PHYSICAL REVIEW B VOLUME 36, NUMBER 13 1 NOVEMBER 1987

Direct evidence of the importance of electron-phonon coupling in La_2CuO_4: Photoinduced ir-active vibrational modes

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(Received 20 July 1987; revised manuscript received 24 August 1987)

We present direct evidence of the importance of the electron-phonon interaction in pure La_2CuO_4. Photoinduced ir-active vibrational modes (IRAV) and associated bleaching of the La_2CuO_4 phonon modes are observed in the spectral range below 700 cm^{-1}. The observation of photoinduced IRAV modes implies the existence of structural deformation around the photoexcited carriers, indicative of coupling of the photoexcitations to the lattice. We find, in addition, a broad photoinduced absorption which peaks at ≈ 0.5 eV, indicating an electronic transition deep within the energy gap.

The high superconducting transition temperature[1] (T_c) of Sr- or Ba-doped La_2CuO_4 has focused attention on the identification of the underlying mechanism which leads to the high T_c. It is of fundamental importance to determine if the mechanism involves pairing via the indirect attractive interaction mediated by phonons, pairing via electronic excitations, or if a fundamentally new mechanism is involved. Recent experimental studies[2] of the optical properties have demonstrated a dopant-induced optical transition at ~ 0.5 eV in $La_{2-x}Sr_xCuO_{4-\delta}$, suggesting an electronically driven mechanism. Although this conclusion is consistent with the absence of an isotope effect[3] in $Y_1Ba_2Cu_3O_7$, a positive isotope effect has recently been reported[4] for doped La_2CuO_4. Even in the case where the high T_c is due to an electronic mechanism, such as in the proposed resonating valence bond state,[5] the electron-phonon interaction can play a critically important role.[6] In more direct experimental terms, one must inquire into the origin of the ~ 0.5 eV dopant-induced electronic transition; does it arise solely from electronic interactions (e.g., an exciton), or is it associated with a localized gap state which originates from a structural distortion resulting from the electron-phonon interaction?

In this paper we report direct experimental evidence of the importance of the electron-phonon interaction in this class of superconducting oxides. By applying the photoexcitation technique, we have observed for the first time photoinduced infrared active vibrational modes (IRAV) in La_2CuO_4. The observation of photoinduced IRAV modes implies the existence of structural deformation around the photoexcited carriers, indicative of relatively strong coupling of the photoexcitations to the lattice. We find, in addition, a broad photoinduced absorption which peaks at ≈ 0.5 eV indicating an electronic transition deep within the energy gap.

When charges are added to quasi-one-dimensional conjugated polymers by doping or by direct optical pumping above the energy gap, the excess charges disrupt the perfect Peierls' bond-alternation pattern and create charged nonlinear excitations; solitons in the case of a degenerate ground state and bipolarons (confined soliton pairs) when the ground-state degeneracy has been lifted.[7] These nonlinear excitations couple to the lattice vibrations and allow the symmetrical (Raman-active) vibrational modes to become infrared active, hence, doping-induced or photoinduced IRAV modes. As a result of the charge-induced structural distortions, electronic states are self-localized and split off into the energy gap leading to doping-induced or photoinduced electronic absorption at $\hbar\omega < E_g$ (the topological nature of the soliton leads to a single induced absorption at $\hbar\omega \approx E_g/2$). In the same spirit, we initiated the photoexcitation experiment in La_2CuO_4 in search of evidence which would specifically demonstrate whether or not the electron-phonon interaction was of importance in the high-T_c copper-oxide superconductors.

The La_2CuO_4 samples were prepared by following the method of Longo and Raccah.[8] After sintering under an oxygen atmosphere, the La_2CuO_4 was characterized by x-ray powder diffraction as single-phase material. For the photoinduced absorption measurements, the sintered La_2CuO_4 pellet was ground into approximately micron size cyrstallites and mixed at a concentration of 1–2 wt.% either with KBr powder (for measurements in the spectral range from 400 to 8000 cm^{-1}) or with CsI powder (120 to 500 cm^{-1}). The random mixtures were then compressed into semitransparent dark grey thin pellets. The compressed pellets were reground and then repressed to improve homogeneity. This grinding-pressing cycle was repeated until satisfactory transparency and homogeneity were achieved.

