Time-Resolved Observation of Coherent Phonons in Superconducting $YBa_2Cu_3O_{7-\delta}$ Thin Films

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We report the observation of coherent optical phonons at 120 and 150 cm^{-1} in superconducting $YBa_2Cu_3O_{7-\delta}$ ($\delta < 0.1$) thin films. These phonons are excited by femtosecond laser pulses and observed by distinct oscillations of the reflectivity signal in real time. Below the transition temperature T_c the amplitude of the Ba mode at 120 cm^{-1} increases drastically in close correlation to the density of optically excited quasiparticles. The dephasing times of the coherent Ba and Cu(2) vibrations exhibit sharp increases below T_c excluding a "second" smaller gap below 150 cm^{-1}.

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Coherent optical phonons can be generated by ultrashort laser pulses, whose duration is shorter than the period of vibration. They are observed in time-domain reflectivity or transmission measurements with femtosecond time resolution. Real-time investigations of coherent phonon modes provide quantitative information on the electron-phonon coupling which is complementary to Raman experiments. The optically induced displacements of atoms are manifested in a modulation of the dielectric constant. Up to now, detailed information about electron-phonon coupling in high-temperature superconductors has been obtained by resonant Raman and ir experiments [1-6]. Abrupt changes in frequency, linewidth, and intensity have been observed for all five A_g modes at and below the transition temperature. These changes have been used to determine the superconducting gap [6]. However, the low-frequency modes of the metallic ions are difficult to investigate quantitatively in Raman scattering experiments. In particular, the linewidths are obscured by large electronic background signals independent of temperature.

Recently femtosecond laser pulses have been used to excite coherent optical phonons in a large variety of highly absorbing semiconductors and metals [7-9]. These coherent modes are launched either by impulsive Raman scattering [7] or by ultrafast screening of surface space-charge fields [8,9]. In semiconducting $YBa_2Cu_3O_{6.3}$, oscillations have been observed in time-resolved transmission and tentatively explained by coherent phonons [10]. Our first clear demonstration of coherent phonon modes in superconducting $YBa_2Cu_3O_{7-\delta}$ ($\delta < 0.1$) has been possible only by the use of highly sensitive detection schemes [11]. A close resemblance to displacive excitation of coherent phonons in metals is found [12].

In this paper, we report on the first quantitative investigation of optically excited coherent phonons in superconducting $YBa_2Cu_3O_{7-\delta}$. Essential properties of the low-frequency modes of metallic ions (Ba,Cu) are compared in the semiconducting and superconducting phase. Special emphasis is paid to the amplitude and dephasing of the observed coherent modes. To exclude any uncertainties of the $YBa_2Cu_3O_{7-\delta}$ system we compared the measurements of ten samples and found identical results within experimental error.

The experiments are performed with femtosecond laser pulses extracted from a dispersion-balanced colliding-pulse mode-locked ring dye laser. Reflectivity changes down to $\Delta R/R_0 = 10^{-7}$ can readily be measured applying an optimized version of the fast scan technique in a standard pump-probe setup [13]. All measurements are performed with $\mathbf{E} \perp \mathbf{c}$ at a fluence of 15 $\mu J/cm^2$. The corresponding temperature increase of the sample is estimated to be less than 2 K. The samples are mounted in a continuous-flow cryostat. The temperature is controlled in the range from 4 to 330 K with an accuracy of 1 K. The laser pulse broadens to 80 fs in the cryostat (measured by the autocorrelation technique).

The samples are $YBa_2Cu_3O_{7-\delta}$ ($\delta < 0.1$) films on $SrTiO_3$ deposited by laser ablation or dc sputtering. The results for laser-deposited samples shown in the figures are identical to those for dc-sputtered samples. All samples are fully c-axis oriented with $T_c = 89-92$ K and $j_c > 10^6$ A/cm^2. The film thickness of 300 nm has been chosen to suppress multiple-interference effects. For comparison, semiconducting $YBa_2Cu_3O_{6.3}$ samples are used which oxygen content has been lowered by annealing the films in N_2 at 450 °C for 40 min. Stoichiometry has been routinely controlled by x-ray diffraction and electron probe microbeam analysis.

