Femtosecond spectroscopic studies of the ultrafast relaxation process in the charge-transfer state of insulating cuprates

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We have investigated the transient absorption spectra of insulating $YBa_2Cu_3O_y$ and Nd_2CuO_4 thin films by the pump and probe method from 1.3 to 2.8 eV with a time resolution of 100 fs. For both insulating samples, a bleaching signal with a 0.6–0.9 ps initial decay time was observed in the spectral range of the O_{2p} to Cu_{3d} charge-transfer transition at around 1.8 eV. This initial decay can be explained as a nonradiative transition through the successive emission of magnons having a comparably large energy quantum. In the photon-energy region lower than the bleaching signal, an induced absorption signal is observed. The origin of the induced absorption by pumping pulses has not necessarily been resolved, but the in-gap states induced by the photodoping effect is suggested as a reason.

I. INTRODUCTION

Recent remarkable progress in short-pulse laser technology enables us to investigate ultrafast relaxation phenomena in various materials, such as the initial stage of the defect formation in alkali halides mediated by self-trapped excitons,[1] and the initial relaxation process of photogenerated carriers in the semiconductor superlattice.[2] Metallic samples have also appeared as objects for optical investigation, because recent progress in the technique of femtosecond light-pulse generation and detection[3] enables us to observe the ultrafast relaxation of electrons even in metals.[4] For superconductors, the ultrafast relaxation in the initial stage of photoexcitation has been already investigated by several groups.[5–11] As yet there has not been any complete consistency or agreement among the proposed mechanisms used by the groups involved. Examples of such disagreement are the previously discussed electron-phonon interaction in the strong-coupling scheme or the lifetime of quasiparticles in nonequilibrium superconductivity, analyzing the data obtained by the pump and probe method. One of the reasons for such inconsistency is that most of the experiments were done using a pump and probe setup with single photon energy around 2 eV. For the insulating phase of the cuprates, few works were done to investigate the photodoping effect, comparing the results for insulating and superconducting phases.

Here we have carried out measurements of the differential absorption spectra on the insulating cuprates by the pump and probe method, with white light in the visible region. This technique is useful for identifying the origin of the electron transitions, and comparably clear-cut results are expected concerning the initial stage of electronic excitation in the highly correlated low-dimensional systems with magnetic excitation, which is characteristic of cuprates.

In this study, we present results on ultrafast relaxation dynamics of the charge-transfer (CT) excited state in $YBa_2Cu_3O_y$ and Nd_2CuO_4. With the pump pulses at 2.05 eV, we have already observed both photobleaching of the CT transition and induced absorption in the near IR (<1.6 eV) within 1 ps. Universal behavior of the time evolution was found for both cuprates at temperatures between 4.2 and 300 K. The possible mechanism giving rise to the nonradiative relaxation with the picosecond time scale will be discussed considering the strong coupling of the CT excited state with magnons.

II. EXPERIMENTAL

Transient absorption spectra with femtosecond time resolution of the insulating $YBa_2Cu_3O_{6.2}$ and Nd_2CuO_4 thin films were measured by the pump and probe method with a white light probe. The laser system consisted of a mode-locked dye oscillator and a four-stage dye amplifier excited by a Nd-YAG laser with a pulse compression system. The time duration and maximum energy of the output light pulse were about 100 fs and 200 μJ per pulse, respectively. The repetition rate was 10 Hz. The output laser beam was split into two, so that one beam was focused onto the D_2O cell to produce visible white light and the other beam for pumping. The pumping beam was passed through an optical delay and directed to the sample with an excitation energy of 20 mJ/cm^2. Crossed polarization between the pumping and probing beam was used to avoid a ghost of the pumping light. All measurements were done in the configuration of transmission. The probing light and the transmitted light were analyzed by two detection systems with polychromators and optical multichannel analyzers. The spectrum of the

transmitted light was divided by the probing light in a real-time operation and was accumulated several times for noise reduction. In all experiments, the photon energy of the pumping light was 2.05 eV.

