Femtosecond Spectroscopy of $YBa_2Cu_3O_{7-\delta}$: Electron-Phonon-Interaction Measurement and Energy-Gap Observation

S. V. Chekalin, V. M. Farztdinov, V. V. Golovlyov, V. S. Letokhov, Yu. E. Lozovik, Yu. A. Matveets, and A. G. Stepanov

Institute of Spectroscopy, U.S.S.R. Academy of Sciences, 142092 Troitsk, Moscow Region, U.S.S.R.

(Received 8 April 1991)

The femtosecond dynamics of reflection and transmission spectra of a $YBa_2Cu_3O_{7-\delta}$ film have been studied in the wavelength range 620–680 nm at initial temperatures T_0 both above and below the critical temperature T_c. A difference has been found to exist between the spectral responses for $T_0 < T_c$ and $T_0 > T_c$, which can be attributed to the presence of an energy gap in the spectrum at $T_0 < T_c$. Based on the experimental data, the electron-phonon-interaction parameter $\lambda\langle\omega^2\rangle$ has been estimated as $(4 \pm 2) \times 10^2$ meV^2.

PACS numbers: 74.30.Gn, 74.70.Vy, 78.20.Nv, 78.47.+p

Real-time studies of the relaxation of charge carriers in oxide superconductors can help to obtain unique information about the nature of superconductivity in such materials, particularly the role of the electron-phonon interaction. In the works reported in Refs. [1–5], there was investigation of the femtosecond charge-carrier dynamics in cuprates using a single wavelength for both pump and probe pulses. In this work, we have studied the femtosecond dynamics of the difference reflection and transmission spectra of a $YBa_2Cu_3O_{7-\delta}$ film in the spectral range 620–680 nm at initial temperatures T_0 above and below the critical temperature T_c. The spectral dependence of the response has been found to reverse sign in the vicinity of the Fermi level. The spectra obtained with delay times between the pump and probe pulses of less than 1 ps at $T_0 < T_c$ differ drastically from those at $T_0 > T_c$, which is believed to be associated with the dynamics of destruction of superconductivity upon the heating of the sample from $T_0 < T_c$ by a high-power femtosecond pulse.

Studying the time history of electron-phonon relaxation throughout the spectral range has allowed us to estimate the electron-phonon interaction parameter [6,7] $\lambda\langle\omega^2\rangle$ as $(4 \pm 2) \times 10^2$ meV^2.

The sample under study was a 150-nm-thick $YBa_2Cu_3O_{7-\delta}$ film deposited on a $SrTiO_3$ substrate and coated with a protective MgO layer 5 nm in thickness. The superconducting and protective layers were grown by high-frequency magnetron sputtering in a single production cycle. The crystallites in the superconducting layer were around 300 nm across, their c axis being oriented normal to the substrate surface. The critical temperature T_c was equal to 80 K.

The sample was excited with a 150-fs laser pulse at 612 nm. The pump pulse intensity on the sample was some 10^{11} W/cm^2. The excited sample area was probed with a weak wide-band continuum pulse of the same duration. The probe pulse that passed through (or reflected from) the sample was detected with a multichannel optical analyzer built around two charge-coupled-device arrays. In our experiment, we measured the difference spectrum $\Delta A(\lambda, \tau)$ at various delay times τ between the pump and probe pulses.

In Fig. 1, which shows some of the experimental difference transmission spectra, one can see the drastic difference between the results for $T_0 > T_c$ and $T_0 < T_c$.