An IBM/98 (Bruker) Fourier-transform infrared interferometer (modified to allow access for the external laser light from an Ar+ ion laser onto the sample) was used to cover the spectral range between 120 cm^{-1} (0.015 eV) and 8000 cm^{-1} (1 eV). The cutoff of the CsI transmission set the frequency limit on the low-frequency side. Fractional changes in the infrared transmission (T) resulting from the external laser light incident onto the sample were determined as described by Blanchet, Fincher, Chung, and Heeger.[9] From the photoinduced change in transmittance (ΔT), the net change in the absorption coefficient (α) can be obtained, for small ΔT, $-(\Delta T/T)=\Delta(\alpha d)$ where d is the sample thickness. Long time signal averging was necessary to resolve all the detailed photoinduced IRAV features above the noise level.

The photoinduced absorption spectrum (time averaged over periods up to 36 h, or 37 376 scans) of La_2CuO_4 at 15 K is shown in Fig. 1 for probe energies between 120 and 8000 cm^{-1}. The laser pumping energy was 2.56 eV (488 nm) with 50 mW/cm^2 power incident on the sample. The spectral resolution was 4 cm^{-1} in the mid ir, 8 cm^{-1} in the near ir, and 2 cm^{-1} in the far ir. Since the background absorption is completely suppressed in the photoinduced absorption spectrum, the only contribution to ($\Delta T/T$) is that resulting from the optically pumped photoexcitations in La_2CuO_4. A series of photoinduced IRAV modes and associated bleaching of the La_2CuO_4 phonon modes are observed in the spectral range below 700 cm^{-1}. In addition, a broad photoinduced electronic absorption is observed with maximum at approximately 0.5 eV. The photoinduced IRAV modes are shown in more detail in Fig. 2; photoinduced absorption bands were found at 285, 398, 486, 560, and 640 cm^{-1} with associated bleaching at 214 and 706 cm^{-1}.

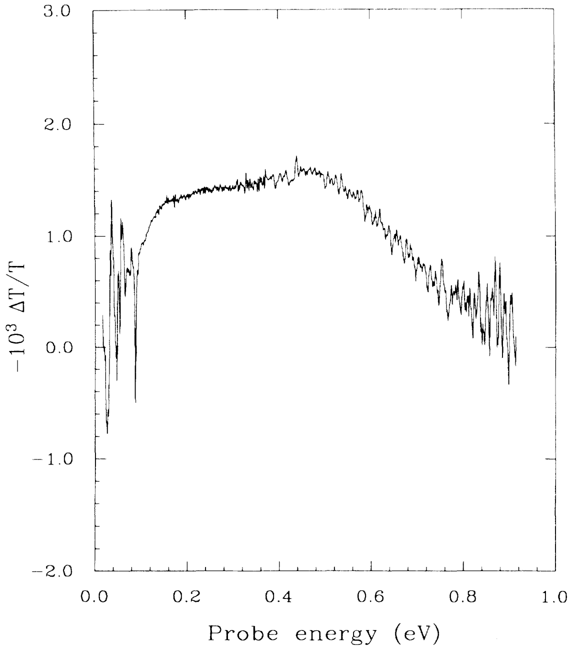

FIG. 1. Photoinduced absorption spectrum, $-(\Delta T/T)=\Delta(\alpha d)$, of La_2CuO_4 at 15 K showing the IRAV modes below about 700 cm^{-1} and the broad electronic absorption which peaks at $\approx$0.5 eV; the laser pump was 50 mW/cm^2 at 2.56 eV (488 nm).