In Fig. 1 the reflectivity signals above and below the transition temperature of superconducting $YBa_2Cu_3O_{7-\delta}$ are compared. The thermomodulation response in reflectivity at room temperature is known from investigations of carrier heating and cooling in metallic systems [14]. The incident pump light pulse excites holes to empty states below the Fermi level. Their excess energy heats the carrier in the metallic phase, opening states below and filling states above the Fermi level. As a consequence an ultrafast rise of the reflectivity signal is observed. After the excitation, the reflectivity drops to a slowly decaying background indicating carrier relaxation.

At the transition temperature T_c, the thermomodulation response is superposed by quasiparticle excitation, which causes a negative reflectivity response [15-17]. Far below T_c, at 40 K, the reflectivity change due to quasiparticle creation dominates the thermomodulation

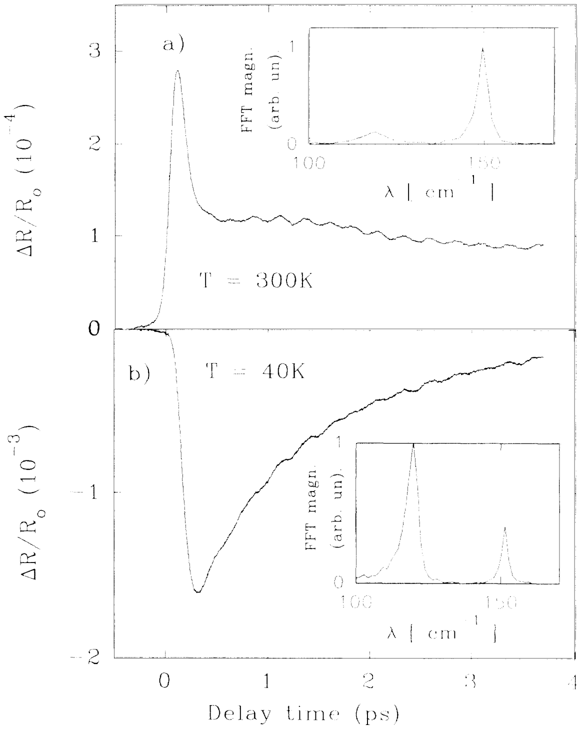

FIG. 1. Time-resolved reflectivity change of a $YBa_2Cu_3O_{7-\delta}$ film on $SrTiO_3$ at (a) 300 K and (b) 40 K. Insets: The fast-Fourier-transformation spectra of the phonon-induced reflectivity modulations.

signatures completely. A detailed explanation of the transient signal dynamics will be discussed in a separate paper. Here, we focus only on the periodic modulations which are visible in the transient reflectivity at all temperatures. A beating of modes becomes clearly visible indicating the concurrent vibration of at least two coherent modes.

We analyze the periodic part of the signals by fast Fourier transformation (FFT). The FFT spectra in the insets of Fig. 1 show pronounced peaks at 120 and 150 cm^{-1} in the case of superconducting $YBa_2Cu_3O_{7-\delta}$. The orthorhombic structure of $YBa_2Cu_3O_{7-\delta}$ supports five A_{1g} Raman modes with respect to the thin film and detection geometry. We identify clearly the low-frequency metallic ion modes, namely, the vibration of Ba (120 cm^{-1}) and the Cu(2) (150 cm^{-1}) along the c axis. The actual bandwidth of the laser pulse as well as the rate at which the quasiparticles are generated limit the detectable phonon modes.

The optical phase locking of various modes in $YBa_2Cu_3O_{7-\delta}$ implies that changes in the dielectric function at 2 eV are governed by the linear superposition of all modes excited. In a first approximation the reflectivity modulation $\Delta R/R_0$ is determined by the change in the dielectric response $\Delta\varepsilon_{ij}$:

$$\Delta\varepsilon_{ij} = \sum_a \alpha_{ij}^a Q^a(t) , \quad (1)$$

TABLE I. Data for the fit of the coherent-phonon-induced reflectivity signatures shown in Fig. 1: lattice temperature T, phonon frequency ω, dephasing time τ, phase Φ, and phonon-induced reflectivity change ΔR.