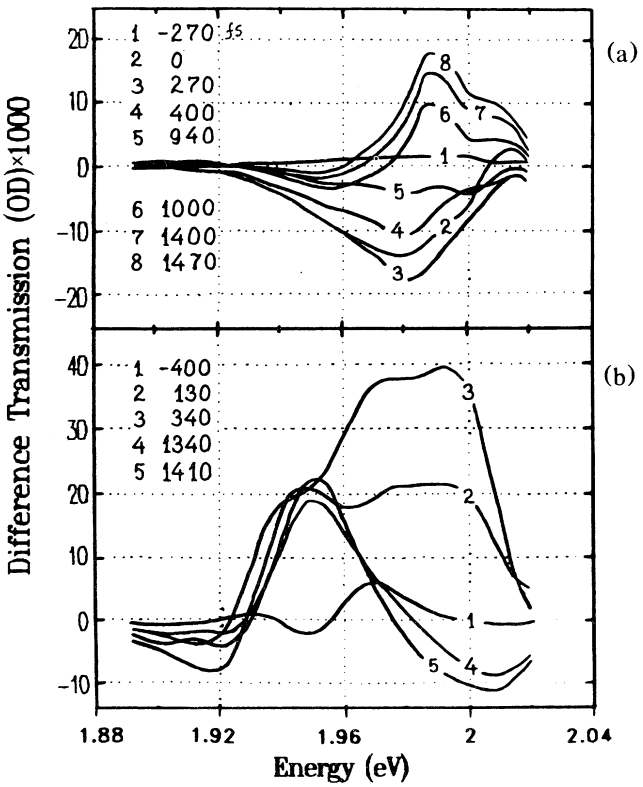

FIG. 1. Difference transmission spectra of the sample for various delay times τ (fs) of the probe pulse: (a) $T_0 = 92$ K, (b) $T_0 = 70$ K. The delay times are presented for an energy of 1.96 eV. The delay of the blue-wing probe continuum (2.02 eV) relative to its red-wing counterpart (1.9 eV) is no more than 60 fs.

While transmission in the former case is observed to decrease during the pump pulse over the entire spectral range under study [Fig. 1(a)], it grows in the region 1.93–2.01 eV in the latter case, there being only a slight drop in transmission in the range 1.89–1.93 eV [Fig. 1(b)]. With the delay time between the pump and probe pulses amounting to around a picosecond, a quasiequilibrium sets in, so that fast ($\simeq$100 fs) changes in the spectra cease. The only difference in the observation conditions between the spectra of Figs. 1(a) and 1(b) was that between the initial temperatures of the samples, and so it is reasonable to suppose that the changes the spectra are seen to undergo at $\tau < 1$ ps [Fig. 1(b)] contain information on the dynamics of destruction of the energy gap as a result of the sample being heated by the powerful femtosecond laser pulse.

Figure 2 shows the relationship between the optical density of the difference transmission spectra ΔA and the delay time τ for the most typical regions. The zero delay time was determined from the results of independent experiments with a semiconductor-doped glass filter RG-8. At $T_0 = 92$ K (Fig. 2, curve *a*), the shape of the curves remains qualitatively the same throughout the spectral range of interest: ΔA is seen to decrease for a characteristic time of the order of 100 fs and then relax during $\tau \leq 1$ ps. The difference between the curves for various regions of the spectrum is that the asymptotic value of ΔA is less than zero at $\hbar\omega < 1.96$ eV and greater than zero at $\hbar\omega > 1.96$ eV. Similar curves, though relaxing to $\Delta A \simeq 0$, were observed at $T_0 = 70$ K for $\hbar\omega < 1.93$ eV (Fig. 2, curve *b*). The curves for $\hbar\omega > 1.93$ eV at this temperature reversed sign (Fig. 2, curve *c*); i.e., ΔA was first observed to increase and then relax to various asymptotic values, depending on wavelength. The relaxation of ΔA in the vicinity of $\hbar\omega = 1.96$ eV was nonmonotonic: Two to three ΔA oscillations were observed to occur on a 300–500-fs scale. More pronounced oscillations in the transient transmissivity profile were observed in Ref. [2] only for a nonsuperconducting $YBa_2Cu_3O_{6+x}$ sample and were explained by the pulsed generation of optical phonons. An essential feature of the curves obtained at $T_0 < T_c$ is the delay of the response for $\simeq$200 fs in the region of 1.93 eV (Fig. 2, curve *c*), compared to that in the region of 1.91 eV (Fig. 2, curve *b*) and the response at $T_0 > T_c$ (Fig. 2, curve *a*). The magnitude of this delay is roughly 3 times the relative lag of the various spectral components of the probe pulse, observed to occur in the experiment as a result of dispersion.

