Pergamon

# FEMTOSECOND RESPONSE OF OPTICAL CONSTANTS DUE TO CHARGE-TRANSFER EXCITATIONS IN $Nd_2CuO_4$

M. Ichida [a,1], K. Hayakawa [a], K. Matsuda [a], A. Nakamura [a] and I. Hirabayashi [b]

[a] Center for Integrated Research in Science and Engineering, and Department of Applied Physics, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
[b] Superconductivity Research Laboratory, Nagoya Division, International Superconductivity Technology Center, 2-4-1, Mutsuno, Atsuta-ku, Nagoya 456-0023, Japan

We have performed femtosecond reflectivity $\Delta R/R$ and transmissivity $\Delta T/T$ measurements in $Nd_2CuO_4$ thin film at 80 and 300 K. We have derived time variations of $\Delta\epsilon'$ and $\Delta\epsilon''$ from transient data of $\Delta R/R$ and $\Delta T/T$. Assuming a Lorentz oscillator model consisting of three oscillators, we obtain spectra of the real part $\epsilon'$ and imaginary part $\epsilon''$ of dielectric function from the measured reflectivity and absorption spectra in the visible-uv region. The absorption bands in the visible region are assigned to in-plane charge-transfer (CT) excitations, and relaxation times of CT excitations are found to be 0.6 and 1.0 ps. © 1998 Elsevier Science Ltd. All rights reserved

## 1. INTRODUCTION

The advent of ultrafast laser spectroscopy has made it possible to observe ultrafast relaxation phenomena of photoexcited states in various materials in the femtosecond time region. The nonequilibrium dynamics of laser-heated conduction electrons in metals and superconductors is a fascinating area of intense research. The studies on ultrafast relaxation dynamics in superconducting cuprates have revealed the electron-phonon coupling strength, the Fermi energy position, the superconducting gap, and the lifetime of quasi-particles in nonequilibrium superconductivity [1–8]. In optical measurements, it is essential to obtain dielectric constants rather than reflectivity $R$ and transmissivity $T$, because the complex dielectric constant in the optical frequency region reflects electronic structures of materials. Brorson *et al.* have given attention to the time response of the imaginary part of dielectric constant $\epsilon''$ in the superconducting and insulating cuprates [2]. The electron-phonon coupling con-

stants were obtained for various high-$T_c$ superconductors with different transition temperatures using Allen's theory [9] which describe the relaxation rate of hot electrons. The Fermi level position has been also discussed from the sign of change in $\epsilon''$ within the frame work of the "Fermi energy smearing" model. For insulating phase, however, a few effort has been made to investigate relaxation dynamics of charge-transfer (CT) excitations from oxygen $2p$ orbitals to an upper Hubbard band (UHB). The CT excitation created by ultrashort optical pulses is relaxed into the ground state with emission of magnons within 1 ps [10, 11]. The dielectric function of insulating cuprates in the visible region is believed to be mainly governed by CT transitions. However, roles of different orbitals of plane oxygen atoms and magnons in optical transitions are not well understood.

In this paper, we have studied the ultrafast optical response of complex dielectric functions and relaxation process of CT excitaitons in $Nd_2CuO_4$ by means of femtosecond reflectivity and transmissivity measurements. We obtain spectra of real part $\epsilon'$ and imaginary part $\epsilon''$ of the dielectric function from the

[1] e-mail: ichida@nuap.nagoya-u.ac.jp

measured reflectivity and absorption spectra, and we derive changes in $\epsilon'$ and $\epsilon''$ by the CT band excitation with fs pump pulses. From these results we assign the absorption bands in the visible region to CT transitions associated with different orbitals, and show the ultrafast relaxation behaviors of the order of 1 ps.

## 2. EXPERIMENTAL SETUP

Thin-film samples of $Nd_2CuO_4$ were prepared by using a laser ablation technique. The thin film was epitaxially grown with c-axis orientation on a MgO substrate and the sample thickness was ~100 nm. We used a pump and probe method with single wavelength to measure fractional changes in both reflectivity $\Delta R/R$ and transmissivity $\Delta T/T$. The laser source was a passively mode-locked Ti-sapphire laser, and the wavelength and the pulse duration were 750 – 780 nm and 120 fs, respectively. The repetition rate and the average power were 76 MHz and 500 mW, respectively. The output beam was split into pump and probe beams with a beam splitter. The pump beam with the average power of ~50 mW was focused onto a spot of 100 $\mu$m diameter, and the average power of the probe beam was ~5 mW. The pump beam was perpendicularly polarized to the probe beam to avoid a coherent artifact in the signal and to reject a stray of the pumping light. Changes in optical constants were detected by a lock-in amplifier with a silicon photodiode and time evolutions were measured as a function of the pump-probe delay times using a variable delay line.

