Femtosecond Study of the Electronic Structure in Semiconducting Y-Ba-Cu-O

We have carried out femtosecond pump-probe studies of the electronic structure of semiconducting $YBa_2Cu_3O_x$ (YBCO). By separating photoinduced bleaching and free-carrier absorption, we have measured the charge-transfer gap. The recovery after the photoexcitation follows a stretched exponential law with a temperature-independent dispersion factor and a temperature-dependent decay time. At probe energies below 1.9 eV, a drastic decrease in bleaching is observed as a consequence of induced free-carrier absorption within the O-2*p* band, which leads us to the conclusion that the bandwidth of the O-2*p* band is approximately 1.9 eV.

Femtosecond spectroscopy has been a powerful tool in probing the properties of high-temperature superconductors (HTS), including the quasiparticle dynamics,[1-3] coherent phonons,[4,5] the electron-phonon coupling constant,[6-8] and the position of the Fermi level.[9-13] In the normal state of oxygen-rich YBCO with $x > 6.8$, the Fermi smearing model has been widely applied in describing the transient optical response, especially the sign change of the differential reflectivity when the probe is tuned across the Fermi level.[9-13] However, there is no general agreement over the dependence of the signal sign on doping, pump intensity, and temperature.

Recent femtosecond studies on insulating cuprates have observed both photobleaching and induced absorption.[14] The initial subpicosecond decay of the bleaching was assigned to two-magnon emission; however, the origin of the induced absorption below 1.6 eV was not fully understood. It is well accepted that semiconducting YBCO ($x < 6.3$) is a Mott-Hubbard insulator with a charge-transfer (CT) gap between the Cu-3*d* upper Hubbard band (UHB) and the O-2*p* band. Several corresponding band diagrams have been proposed based on Raman,[15] photoconductivity,[16] and photoluminescence[17] studies. Moreover, transient photoconductivity investigation has shown a long lifetime (>10 ns) for photoexcited carriers in insulating YBCO.[18]

In the present study, we explore the mechanisms of the nonequilibrium optical response in oxygen-poor semiconducting YBCO. We observe a stretched exponential recovery of the bleaching signals. We find that photoinduced, free-carrier absorption occurs at probe energies smaller than the bandwidth of the O-2*p* band. The interplay of free-carrier absorption and bleaching results in a significant enhancement of the recovery rate of the signal near the band edge. By investigating the relative contributions of the induced absorption and bleaching, we estimate that the bandwidth of the O-2*p* band is approximately 1.9 eV.

Experiments

Our experiments were performed on 200-nm-thick epitaxial semiconducting YBCO films, which were deposited on MgO substrates using RF magnetron sputtering. Oxygen depletion was achieved by *in-situ* annealing of as-deposited films in 100 mTorr of Ar. Cryogenic testing of their electronic transport showed a behavior typical for a variable-length hopping.[19] The optical density was obtained using a Perkin-Elmer Lambda-9 spectrometer. The femtosecond response was investigated between room temperature and 12 K using a conventional pump-probe technique. Laser pulses of 120 fs in duration were generated by a colliding-pulse, mode-locked laser and further amplified by a copper vapor laser at an 8.5-kHz repetition rate. While the pump energy was fixed at 2 eV, variable probe energies were obtained from a white-light continuum. Pump and probe beams were cross polarized and focused on the 30-μm sample surface. With the pump energy of 10 nJ per pulse, the injected carrier density is estimated to be $\sim 10^{20}$ cm^{-3}. Lock-in and differential detection techniques were used to enhance the signal-to-noise ratio. Time-resolved transient changes in both reflection and transmission were measured simultaneously so that both the transient absorption ($\Delta\alpha$) and the unperturbed absorption coefficient (α_0) could be obtained by a numerical fitting that included Fabry-Perot interferences.[20] The low-temperature measurements were

performed in a continuous-He-flow optical cryostat using 2-eV pump and probe pulses.

