

Photoinduced self-localized structural distortions in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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Photoinduced absorption measurements of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) from 150 to 4000 cm^{-1} are reported. We observed photoinduced infrared-active vibrational modes, associated phonon bleachings, and an electronic transition from a self-localized gap state. The results indicate a local tetragonal to orthorhombic distortion around the charge carriers. The dynamic mass associated with the distortion is smaller in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ than in La_2CuO_4 . The photoinduced structural distortion and the associated self-localized gap state demonstrate that the photoexcitations are polarons or bipolarons. Since these photoinduced absorption features are not observed in the isostructural compound La_2NiO_4 we conclude that polaron (or bipolaron) formation may play an important role in the high-temperature superconductivity.

INTRODUCTION

Research on the superconducting copper oxides has focused on identifying the mechanism(s) responsible for high T_c . Determining whether the mechanism involves pairing via phonons, pairing via electronic excitations, or whether a totally new mechanism is involved is of fundamental importance. The absence of an isotope effect¹ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and the relatively weak isotope effect² in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ were interpreted as evidence that the electron-phonon interaction is not the dominant pairing mechanism. On the other hand, photoinduced infrared (ir) absorption data³ on La_2CuO_4 provided direct evidence of the electron-phonon interaction and demonstrated the formation of a unique local distortion around the carriers.

For strong electron-phonon coupling, charge carriers (introduced by doping or photoexcitation) form polarons which attract one another via overlap of their structural distortions. This attractive interaction can lead BCS-like superconductivity with an enhanced T_c (due to the relatively long range of the localized distortion);⁴ or to formation of polarons or bipolarons that Bose condense⁵ or pair.⁶ Even if other pairing interactions dominate (e.g., resonating valence bond,⁷ electronic exciton,⁸ or magnetic⁹ mechanisms, etc.), the electron-phonon interaction could still play an important role.

In the previous study³ of the photoinduced ir absorption in La_2CuO_4 , the importance of the electron-phonon interaction was emphasized. Photoinduced infrared-active vibrational (IRAV) modes and phonon bleachings were observed, together with a broad photoinduced electronic absorption that peaked at ~ 0.5 eV. The former indicated the formation of a localized structural distortion, while the latter indicated the formation of a localized electronic state in the energy gap. The association of this gap state with the localized structural distortion formed around the

photoinjected charge carriers was implied by the common temperature and intensity dependences of the photoinduced spectral features.

To probe more deeply into these phenomena, we have expanded this study to the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system; we report the presence of photoinduced ir absorption in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) implying the existence of a tetragonal-to-orthorhombic structural distortion around the photogenerated charge carriers and an associated photoinduced electronic absorption peaked at ~ 0.13 eV. These data provide direct evidence of the importance of the electron-phonon interaction in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system. Moreover, the smaller dynamic mass ($\sim 11.4m_e$) and the more weakly bound gap state (~ 0.13 eV) found in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as compared with La_2CuO_4 ($\sim 23.8m_e$ and ~ 0.5 eV, respectively) suggest a longer-range distortion around the carriers in the higher- T_c system. The broad 0.13-eV peak and a partial IRAV mode spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been independently reported in a publication¹⁰ that appeared after the completion of our studies.

In both $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, a structural phase transition occurs as the number of carriers is increased either by doping (increasing x causes a transition from orthorhombic to tetragonal) or by removal of the oxygen vacancies (decreasing δ causes a transition from tetragonal to orthorhombic), respectively. In both cases, the correlation of the orthorhombic-tetragonal phase transition with T_c demonstrates the importance of structural distortions (caused by changes in x or δ) to the superconductivity. Our results demonstrate that even when charge carriers are injected by photoexcitation, a *localized* distortion forms around the carrier, and that associated with this localized distortion there is a localized electronic state in the energy gap. These spectral features demonstrate the formation of self-localized polarons (or bipolarons), and they imply that the semiconducting phase is

sufficiently close to the structural instability that even a single carrier locally changes the structure to that characteristic of the metallic (and superconducting) phase.

