Dynamics of Photogenerated Charge Carriers in Cuprates

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New results of infrared photoexcitation experiments on undoped La_2CuO_4 and Nd_2CuO_4 are reported. We observed two broad electronic excitations within the charge-transfer energy gap and an associated phonon bleaching, possibly originating from strong charge-lattice coupling. Our results are discussed in terms of the condensation of self-localized photocarriers in the CuO_2 planes at low temperatures.

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One of the remarkable properties of layered cuprates is the transition from magnetic insulator to superconductor with high transition tempertures (T_c) upon chemical doping. Therefore, one must inquire into the role of charge carriers that leads to the high T_c regardless of specific theoretical models. In this Letter, we report newly found remarkable properties of charge carriers in the CuO_2 planes that provide a deep insight into the nature of charge carriers and dynamic properties.

The nature of charge carriers and their interactions with the lattice in these unusual superconducting cuprates may be directly probed by standard infrared reflectivity measurements. However, because of the free-carrier contribution to the infrared conductivities, one can discern the residual contributions buried under the Drude-type conductivities only when all the free carriers are condensed into the superconducting state at $T < T_c$ [1]. Therefore, it is not straightforward to verify the relevance of the background conductivities to the superconductivity.

In an attempt to address specific issues concerning the infrared properties of high-T_c cuprates, we employed the steady-state infrared photoexcitation technique to measure the infrared absorptions due to the photogenerated charge carriers (photocarriers) in the CuO_2 planes of undoped La_2CuO_4 and Nd_2CuO_4, with which we can change the charge-carrier densities *in situ* at various temperatures.

We found two photoinduced electronic excitations, one at lower energy (LE) and the other at higher energy (HE), within the charge-transfer (CT) energy gap and a phonon bleaching associated with the Raman-active in-plane breathing mode of the CuO_2 plane. At $T < 40$ K, we observed a spectral weight transfer from the far infrared ($\omega < 500$ cm^{-1}) to LE, suggesting that LE at ~ 0.12 eV in La_2CuO_4 and at ~ 0.16 eV in Nd_2CuO_4 are directly involved in the charge transport. The change in the intensity dependence of the photoinduced signal from $I^{0.5}$ at 45 K to $I^{0.25}$ at 4.2 K indicates a possible change in the state of the photocarriers.

The essential physical equivalence of the role of photocarriers with that of doping-induced charges in the CuO_2 planes has been verified through previous photoexcitation and doping studies of high-T_c cuprates [2,3]: the one-to-one correspondence between the photoinduced infrared-active vibrational (IRAV) modes and the doping-induced IRAV modes, and the existence of the associated LE and HE within the CT gap (~ 2.0 eV) of cuprates. It has been also verified that the photoinduced IRAV modes are directly related to the Raman-active modes of the undoped cuprates [2,3].

A La_2CuO_4 pellet was synthesized with the conventional solid-state reaction and single crystals of Nd_2CuO_4 were grown with the flux technique from excess CuO in a platinum crucible. Excess oxygen in the La_2CuO_4 specimen was removed by N_2 annealing at 650 °C. For the infrared photoinduced absorption measurements (400–8000 cm^{-1}), the specimens were ground to produce ~ 1-μm-size grains of each compound and dispersed in KBr at a concentration of ~ 2 wt.%. The homogeneous mixture was compressed into semitransparent, ~ 0.7-mm-thick, greyish black pellets.

Photoinduced absorption spectra were obtained by measuring fractional changes ($\Delta\mathcal{T}$) in the infrared transmission ($\mathcal{T}$) of the semitransparent sample [$-\Delta\mathcal{T}/\mathcal{T} \approx \Delta(\alpha d)$, where α is the absorption coefficient and d is the optical absorption depth at the pump energy] in response to the external laser incident on the sample for 4 sec by using a Bruker 113v infrared spectrometer for frequencies from 400 cm^{-1} (0.05 eV) to 8000 cm^{-1} (1 eV). The spectral resolution was set to 2 cm^{-1}.