Results and Discussion

Figure 64.39 shows the room-temperature linear absorption spectrum of an oxygen-depleted YBCO ($x \sim 6.0$) film. Two main absorption features near 1.78 and 2.8 eV are clearly resolved. These two peaks are related to the CT transition between the filled Cu-3*d* UHB and the empty O-2*p* band (in the hole picture).[15,16] In addition, a broad bandtail is observed below the fundamental absorption peak near 1.78 eV. Low-temperature photoconductivity studies have indicated that the lowest interband transition occurs at 1.5 eV.[17] Therefore, it can be concluded that all the probe energies (>1.65 eV) used in the present study are greater than the CT gap, and thus bleaching is expected as a result of band filling. Also shown in Fig. 64.39 are the values of α_0 (solid dots) obtained from the numerical fitting of the pump-probe data. The good agreement between α_0 from pump-probe experiments and the linear absorption curve demonstrates the effectiveness of the fitting program and gives additional confidence in our experimental results.

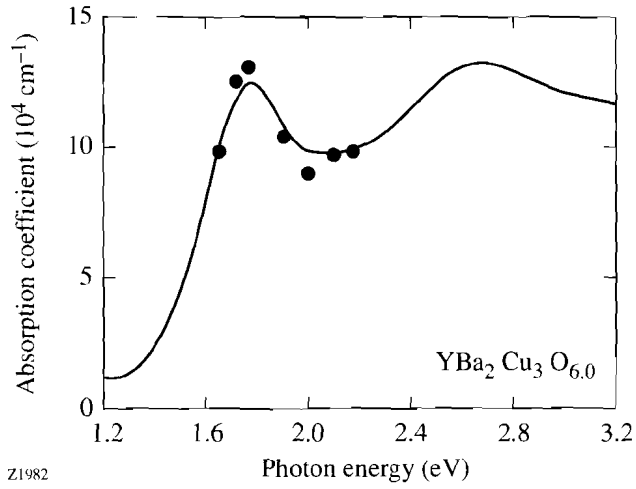

Figure 64.39
Absorption spectrum of semiconducting YBCO at room temperature. The solid dots are the values of linear absorption obtained from the pump-probe data.

Figure 64.40 displays the normalized transient absorption at probe energies from 1.65 eV (750 nm) to 2.1 eV (570 nm). As expected, bleaching ($\Delta\alpha < 0$) is observed at all wavelengths immediately after the excitation. The pulse-width-limited rise of the bleaching is due to the efficient redistribution of photoexcited carriers by carrier-carrier (CC) scattering. As in the case of conventional semiconductors, such as GaAs,[21] CC scattering occurs on a sub-100-fs time scale when the injected density is higher than 10^{19} cm^{-3}. The redistributed carriers occupy the previously empty states and, hence, block the possible transitions across the CT gap.

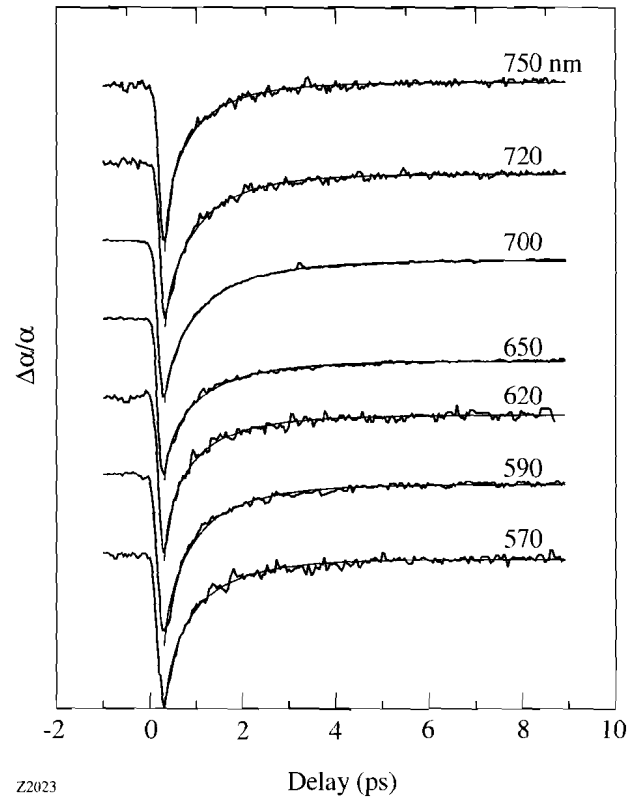

Figure 64.40
Time-resolved differential absorption ($\Delta\alpha/\alpha$) of semiconducting YBCO at several probe wavelengths. The data are normalized and shifted vertically for clarity. The smooth lines are the fits using a stretched exponential.