The detailed changes in the midinfrared absorption during photoexcitation are compared with the absorption spectra of La_2CuO_4 (at 300 and 80 K) and 16% Sr-doped La_2CuO_4 (80 K) in Fig. 2. Four major infrared vibrational modes, at 218, 375, 513, and 683 cm^{-1}, were found[10-12] for La_2CuO_4 at 300 K. On cooling the La_2CuO_4 sample to 15 K, the 683 cm^{-1} mode was blue shifted by 21 cm^{-1}, whereas the others do not change frequency. On cooling, the oscillator strength of the 513 cm^{-1} mode increased by about 30% while that of the 683 cm^{-1} mode increased by only about 10%. There are three additional weak spectral features, at 332, 436, and 594 cm^{-1}, that can be seen in the La_2CuO_4 absorption at low temperatures. After 16% Sr doping, the 218 and 683 cm^{-1} modes disappear leaving two principal absorptions at 343 and 505 cm^{-1}. The only temperature dependence found for the Sr-doped sample was a modest increase in the oscillator strength of the 505 cm^{-1} mode on cooling from 300 to 80 K.

The splitting of the vibrational modes of the CuO_6 octahedra in La_2CuO_4 is characteristic of the orthorhombic symmetry of the quasi-two-dimensional K_2NiF_4 distorted perovskite structure. The suppression of the 218 and 683 cm^{-1} absorptions upon doping is a result of the stabilization of the undistorted (tetragonal) phase; for example, in the tetragonal phase, the two in-plane stretching modes of the CuO_6 become degenerate.[11,12]

The principal source of experimental artifacts in the photoinduced absorption experiment is sample heating by the laser pump beam. If there are temperature-dependent absorptions in the "dark spectra," these can show up as apparent photoinduced absorption. Decreases in intensity with increasing temperature appear as bleaching artifacts, wheres shifts in frequency with temperature appear in the photoinduced absorption as derivativelike artifacts. Extensive experience with this technique as applied to conducting polymers[9,13] gives us confidence that the photoinduced spectral changes in Figs. 1 and 2 are not due to sample heating. There are a number of specific aspects of the data which demonstrate that the photoinduced spectrum at 15 K as shown in Fig. 2 is not due to laser-induced heating. For example, there is no bleaching near 513 cm^{-1} even though the 513 cm^{-1} exhibits the strongest temperature dependence. Although there is a shift of the 704 cm^{-1} absorption on heating, the photoinduced bleaching at 706 cm^{-1} does not have a derivative shape. Moreover, the possible role of laser-induced heating has been carefully checked by directly generating a series of difference curves from ir absorption data taken as a function of temperature, and comparing these with the photoinduced spectrum.[14] Our conclusion is that the IRAV modes, the bleaching at 214 and 706 cm^{-1}, and the broad photoinduced transition which peaks at $\approx$0.5 eV are real spectral features which arise from photoexcitations in the material.

The observation of photoinduced IRAV modes implies the existence of structural deformation around the photoexcited carriers, indicative of relatively strong coupling

