

Femtosecond Spectroscopy Studies of Ultrafast Dynamics in $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Thin Films at Different Temperatures

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We have systematically measured the transient reflectivity ($\Delta R/R$) in Pr-doped YBCO ($\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$) and partially oxygen deficient YBCO ($\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$) thin films at temperatures ranging from 300 K to 12 K by using the femtosecond pump-probe technique. At room temperature, the electron-phonon coupling strength and the position of Fermi-level as a function of Pr doping concentration and oxygen content have been studied. Measurements performed at low temperatures indicate that the magnitude, polarity, and relaxation time of the transient reflectivity is strongly dependent on the photon energy and pumping intensity of the optical excitation, the ambient temperature, and the doping level of the superconducting thin films. Moreover, the temperature dependence of the Fermi-level position was also observed.

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I. Introduction

Understanding the normal and superconducting state properties of high T_c superconductors (HTSCs) and the physical mechanism governing superconductivity, as well as exploiting these properties in optical detectors and superconducting electronics have been the most challenging issues in this field over the past decade. The ultrafast optical response, dealing with the role of electrons, phonons, and their interaction and the dynamics of charge carriers in either normal or superconducting state, is particularly important in these studies. The femtosecond optical spectroscopy using pump-probe technique, which has temporal resolution of subpicosecond, has served as a powerful tool to investigate the nonequilibrium dynamics of HTSCs.

For femtosecond pump-probe experiments performed at room temperature, the measured time-resolved transient reflectivity ($\Delta R/R$) or transient transmissivity ($\Delta T/T$), has been used ubiquitously to extract parameters such as the strength of carrier-phonon coupling, the relaxation behavior of hot carriers, and the position of Fermi level by using the thermomodulation model [1-3]. However, at temperatures near T_c , $\Delta R/R$ may contain more complicated nonequilibrium dynamics [4-8]. The abrupt change of the density of states near the Fermi level [6], the photogeneration and relaxation of quasiparticles [4], and the opening of the superconducting gap [7] or pseudogap [8] may all come into play simultaneously. Therefore, the relationship between the optical response and the nature of the nonequilibrium superconducting dynamics has not been clearly elucidated in this regime. For example, as pointed out by Reitze et al [6], when a fully-oxygenated YBCO sample was either pumped or probed by a photon energy of 2.0 eV, which is close to the position of

Fermi level (E_f) relative to the Cu upper Hubbard band UHB (E_d), the magnitude and change of polarity found in $\Delta R/R$ at temperature below T_c cannot be explained by a simple two-fluid model. The relaxation process of the optical response in the superconducting state apparently involves not merely the generation and recombination of quasiparticles. On the other hand, more recently experimental results [8] showed that, when the fully-oxygenated YBCO sample was probed by a photon energy of 1.5 eV, $\Delta R/R$ had the same sign as the sample probed at room temperature even when the sample was lowered to 20 K. These results imply that other mechanisms may contribute to the negative component of measured ΔR if the probe energy is near $E_f - E_d$. It is suggestive that, further femtosecond-spectroscopy measurement using the pump and probe beams with different photon energies might be needed to reveal more information about the optical response and the band structure of HTSCs.

In the present work, we have systematically measured $\Delta R/R$ versus delay time in $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films at temperatures ranging from 300 K to 12 K by using the femtosecond pump-probe technique. A passively mode-locked Ti-sapphire laser with photon energies tuning from 1.45 eV to 1.65 eV was used. It thus provides a different spectral range to monitor the optical response.