Typical photoinduced absorption spectra of each compound obtained at 4.2 K are shown in Fig. 1. There are three common features that are readily seen in each absorption spectrum: an absorption dip (bleaching) at ~ 580 cm^{-1} and LE peaked at ~ 1300 cm^{-1} (~ 0.16 eV) and HE located at ~ 5000 cm^{-1} (~ 0.62 eV) for Nd_2CuO_4, and the similar bleaching at ~ 682 cm^{-1} and LE at ~ 1000 cm^{-1} (~ 0.12 eV) and HE at ~ 3800 cm^{-1} (~ 0.47 eV) for La_2CuO_4 [4], consistent with the doping studies [5,6].

The photoinduced absorption spectra of La_2CuO_4 and Nd_2CuO_4 obtained at two temperatures are shown in Fig. 2. For $T > 40$ K, there exists a substantial spectral weight in the far-infrared range (see the inset). As the

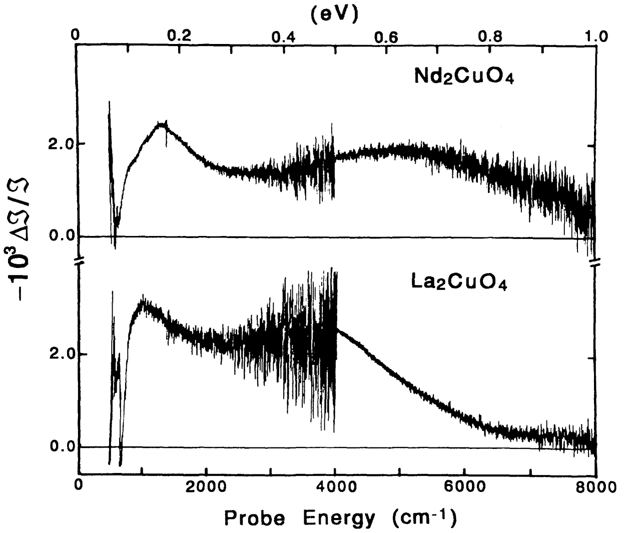

FIG. 1. Photoinduced absorption spectra measured at $T=4.2$ K (500–8000 cm^{-1}); the laser pump intensity was 30 mW/cm^2 at 2.7 eV. Note the change of the beam splitter and detector at 4000 cm^{-1}.

sample is cooled below 40 K, the absorption strength of LE of La_2CuO_4 and of Nd_2CuO_4 increases and the far-infrared spectral weight diminishes substantially. Figure 3 shows details of the temperature dependences. We note that the absorption of LE abruptly gains strength for $T < 40$ K while HE has moderately increased its oscillator strength only by ~20% at 4.2 K.

The photoinduced signal is proportional to the number of photocarriers in the CuO_2 planes (n_p) which is determined by balancing the recombination rate with the generation rate ($\propto I$, optical pump intensity) in the steady state. Therefore, the intensity-dependence measurements can directly probe the detailed characteristics of charge carriers. As displayed in Fig. 4, the intensity dependence of LE measured at 45 K exhibits $\propto I^{0.5}$ behavior, presumably resulting from the bimolecular recombination [7]. At 4.2 K, we observe $\propto I^{0.25}$ behaviors for LE of both La_2CuO_4 and Nd_2CuO_4. We note that HE is insensitive to temperature changes, unlike LE (see Fig. 3); however, we observed the same intensity dependence for both LE and HE (not shown here) [8], implying that LE and HE share the same physical origin [2,3,7].

Based on our results, we attempt to answer the following specific issues:

(1) Are these photoinduced spectral changes attributable to charges in the CuO_2 planes?—The photoexcitation process, generating both electrons and holes, induces virtually identical infrared activities to those from chemical doping where only either holes (*p*-type doping) or electrons (*n*-type doping) are involved, suggesting that the photogenerated electrons (holes) in La_2CuO_4 (Nd_2CuO_4) are localized outside the CuO_2 planes after the charge separation.

