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Photoexcitations in La_2CuO_4: 2-eV energy gap and long-lived defect states

J. M. Ginder, M. G. Roe, Y. Song, R. P. McCall, J. R. Gaines,* and E. Ehrenfreund†
Department of Physics, The Ohio State University, Columbus, Ohio 43210-1106

A. J. Epstein
Department of Physics and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210-1106

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We report the photoinduced optical-absorption spectrum of La_2CuO_4. Two photoinduced absorptions are observed, peaking at 0.5 and 1.4 eV, with a crossover to photoinduced bleaching above 2.0 eV. These data, together with observed luminescence at ~2 eV, confirm the presence of an energy gap at or above this energy, as well as the existence of long-lived stable electronic defect states in this system.

The report of high-temperature superconductivity in the La-Ba-Cu-O system by Bednorz and Müller[1] has stimulated intensive study of these and related materials. It is important to understand the electronic structure involved in this system and its relationship to the high T_c for superconductivity. Toward this direction there have been numerous experimental studies of the optical properties of the $La_{2-x}(Sr,Ba)_xCuO_{4-\delta}$ system in an effort to identify the origins of the high-temperature superconductivity.[2–4] There have also been a number of band-structure calculations[5,6] for this material as well as several models proposed for the unusually high T_c.[7–10,13] Though most work to date has emphasized the doped material ($x > 0$) it is important to understand the electronic structure of the parent La_2CuO_4 compound and the defect states that are introduced into the system upon addition or removal of electrons.

We report here an experimental study of the photoinduced optical phenomena in La_2CuO_4 for probe photon energies between 0.4 and 2.4 eV, using a pump laser at energy 2.54 eV. Several features are reported for the first time. These include the observation of *two* photoinduced absorption peaks, at 0.5 and at 1.4 eV. A crossover from photoinduced absorption to photoinduced bleaching is observed near 2 eV. The intensity of the absorption and bleaching bands decreases with increasing temperature with a similar temperature dependence. The intensity of the photoinduced absorption and bleaching bands are roughly proportional to the square root of the incident laser power, indicating a bimolecular-type decay, though the chopping frequency behaviors of the two photoinduced absorption peaks differ. The data, together with the first report of luminescence at ~2 eV, confirm the presence of an energy gap of ~2 eV. The presence of the two photoinduced absorptions as well as the photoinduced bleaching are discussed in terms of the predictions of available models.

The La_2CuO_4 material used in this study was prepared by the solid-state reaction method. Details of the preparation and characterization of these compounds are provided elsewhere.[11] X-ray diffraction studies of the material used for these experiments revealed it to be single-phase material, and temperature-dependent magnetic susceptibility measurements showed the presence of less than 0.02% by volume of a superconducting ($T_c = 40$ K) phase. Powdered La_2CuO_4 consisting of micron-sized crystallites was mixed in a concentration of ~0.1% by weight with KBr in a freezer mill and then compressed into a pellet. Samples were reground several times until the desired uniformity was achieved. The near steady-state photoinduced absorption experiments were carred out using an Ar^+ ion laser to excite the sample; the probe beam, produced by an incandescent lamp, was filtered through a monochromator and detected by the appropriate semiconducting photodiodes. The laser beam was mechanically chopped and a lock-in amplifier was used to measure the change in transmission, ΔT, of the sample induced by the photoexcitations. The uncorrected sample transmission, T, was measured simultaneously in order to compute $\Delta T/T$, which is independent of the response of the measuring apparatus, and which is proportional to the change in the absorption coefficient of the sample. The difficulties in measuring the absolute transmission of powder samples dispersed in KBr are minimized in this photoinduced transmission experiment, since it is a differential measurement. The photoluminescence spectra were normalized to the uncorrected transmission spectrum; consequently, they are corrected for sample transmisison and detector and grating response, but not for the spectral dependence of the probe beam.