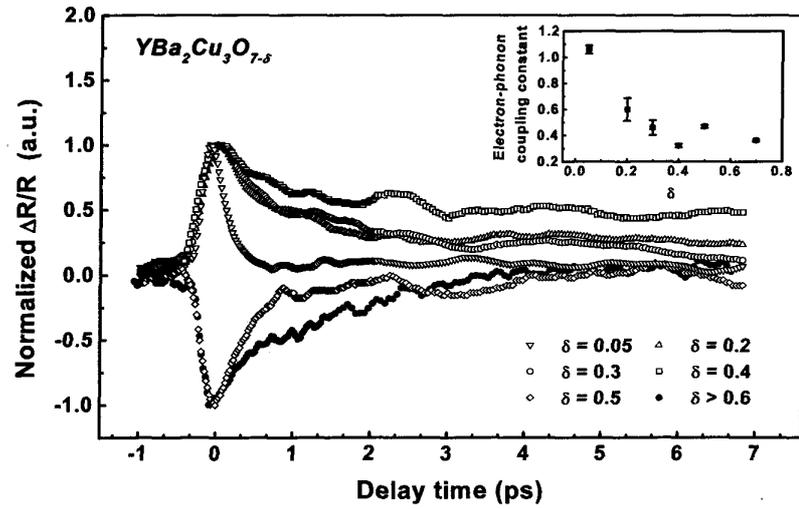
II. Experimental

The $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ thin films with $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8,$ and 1.0 were prepared on (100) LaAlO_3 substrates using pulsed laser deposition. The detailed deposition conditions were reported previously [9]. Briefly, a KrF excimer laser operating at a repetition rate of 3-8 Hz with an energy density of 2-4 J/cm² was used. The oxygen partial pressure during deposition was maintained at 250 mTorr. The substrate temperature was kept at 790 °C for $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ films deposited on LaAlO_3 . All samples were about 300 nm to 350 nm thick. In comparison, the oxygen stoichiometry of a sole $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin film was controlled to vary δ ($\delta = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.55, < 0.6$) in a precise and reproducible fashion [10]. This is to guarantee other factors that may arise from individual film microstructures and thickness are minimized, and the changes in physical properties should be due mainly to the effects associated with the oxygen content of the film.

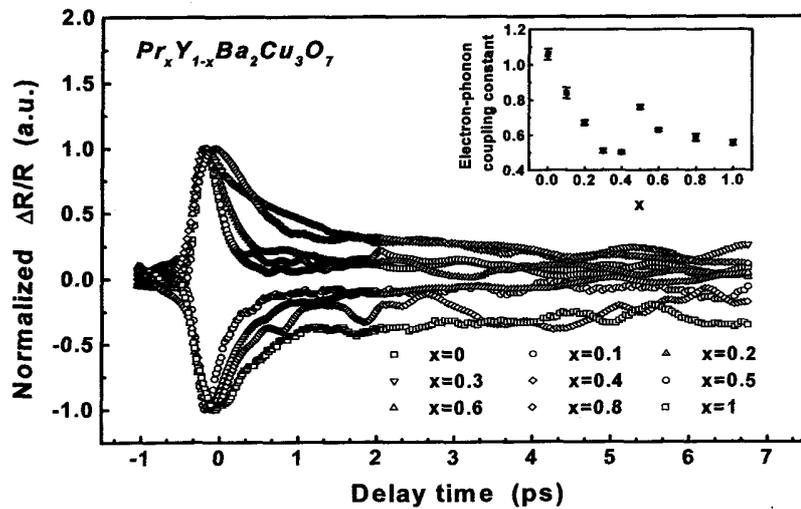
A passively mode-locked Ti-sapphire laser with saturable Bragg reflector was used in the present study. The laser system produces an 85 MHz train of 150 fs pulses and a tunable wavelength ranging from 750 nm to 860 nm (corresponding to the photon energy from 1.45 eV to 1.65 eV). The laser beam was divided into an intensive pump and a weak probe beam by a continuous variable beam-splitter. The average pump power was kept at 10 to 30 mW while the probe power was kept at 2 to 5 mW. The probe pulses were delayed with respect to the pump pulses by a computer-controlled delay stage with a step size resolution of 0.1 μm . The pump beam was incident onto the sample at an angle of $\sim 30^\circ$ to the surface normal and focused into a spot with diameter of 200 μm while the probe beam was incident normal to the surface and focused to a diameter of 100 μm . The reflected signals were detected using a lock-in amplifier referenced at the 3.5 kHz chopping frequency. For low temperature pump-probe measurements, the samples were cooled using a Janis flow-through cold-finger cryostat, and the temperature was monitored by measuring the resistance of the attached thermometers.

III. Results and discussion

Figs. 1(a) and 1(b) show the normalized $\Delta R/R$ versus delay time of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, < 0.6$) and $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8$,



(a)



(b)

FIG. 1. The normalized time-resolved reflectivity $\Delta R/R$ curves at room temperature for the (a) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films with $\delta = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, < 0.6$ and (b) $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ films with $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0$. The photon energy was 1.55 eV and average pump power was 10 mW. The insets show the derived results of carrier-phonon coupling strength as a function of δ and x , respectively.

