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Absorption and photoinduced-absorption spectroscopy in semiconducting $YBa_2Cu_3O_{6+x}$

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Semiconducting $YBa_2Cu_3O_{6+x}$ thin films with $x=0.0$ and 0.3 have been studied extensively via direct-absorption (0.2–5.5 eV) and photoinduced-absorption (0.5–3.3 eV) techniques. Optical absorptions at ~0.5, ~1.7, ~3.0, ~4.3, and ~4.8 eV were observed in direct-absorption studies for $x=0.0$. With addition of oxygen to form the $x=0.3$ composition, these absorptions evolved to ~0.5, ~1.7, ~3.0, ~4.3, and ~5.2 eV. The photoinduced-absorption spectra showed several common features: Two broad photoinduced-absorption bands peaked at 1.1 and 1.4 eV and two strong photoinduced-bleaching peaks at 1.9 and 2.6 eV. The photoinduced-absorption peaks are assigned to optical transitions from O p bands to a photoinduced charged-defect state. This self-localized positively charged defect state may be direct evidence of the presence of an oxygen $2p$ hole *polaronic* state in semiconducting $YBa_2Cu_3O_{6+x}$ upon photoexcitation. Within this model, the double peaks of photoinduced absorption reflect the excitation spectrum of the Zhang-Rice singlet predicted by Chen and Schüttler for the strong-coupling-limit t-J model. Possible alternative origins of the photoinduced-absorption peaks are pointed out. A photoinduced absorption peaked at 0.13 eV and varying with oxygen content is suggested to be associated with excitation within the CuO chains in the preceding paper (Ye *et al.*). The photoinduced-absorption spectra together with the pump-laser power and modulation frequency dependence of each of the photoinduced features suggest that the 1.9- and 2.6-eV photoinduced-bleaching peaks arise from in-plane O $p\sigma$ band to Cu $d_{x^2-y^2}$ and from in-plane O $p\pi_{x,y}$ to Cu $d_{x^2-y^2}$ and/or out-of-plane O $p\pi_z$ to Cu $d_{3z^2-r^2}$ band transitions, respectively.

I. INTRODUCTION

Since the discovery of high-temperature superconductors of $La_{2-x}Sr_xCuO_{4-\delta}$ and $YBa_2Cu_3O_{6+x}$, a variety of optical studies on the electronic structure have been made to provide a fundamental understanding of the mechanism responsible for high-temperature superconductivity and the insulator-to-metal transitions that occur in these systems upon Sr (or Ba) and oxygen doping, respectively.[1–10] To date, the mechanism of pairing in the high-T_c materials is still unclear. Band-structure calculations based on a single-electron approximation show that the valence bands of semiconducting La_2CuO_4 and $YBa_2Cu_3O_6$ are half-filled and fail to describe these materials as antiferromagnetic insulators, indicating the importance of strong electron-electron correlation effects in these materials.[11–13] These calculations consistently predict that the valence bands of La_2CuO_4 and $YBa_2Cu_3O_6$ are primarily composed of Cu $d_{x^2-y^2}$ and O p_x,p_y orbitals ($pd\sigma$).[11–13] It is generally accepted that an Anderson lattice model developed for transition metals should be employed to describe the electronic structure of these high-T_c materials.[14–17] In this model, parameters such as on-site Coulomb energy U_{dd}, charge-transfer energy for transition from an O p orbital to a Cu d orbital, Δ, and Cu d and O p hybridizing interaction t_{pd} are entered as inputs for the electronic-structure calculations.[16,17] In the Zaanan-Sawatzky-Allen (ZSA) phase diagram, the ground state of semiconducting $YBa_2Cu_3O_6$ has been described as a charge-transfer gap rather than a Mott-Hubbard insulator, based on the experimental and theoretical estimations of these parameters.[3,15–17] Optical measurements like spectroscopic ellipsometry[18–22] and absorption spectroscopy[23,24] are also reported. However, interpretations of the observed features are highly controversial.[18–22] It is therefore very important to resolve these controversies unambiguously.