To recover $\Delta\epsilon_2$ from the difference transmission and

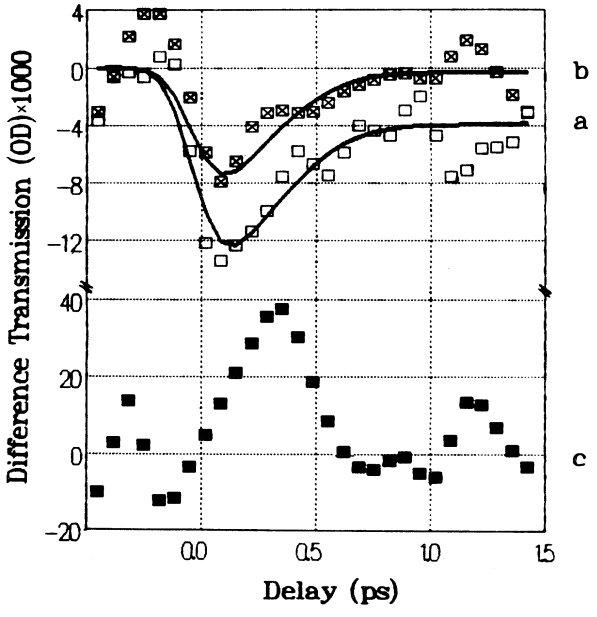

FIG. 2. Difference transmission of the sample as a function of delay time for various photon energies of the probe pulse, $\hbar\omega$ (eV): Curve *a*, $T_0 = 92$ K, $\hbar\omega = 1.95$ eV; curve *b*, $T_0 = 70$ K, $\hbar\omega = 1.91$ eV; curve *c*, $T_0 = 70$ K, $\hbar\omega = 1.98$ eV. The curves are the numerical fits to the experimental data for $\lambda\langle\omega^2\rangle = 450$ meV^2, $C_e = 16$ mJ/mol K^2, and $I_p = 2\times10^{11}$ W/cm^2.

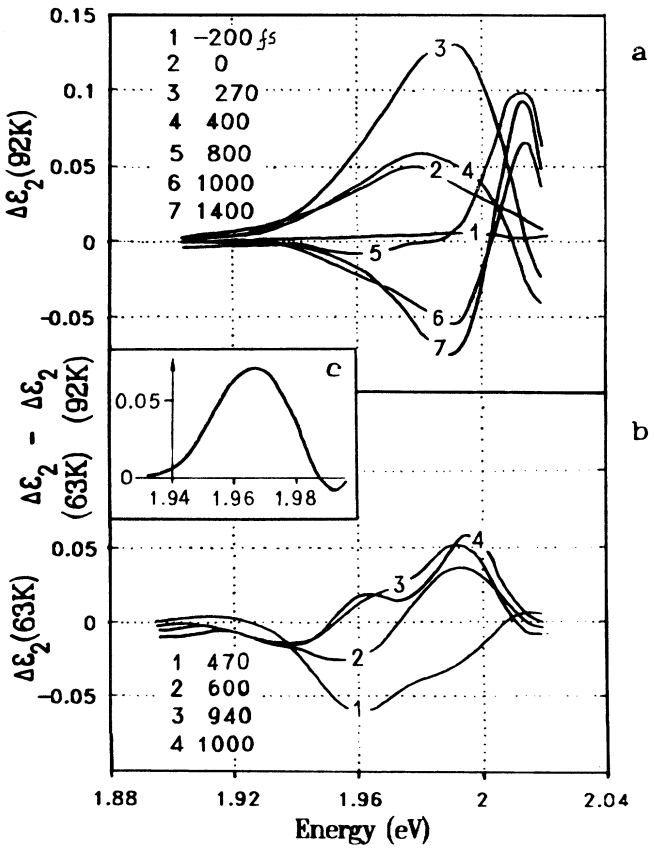

FIG. 3. Difference spectra of the imaginary part of the dielectric constant ϵ_2 for various delay times τ (fs) of the probe pulse: (a) $T_0 = 92$ K, (b) $T_0 = 68$ K, (c) the result of subtracting the spectra of $\Delta\epsilon_2$ for $T_0 = 63$ K and $T_0 = 92$ K ($\tau = 1000$ fs).