1.0) thin films at room temperature, respectively. The probe photon energy was 1.55 eV. The carrier-phonon coupling constant can be extracted from the $\Delta R/R$ curves [10]. The insets in Fig. 1 show the derived results of carrier-phonon coupling constant as a function of δ and x , respectively. It reveals that the relaxation rate and the coupling constant decreased dramatically with decreasing oxygen content or increasing Pr-doping concentration. It is also noted that the sign of the measured $\Delta R/R$ at 1.55 eV was reversed for the samples with either $\delta \sim 0.5$ or $x \sim 0.5$. According to the Fermi distribution smearing effect [1,10], the results imply that the Fermi level of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ films should be about 1.55 eV above UHB, when $\delta \sim 0.5$ and $x \sim 0.5$.

The temperature-dependent $\Delta R/R$ curves of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ samples has been systematically measured. Figs. 2(a)-2(c) show the temperature-dependent normalized $\Delta R/R$ curves of a single $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ film with $\delta = 0.05, 0.3, 0.6$. The average power of the pump and probe beams are 10 mW and 2 mW, respectively. Figs. 3(a)-3(c) show the $\Delta R/R$ curves for varying Pr-doping $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ thin films with $x = 0.1, 0.2, 0.6$. From the present results, it is found that the sign of ΔR always remains positive in the whole temperature range for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films with $\delta \leq 0.2$ and $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ films with $x \leq 0.1$. On the other hand, for samples with $\delta = 0.3$ (Fig. 2(b)) or $x = 0.2$ (Fig. 3(b)) and 0.3, a positive ΔR is observed when the temperature is larger than T_c and an additional component of negative ΔR is appeared when the temperature is lowered then $T_c - \Delta T$, where ΔT is the arise of temperature due to laser pulse. The magnitude of the negative ΔR increases while the positive ΔR decreases as the temperature is lowered further. It is also noted that the relaxation of ΔR change significantly.

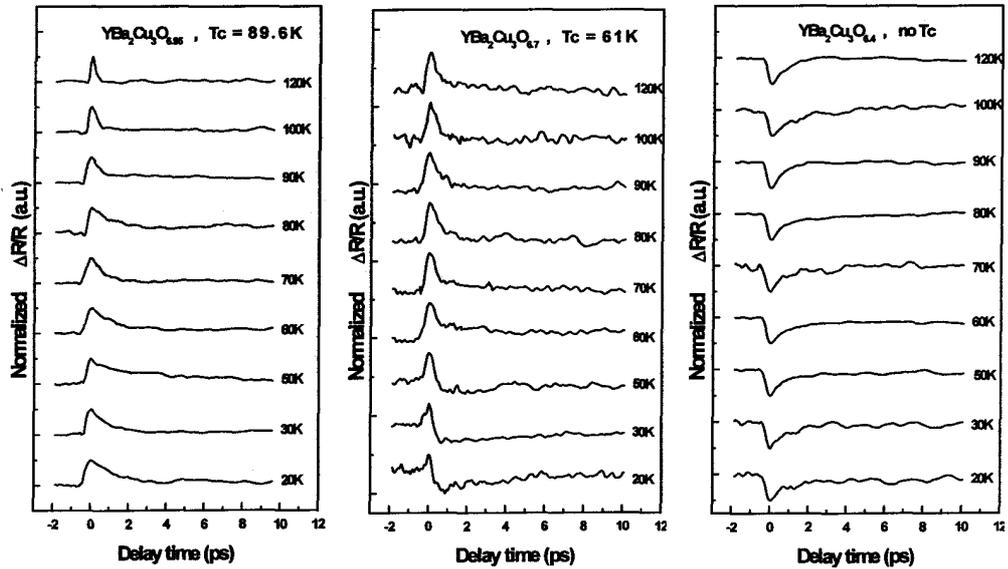


FIG. 2. The temperature dependence of the normalized time-resolved reflectivity $\Delta R/R$ curves for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films with $\delta =$ (a) 0.05, (b) 0.3, and (c) 0.6. The average pump power was 10 mW and probe beam was 2 mW.