Photoinduced-absorption spectroscopy has long been recognized as a sensitive probe of local charge excitations in semiconducting quasi-one-dimensional polymers and amorphous silicon without perturbing the lattice through doping.[25–28] This method was employed to study the photoexcitations in semiconducting $La_{2-x}Sr_xCuO_{4-\delta}$ and proved to be a powerful probe of the band-gap presence and localized charged-defect states within the gap of this material.[4,5] Photoinduced ir spectra of semiconducting $YBa_2Cu_3O_{6+x}$ have also been reported for $0.2 \leq x \leq 0.3$, showing a series of photoinduced ir modes and a localized gap state at about 0.13 eV.[6–9] However, there are few reports on photoinduced absorption in the visible to near-infrared range[8,9] and no reports in ultraviolet to visible region, to our knowledge.

In this paper we report absorption and photoinduced-absorption spectra of semiconducting $YBa_2Cu_3O_{6+x}$ thin-film samples in the uv–visible–near-ir range. Direct-absorption specta were recorded at room temperature in the photon-energy range of 0.2–5.5 eV, showing one low-lying absorption at 0.5 eV, a shoulder around 1.7 eV, and a higher-energy peak at approximately 3.0 eV, which are assigned to Cu *d-d* transition (0.5-eV feature) and oxygen-*p*-band–to-copper-*d*-band charge-transfer excitations (1.7- and 3.0-eV features). Absorption peaks at 4.2 and 4.8 eV are also reported, which are assigned to optical transitions involving O 2*p* to Ba 5*d* orbitals and transitions of the O—Cu—O complex that comprises the chain segments, respectively. The 4.8-eV peak position is sensitive to oxygen content. Photoinduced-absorption experiments were carried out in the range of 0.5–3.3 eV at a temperature of 10 K. The photoinduced absorption in the ir (0.05–0.5 eV) range are reported in the preceding paper.[10] The pumping photon energy is chosen at 2.71 eV, which is much higher than the charge-transfer gap of this material. Photoexcitation spectra of $YBa_2Cu_3O_{6+x}$ showed two photoinduced-absorption (PA) peaks at 1.1 and 1.4 eV, with the crossover to a photoinduced-bleaching energy at 1.6 eV, and two strong photoinduced-bleaching (PB) peaks at 1.9 and 2.6 eV. The intensity dependences of the magnitudes of the photoinduced-absorption and -bleaching peaks are similar, increasing as $I^{\sim 0.6}$, where I is the pumping-light intensity. At higher light intensity ($I_0 \geq 100$ mW/cm^2), the power law is closer to 0.5, indicating that the dynamic process of the photoinduced species responsible for each peak is predominantly bimolecular. The chopper-frequency dependence (4–300 Hz) of the photoinduced-absorption peaks differs from those of the photoinduced-bleaching peaks at low frequency, showing that the magnitude of each bleaching peak is more strongly frequency dependent than the absorption peaks. We suggest that the photoinduced-bleaching peak at 1.9 eV corresponds to transitions from the O $p\sigma$ to the Cu $d_{x^2-y^2}$ band and the photoinduced-bleaching peak at 2.6 eV corresponds to the in-plane O $p\pi_{x,y}$ to the Cu $d_{x^2-y^2}$ and/or out-of-plane O $p\pi_z$ to Cu $d_{3z^2-r^2}$ band of Cu-O planes. Photoinduced-absorption peaks at 1.1 and 1.4 eV are photoexcitations from O *p* bands to a photoexcited defect state which is 1.1 eV above the O *p* band. This localized positively charged defect is proposed as a hole polaron state in semiconducting $YBa_2Cu_3O_{6+x}$ upon photoexcitation. The possible origin of the splitting of the 1.1- and 1.4-eV photoinduced absorptions is discussed in terms of strong-coupling models.