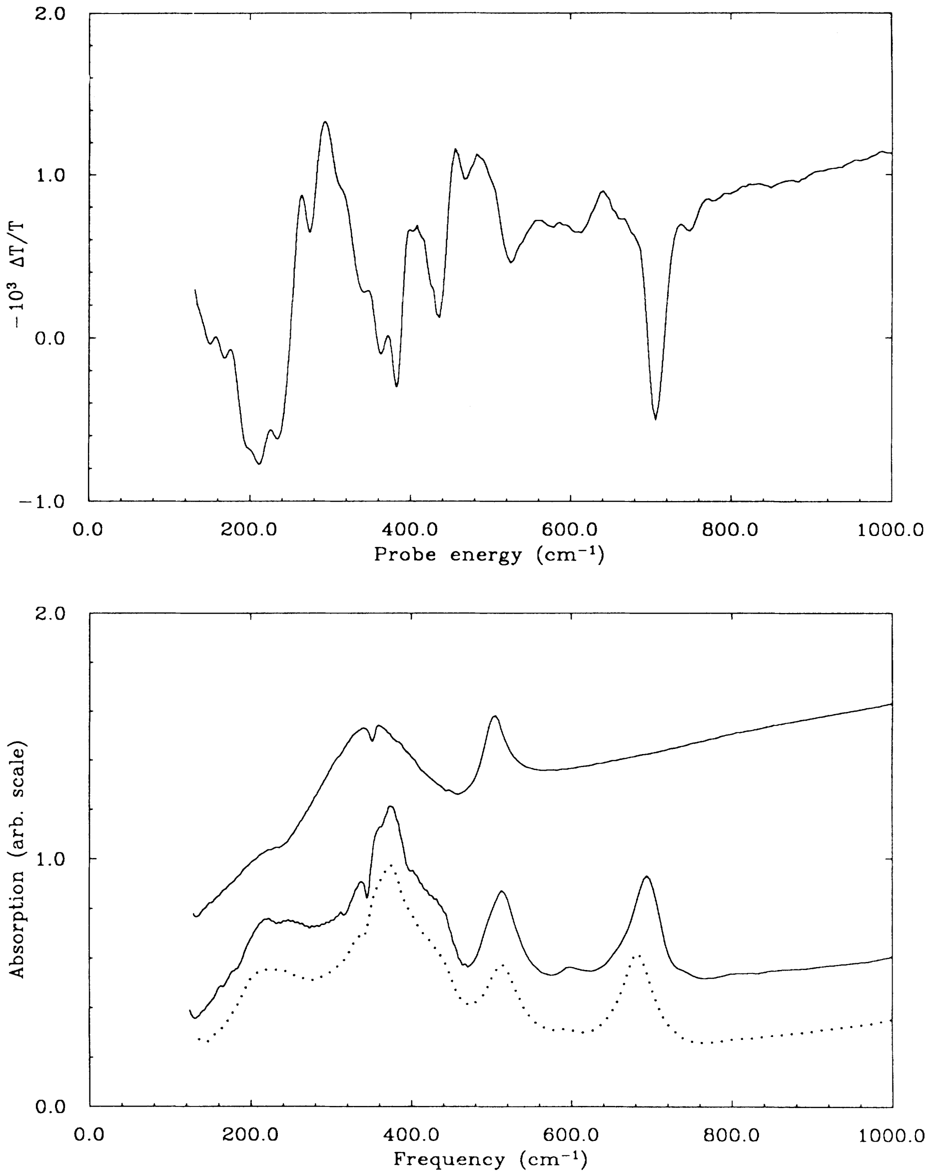

FIG. 2. Comparison of detailed changes in the midinfrared absorption during photoexcitation at 15 K (upper panel), with the absorption spectra of La_2CuO_4 at 300 K (lower panel, dotted curve at bottom), and 80 K (lower panel, solid curve second from bottom), and with the absorption spectrum of 16% Sr-doped La_2CuO_4 at 80 K (lower panel, solid curve on top).

of the photoexcitations to the lattice. On the other hand, the broad absorption with maximum at ≈ 0.5 eV is a signature of a photoinduced electronic transition to an energy level located deep within the energy gap. This may be the photoinduced analog of the ~ 0.5 eV doping-induced absorption reported earlier.[2] We suggest that similar to the case in conducting polymers the photoinduced (and perhaps also the doping-induced) *electronic* absorption may be associated with a localized gap state which originates from a structural distortion resulting from the electron-phonon interaction. Initial confirmation of this point of view comes from comparison of the temperature dependence and the pump laser intensity (I) dependence of the photoinduced absorption. We find that the IRAV modes and the electronic absorption are proportional as the temperature is changed and that both increase as the square root of the incident laser power. The $I^{0.5}$ dependence provides additional evidence that the IRAV modes do not arise from laser-induced heating.