T (K)	ω (cm^{-1})	τ (ps)	Φ (deg)	ΔR
300	150	3.5	0	0.5×10^{-5}
	120	1	180	0.5×10^{-6}
40	152	5.8	0	0.25×10^{-5}
	122	2.6	180	0.16×10^{-4}

where α_{ij} are the Raman polarizabilities, and Q are the amplitudes of coherent vibrations. We are able to track the phases of single-phonon modes and their superposition since our time-resolved detection scheme directly samples the temporal variations in the dielectric function. In our specific case, we fit the oscillatory part of the reflectivity by the superposition of two sine waves, decaying with a characteristic time τ_i:

$$\Delta R(t) = \sum_{i=1}^{2} \Delta R(t)_i \sin(\omega_i t + \Phi_i) e^{-t/\tau_i} , \quad (2)$$

where ω_i are the frequencies of the fundamental modes, ΔR_i the specific phonon-induced reflectivity changes, Φ_i the phase of starting, and τ_i the dephasing times. The fit parameters used to reconstruct the reflectivity data of Fig. 1 are summarized in Table I. The phonon frequencies increase continuously with decreasing temperature from 150 cm^{-1} (120 cm^{-1}) at 300 K to 153 cm^{-1} (122 cm^{-1}) at 10 K. No anomalous hardening is observed at T_c within our experimental accuracy. Similar behavior is found in Raman experiments [1,3]. According to the theoretical predictions [6] the superconducting gap has to be significantly larger than 150 cm^{-1} in our $YBa_2Cu_3O_{7-\delta}$ films.

The amount of phonon-induced reflectivity modulation depends strongly on the sample temperature. The Raman tensors as well as the amplitudes Q may change with temperature [18]. As shown in Fig. 2 the phonon-induced reflectivity modulation through the 150-cm^{-1} Cu(2) mode remains fairly constant upon cooling down to 120 K. Already above T_c the phonon-induced reflectivity modulation starts to drop and passes through a minimum at 50 K. From the published temperature dependence of Raman efficiencies [18] we deduce a decrease of the c-axis motion of Cu(2) upon cooling down to T_c, followed by a distinct discontinuity at T_c.

The Ba-mode-induced reflectivity modulation, however, is barely discernible above T_c, and rises by an order of magnitude at 20 K. This sharp increase cannot be explained by the slight increase of Raman efficiencies alone [18]. In addition, a strong increase of the amplitude of the photon-induced Ba vibration along the c axis has to be concluded as a specific feature of the superconducting state. Particularly striking is the close correlation between the reflectivity change $(\Delta R/R_0)_{phonon}$ associated

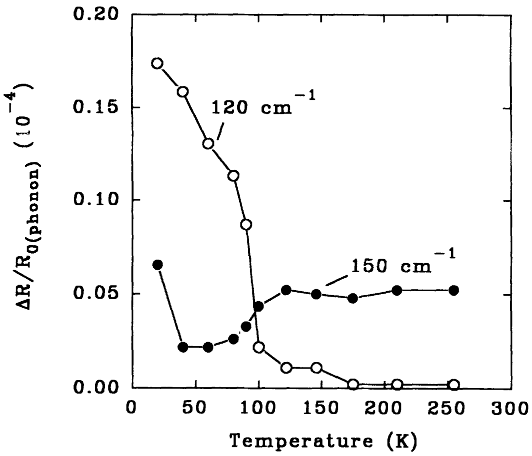

FIG. 2. Temperature dependence of the phonon-induced reflectivity change $(\Delta R/R_0)_{phonon}$ of the 120- and 150-cm^{-1} modes in superconducting $YBa_2Cu_3O_{7-\delta}$. The size of the symbols includes error bars.

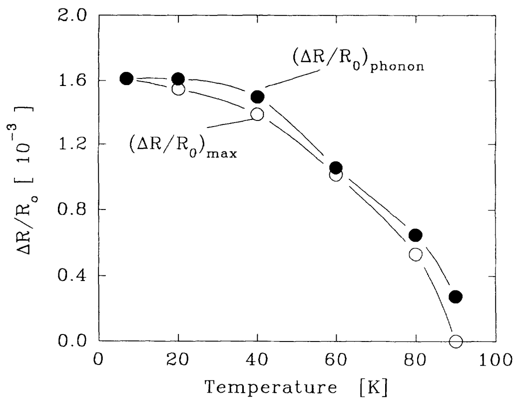

FIG. 3. Comparison between maximum negative reflectivity change $(\Delta R/R_0)_{max}$ and Ba-phonon-induced reflectivity change normalized to a value at 10 K. The size of the symbols includes error bars.