EXPERIMENTAL TECHNIQUES

The tetragonal semiconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) samples were prepared by heating orthorhombic superconducting material ($T_c=92$ K: $a=3.8170$ Å, $b=3.8888$ Å, $c=11.6721$ Å, $V=173.26$ Å³) in air at 850°C in an alumina boat for 3 h followed by rapid quenching to room temperature. The resulting sample was not a superconductor; resistivity measurements gave the high dc value and characteristic temperature dependence of $\delta \approx 0.75$. X-ray powder patterns indicated a tetragonal unit cell: $a=3.8590$ Å, $b=3.8590$ Å, $c=11.7949$ Å, $V=175.65$ Å³. The oxygen content was determined by comparing these values with the lattice constants given by Tarascon *et al.*¹¹ For photoinduced absorption, the sintered pellet was then reground to micrometer-sized crystallites and mixed at a concentration of 2 wt.% with KBr powder (for the spectral range from 400–4000 cm^{-1}) or 1 wt.% with CsI powder (120–500 cm^{-1}). The mixture was pressed into thin dark grey semitransparent pellets, which were then reground and repressed to achieve greater homogeneity. This process was repeated until satisfactory transparency and homogeneity was achieved.

An IBM/98 (Bruker) Fourier-transform ir interferometer, modified to allow access onto the sample of the external beam from an Ar^+ laser, was used to cover the spectral range from 120 (0.015 eV) to 4000 cm^{-1} (1 eV); the CsI cutoff set the low-frequency limit. For temperature control, the sample was placed on the cold finger of an Air Products Heli-tran system. The sample was optically pumped by the laser at 2.7 eV with a power level of 30 mW/cm^2 , and the fractional changes in ir transmission were measured¹² (with resolution of 2 cm^{-1} in the far-infrared region and 4 cm^{-1} in the mid-infrared region). The net change in the absorption coefficient ($\delta\alpha$) was determined from the photoinduced change in transmission (ΔT); for small ΔT , $-\Delta T/T = \delta(ad)$ where d is the sample thickness. To obtain an acceptable signal-to-noise ratio, signal averaging (~ 2 h) was required.

EXPERIMENTAL RESULTS

Figure 1 shows the photoinduced absorption spectra for the semiconducting tetragonal phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) obtained in the spectral range from 120 to 4000 cm^{-1} at 15 K, with the inset showing the photoinduced IRAV modes in greater detail. We found three major IRAV modes at 396, 436, and 520 cm^{-1} and four major photoinduced bleachings at 192, 219, 362, and 598 cm^{-1} . In addition, a broad electronic absorption peak at 1050 cm^{-1} (~ 0.13 eV) was observed.

In Fig. 2 we compare the ir spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) at 15 and 300 K, with the ir spectrum of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta < 0.2$). For $\delta=0.75$, vibrational modes were found at 164, 191, 216, 252, 361, 472,

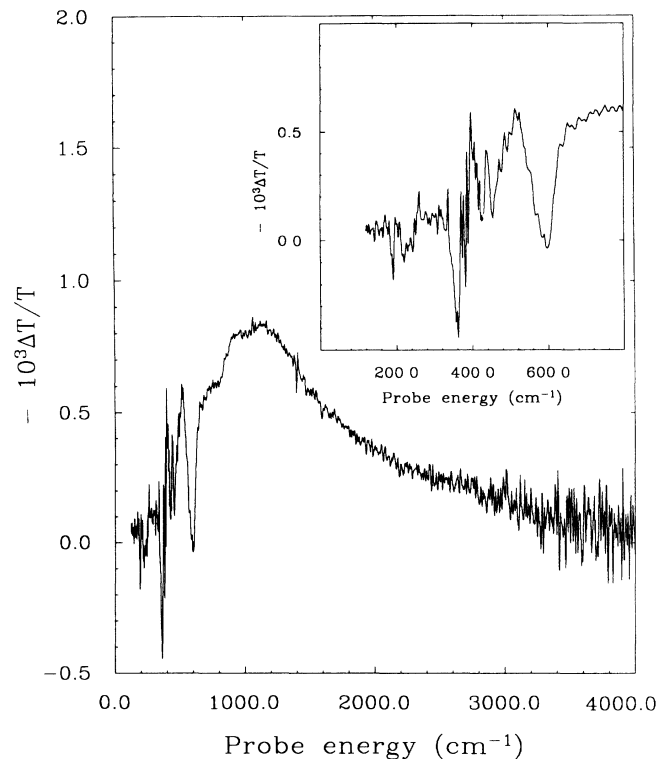


FIG. 1. Photoinduced absorption spectrum of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) at 15 K (2.7-eV pump at 30 mW/cm^2); inset shows detailed IRAV features.