## 3. RESULTS AND DISCUSSION

Figure 1(a) shows the reflectance and the absorption spectra in $Nd_2CuO_4$ thin film at 80 K. In the absorption spectrum, we see three absorption bands; the band around 1.7 eV is assigned to the CT transition from the oxygen 2$p$ band to the copper 3$d$ upper Hubbard band in the $CuO_2$ plane [12]. The origin of the broad absorption bands around ~ 2.2 eV and ~ 3.4 eV have not been well understood.

Here, we tentatively assign these bands to the in-plane CT transitions, and the origin will be discussed later in more detail considering the results of the femtosecond pump and probe experiments.

We analyze the optical spectra assuming a Lorentz oscillator model. The complex dielectric function is described as

$$\epsilon(\omega) = \epsilon_0 + \sum_j \frac{\omega_p^2 f_j}{\omega_j^2 - \omega^2 - i\gamma_j\omega}, \qquad (1)$$
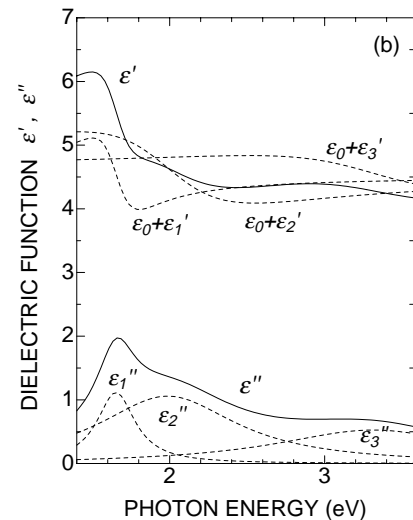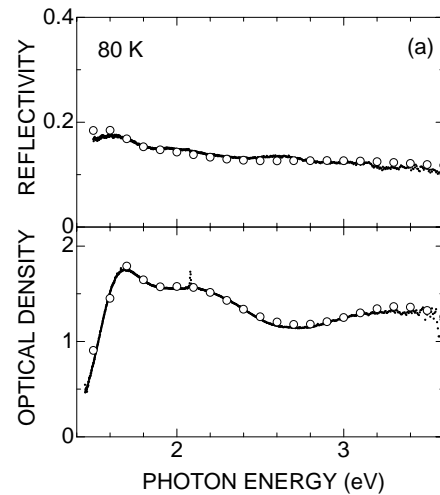


Fig. 1. (a) Absorption and reflection spectra of $Nd_2CuO_4$ thin film at 80 K. The model calculations are shown by open circles with the fitting parameters listed in Table 1. (b) $\epsilon'$ and $\epsilon''$ spectra derived from the fitting analysis of reflectivity and absorption spectra. Components due to the $j = 1$ ($\epsilon_1'$, $\epsilon_1''$), 2 ($\epsilon_2'$, $\epsilon_2''$), and 3 ($\epsilon_3'$, $\epsilon_3''$) oscillators are displayed by the broken curves: $\epsilon' = \epsilon_0 + \epsilon_1' + \epsilon_2' + \epsilon_3'$ and $\epsilon'' = \epsilon_1'' + \epsilon_2'' + \epsilon_3''$. $\epsilon_0$ is the background dielectric constant.

Table 1. The best fitted parameters of reflection and absorption spectra in Fig. 1(a). Parameters $\omega_j$, $\omega_p$, $f_j$, and $\gamma_j$ are the resonant energy, the plasma frequency, the oscillator strength, and the damping constant of the $j$-th oscillator, respectively. The frequency-independent dielectric constant $\epsilon_0$ was taken as 4.5

| $j$ | $\omega_j$(eV) | $\omega_p^2 f_j$ | $\gamma_j$(eV) |
|---|---|---|---|
| 1 | 1.66 | 0.55 | 0.30 |
| 2 | 2.06 | 2.33 | 1.10 |
| 3 | 3.40 | 2.70 | 1.55 |

where $\epsilon_0$ is the frequency-independent term, and $\omega_p$, $f_j$, $\omega_j$, and $\gamma_j$ are the plasma frequency, the oscillator strength, the resonant frequency, and the damping constant of the $j$-th oscillator, respectively. The real and imaginary parts of the dielectric constant, $\epsilon'$ and $\epsilon''$ are written by

$$\epsilon' = n^2 - \kappa^2, \tag{2}$$

$$\epsilon'' = 2n\kappa, \tag{3}$$

where $n$ and $\kappa$ are the refractive index and the extinction coefficient, respectively. The normal-incidence reflectivity, $R$, can be described by