with the amplitude of Ba motion and the maximum of reflectivity change $(\Delta R/R_0)_{max}$ induced by the femtosecond excitation as shown in Fig. 3. The ratio of $\Delta R_{phonon}/\Delta R_{max}$ of 10^{-2} remains constant at all temperatures below T_c. The negative maximum reflectivity change is determined by the density of optically broken superconducting charge pairs. They are destroyed by the optical injection of hot carriers via charge-transfer processes within the CuO_2 planes and subsequent carrier-carrier collisions. At constant optical excitation level, the number of quasiparticles is determined by the $1-(T/T_c)^4$ law of the two-fluid model. The close correlation between the Ba amplitude and the maximum negative reflectivity change indicates that the driving force is determined by the number of optically broken charge pairs for $T \rightarrow 0$ K. Similar carrier-induced processes have been invoked to explain the displacive excitation in metals and Ti_2O_3 [12].

In Fig. 4 the dephasing times τ_i of the two metallic modes are plotted versus temperature. Approaching T_c from room temperature the dephasing time increases linearly due to the freeze-out of decay channels with decreasing temperature [3]. The change in the electronic states below T_c induces noticeable variation of dephasing of all modes: Phonons with energy smaller than the gap are supposed to reduce their coupling to the electronic system below T_c [6]. While the dephasing of the Ba mode (120 cm^{-1}) slows down to 3.5 ps (3.1 cm^{-1}), the maximum dephasing time for the 150-cm^{-1} mode is increased up to 7.3 ps, corresponding to a linewidth of 1.5 cm^{-1} at 20 K.

The linear temperature dependence of dephasing for $T < T_c$ clearly rules out the existence of a "second" superconducting gap in the energy range of the phonon modes observed here besides the "normal" superconducting gap at 39 meV (316 cm^{-1}) [3].

Below T_c the linewidths in our experiments are clearly smaller than those reported in cw Raman experiments, which are subject to Landau damping [19]. The wave vectors of the low-frequency modes excited in fs experiments are lower than those of Raman experiments in backward geometry, crossing the demarcation line of the Landau damping determined by $v_F = 6\times10^7$ cm/s. The wave vectors of the low-frequency phonon modes excited in fs experiments are too low to reach the Landau damping region [19].

In addition to the superconductivity-induced changes in coherent phonon modes, the amplitude and frequency are sensitive to symmetry changes of $YBa_2Cu_3O_{7-\delta}$ due to removal of oxygen. The amplitude of the Cu(2) (150 cm^{-1}) oscillation increases by a factor of 2, and the frequency drops to 143 cm^{-1}, in agreement with a previous measurement [10]. The 120-cm^{-1} Ba mode is not visible in the $z(xx)\bar{z}$ geometry used in our femtosecond experi-

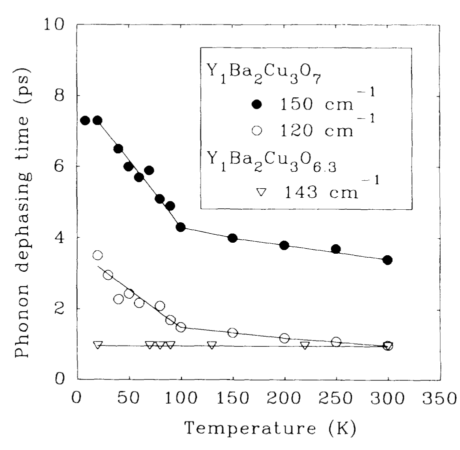

FIG. 4. Phonon dephasing times of the 120- and 150-cm^{-1} phonon modes as a function of lattice temperature. The lines are guides for the eye. The size of the symbols includes error bars.

ments. Raman data of single crystals show clearly that this mode loses intensity in $z(xx)\bar{z}$ polarization whereas it remains easily visible in $x(zz)\bar{x}$ geometry [20]. The dephasing time remains fairly constant in a wide range of temperatures as shown in Fig. 4.

In conclusion, we have observed for the first time coherent phonons in superconducting $YBa_2Cu_3O_{7-\delta}$ in the time domain through reflectivity modulation. The low-lying A_{1g} metallic ion modes are coherently excited by femtosecond laser pulses. Below T_c the increase of the Ba vibration is related to the number of optically excited quasiparticles. The dephasing times of both phonon modes increase linearly in the superconducting state. A "second" gap below 150 cm^{-1} can be excluded.

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