532, 583, and 632 cm^{-1} with the sample at 300 K. Upon cooling to 15 K, we observed an increase in oscillator strength of the 359- cm^{-1} mode and a 19- cm^{-1} blueshift of the 583- cm^{-1} mode, consistent with values reported earlier.¹³ For the orthorhombic phase ($\delta < 0.2$), we observed relatively weak ir vibrational features at 336, 454, 493, 528, and 602 cm^{-1} at 300 K. They appear weak in transmission due to the strong free-carrier background in the highly conducting sample. Reflectivity data¹⁴ show quantitatively that the 528- and 602- cm^{-1} absorptions are relatively weak compared to the modes below 400 cm^{-1} . In contrast, for the tetragonal phase we find that the modes at 532, 586, and 632 cm^{-1} are much stronger than those in the far-infrared region. The ir modes associated with the two structures can be compared with the photoinduced features shown in Fig. 1 (IRAV modes at 396, 436, and 520 cm^{-1} and bleachings at 192, 219, 362, and 598 cm^{-1}). In particular, the bleaching frequencies suggest that photoexcitation locally converts the structure from tetragonal to orthorhombic.

Artifacts associated with the photoinduced absorption technique can be generated by sample heating by the incident laser pump beam. In systems such as oxide superconductors, small changes in the "dark" ir absorption caused by a strong temperature dependence can be incorrectly interpreted as photoinduced absorptions. Small shifts in frequency with changes in temperature would appear as derivative-shaped signals in the photoinduced spectra; changes in linewidth would appear as second-derivative-shaped signals. Similarly, a decrease in intensi-

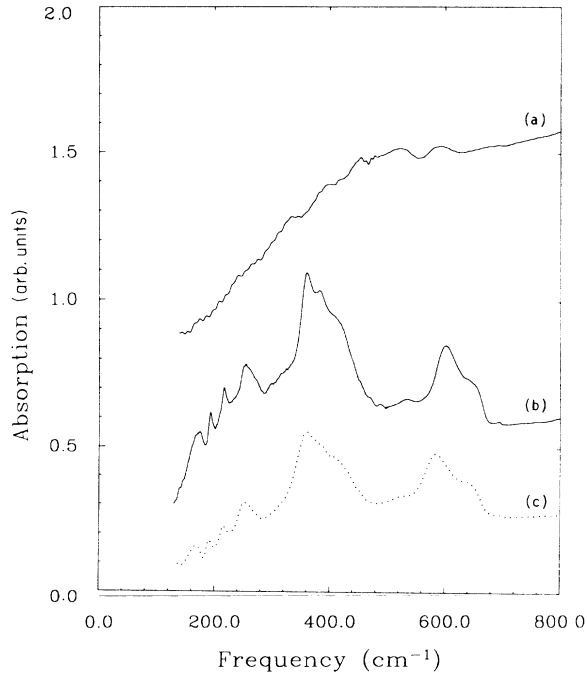


FIG. 2. Infrared spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: (a) $\delta < 0.2$ at 300 K (top); (b) $\delta = 0.75$ at 15 K (center); (c) $\delta = 0.75$ at 300 K (dotted curve).

ty accompanying an increase in temperature will appear as photoinduced bleaching. That the photoinduced features observed in Fig. 1 result from the photogenerated charge carriers (and do not arise from sample heating) can, therefore, be inferred from the lack of a derivative shape to the photoinduced bleachings and from the absence of second derivative features even though the tetragonal phase modes exhibit a strong temperature dependence.

Nevertheless, as confirmation, we carried out detailed measurements of the dark ir spectrum as a function of temperature and generated from these data numerical ($-\Delta T/T$) spectra that would arise from heating. As shown from the comparison of the two spectra in curves (a) and (b) in Fig. 3, the heating-induced spectral changes are clearly different from those in the photoinduced absorption spectrum. The thermal difference spectrum shows all the derivative features expected from sample heating artifacts; compare curve (b) with the ir absorption spectrum reproduced as curve (c) in Fig. 3. Moreover, the broad electronic transition that peaked at 0.13 eV is completely absent in the thermal difference spectrum. We conclude that the photoinduced spectrum of Figs. 1 and 3(a) is a genuine indication of the change in ir absorption due to photogenerated carriers.