reflection spectra, use was made of ellipsometric data on the equilibrium dielectric constant, ϵ_1 and ϵ_2, of $YBa_2Cu_3O_{7-\delta}$ [8]. The difference spectra of $\Delta\epsilon_2$ are shown in Figs. 3(a) and 3(b). As can be seen from the figures, the spectra for $T_0 > T_c$ again differ greatly from those for $T_0 < T_c$. At $\tau \geq 700$ fs, the spectral dependence of the response for $T_0 = 92$ K becomes alternating: $\Delta\epsilon_2 < 0$ for $\hbar\omega \leq 1.99$ eV and $\Delta\epsilon_2 \geq 0$ for $\hbar\omega \geq 1.99$ eV. Subsequently, starting from $\tau \simeq 1$ ps, the shape of the spectrum ceases to change—it remains alternating, with $\Delta\epsilon_2 = 0$ at $\hbar\omega = 2$ eV [Fig. 3(a)]. An alternating response is characteristic of the spectral range corresponding to transitions either into or out of the Fermi level region [9,10] and is associated with the temperature smearing of the charge-carrier distribution function in the vicinity of the Fermi level. The position of the Fermi level in the spectral region $\hbar\omega \simeq 2$ eV agrees with the data of Ref. [4]. The decrease of transmission (ϵ_2 rise) for short delay times over a wide spectral range [Fig. 3(a)] is to all appearances due to the shift of the Fermi level as a result of strong heating of the charge carriers. The absence of any substantial changes in the $\Delta\epsilon_2$ spectrum at $\tau \geq 1$ ps points to the establishment of a quasiequilibrium. By this moment, the temperature of the sample reaches 500 K, and the system loses its memory of the initial conditions, so that the difference of a mere 30 K between the initial temperatures cannot bring about any significant dissimilarities in the spectra of the excited sample. It can therefore be argued that the diversities observed in the difference spectra at $\tau \geq 1$ ps [see Figs. 3(a) and 3(b)] can only result from the differences between the spectra of the sample in the initial (unexcited) state. This can be explained by the presence of an energy gap in the vicinity of the Fermi level for $T_0 = 63$ K and the shift of this level because of the difference between the T_0 values.

Subtracting the difference spectrum $\Delta\epsilon_2$ for $T_0 = 92$ K at $\tau = 1$ ps from that for $T_0 = 63$ K, we obtain a peak about 30 ± 10 meV wide in the neighborhood of 1.97 eV [Fig. 3(c)]. Relating the width of this peak to the width Δ of the energy gap (in a way similar to that used in the experiments on photoelectron spectroscopy [11,12]), we get $2\Delta_0/T_c = 8 \pm 3$, which agrees well with the data reported in Ref. [11].

The presence of an energy gap in the initial state can also explain the lag of the optical response maximum observed to occur for $T_0 < T_c$ in the vicinity of the Fermi level. The magnitude of this lag ($\simeq 200$ fs) matches the time it takes for superconductivity to be destructed (see also Ref. [5]).

The experimental curves of Fig. 2 were used to estimate the electron-phonon-interaction parameter $\lambda\langle\omega^2\rangle$ as follows. The dielectric constant of the sample varies as a result of the heating of charge carriers and the shifting of energy bands due to the heating of the lattice and thermoelasticity effects. Within the framework of linear response, this variation (the change of transmission in our case) can be represented in the form [13] $\Delta A \simeq a\Delta T_e(t) + b\Delta T_L(t)$, where T_e is the charge-carrier temperature and T_L the lattice temperature. To calculate the dynamics of ΔA, the temporal variations of T_e and T_L were determined from the set of equations [7,13]

$$dT_e/dt = [(1 - R_f - T_f)/L_{sc}C_e(T_e)]I_p(t) - \gamma(T_e, T_L)(T_e - T_L), \quad (1)$$

$$dT_L/dt = \gamma(T_e, T_L)[C_e(T_e)/C_L(T_L)](T_e - T_L) - (1/\tau_{esc})(T_L - T_0), \quad (2)$$

where R_f is the reflectivity of the multilayer system, T_f the transmissivity of the superconductor layer, L_{sc} the superconductor layer thickness, I_p the pump pulse intensity, C_e and C_L the electronic and lattice heat capacities, and τ_{esc} the time it takes for phonons to escape into the substrate.