The $YBa_2Cu_3O_y$ films were deposited by the chemical-vapor-deposition method on the MgO substrates at 800 °C for 30 min. The thickness of the samples was about 100 nm. At these conditions, they were *c*-axis oriented and epitaxially grown on the substrates. The superconducting transition temperature was about 85 K for as-grown samples, and oxygen-deficient samples were prepared by vacuum annealing, monitoring the resistivity at low temperatures. From the comparison with the transport and optical properties of the previously reported data, the oxygen content of the oxygen-deficient $YBa_2Cu_3O_y$ sample was estimated to be $y \cong 6.2$. On the other hand, the Nd_2CuO_4 sample was prepared by the laser ablation technique. Epitaxially grown *c*-axis-oriented samples of about 100 nm in thickness were prepared on the MgO substrate at 800 °C.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the absorption spectrum (shown by optical density D) in the insulating $YBa_2Cu_3O_{6.2}$ sample at 4.2 K as well as the differential absorption spectra (ΔD) for various delay times. The optical density (D) relates to optical conductivity $\sigma(\omega)$ by the relation $\sigma(\omega)=[n(\omega)(c/4\pi)\log_{10}e]\,D/d$, where $n(\omega)$ is the refractive index and d is the sample thickness. The optical density spectrum shows a peak at around 1.8 eV, which is the charge transfer (CT) transition from oxygen $2p$ to the copper $3d^9$-$3d^{10}$ upper Hubbard band in the CuO_2 plane. There are two different features in the differential absorption spectra. The most prominent signal is a photoinduced bleaching (PB) signal centered at 1.8 eV, which agrees with the CT transition of the peak in the optical density spectra. The spectral width (full width at half minimum) of the PB signal is about 1300 cm^{-1} being comparable to that of the two-magon Raman scattering signal.[12–14] The decay behavior of the induced bleaching will give us a lifetime of excited states created by the charge-transfer transition. In the lower photon energy region below 1.7 eV, the induced signal changes its sign from a bleaching signal ($\Delta D<0$) to an absorption signal ($\Delta D>0$). The origin of this photoinduced absorption (PA) signal is not clear, but as discussed later, it may be related to the so-called in-gap states induced by the pumping light pulse. We have also measured the induced spectra at 80 K. There is not a qualitative difference in the overall spectral features, as compared to the spectra measured at 4.2 K, for insulating $YBa_2Cu_3O_{6.2}$ samples.

Likewise, Fig. 1(b) shows the result on the Nd_2CuO_4 sample. There is a trace of charge-transfer excitation at around 1.7 eV in the optical density spectrum, which is similar to the insulating $YBa_2Cu_3O_y$ sample. The PB signal at 1.7 eV appears as a main signal of the spectra, which is essentially the same as $YBa_2Cu_3O_{6.2}$. The PA signal is also observed at a lower energy. The temporal behavior also seems to be similar to the case of $YBa_2Cu_3O_{6.2}$.

Figures 2(a)–2(c) shows the temporal behavior of ΔD signal of $YBa_2Cu_3O_{6.2}$ monitored at 2.5, 1.8, and 1.6 eV, respectively. The decay signal monitored at 2.5 eV that is higher than the CT gap energy shows a PB signal with a fast-decay component of 0.6 ps, whereas the signal monitored at the CT gap energy shows two-component decay. The fast-decay component of the PB signals has a