It is known that small *metallic* particle effects arising from random depolarization factors in highly anisotropic metallic grains in ceramic samples can lead to artifacts in the infrared reflection (and absorption) spectrum.¹⁵ In such a case, the features in $\Delta T/T$ should be in one-to-one correspondence with the features in T . As shown in Fig. 3, curves (a) and (c), this is not the case. Since the samples used in the photoinduced absorption experiments are

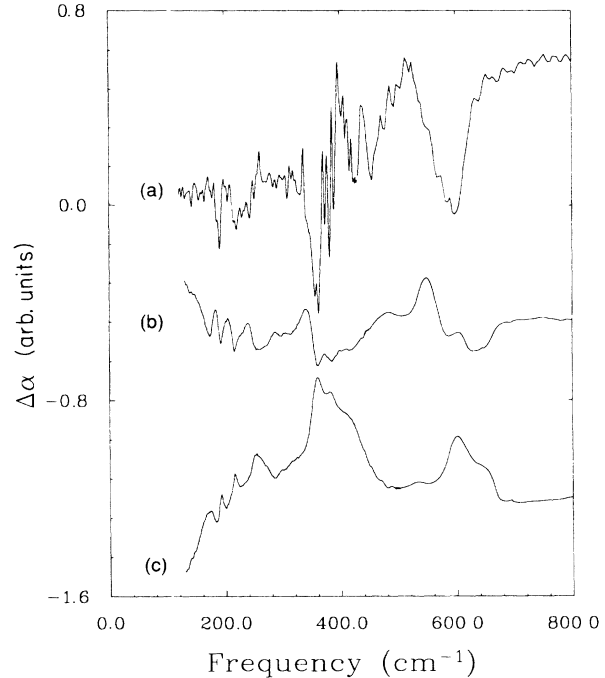


FIG. 3. (a) Photoinduced absorption spectrum (15 K); (b) thermal difference spectrum (between 15 and 300 K); (c) ir absorption spectrum obtained at 15 K.

insulating micrometer-sized crystallites embedded in an insulating medium, such small particle effects will not affect either the infrared spectrum or the photoinduced ir absorption spectrum where the measured $\Delta T/T$ are of order 10^{-3} .

In Fig. 4 we compare the temperature dependences of the IRAV mode at 520 cm^{-1} , the phonon bleaching at 598 cm^{-1} , and the broad electronic absorption that peaked at 1050 cm^{-1} ($\sim 0.13 \text{ eV}$). The common temperature dependence indicates that all originate from the same charged species (the dependence in Fig. 4 is probably due to the temperature dependence of the carrier lifetime). This was confirmed through the intensity dependence; an $I^{1/2}$ dependence was observed for all of the spectral features. We conclude that the IRAV modes, the mode bleachings, and the broad electronic transition that peaked at 1050 cm^{-1} ($\sim 0.13 \text{ eV}$) arise from the same photogenerated charged excitation. This implies that the gap state is self-localized and originates from the carrier-induced structural distortion as a result of electron-phonon coupling.

POLARON (OR BIPOLARON) PHOTOEXCITATIONS

The nature of the structural distortion associated with photogenerated charge carriers can be inferred from the photoinduced spectra. The four photoinduced bleachings at $192, 219, 362,$ and 598 cm^{-1} correspond to ir active modes in the tetragonal phase ($\delta = 0.75$), and the three major photoinduced IRAV modes at $396, 436,$ and 520 cm^{-1} correspond to Raman modes of the tetragonal phase which are in 1:1 correspondence with the ir modes of the

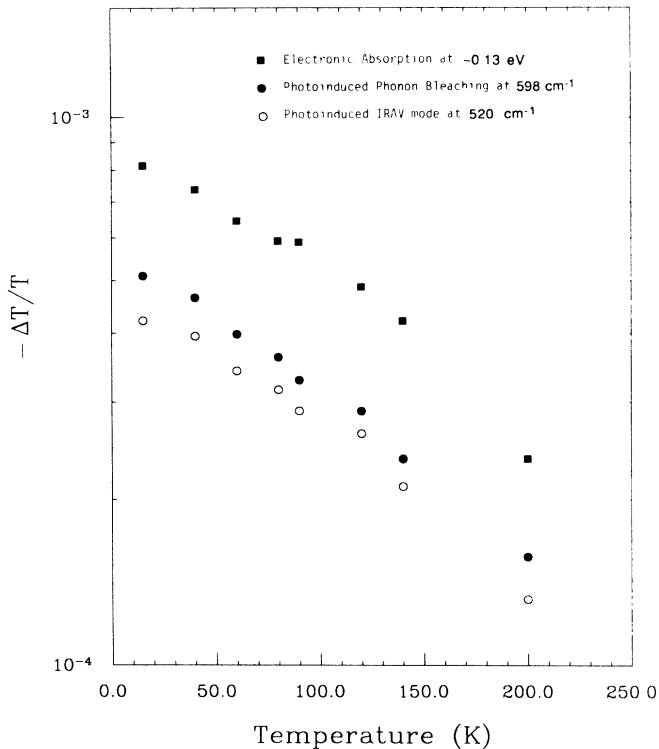


FIG. 4. Temperature dependence of the photoinduced electronic absorption at ~ 0.13 eV, the photoinduced bleaching at 598 cm^{-1} , and the photoinduced IRAV mode at 520 cm^{-1} .

orthorhombic phase. We conclude that the presence of a photoinduced charge carrier distorts the original tetragonal structure, locally forming the orthorhombic phase. Thus the photogeneration of charge carriers is qualitatively equivalent to increasing the number of carriers by reducing δ .