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}. \tag{4}$$

The transmissivity is written by

$$T = (1-R)^2 \exp(-\alpha L), \tag{5}$$

where $\alpha = 4\pi\kappa/\lambda$ is an absorption coefficient at wavelength $\lambda$, and $L$ is a sample thickness. We neglected the effect of multiple reflection in the thin film and the contribution of the substrate, because the optical density ($\alpha L$) is larger than unity in the spectral region studied here. Using these formula, we can calculate reflection and absorption spectra with the assumption of three different oscillators. The calculated spectra are illustrated by the open circles in Fig. 1(a) and the fitting parameters are listed in Table 1. Both reflectivity and absorption spectra are well reproduced by the three-oscillator model. Shown in Fig. 1(b) are $\epsilon'$ and $\epsilon''$ spectra and the contributions of these oscillators are displayed in the figure. The peak values of $\epsilon'$ and $\epsilon''$ at 1.65 eV are 5.7 and 2.0, respectively, which are in good agreement with the values in the literature [13]. We note that around the $j = 1$ oscillator peak (CT band) in the $\epsilon''$ spectrum, the contribution of $j = 3$ oscillator is very small, whereas all three oscillators contribute to the $\epsilon'$ spectrum below $\sim 2$ eV except for the resonance energies of the $j = 1$ and 2 oscillators. For example, $\epsilon_1' = 0.3$, $\epsilon_2' = 0.7$, $\epsilon_3' = 0.4$ for 1.60 eV, and $\epsilon_1' = 0.1$, $\epsilon_2' = 0.7$, $\epsilon_3' = 0.3$ for 1.65 eV.

Figure 2(a) shows $\Delta R/R$ and $\Delta T/T$ signals measured at 1.65 eV as a function of delay times at 80 K. The positive $\Delta T/T$ coincides with the result of
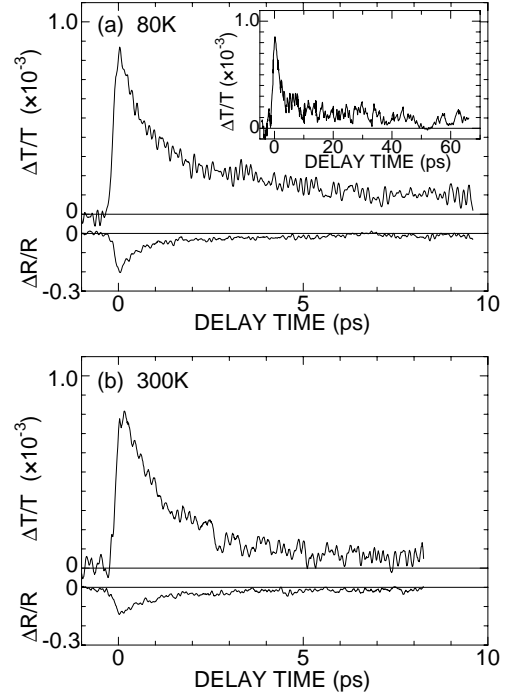


Fig. 2. Decay curves of the fractional change in the reflectivity $\Delta R/R$ and in the the transimissivity $\Delta T/T$ at 80 K (a) and 300 K (b). Inset: Decay curves of $\Delta T/T$ at 80K in an extended time scale.

the photo-induced bleaching of the CT band which was observed by the pump-probe spectroscopy using a white continuum light as a probe light [10]. The negative $\Delta R/R$ is opposite to that observed for superconducting Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$ [7], which indicates that the optical response after the intense pulse excitation is strongly depend on the the electronic structure. As seen in Fig. 2(a) and the inset, both $\Delta T/T$ and $\Delta R/R$ signals exhibit a two-component decay. The fast and slow decay times of $\Delta T/T$ are $\sim 1$ ps and $\gtrsim 100$ ps, respectively. The fast decay component of $\Delta R/R$ has a decay time of $\sim 0.6$ ps and that of the slow component is $\gtrsim 100$ ps. The observed temporal behaviors are in good agreement with our previous results, the relaxation process is ascribed to the nonradiative relaxation of CT excitation with emission of magnons [10]. The decay behavior is almost independent of temperatures below and slightly above the Néel temperature (240 K), as shown in Fig. 2(b). This result is explained in terms of antiferromagnetic spin fluctuations existing around the Néel temperature [10].

