectrum. However, the spectrum was the same even when we decreased the shaker amplitude to a minimum. The next reason to be addressed is the pulse duration at the sample site in *cryostat*. The pulse duration of 25 fs was measured on the sample site in the air, and the cryostat windows could result in some broadening of the laser pulse. However, such broadening is hardly expected to be the main reason for the lack of the high-frequency modes. As a matter of fact, the measurements carried out without cryostat still showed no trace of the oxygen-related phonons. Thus, we conclude that the absence of high-frequency phonons remains unexplained signaling that the excitation mechanism for coherent phonons in Y123 may not be related to Raman process. Nevertheless, we would like to draw attention to the following feature of Raman spectra that might be responsible for the lack of high-frequency modes. The oxygen-related modes are considerably broader than the metal-ions phonons.[15] If their decay time is somehow proportional to the linewidth in frequency domain then the modes would decay just after a few hundreds of femtotoseconds, and therefore do not appear in the Fourier transformed spectra.

VI. CONCLUSION

We have experimentally studied the phonon spectra in $YBa_2Cu_3O_{7-x}$ by time- and frequency-domain spectroscopies. The spectra were obtained over a wide temperature range including both normal and superconducting states. In the time-domain spectra we have revealed the asymmetric line shape for low-frequency mode, similar to that observed in the frequency-domain spectra. This asymmetry most probably stems from Fano interference. Temperature affects the coherent and thermal phonons in a qualitatively similar, but quantitatively different way. Namely, the FT amplitude and Raman intensity for Ba mode increase as the sample goes superconducting, however, the relative intensity of the Ba and Cu modes remains different for time- and frequency-domain measurements through the whole temperature range from room down to helium temperatures. Although the frequencies of coherent and thermal phonons coincide within experimental accuracy, their linewidths are different.

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