The origin of the photoinduced IRAV modes in conducting polymers and their relation to resonant Raman active modes has been clearly established.¹⁶ The 1:1 correspondence between IRAV and Raman modes arises because photogenerated charges induce ir-active localized phonons associated with the symmetric Raman modes. Examination of the Raman spectrum¹² of the tetragonal phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ reveals a similar 1:1 correspondence. Assignments of some of the photoinduced IRAV features can be made based upon the ir studies¹⁷ of $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$. For example, the photoinduced bleaching at 598 cm^{-1} and the IRAV mode at 520 cm^{-1} are a specific fingerprint of the structural change from tetragonal to orthorhombic of the Cu-O plane. The bleachings at 190 and 219 cm^{-1} can be assigned to deformation of the Cu-O plane coupled to the Y sites in the tetragonal phase. Thus, when charge carriers are added, they couple to the Cu-O plane which then locally distorts.

An estimate of the dynamic mass of the photoinduced structural distortion was obtained from the ratio of the integrated oscillator strength of all the IRAV modes (I_{IRAV}) to that of the subgap electronic transition (I_e), $m_d = (I_d/I_{\text{IRAV}})m_e$, where m_e is the electronic band effective mass. We find $m_d \sim 11.4m_e$, which is consider-

ably smaller than the corresponding dynamic mass obtained for La_2CuO_4 of $\sim 23.8m_e$. This result and the smaller energy of the electronic transition (0.13 eV as compared with 0.5 eV for La_2CuO_4) suggest that the distortion around a charge carrier is more widely spread in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Based on our experience obtained from analogous studies of conductive polymers,¹⁸ in order to transfer so much oscillator strength into the IRAV modes, the distortion must extend over several lattice units.

The photoinduced ir absorption features observed in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and La_2CuO_4 appear to be characteristic of the superconducting oxide systems. Our initial infrared photoinduced absorption studies of metallic La_2NiO_4 (tetragonal phase) gave null results while the semiconducting La_2NiO_4 (orthorhombic phase) yielded extremely weak signals (essentially at the noise level) that are much smaller in magnitude than $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ or La_2CuO_4 . This implies that the dynamic mass of the self-localized excitation (if any) in La_2NiO_4 is an order of magnitude larger than that of the copper-oxide systems.

SUMMARY AND CONCLUSIONS

In summary, we have demonstrated that the charge carriers in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are polarons (or bipolarons) which have a relatively small dynamic mass, $m_d \sim 11.4m_e$. Photoinduced IRAV modes and associated phonon bleachings were observed, indicative of a local distortion from tetragonal to orthorhombic in the vicinity of the charge carrier. The subgap electronic transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta = 0.75$) implies a self-localized electronic state and occurs at a significantly lower energy ($\sim 0.13\text{ eV}$) than that observed for La_2CuO_4 ($\sim 0.5\text{ eV}$). The reduced dynamic mass, the smaller gap-state binding energy, and the implied spatially extended distortion are important components to an understanding of the high T_c .

Based on the results obtained from the dilute concentration of photogenerated carriers, we speculate on what happens at a higher concentration of holes corresponding to $x > 0.15$ or $\delta < 0.2$. At these high carrier concentrations, there is no well-defined peak in the ir absorption (nor in the frequency-dependent conductivity) for high-quality samples;¹⁹ the oscillator strength associated with the electronic transition shifts toward zero frequency and becomes (at least a part of) the free-carrier absorption. This implies that the hole polaron (or bipolaron) level broadens and probably merges with the valence band. On the other hand, the IRAV modes remain, with enhanced intensity,²⁰ a situation remarkably similar to the metallic state in conducting polymers.¹⁸ The enhanced IRAV modes suggest that in the superconducting phase the holes carry overlapping distortions (like polarons or bipolarons), leading to an average distortion plus large local fluctuations about that average. Whether the implied attractive interaction is sufficient to yield high- T_c superconductivity remains to be seen. However, since these features are not observed in the isostructural compound La_2NiO_4 , we conclude that polaron (or bipolaron) formation may play an important role in the high-temperature superconductivity.

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