For very small volume fraction (f) of spherical parti-

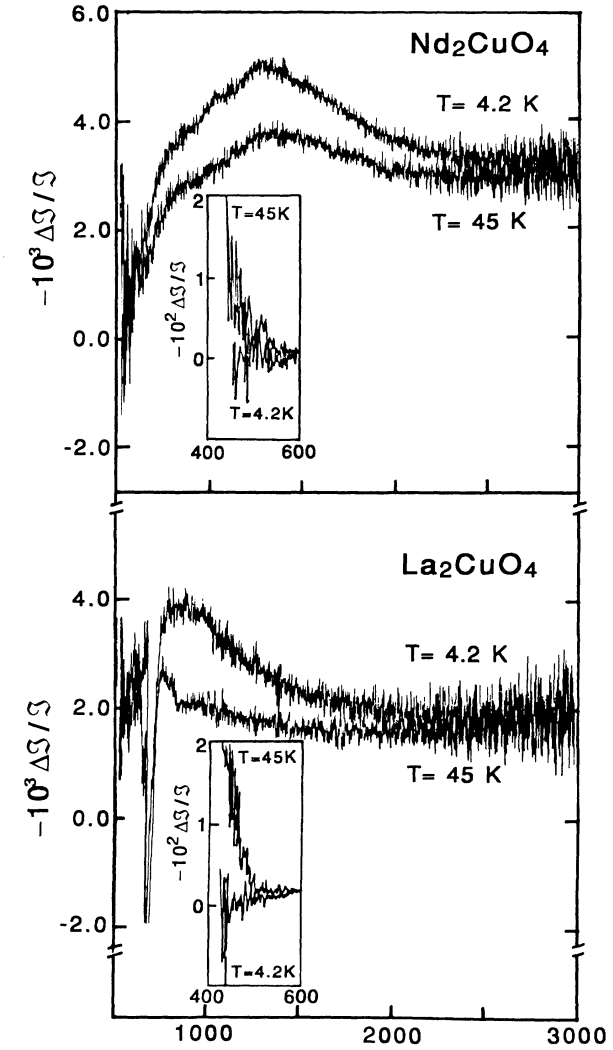

FIG. 2. Comparison of the photoinduced electronic excitations at ~0.16 eV of Nd_2CuO_4 (70 mW/cm^2) and at ~0.12 eV of La_2CuO_4 (100 mW/cm^2) for two temperatures. Insets: The corresponding far-infrared tail for frequencies between 400 and 600 cm^{-1} (note the scale difference on the vertical axis).

cles in an insulating medium of ε_{KBr}, the absorption coefficient α can be approximated [9] as $\alpha/\varepsilon_{KBr}^{3/2} \approx f(36\pi/c)\sigma_1(\omega)/\varepsilon_1^2$ in the $\varepsilon_1 \gg \varepsilon_2 = 4\pi\sigma_1/\omega$ limit. By taking $f \sim 0.008$ (~2 wt%), $\varepsilon_{KBr} \approx 2.1$ at 1000 cm^{-1}, and $\Delta(\alpha d) \sim 2.0\times10^{-3}$ ($T > 40$ K) at 1000 cm^{-1}, we estimate the real part conductivity due to photocarriers $\sigma_{p1} \approx 120$ Ω^{-1}cm^{-1} for La_2CuO_4, with $\varepsilon_1^2 \sim 100$ at 0.1 eV [6] and optical density ~3 for a 1-mm-thick sample ($d \sim 0.5$ μm) at 2.4 eV. From σ_1(1000 cm^{-1})~800 Ω^{-1}cm^{-1} with carrier density ~1.6×10^{21}/cm^3 at 15% Sr doping [6], we find the lower bound to photocarrier density $n_p \geq 2.4\times10^{20}$/cm^3. Therefore, the photocarrier concentration in the CuO_2 planes is equivalent to ~2.2% doping level, which is consistent with the observed large