We now derive changes in dielectric constant ($\Delta\epsilon'$ and $\Delta\epsilon''$) from the measured $\Delta R/R$ and $\Delta T/T$. $\Delta R/R$ and $\Delta T/T$ can be expressed as [2]

$$\frac{\Delta R}{R} = \alpha_1 \Delta \epsilon' + \alpha_2 \Delta \epsilon'', \quad (6)$$

$$\frac{\Delta T}{T} = \beta_1 \Delta \epsilon' + \beta_2 \Delta \epsilon''. \quad (7)$$

$\alpha_i$ and $\beta_i$ ($i = 1, 2$) are transformation parameters which can be calculated from the dielectric constant. Taking the values of 5.7 for $\epsilon'$ and 2.0 for $\epsilon''$ at 1.65 eV (Fig. 1(b)), we obtain $\alpha_1 = 0.13$, $\alpha_2 = 0.09$, $\beta_1 = 0.15$, and $\beta_2 = -1.00$. Using Eqs. (6) and (7), we convert the observed time variations of $\Delta R/R$ and $\Delta T/T$ into those of $\Delta \epsilon'$ and $\Delta \epsilon''$. As shown in Fig. 3 the temporal behaviors of $\Delta \epsilon'$ and $\Delta \epsilon''$ exhibit a two-component decay. The decay time of the fast component of $\Delta \epsilon'$ is 0.6 ps, while that of $\Delta \epsilon''$ is 1 ps. The different decay behaviors of $\Delta \epsilon'$ and $\Delta \epsilon''$ suggest that origins of $\Delta \epsilon'$ and $\Delta \epsilon''$ are not the same. As the excitation photon energy corresponds to the resonance energy of the $j = 1$ oscillator, i.e., the CT transition, the $j = 1$ and 2 oscillators cause a change of $\epsilon''$ (see Fig. 1(b)). As the $\epsilon'$ value of the $j = 2$ oscillator ($\epsilon_2'$) is about two times larger than that of the $j = 3$ oscillator, $\Delta \epsilon'$ is mainly governed by the $j = 2$ oscillator, and the decay time of $\Delta \epsilon'$ (0.6 ps) corresponds to the relaxation time of the $j = 2$ oscillator. Taking into account the different decay behaviors between $\Delta \epsilon'$ and $\Delta \epsilon''$, we attribute $\Delta \epsilon''$ to the $j = 1$ oscillator, i.e., CT excitation. The decay time of $\Delta \epsilon''$ is in good agreement with the recovery time of the bleaching of the CT band [10]. Such a fast relaxation of CT excitation is interpreted in terms of the nonradiative relaxation with emission of magnons in the antiferromagnetic phase.

Now, we discuss the origin of the $j = 2$ oscillator with the resonance energy of 2.06 eV. As the decay behavior of the $j = 2$ oscillator is different from the CT band at 1.7 eV, the assignment to the magnon-assisted transition of the $j = 1$ oscillator is ruled out. If it were the magnon sideband, the decay time should be the same. In the insulating YBa$_2$Cu$_3$O$_6$, three absorption bands observed at 1.7, 2.1 and 2.5 eV are assigned to the CT excitations from the band consisting of the O(2)$p_x$ (or $p_y$) and O(3)$p_x$ (or $p_y$) orbitals to the upper Hubbard band with the Cu(2)$d_{x^2-y^2}$ character [14, 15]. As shown in fig. 4 of Ref. [14], these transitions are in-plane transitions and the participating bands have no contribution from the Ba or O(4) orbitals. Keeping in mind this assignment for YBa$_2$Cu$_3$O$_6$, the $j = 2$ oscillator is attributable to the in-plane CT excitation which involves orbitals different from the CT excitation of the $j = 1$ oscillator. The bands which contribute to the excitations corresponding to the $j = 1$ and 2 oscillators have O(2)$p_x$ (or $p_y$), O(3)$p_x$ (or $p_y$) and Cu(2)$d_{x^2-y^2}$ character.
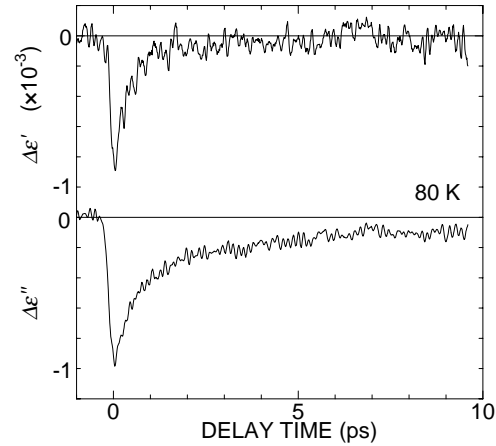


Fig. 3. Decay curves of the fractional change in the real part of the dielectric constant $\Delta \epsilon'$ and in the imaginary part of the dielectric constant $\Delta \epsilon''$ at 80 K.