In conducting polymers, the photoinduced IRAV modes have a 1:1 correspondence with the Raman frequencies.[7] As developed formally within the amplitude mode formalism,[15] this 1:1 correspondence arises since the photogenerated charges change the local symmetry and make the Raman-active modes (slightly shifted) infrared active. Initial examination of the Raman spectra[16] of La_2CuO_4 suggests a similar 1:1 correspondence between the photoinduced absorption modes and the Raman modes. In other words, when charges are added to the system, they couple to the CuO_6 octahedra and make the symmetric Cu-O associated Raman modes become infrared active, as observed in this study.

Some specific insight into the nature of the distortion around the photoexcitations can be obtained from comparison of the photoinduced bleaching (at 218 and 706 cm^{-1}) and the doping-induced bleaching (at 218 and 704 cm^{-1}) shown in Fig. 2. This remarkable similarity implies that locally in the vicinity of a photogenerated carrier, the CuO_6 octahedra become tegragonal (as in the Sr-doped case). The possible importance of such a specific large local structural deformation around a carrier to the occurrence of high-temperature superconductivity is quite obvious.

We thank S. Etemad and J. Orenstein for providing us with copies of their work prior to publication and for freely discussing their results. We thank N. Colaneri and D. Spiegel for important discussions and C. Foster for help with the data collection. This research was supported by the Office of Naval Research Grants No. N00014-83-K-0450 and No. N00014-87-K-0457.

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[1] J. G. Bednorz and K. Müller, Z. Phys. B **64**, 18 (1986).

[2] S. Etemad *et al.* (unpublished); J. Orenstein *et al.* (unpublished); S. L. Herr *et al.*, Phys. Rev. B **36**, 733 (1987).

[3] B. Batlogg *et al.*, Phys. Rev. Lett. **58**, 2333 (1987); L. C. Bourne *et al.*, *ibid.* **58**, 2337 (1987).

[4] B. Batlogg *et al.*, Phys. Rev. Lett. **59**, 912 (1987); T. A. Faltens *et al.*, *ibid.* **59**, 915 (1987).

[5] P. W. Anderson, Science **235**, 1196 (1987).

[6] S. Kivelson, D. S. Rokhsar, and J. P. Sethna, Phys. Rev. B **35**, 8865 (1987).

[7] For reviews, see *Handbook of Conducting Polymers,* edited by T. A. Skotheim (Marcel Dekker, New York, 1986), Vols. 1 and 2.

[8] J. M. Longo and P. M. Raccah, J. Solid State Chem. **6**, 526 (1973).

[9] G. B. Blanchet, C. R. Fincher, T. C. Chung, and A. J. Heeger, Phys. Rev. Lett. **50**, 1938 (1983); G. B. Blanchet, C. R. Fincher, and A. J. Heeger, *ibid.* **51**, 2132 (1983).

[10] K. K. Singh, P. Ganguly, and J. B. Goodenough, J. Solid State Chem. **52**, 254 (1984).

[11] M. Stavola, R. J. Cava, and E. A. Rietman, Phys. Rev. Lett. **58**, 1571 (1987).

[12] H. Sawada *et al.*, Jpn. J. Appl. Phys. **26**, L426 (1987).

[13] H. S. Schaffer and A. J. Heeger, Solid State Commun. **59**, 415 (1986); Y. H. Kim, S. Hotta, and A. J. Heeger, Phys. Rev. B (to be published).

[14] At higher temperatures (80 K and above) there is an observable heating contribution to the bleaching near 706 cm^{-1} which arises from the shift in mode frequency as the temperature is increased. This is indicated by the development of a shoulder at 683 cm^{-1} (and thus a derivativelike line shape) not seen in the 15 K data shown in Fig. 2. Details will be published elsewhere.

[15] B. Horovitz, Solid State Commun. **41**, 729 (1982).

[16] S. Sugai, M. Sato, and S. Hosoya, Jpn. J. Appl. Phys. **26**, L495 (1987).