The component of photoinduced absorption that is in phase with the pump laser pulses, measured at a sample holder temperature of 15 K, is shown as the solid-line spectrum in Fig. 1. It has three features: a photoinduced absorption peaking at 0.5 eV, a second photoinduced absorption peaking at 1.4 eV and extending up to 2.0 eV, and a small photoinduced bleaching response above 2.0 eV. The gap in the photoinduced absorption spectrum in the region of 0.8 through 1.0 eV is due to a combination of strong scattering of the ~1-μm-wavelength probe light by the micron-sized ceramic particles and the reduced sensitivity of the detectors in this wavelength range, causing extremely poor signal-to-noise ratios. In addition to the photoinduced absorptions and bleaching, a significant temperature-dependent photoluminescence is observed at ~2 eV, as plotted in arbitrary units as the dotted-line

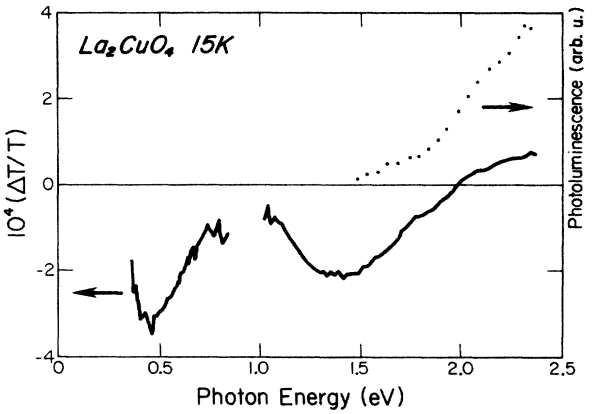

FIG. 1. Solid line: photoinduced absorption spectrum of La$_2$CuO$_4$ at 15 K, taken with a laser intensity of 0.8 W/cm^2 and a pump photon energy of 2.54 eV. Dotted line: photoluminescence spectrum in abitrary units.

spectrum in Fig. 1.

In order to investigate these spectral features, measurements were taken of $|\Delta T/T|$ as a function of incident laser intensity, chopper frequency, and temperature for each of the three features. Figure 2 is a plot of the magnitude of the photoinduced signals at 0.5, 1.4, and 2.2 eV vs temperature. The results show a fairly constant behavior up to a sample holder temperature of ~40 K, and a gradual decrease with increasing temperature thereafter. All three features have similar temperature behavior, though the error in the photoinduced bleaching is significantly larger due to the presence of luminescence.

The variation of the magnitude of the three photoinduced features with incident laser power is shown in Fig. 3. All three features scale approximately as the square root of the laser intensity in the intensity range studied.

Though all three photoinduced features have similar temperature and laser intensity behavior, they have somewhat different dependences on chopper frequency, as illustrated in Fig. 4. The 2.2 eV induced bleaching has the weakest dependence on chopper frequency, indicating it has the fastest temporal behavior. The 0.5 eV induced absorption has the next fastest behavior, and the 1.4 eV induced absorption has the slowest temporal behavior. This result suggests that the features of the photoinduced spectrum are not all due to the same photoexcited species.

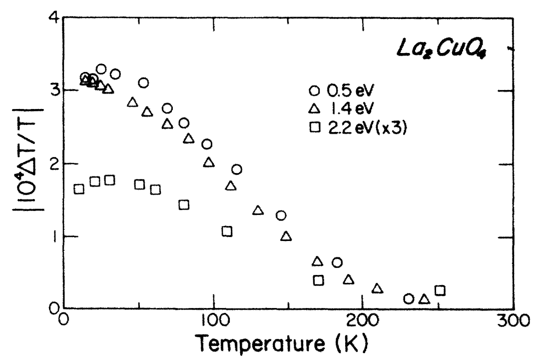

FIG. 2. Magnitude of photoinduced absorptions at 0.5 and 1.4 eV, and of photoinduced bleaching at 2.2 eV (enlarged by a factor of 3 for clarity) vs temperature.