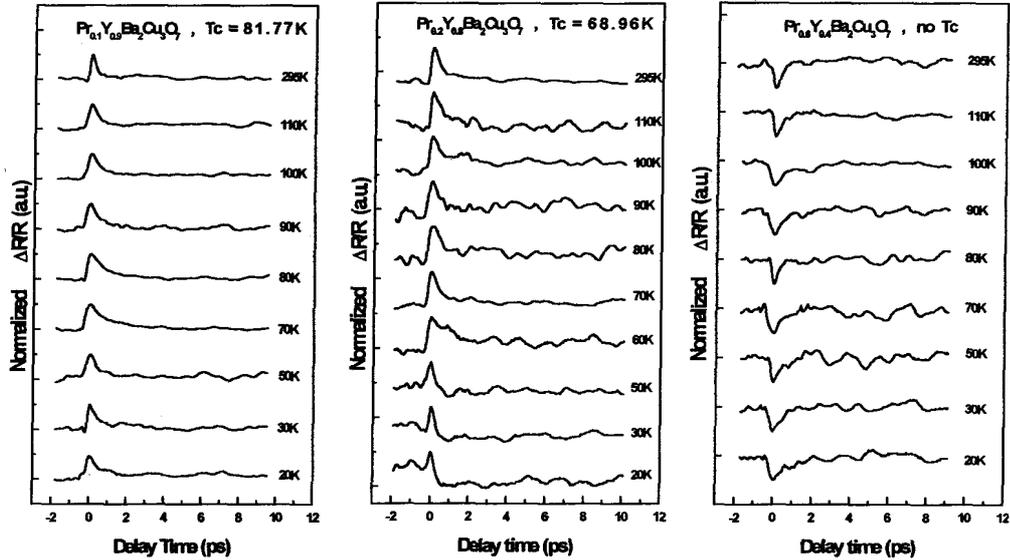


FIG. 3. The temperature dependence of the normalized time-resolved reflectivity $\Delta R/R$ curves for $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ thin films with $x =$ (a) 0.1, (b) 0.2, and (c) 0.6. The average pump power was 10 mW and probe beam was 2 mW.

The temperature-dependent of the relaxation time for different samples will be further investigated and reported elsewhere. For samples with $\delta > 0.5$ or $x > 0.5$, the sign of ΔR becomes negative in the whole temperature range.

However, for the films with $\delta \leq 0.2$ or $x \leq 0.1$, the present results are quite different from those reported previously [4-6] where higher photon energy (about 2.0 eV) was used and larger, negative ΔR was obtained. This implies that other mechanisms may have contributed to the negative component of measured ΔR if the probe energy is near $E_r - E_d$. Indeed, as is evident from Figs. 2(b) and 3(b). when $E_f - E_d$ was near the probing photon energy (1.55 eV in our case), ΔR had negative component at $T_c - \Delta T$ for samples with $\delta = 0.3$ or $x = 0.2$. One of the explanation for this is, when the sample in the superconducting state is illuminated by ultrashort pulses, the density of states lying near the Fermi level, with the distribution of van Hove singularity [12], will change drastically and then modify the Fermi smearing. This abrupt change can be monitored only when the probe energy is near $E_r - E_d$ and leads to the sign reversal of ΔR .

It is also noted that in nonsuperconducting film, such as $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ film with $x > 0.6$ or $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ film with $\delta > 0.6$, the sign of ΔR were strongly related to the pumping intensity and the ambient temperature. As shown in Fig. 4, when a $\text{PrBa}_2\text{Cu}_3\text{O}_7$ film was illuminated by a pumping power of 20 mW, the sign of ΔR was positive while the pump power was reduced to 10 mW, it became negative. Moreover, Fig. 5 shows that the change of ΔR sign also occurred when the ambient temperature was cooled to below 233 K. The change of

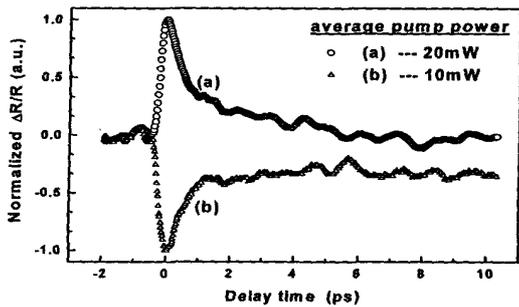


FIG. 4. The normalized time-resolved reflectivity $\Delta R/R$ curves at room temperature for $\text{PrBa}_2\text{Cu}_3\text{O}_7$ film. The average pump power was (a) 20 mW and (b) 10 mW.