## 4. CONCLUSIONS

We have investigated the ultrafast optical response in Nd$_2$CuO$_4$ thin film by means of the fs pump and probe method. The absorption and reflectivity spectra in the visible-UV region were analyzed assuming three oscillators, and $\epsilon'$ and $\epsilon''$ spectra were obtained. Using the $\epsilon'$ and $\epsilon''$ spectra and the formula of optical constants, we derived the time evolutions of $\Delta \epsilon'$ and $\Delta \epsilon''$, and the decay times of $\Delta \epsilon'$ and $\Delta \epsilon''$ were found to be 0.6 and 1 ps, respectively. From these results we assign the transitions at 1.66 and 2.06 eV to the in-plane CT transitions from the O(2) and O(3) $2p$ orbitals to the upper Hubbard band (Cu(2)$d_{x^2-y^2}$). The relaxation times of 1.66 and 2.06 eV bands are 1.0 and 0.6 ps, respectively, and they are governed by the nonradiative relaxation with emission of magnons.

## REFERENCES

1. Brorson, S.D., Kazeroonian, A., Moodera, J.S., Face, D.W., Cheng, T.K., Ippen, E.P., Dresselhaus, M.S. and Dresselhaus, G., *Phys. Rev. Lett.*, **64**, 1990, 2172.
2. Brorson, S.D., Kazeroonian, A., Face, D.W., Cheng, T.K., Doll, G.L., Dresselhaus, M.S., Dresselhaus, G., Ippen, E.P., Venkatesan, T., Wu, X.D. and Inam, A., *Solid State Commun.*, **74**, 1990, 1305.
3. Eesley, G.L., Heremans, J., Meyer, M.S., Doll, G.L. and Liou, S.H., *Phys. Rev. Lett.*, **65**, 1990, 3445.
4. Chwalek, J.M., Uher, C., Whitaker, J.F., Mourou, G.A., Agostinelli, J. and Lelental, M., *Appl. Phys. Lett.*, **57**, 1990, 1696.
5. Han, S.G., Vardeny, Z.V., Symko, O.G. and Koren, G., *IEEE Trans. Magn.*, **27**, 1991, 1548.
6. Gong, T., Zheng, L.X., Xiong, W., Kula, W., Kostoulas, Y., Sobolewski, R. and Fauchet, P.M. *Phys. Rev. B*, **47**, 1993, 14495.
7. Liu, Y., Whitaker, J.F., Uher, C., Peng, J.-L., Li, Z.Y. and Greene, R.L., *Appl. Phys. Lett.*, **63**, 1993, 979.
8. Shi, L., Gong, T., Xiong, W., Weng, X., Kostoulas, Y., Sobolewski, R. and Fauchet, P.M., *Appl. Phys. Lett.*, **64**, 1994, 1150.
9. Allen, P.B., *Phys. Rev. Lett.*, **59**, 1987, 1460.
10. Matsuda, K., Hirabayashi, I., Kawamoto, K., Nabatame, T., Tokizaki, T. and Nakamura, A., *Phys. Rev. B*, **50**, 1994, 4097.
11. Matsuda, K., Ichida, M., Nakamura, A., Kawamoto, K., Nabatame, T. and Hirabayashi, I., *Physica C*, **280**, 1997, 84.
12. Tokura, Y., Koshihara, S., Arima, T., Takagi, H., Ishibashi, S., Ido, T. and Uchida, S., *Phys. Rev. B*, **41**, 1990, 11657.
13. Kelly, M.K., Barboux, P., Tarascon, J.M. and Aspnes, D.E., *Phys. Rev. B*, **40**, 1989, 6797.
14. Heyen, E.T., Kircher, J. and Cardona, M., *Phys. Rev. B*, **45**, 1992, 3037.
15. Kircher, J., Kelly, M.K., Rashkeev, S., Alouani, M., Fuchs, D. and Cardona, M., *Phys. Rev. B*, **44**, 1991, 217.