According to Allen [7], the electron-phonon relaxation rate is described by the expression ($\hbar = 1$, $k_B = 1$)

$$\gamma(t_e, T_L) = (3/\pi T_e)\lambda\langle\omega^2\rangle(1 - \langle\omega^4\rangle/12\langle\omega^2\rangle T_e T_L). \quad (3)$$

According to the calculation results on the band structure of $YBa_2Cu_3O_{7-\delta}$ (Refs. [14,15]), the energy interval from -6 to $+2$ eV relative to the Fermi level contains a 36-band complex made up of highly hybridized Cu $3d$ and O $2p$ states. Transitions across the forbidden gap in the electronic band structure start from an energy of around 3 eV. For this reason, it can be assumed that practically all of the absorbed pump pulse energy goes to the heating of the charge carriers. The quantity τ_{esc} can be estimated as ≥ 10 ps. For $C_L(T)$, we interpolated the data reported in Refs. [16,17]. The data for $C_e = \gamma T$ differ greatly (from 13 to 54 mJ/mol K) [14,18], and this contributes the most to the error in determining $\lambda\langle\omega^2\rangle$. According to our calculation results, the maximum temperature of charge carriers reaches some 3000 K. The maximum temperature of the lattice is around 600 K. The theoretical functions $\Delta A(t)$, calculated with due regard for the Gaussian shape of the pump and probe pulses, were compared to the experimental curves (see Fig. 2). Comparison was made for the spectral range 1.92–1.95 eV far from the Fermi level in order to avoid the possible nonlinear effects associated with the shift of the level as a result of strong heating of electrons. The parameters a and b were selected so as to make the calculated curves approximate the experimental data for the maximum ($\tau \simeq 100$ fs) and asymptotic ($\tau \geq 1$ ps) values, the temporal behavior of the experimental curves being approximated by means of the parameter $\lambda\langle\omega^2\rangle$. The resultant estimate is $\lambda\langle\omega^2\rangle = (4 \pm 2) \times 10^2$ meV^2. Using for $\langle\omega^2\rangle$ the estimate $\langle\omega^2\rangle = \Theta_D^2/2$ and taking the Debye temperature Θ_D as 350 K [17], we get the following esti-

mate for the electron-phonon coupling constant: $\lambda = 0.9 \pm 0.4$. Our data fit the results of the femtosecond pump-probe measurements [7] and the value of $\lambda \simeq 1$ found in Ref. [19] by the local-density-functional method.

We would like to thank M. E. Gershenzon and M. I. Falei for kindly providing the samples, I. B. Kedich and A. P. Yartsev for their assistance in the experiment, and also L. B. Kislichenko for her aid in calculations.

[1] S. D. Brorson, A. Kazeroonian, J. S. Moodera, D. W. Face, T. K. Cheng, E. P. Ippen, M. S. Dresselhaus, G. Dresselhaus, G. L. Doll, T. Venkatesan, X. D. Wu, and A. Inam, in *Ultrafast Phenomena VII,* edited by C. B. Harris, E. P. Ippen, G. A. Mourou, and A. H. Zewail (Springer-Verlag, Berlin, 1990), p. 354.

[2] J. M. Chwalec, C. Uher, J. F. Whitaker, G. A. Mourou, J. Agostinelli, and M. Lelental, Appl. Phys. Lett. **57**, 1696 (1990); J. M. Chwalec, C. Uher, J. F. Whitaker, G. A. Mourou, and J. Agostinelli, Appl. Phys. Lett. **58**, 980 (1990).

[3] S. G. Han, Z. V. Vardeny, K. S. Wong, O. G. Symko, and G. Koren, Phys. Rev. Lett. **65**, 2708 (1990).