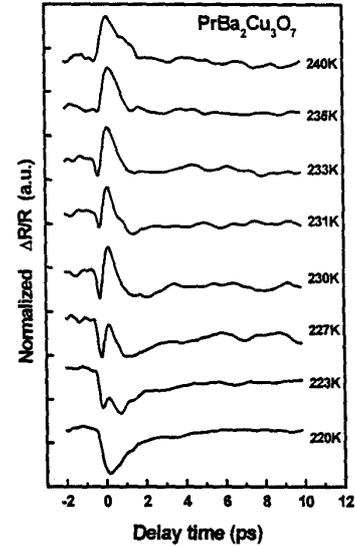


FIG. 5. The temperature dependence of the normalized time-resolved reflectivity $\Delta R/R$ curves for a nonsuperconducting $\text{PrBa}_2\text{Cu}_3\text{O}_7$ film. The average pump power was 10 mW and probe beam was 2 mW.

ΔR sign in both cases can be interpreted as the temperature dependence of the Fermi level shift. It is measurable especially when the Fermi temperature is low ($\sim 10^3$ K) for the nonsuperconducting films [11]. Therefore, any reasons cause the change of the initial carrier temperature can significantly affect the position of E_f , leading to the pump intensity or temperature dependent $\Delta R/R$ response. The change sign of ΔR can be further interpreted as follows: In the hole picture, the Fermi level moves downward related to the UHB as the temperature increases [11]. If the probe energy $h\nu$ is larger than $E_{f1} - E_d$, where E_{f1} is the position of Fermi level of the sample under laser illuminated, then the measured $\Delta R/R$ is negative. On the other hand, if the pump power increases to an average level (corresponding to Fermi level E_{f2}) such that $h\nu$ is lower than $E_{f2} - E_d$, then $\Delta R/R$ would change sign from negative to positive. Similarly, when the sample was cooled down, $\Delta R/R$ would change sign from positive to negative if the relative Fermi level shift corresponding to a temperature varying from $E_f - E_d > h\nu$ to $E_f - E_d < h\nu$.

IV. Conclusions

We have systematically measured the transient reflectivity ($\Delta R/R$) in Pr-doped and partially oxygen deficient YBCO thin films at temperatures ranging from 300 K to 12 K by using the femtosecond pump-probe technique. At room temperature, the electron-phonon coupling strength and the position of Fermi-level as a function of Pr doping concentration and oxygen content have

been studied. The measured results reveal that the relaxation rate and the carrier-phonon coupling constant [10] decreased dramatically with decreasing oxygen content or increasing Pr-doping concentration. Although the pairing mechanism in HTSCs may not be related to the carrier-phonon coupling directly, the measured results show that the magnitude of coupling strength does depend on the Pr-doping concentration or oxygen content of these materials. From the change sign of measured ΔR , the position of Fermi level of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ films with either $\delta = 0.5$ or $x = 0.3$ should be about 1.55 eV above the UHB.

Measurements performed at low temperatures indicate that both the sign and relaxation time of $\Delta R/R$ are strongly dependent on the energy difference between the photon energy $h\nu$ and $E_f - E_d$ of the superconducting thin film. When $h\nu$ is far away from $E_f - E_d$, the sign of ΔR was unchanged and the quasiparticles relaxation is the dominant process for ΔR . On the other hand, when the $h\nu$ is close to $E_f - E_d$, the sign of ΔR is reversed and other mechanisms, such as modified Fermi smearing and Van Hove singularity effects, may also contribute to the negative component of measured ΔR . The results demonstrate that femtosecond-spectroscopy measurements with different photon energies for the pump and probe beams should be useful for delineating the detailed processes of quasiparticle excitations and relaxations.

The effects of pumping intensity and temperature on the polarity of $\Delta R/R$ for samples with $x > 0.6$ or $\delta > 0.6$ were also investigated. The result was attributed to the temperature dependence of the Fermi level shift. In principle, the temperature dependence of the Fermi-level position can be determined by the time-resolved $\Delta R/R$ measurement provided that the probe energy can be tuned over a wide range.

Acknowledgment

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