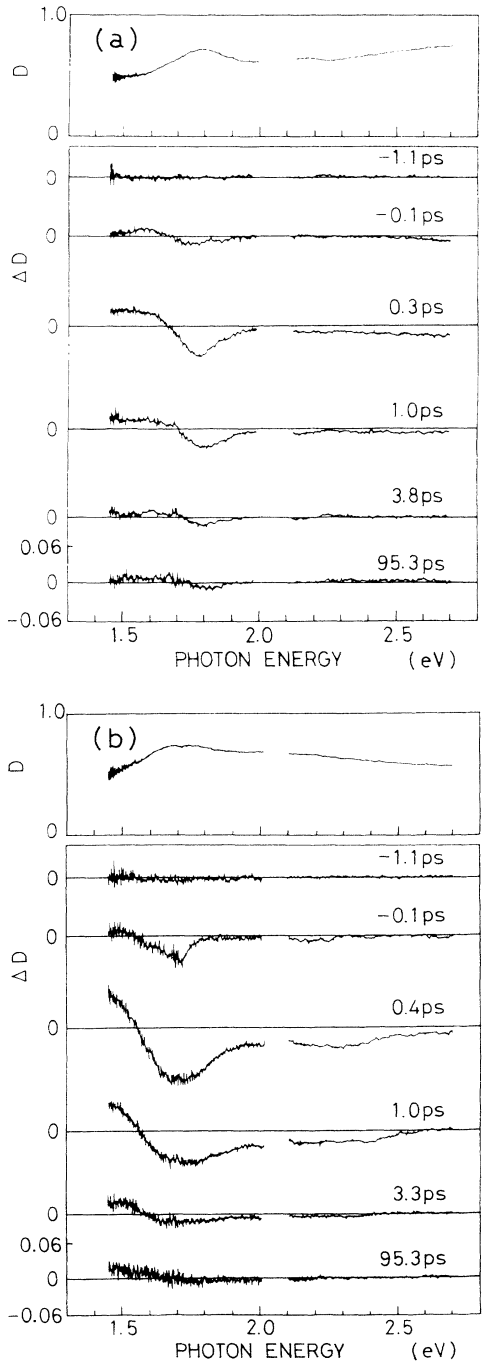

FIG. 1. (a) Delay-time dependence of transient absorption spectra of $YBa_2Cu_3O_{6.2}$ at 4.2 K. (b) Delay-time dependence of transient absorption spectra of Nd_2CuO_4 at 4.2 K.

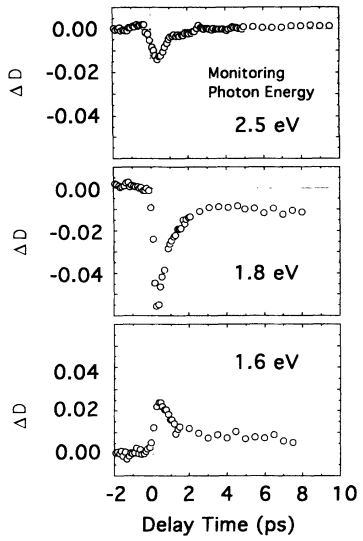

FIG. 2. Decay curves of transient absorption of $YBa_2Cu_3O_{6.2}$ at 4.2 K monitored at 2.5, 1.8, and 1.6 eV, respectively.

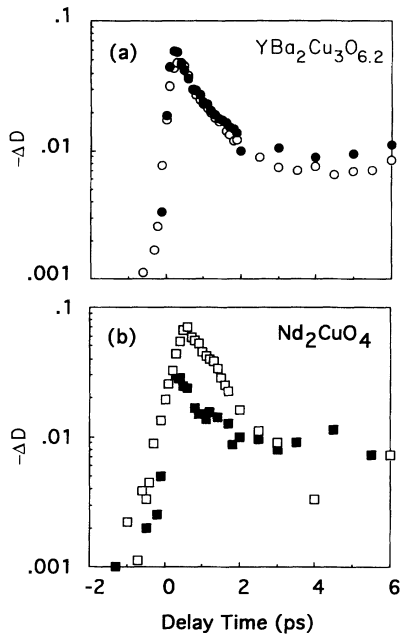

FIG. 3. (a) Decay curves of the PB spectra observed at the CT transition for $YBa_2Cu_3O_{6.2}$, at different temperatures. Open circles and filled circles in the figure denote the data at 4.2 and 77 K, respectively. (b) Decay curves of PB spectra observed at the CT transition for Nd_2CuO_4. Open squares and filled squares in the figure denote the data at 4.2 and 300 K, respectively.

decay time τ_d of 0.7 ps and the decay time of the slow component is longer than 100 ps. The decay constants of the PB signal do not change greatly at different energy levels. The decay behavior of the PA signal at 1.6 eV also exhibits the two-component decay. The decay time of the fast component is 0.7 ps and that of the slow-decay component is also longer than 100 ps. That is similar to the PB signal at 1.8 eV, but the polarity of the signal is inverse.