[4] S. D. Brorson, A. Kazeroonian, D. W. Face, T. K. Cheng, G. L. Doll, M. S. Dresselhaus, G. Dresselhaus, E. P. Ippen, T. Venkatesan, X. D. Wu, and A. Inam, Solid State Commun. **74**, 1305 (1990); A. Kazeroonian, T. K. Cheng, S. D. Brorson, E. P. Ippen, X. D. Wu, T. Venkatesan, S. Etemad, M. S. Dresselhaus, and G. Dresselhaus, Solid State Commun. **78**, 95 (1991).

[5] G. L. Eesley, J. Heremans, M. S. Meyer, G. L. Doll, and S. H. Liou, Phys. Rev. Lett. **65**, 3445 (1990).

[6] G. M. Eliashberg, Zh. Eksp. Teor. Fiz. **38**, 966 (1960); **39**, 1437 (1960) [Sov. Phys. JETP **11**, 696 (1960); **12**, 1000 (1960)].

[7] P. B. Allen, Phys. Rev. Lett. **59**, 1460 (1987).

[8] A. Bjørneklett, A. Borg, and O. Hunderi, Physica (Amsterdam) **157A**, 164 (1989).

[9] G. L. Eesley, Phys. Rev. B **33**, 2144 (1986).

[10] M. E. Gershenzon, V. V. Golovlyov, I. B. Kedich, V. S. Letokhov, Yu. E. Lozovik, Yu. A. Matveets, E. G. Sil'kis, A. G. Stepanov, V. D. Titov, M. I. Falei, V. M. Farztdinov, S. V. Chekalin, and A. P. Yartsev, Pis'ma Zh. Eksp. Teor. Fiz. **52**, 1189 (1990) [JETP Lett. **52**, 602 (1990)].

[11] Y. M. Imer, F. Patthey, B. Dardel, W.-D. Schneider, Y. Baer, Y. Petroff, and A. Zettl, Phys. Rev. Lett. **62**, 336 (1989); J. Shutzmann, W. Ose, J. Keller, K. F. Renk, B. Roas, L. Shulz, and G. Saeman-Ischenko, Europhys. Lett. **8**, 679 (1989); R. T. Collins, Z. Schlezinger, F. Holzberg, and C. Freidl, Phys. Rev. Lett. **63**, 422 (1989).

[12] E. G. Maksimov and S. Yu. Savrasov, Usp. Fiz. Nauk **160**, 155 (1990) [Sov. Phys. Usp. **33**, 86 (1990)].

[13] S. D. Brorson, A. Kazeroonian, J. S. Moodera, D. W. Face, T. K. Cheng, E. P. Ippen, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. Lett. **64**, 2172 (1990).

[14] H. Krakauer, W. E. Pickett, and R. E. Cohen, J. Supercond. **1**, 111 (1988).

[15] S. Massidda, J. Yu, A. J. Freeman, and D. D. Koeling, Phys. Lett. A **122**, 198 (1987); G.-L. Zhao, Y. Xu, W. Y. Ching, and K. W. Wong, Phys. Rev. B **36**, 7203 (1987); W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989); W. E. Pickett, R. E. Cohen, and H. Krakauer, Phys. Rev. B **42**, 8764 (1990).

[16] V. E. Lyusternik, B. E. Peletskii, V. S. Bakunov, and A. V. Bolotnikov, Sverkhprovodimost' **3**, 2037 (1990) (in Russian).

[17] K. A. Kvavadze, D. D. Igitkhanishvili, M. M. Nadareishvili, L. A. Tarkhnishvili, G. A. Zinzadze, and M. Y. Chubabriya, Sverkhprovodimost' **3**, 1628 (1990) (in Russian).

[18] M. V. Nevitt, G. W. Crabtree, and T. E. Klippert, Phys. Rev. B **36**, 2398 (1987).

[19] C. O. Rodriguez, A. I. Liechtenstein, I. I. Mazin, O. Jepsen, O. K. Andersen, and M. Methfessel, Phys. Rev. B **42**, 2692 (1990).