The remainder of the paper is organized as follows. The experimental techniques will be discussed in the next section. Experimental results for both direct- and photoinduced-absorption spectroscopy will be presented in Sec. III. The data will be discussed in Sec. IV together with a proposed model. The paper will be summarized in Sec. V.

II. EXPERIMENT

Samples used in the experiment were thin films of $YBa_2Cu_3O_{6+x}$ of thickness of 2500–5000 Å on MgO substrates with the *c* axis out of plane, produced by annealing films of cosputtered reactants; details of the preparation and characterization of these thin films are provided elsewhere.[29] Samples that had good quality as observed under an optical microscope and by Raman spectroscopy were chosen to carry out the optical measurements. Near-steady-state photoinduced-absorption as well as direct-optical-absorption spectra were measured in the range of the near-ir through near-uv region (0.2–5.5 eV for direct absorption and 0.5–3.3 eV for photoinduced absorption). The photoinduced-absorption measurement was carried out by pumping the sample with an argon-ion laser at 2.71 eV (457.9 nm), with intensity at the sample of 40–250 mW/cm^2; the probe beam, produced by an incandescent lamp or a deuterium lamp, was filtered through a monochromator and detected by the appropriate semiconducting photodiodes. The pumping beam was mechanically chopped with chopper frequencies in the range 4–300 Hz. A lock-in amplifier was used to measure the change in transmission, ΔT, of the sample induced by the photoexcitations. The transmission T of the sample was measured simultaneously in order to obtain $-\Delta T/T$, which is independent of the response of the measuring apparatus and is proportional to the change in absorption coefficient of the sample. For the photoinduced-absorption measurements, the sample was held at low temperature of ~ 10 K to achieve the best signal-to-noise ratio. The recombination of photoinduced defects was investigated by varying chopping frequency and laser-light intensity. A set of calibrated neutral density filters was used to measure the power dependence of the photoinduced features, varying the intensity of the laser light by factors of 0.03–1.

III. EXPERIMENTAL RESULTS

Shown in Fig. 1 is the direct-optical-absorption spectra of $YBa_2Cu_3O_{6+x}$ for $x = 0.0$ and 0.3 measured at room temperature. A significant absorption peak was observed in both spectra at about 0.5 eV. Both spectra have a nearly linear increase of the band-edge absorption starting at 1.4 eV with a shoulder at 1.7 eV. A second linear increase of absorbance begins at 2.2 eV with a plateau at ~ 3.0 eV. With the increase of photon energy, two additional strong peaks were recorded at 4.3 and 4.8 eV for $x = 0.0$. When the oxygen content was increased from $x = 0.0$ to 0.3, the 4.8-eV peak shifted to 5.2 eV and increased in relative intensity, while the four lower-energy peaks remained unshifted and decreased in relative intensity. An interpretation of these data will be given in Sec. IV.

Shown in Fig. 2 is the photoinduced-absorption spectrum of $YBa_2Cu_3O_{6.3}$, measured on the same sample used

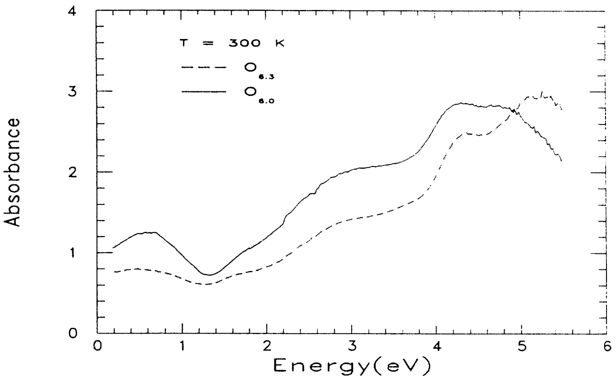

FIG. 1. Room-temperature optical absorbance of $\mathrm{YBa_2Cu_3O_{6+x}}$ with $x=0.0$ (dashed curve) and 0.3 (solid curve). The thickness of each sample is ~2500 Å.