Next, we will make a qualitative analysis on the temporal behavior comparing the results obtained from the different samples and temperatures. Summarized in Figs. 3(a) and 3(b) are the temporal decay curves of $YBa_2Cu_3O_{6.2}$ and Nd_2CuO_4, measured at the CT transition peak and different temperatures. The decay curves show universal features irrespective of the kinds of materials and the temperatures. The fast-decay component has a decay time τ_d of 0.6–0.9 ps. This decay time is independent of temperature between 4.2 and 300 K. We should note that the decay behavior of Nd_2CuO_4 does not change even at a temperature higher than the Néel temperature of 240 K.

The decay time of the PB signal reflects the lifetime of the excited states, because it represents the decrease in the number of electrons in the ground state. In this case, the energy of the pumping light is just above that of the charge-transfer transitions, therefore, it is presumed that the excited state goes back to the ground state, with the decay time of the PB signal. This corresponds to the lifetime of the excited state of the charge-transfer excitation, i.e., $\tau_d = \tau_{CT}$. The relaxation time of 0.6–0.9 ps in $YBa_2Cu_3O_{6.2}$ and Nd_2CuO_4 is comparably fast, and radiative recombination can be excluded as an explanation for this recombination process. If it is an example of the nonradiative multiphonon process with weak coupling, the decay rate may be expressed by the energy-gap law,[15] i.e.,

$$\tau_d^{-1} = W_0 \exp(-\gamma \Delta / \hbar \Omega_0) , \quad (1)$$

where W_0, γ, Δ, and Ω_0 are zero-phonon transition rate, arithmetic factor of order 1, energy gap, and maximum photon energy, respectively. If we assume W_0 of order 10^{13} $\sec^{-1}$, $\Omega_0 \approx 1000$ cm^{-1}, and $\Delta \approx 2$ eV, we obtain τ_d of the order of μs. Therefore, the electron-phonon interaction should result in the strong-coupling case. Moreover, the decay time measured at 1.98 eV for both pump and probe pulses for insulating samples, which is reported in Fig. 2(a) of Ref. 5, shows weak temperature dependence. As temperature decreases, the decay time becomes slightly faster for temperatures from 10 to 150 K. This is contradictory to the case of the nonradiative recombination in the strong-coupling scheme, where there is a considerable magnitude of activation energy. Therefore, if the nonradiative recombination is due to the phonon process, it should be a case of strong coupling with small or no activation energy in the excited states. Remembering that the insulating cuprates are typically antiferromagnet, we should examine other possibilities for the nonradiative process that are accompanied by magnetic elementary excitation.

The excited state after CT excitation is the $Cu_{3d^{10}}$-O_{2p} (hole) state in the localized scheme. Here if the electron in the doubly occupied highest Cu d state is localized, the hole at the oxygen site is extended to form the Zhang-Rice singlet band.[16] Therefore, from the standpoint of Cu spins, it is essentially equal to the problem of one-hole doping to incomplete antiferromagnetic order. It is

known that antiferromagnetism is unstable for one-hole doping.[17] Thus if CT excitation occurs, the neighboring antiferromagnetic exchange interaction around the hole is turned off, and at the same time a large spin fluctuation should be inevitably induced on the spin system. In other words, magnon emission might be the most important channel through which the CT excited states could be relaxed nonradiatively to the ground state. In this way, it seems to be natural to consider that this mechanism of magnon emission should be the most suitable nonradiative decay channel for the charge-transfer excitation. It is well known that coupling between electronic excitation and magnetic excitation is very strong in this system, as was observed in the extraordinarily strong two-magnon line of Raman scattering.[12–14,21] Reflecting the large exchange interactions of the copper oxide, the energy quantum of the two-magnon is as large as 2650 cm^{-1}, so that the CT transition energy of 1.8 eV can be taken over by only 5 quanta of two-magnon excitation. This high-energy magnon corresponds to the zone-boundary magnon that plays an analogous role to optical phonon modes in the initial nonradiative decay mechanism from an optically excited state. The interpretation for the nonradiative relaxation with emission of magnons does not conflict with the observation of the same decay behavior for $T > T_N$ in Nd_2CuO_4, if we consider that the results of the Raman signal due to the two-magnon emission can be observed even at $T > T_N$. This is due to the fact that the antiferromagnetic spin fluctuation still exists if the temperature is not far from T_N.