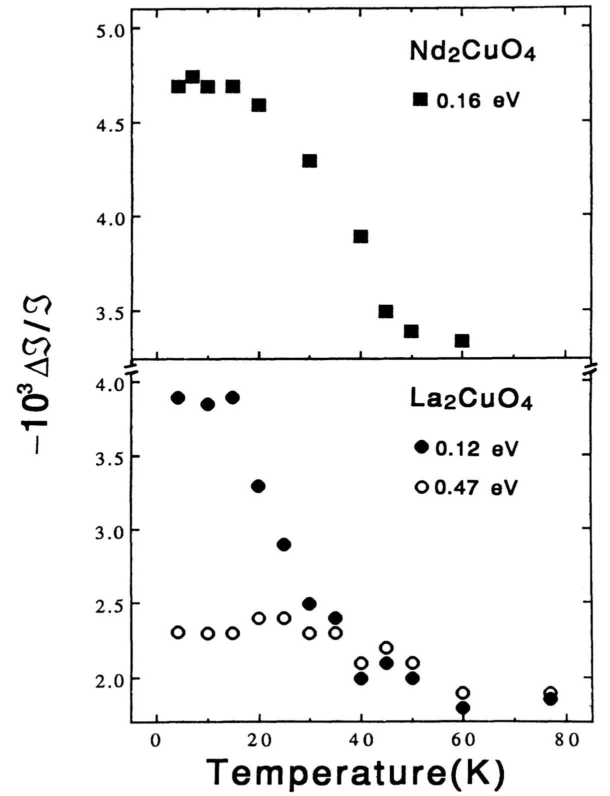

FIG. 3. Temperature dependence of the photoinduced electronic excitations of Nd_2CuO_4 (70 mW/cm^2) and of La_2CuO_4 (100 mW/cm^2) with 2.4-eV pump.

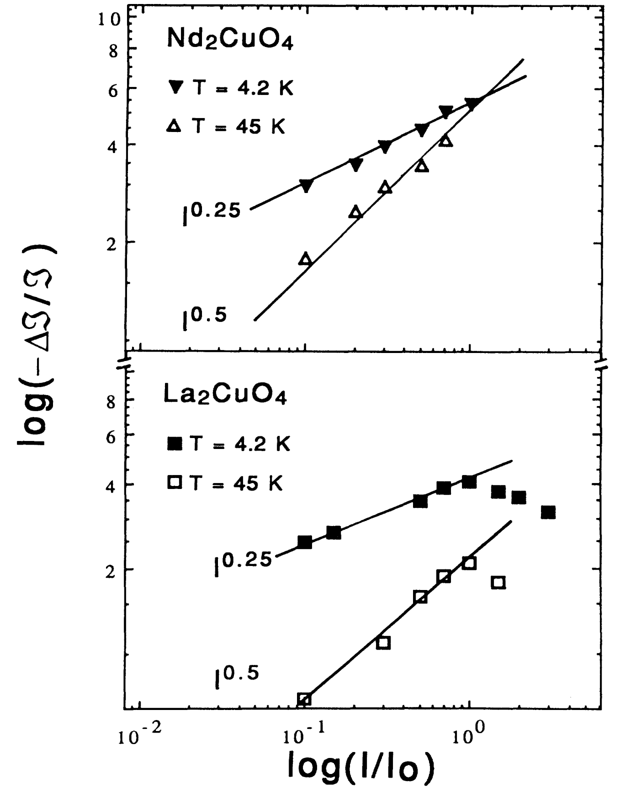

FIG. 4. Pump-intensity dependence of the photoinduced lower-energy electronic excitation at two temperatures ($I_0 = 100$ mW/cm^2). The solid lines are guides for eyes and error bars are about the size of the symbol. (The tendency of saturation at high pump intensity is not clearly understood; however, we observed local heating effects at the intensity as monitored through the thermal sensitivity of the 698-cm^{-1} infrared mode of undoped La_2CuO_4.)

spectral weight due to free carriers in the far infrared (see the inset in Fig. 2) for $T > 40$ K.

In principle, one can estimate the photocarrier concentration from the carrier generation rate ($\sim 2.5 \times 10^{21}$ charges/cm^{3}sec with photon flux $\sim 1.2 \times 10^{17}$ photons/cm^{2}sec corresponding to 100 mW/cm^2 at 2.53 eV by assuming unit quantum efficiency) if the bimolecular recombination rate is given. However, the bimolecular recombination rate in cuprates is not known at this stage, and we anticipate that the rate in cuprates is dramatically different from that due to trapped charges in conventional 3D systems, such as amorphous hydrogenated silicons [10], because of the unusual layered structure of cuprates consisting of CuO_2 sheets with La (or Nd) ions in between that may provide the trapping centers of oppositely charged particles at elsewhere out of the plane. We speculate that the unusual structure of cuprates accounts for the observed high concentration of photocarriers in the CuO_2 planes with the lifetime order of ~ 1 msec. Such long-lived photocarriers in layered cuprates have also been observed in photoconductivity measurements [11].