The excess energy of the excited carriers is then transferred to the lattice. Since the carrier lifetime (~10 ns) is much longer than our 10-ps sampling window, one would expect carrier accumulation near the band edge prior to recombination. As a consequence, for photon energies near the band edge, the recovery of bleaching should become a slow process. In some cases, the bleaching could even increase with time as the carriers slowly cool down to near room temperature. We observe instead that the recovery is slowest around 1.9 eV (650 nm), rather than near the band edge (1.65 eV or 750 nm). Close to the band edge, the bleaching disappears in a few picoseconds, and the signal becomes positive after 5 ps

(Fig. 64.40), indicating induced absorption. The appearance of induced absorption at 1.65 eV suggests that the excited carriers can be further excited.

The relaxation measured by the recovery of the bleaching follows a stretched exponential and not a simple exponential. The smooth solid lines in Fig. 64.40 are fitted by a normalized stretched exponential plus a constant term, i.e., $-\Delta\alpha/\alpha = \exp\left[-(t/\tau)^{\beta}\right] + C_1$. While the first term models the relaxation of hot carriers, C_1 represents the excess heat that escapes by the much slower process of heat diffusion (bolometric process). The fitting provides constant values for $\tau \approx 0.6$ ps and $\beta \approx 0.7$ over the whole spectral range at room temperature. The stretched-exponential decay indicates the coexistence of multiple processes that cannot be represented by a unique time constant.[22,23]

In Fig. 64.41, the transient absorption spectra from Fig. 64.40 are plotted for different time delays. It takes 300 fs to reach the maximum bleaching, consistent with the pulse-width-limited rise time and fast CC scattering. Spectrally, the maximum bleaching is at 1.9 eV, an energy at which there is no peak in the linear absorption. There is also no observable spectral shift of the 1.9-eV peak with time over a 10-ps window. The decay in Fig. 64.41 shows that the slowest recovery occurs near 1.9 eV instead of at the band edge. In fact, at the band edge (1.65 eV) there is even a small increase in absorption after 5 ps, which indicates that, in this case, induced absorption overcomes bleaching. Therefore, the increase of the recovery rate below 1.9 eV results from induced absorption that cancels the bleaching. From the injected density of about 10^{20} cm^{-3} and the magnitude of the induced absorption (about 300 cm^{-1}), we deduce a transition cross section of $\sim 3 \times 10^{-18}$ cm^2. Due to the partial cancellation of the induced absorption by the bleaching, the real transition cross section for free-carrier absorption could be larger than this. Nevertheless, the value of $\sim 3 \times 10^{-18}$ cm^2 is consistent with free-carrier absorption involving extended states and is much smaller than dipole-allowed absorption by carriers trapped in localized states. Therefore, the most likely bleaching cancellation process is free-carrier absorption inside the O-2p band.

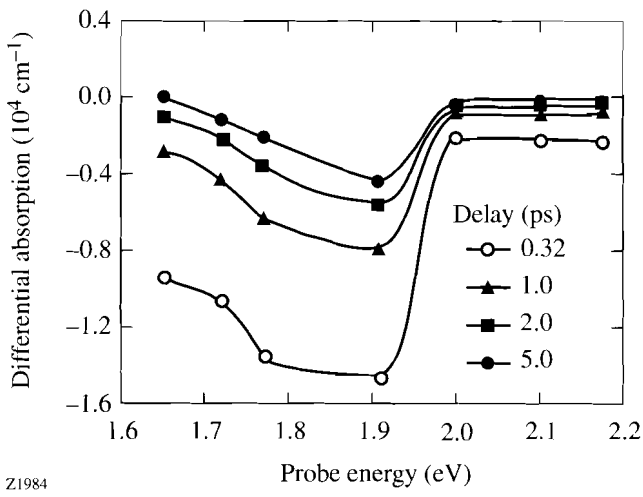

Figure 64.41
Differential absorption spectra at several delay times after the maximum bleaching.

Free-carrier absorption inside the O-2p band must depend strongly on the probe energy. At probe energies larger than the bandwidth of the O-2p band, no intraband transition is possible and only bleaching exists. Below that threshold energy, however, induced absorption and bleaching coexist and compensate each other. The net result is an increase in the recovery rate of bleaching and eventually induced absorption. Consequently, the fact that the fastest absorption recovery occurs near 1.9 eV corresponds to the threshold for free-carrier absorption and should be related to the bandwidth of the O-2p band. For smaller probe energies, the induced absorption becomes progressively stronger than bleaching because more occupied states are available for intraband transitions. As a result, the recovery rate of the differential signal increases drastically toward the lower energies (band edge) and starts to dominate at 1.65 eV (see Fig. 64.41).