To thermalize into the ground state, the energy of the emitted zone-boundary magnon should be taken over by many lower energy modes of magnons or phonons. Otherwise, it is probable that excitation back to the CT excited states will occur, and it may elongate the lifetime of the CT excited states. This condition seems to have been satisfied from the analysis of the two-magnon excitation lines of Raman scattering. As Knoll *et al.* discussed,[13] the spin excitation in the cuprates is drastically different from the conventional antiferromagnets, whose spin-excitation energy is less than that of typical optical-phonon energies. In the cuprates, the exchange energy is so high that the short-wavelength spin excitations have large energies that are more than twice that of the maximum phonon energy. Therefore, emission of optical phonons with comparably large energy is suggested for a large decay channel of the spin excitation. It is reflected as a short lifetime for spin excitation and small temperature dependence, as compared to those of the conventional antiferromagnets. The short lifetime of the zone-boundary spin excitation is estimated for RBaCuO (R=Eu,Y) as 29 and 5.8 fs at 10 and 600 K, respectively. This result justifies the prohibition of backward excitation noted above.

Contrary to the estimation by Raman scattering, Hayden *et al.* estimated[18] the lifetime of the zone-boundary magnon τ_m to be about 0.9 ps from the half width of the pulsed neutron-diffraction spectra of La_2CuO_4. There is a large discrepancy between this result and that of Raman scattering. However, considering that it is probable that this time scale is valid also for $YBa_2Cu_3O_y$ and Nd_2CuO_4, the backward excitation to the CT excited state is completed within 0.9 ps, which is the same order as the observed τ_{CT}=0.7–0.9 ps. Therefore, the magnon-relaxation mechanism is acceptable as a way of nonradiative relaxation of the CT excited state, even if the possibility of the backward excitation is taken into account.

Next we consider the PA signal with lower photon energies than that of the CT excitation. On the origin of the optical response of this range, some uncertainty still exists. If we consider that this transient optical response is a certain monitoring of the photodoping effect, optical conductivity of the doped sample is important as a reference.[19–21] If the sample is doped, the CT transition fades out as the doping level increases, and at the same time the Drude-like signal appears and is accompanied by non-Drude tails or so-called in-gap states that may extend up to the visible region. The latter in-gap state signal is clearly demonstrated in the La system,[20] but in the Y system there is some controversy over the existence of the isolated in-gap states.[21] These in-gap states are believed to be an excitation of the so-called Zhang-Rice singlet states,[16] which are accompanied by spin fluctuation of Cu d electrons. Regardless of the models, if the observed PA signal can be identified as in-gap states, the fast rise of the PA signal may represent the photocreation of the Zhang-Rice singlet states.

IV. CONCLUSIONS

We have investigated the transient absorption spectra of insulating $YBa_2Cu_3O_{6.2}$ and Nd_2CuO_4 thin films by the pump and probe method with 100-fs time resolution. For each sample, a PB signal was observed at the spectral range of the charge-transfer transition between O_{2p} and Cu_{3d} at 1.7–1.8 eV, and the spectral width of the CT band was also resolved. The relaxation time of the PB signal is as short as 0.6–0.9 ps at temperatures between 4.2 and 300 K. This short lifetime of the CT excited state indicates a very low-energy barrier between the relaxed excited state and the ground state in the configuration coordinate scheme, or the nonradiative transition, through the emission of magnons having comparably large energy quanta. In addition, the PA signal at lower photon energies than that in the CT gap suggests the formation of the in-gap state by femtosecond pulse irradiation.

To enable further discussion, it is indispensable that experimental information of different kinds of systems by various kinds of measurements are made available, as well as sophisticated theories which are not only effective to low-energy excited states but are able to include highly (optically) excited states. We should take into account the coexistence of electron- and holelike excitations (or quasiparticles) and their recombination processes on the highly correlated low-dimensional electronic system, such as photoexcited cuprates.[22,23] Femtosecond spectroscopy will be helpful for such investigations, if the progress of laser technology enables us to make experiments with higher time resolution and arbitrary changes of excitation and probing energies from the UV to the far-infrared region.

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