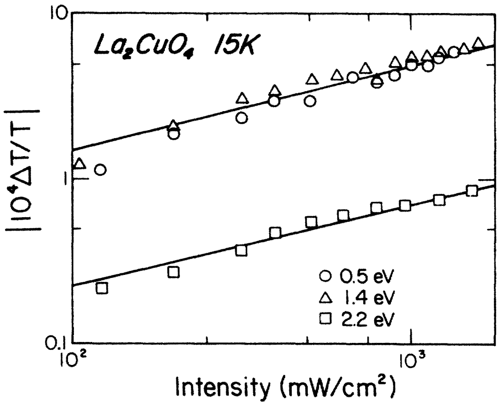

FIG. 3. Log-log plot of the photoinduced peak amplitudes vs pump intensity at 15 K. Straight lines exhibit the square-root dependence of the amplitudes on pump intensity.

Several tests confirm that the data presented here are not artifacts that result from heating of the sample by the laser. We observe an 11-cm^{-1} red shift of the infrared mode at 698 cm^{-1} as the sample is warmed from 80 to 300 K, in qualitative agreement with the results of Kim *et al.*[12] Under conditions similar to those of the photoinduced absorption experiments reported here, no laser-induced shift of this peak is observed, indicating that there is no substantial temperature increase on time scales comparable to the laser chopping period. That heating effects cause both the photoinduced bleaching and absorptions reported here is inconsistent with the temperature dependence of the transmission of the samples studied. In addition, the proportionality of the photoinduced features to the square root of the incident laser intensity as well as the

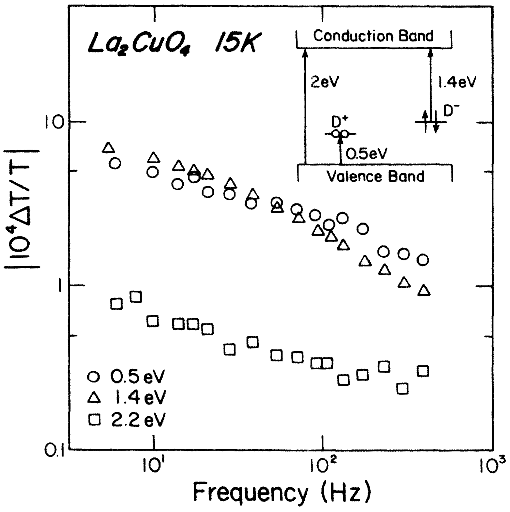

FIG. 4. Log-log plot of the photoinduced peak amplitudes vs chopper frequency at 15 K. Inset: Possible energy-level diagram for photoinduced defect states in the energy gap of La$_2$CuO$_4$.

differences in the chopping-frequency behavior of the features also support that the data reported are not caused by heating effects.

The observation of luminescence at ∼2 eV is a direct confirmation of the existence of an energy gap in La_2CuO_4. This luminescence is broad, extending up beyond 2.4 eV, and is also temperature dependent, being largest at low temperature and undetectable at room temperature. The observation of the crossover from photoinduced absorption to photoinduced bleaching at 2.0 eV is further confirmation of an allowed electronic transition in this region, which is reasonably associated with an interband transition. A 2-eV wide reduction in the density of states near the Fermi energy has been calculated[5] for La_2CuO_4. However, a residual density of states would make it unlikely that photoinduced excitations such as those reported here would be stable. More recently, several groups[7-10,13] have suggested that a Coulomb gap is present in the electronic structure of La_2CuO_4. The existence of an energy gap is consistent with our reported photoluminescence and photoinduced bleaching as well as the doping-induced decrease in oscillator strength of the 2 eV feature observed[3] in optical spectra of $La_{2-x}Sr_xCuO_4$.

Photoinduced absorption spectroscopy has become a productive probe in the study of the electronic defect states that can be produced within the energy gaps of semiconductors[14] and polymers.[15-18] Electrons photoexcited across the band gap and holes that remain in the valence band eventually form long-lived defect states such as solitons, polarons, and bipolarons. The optical absorption of valence electrons to unoccupied levels of these defect states and of electrons from occupied defect states to the conduction band lead to photoinduced optical absorptions. The energies and dynamics of the observed optical absorptions are, therefore, a sensitive tool to determine the origins of the electronic energy gap within which these photoinduced absorptions are observed. The presence of two relatively narrow distinct photoinduced absorption levels differs from that normally expected for crystalline or amorphous semiconductors.[14] In polymers, a variety of relatively sharp photoinduced absorption levels have been observed, indicative of solitons in degenerate polymers and polarons and/or bipolarons in nondegenerate polymers. These defect states are stabilized by the one-dimensional nature of the polymer electronic structure and the presence of a strong electron-phonon interaction in these systems.