Figure 64.42 shows the dependence of the time-resolved differential transmission $\Delta T/T$ on temperature. We note that the recovery of $\Delta T/T$ is faster at lower temperatures. As in Fig. 64.40, the relaxation process can be accurately fitted by a stretched exponential law (the smooth solid lines in Fig. 64.42). Figure 64.43 plots the time constant τ and the dispersion factor β used for the stretched exponential fitting in Fig. 64.42. Unlike in the case of trapping where $\beta = T/T_0$,[22,23] our value of β is independent of temperature. Simultaneously, τ shows a decrease with the temperature decrease, rather than an exponential increase. Therefore, our signals cannot be explained by a distribution of trapping states. The increased decay rate at low temperatures may be related to the emission of acoustic phonons.

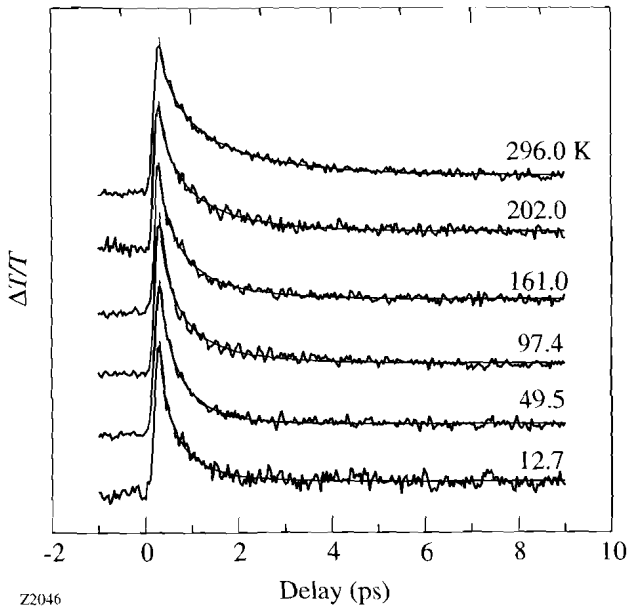

Figure 64.42
Time-resolved differential transmission $(\Delta T/T)$ of semiconducting YBCO at different temperatures. As in Fig. 64.40, the fitting by a stretched exponential is shown as smooth lines.

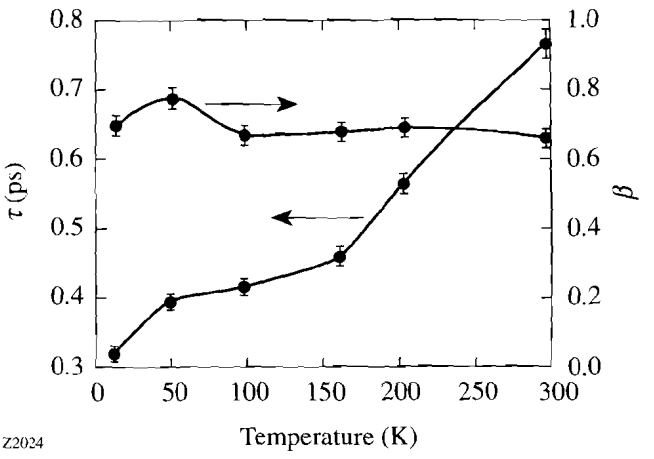

Figure 64.43
Stretched exponential parameters for transient transmission in Fig. 64.42 as a function of temperature. The solid lines are a guide to the eye.

Conclusions

We have measured the transient optical response of semiconducting YBCO by femtosecond spectroscopy. Using probe pulses of different wavelengths, we have measured the free-carrier absorption within the O-2p band and bleaching across the CT gap. The hot carrier dynamics is described precisely by a stretched-exponential law. The temperature-independent dispersion factor (β) excludes transitions involving the trapping states within the CT gap. For probe energies above 1.9 eV, only bleaching contributes to the transient signals. Below 1.9 eV, photoinduced absorption due to free-carrier absorption inside the O-2p band coexists with the bleaching and results in a drastic decrease in the recovery time. Hence, the peak position of the bleaching at 1.9 eV is considered to be a measure of the bandwidth for the O-2p band.

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