(2) Are these electronic excitations directly related to the superconductivity?—The carrier recombination dynamics bears directly on the state of charge carriers. For the recombination between two uncorrelated, oppositely charged carriers, we anticipate $n_p \propto I^{0.5}$ and $\propto I^{1.0}$ for correlated (bound) electron-hole pairs. For real-space bound pairs of holes and pairs of electrons, we expect $I^{0.5}$ again, which is the case of photogenerated bipolarons of conducting polymers [12].

Therefore, we may exclude the possibility of real-space pairing because we would expect $\propto I^{1/3}$ dependence for the recombination process between bound hole (or electron) pairs and unpaired electrons (or holes) or $\propto I^{0.5}$ for the real-space bound pairs of holes and electrons below $T < T_c$. Hence, the observed $I^{0.25}$ dependence is significant. It might, possibly, be explained by the recombination process between momentum-space-paired holes (electrons) in the CuO_2 planes and trapped electrons (holes).

Based on the observation of the oscillator strength upturn of LE that scales rather well with $T_c \approx 40$ K and the change of the intensity dependence at $T < 40$ K, we speculate that the photocarriers are condensed into the superconducting state [13] at $T < 40$ K.

Another point we suggest is that, because our sample is globally insulating, the oscillator strength in the far infrared may not collapse into a delta function at $\omega = 0$ even though the charge carriers in each cuprate grain are in the condensed state. The free-carrier spectral weight appears to be transferred to LE while HE remains nearly constant (see Figs. 2 and 3), implying that the carrier involved in the charge transport carries LE with it.

(3) What is the origin of the electronic excitations? —It has been suggested that LE is due to hopping in the antiferromagnetic background of the CuO_2 plane, the charge motion necessarily involving spin interactions that cost an energy on the order of $J \sim 0.1$ eV. HE is then associated with the Coulomb binding of a charge in the CuO_2 plane with the dopant ion [5]. Our findings appear to disagree with these suggestions because (1) we anticipate a substantial change in the energy when the charge carriers are paired at $T < T_c$ and (2) if we assume that HE in the photoinduced absorption spectra is due to the Coulomb binding between a hole in the plane and a trapped electron out of the plane, we expect $\propto I^{1.0}$, which is not the case.

In this experiment, we observed that the electronic excitations are tied to the IRAV modes, suggesting that the self-localization of charges breaks the local symmetry around charge carriers [2,3]. In addition, we found evidence that LE is directly involved in the charge transport. The bleaching at ~ 682 cm^{-1} in La_2CuO_4 and at ~ 580 cm^{-1} of Nd_2CuO_4 spectra (see Fig. 1) is probably due to the Fano-like interference between LE and the IRAV mode [14] associated with the symmetric breathing mode in the CuO_2 plane [15], implying the presence of strong charge-lattice coupling.

Therefore, one possible scenario is that the charges in the CuO_2 planes gain stability in a self-localized state with a binding energy which develops a gap state(s) within the CT gap as evidenced by the observed electronic states and the associated IRAV modes. At $T < T_c$, these self-localized charged excitations more likely form a bound pair state in the momentum space via many-body interactions [16] as evidenced by the recombination dynamics.

In summary, we have observed two photoinduced electronic absorptions within the CT gap and a phonon bleaching associated with the Raman-active breathing mode of the CuO_2 plane, resulting probably from the strong charge-lattice coupling. At $T < 40$ K, we observed spectral weight transfer from the far-infrared range ($\omega < 500$ cm^{-1}) to LE and changes in the intensity dependence of the photoinduced signal from $I^{0.5}$ to $I^{0.25}$, indicating a possible change in the state of the charge carriers into a momentum-space-paired state. Our results suggest that the electronic excitations in cuprates are charged and directly involved in the transport.

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