We have reported here the presence in La_2CuO_4 of two photoinduced absorption peaks of roughly equal intensity at 0.5 and 1.4 eV. Our observation of the 0.5 eV peak confirms the earlier report by Kim *et al.* of a broad photoinduced absorption peak at ∼0.5 eV.[13] We have also observed photoinduced infrared active vibrational modes (IRAV) as reported by Kim *et al.*, which supports the existence of structural deformation around the photoexcited charged carriers indicative of a coupling of the photoexcitations to the lattice. That the 0.5 eV and IRAV features[13] have the same laser intensity dependence as the photoinduced peaks we report suggests that they are directly associated.

In general, photoexcited electrons and holes may form localized defects, D^- and D^+, whose levels are split off from the conduction and valence-band edges by their respective binding energies, E_{D^-} and E_{D^+}. The energies of the observed photoinduced absorption peaks and the onset of photoinduced bleaching suggest a splitting of ∼0.1 eV between the positive and negative defect levels, as illustrated schematically in the inset of Fig. 4. Alternatively, since the optical spectra of $La_{2-x}Sr_xCuO_4$ exhibit dopant-induced features at ∼0.4 and 1.4 eV (Refs. 2 and 3) that may correspond with the photoinduced features reported here, contributions to both photoinduced absorptions may be made by the D^+ defects.

It is noted that the sum of the two photoinduced absorption peak energies adds up to ∼1.9 eV, nearly the value of the crossover to photoinduced bleaching. This result is what might be expected if bipolarons possessing a substantial confinement energy[19] were photoexcited within the gap of La_2CuO_4. However, the La_2CuO_4 system is not charge-conjugation symmetric; i.e., the valence band is much broader than the conduction band.[5-11] Incorporation of Sr and incorporation of oxygen deficiencies have quite different effects on the photoinduced absorption.[20] This lack of symmetry is expected to make the defect energy levels asymmetric about the energy-gap center, producing a more complex photoinduced spectrum (as observed, for example, in the emeraldine base polymer[17]) than that reported here. The subtle differences in the frequency dependence of the observed photoinduced absorption peaks also suggest that they are not due solely to two dinstinct electronic absorptions of a single type of photoinduced defect.

It is conceivable that the photoexcited electrons and holes behave similarly to the long-lived electrons and holes that are excited in polyacetylene, in that they diffuse until recombination with neutral defects to form charged defects.[18] These neutral defects may be related to the presence of grain boundaries, structural defects, and nonstoichiometry in the ceramic material. The square-root dependence of the 0.5 and 1.4 eV photoinduced peaks on laser intensity is suggestive of bimolecular recombination of positive and negative defects. However, the difference in the chopper frequency behavior of these two peaks is indicative of more complex generation or decay processes. For example, D^+ states resulting from small nonstoichiometries may participate in the recombination process, leading to small difference in the temporal behaviors of the photoinduced D^+ and D^-. Further photoinduced absorption studies on the picosecond through second-time scales are necessary to identify the actual recombination mechanisms involved. The appropriate description of the electronic ground state of La_2CuO_4 must admit the presence of localized charged defect states (see, for example, Ref. 7).

In sum, we have reported the first direct observation of two photoinduced absorptions, photoinduced bleaching and luminescence in La_2CuO_4. These data confirm the presence of an energy gap at ∼2 eV and show the existence of long-lived defect states within the gap. The presence of two photoinduced absorptions suggests the relevance of models that can support the existence of localized defect states.

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[*] Permanent address: Department of Physics, University of Hawaii, Honolulu, Hawaii 96844.

[†] Permanent address: Department of Physics, Technion-Israel Institute of Technology, Haifa, Israel.

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