for the absorption spectra in Fig. 1. (The photoinduced-absorption spectrum for $x=0.0$ measured in the range of 1.1–3.3 eV shows similar features, though weaker.) By pumping at 2.71 eV well above the band gap [determined by the crossover from photoinduced absorption (PA) to photoinduced bleaching (PB) (see Sec. IV)], photoinduced absorptions were observed over a wide range of energies from far-ir to near-ir, with two peaks at approximately 1.1 and 1.4 eV. Photoinduced ir modes and a peak at ~0.13 eV are discussed in the companion paper by Ye *et al.*[10]. The crossover energy from photoinduced absorption to photoinduced bleaching is at 1.6 eV. Two strong photoinduced-bleaching peaks were recorded at the energies of 1.9 and 2.6 eV. The discontinuity of the photoinduced-bleaching peak in the range 2.65–2.9 eV was caused by a strong pump-laser-light background centered at 2.71 eV. Our study of the change of direct absorbance with sample temperatures shows a small increase of absorbance due to heating at ~1.8 eV, in contrast with the photoinduced-bleaching peak observed in the same energy region, demonstrating that the heating effects are not the origin of the photoinduced-absorption spectrum shown in Fig. 2.

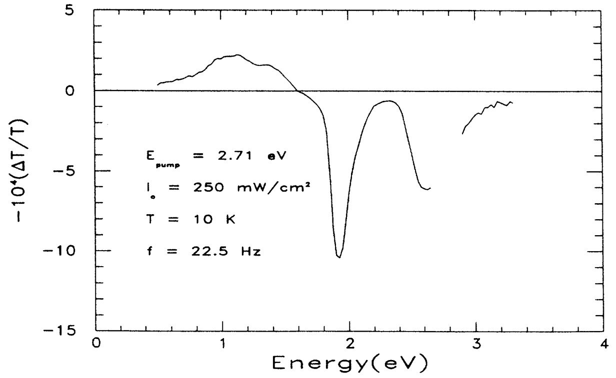

FIG. 2. Photoinduced absorption of $\mathrm{YBa_2Cu_3O_{6.3}}$ with a pumping energy of 2.71 eV, intensity of ~250 mW/cm^2, and chopping frequency of 22.5 Hz, at a temperature of 10 K.

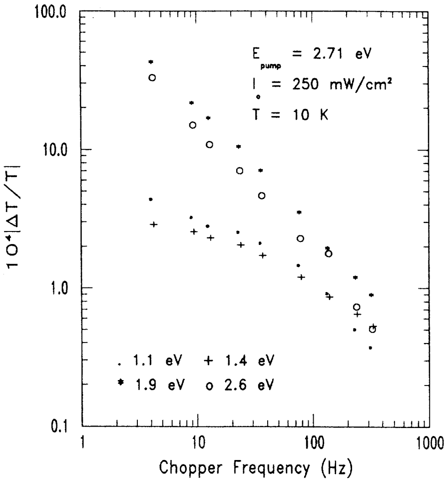

FIG. 3. Frequency dependence of each of the peaks of $\mathrm{YBa_2Cu_3O_{6.3}}$ at a laser intensity of ~250 mW/cm^2 and temperature of 10 K.

The chopper-frequency dependences of the two photoinduced-absorption peaks at 1.1 and 1.4 eV, as well as the two photoinduced-bleaching peaks at 1.9 and 2.6 eV, are presented in Fig. 3. In this log-log plot of $|\Delta T|/T$ versus chopping frequency f, it is observed that the 1.1- and 1.4-eV peaks follow a power law for frequencies below 100 Hz, with a slope of ~ -0.4; however, for frequencies greater than 100 Hz, $|\Delta T|/T \propto f^{-0.7}$, closer to the behavior of the photoinduced-bleaching peaks at 1.9 and 2.6 eV. At low chopper frequencies, the bleachings peaks maintained the stronger $f^{-0.7}$ dependence. The variation of the PA and PB peaks with pump-laser intensity I is shown in Fig. 4. All of the peaks follow a

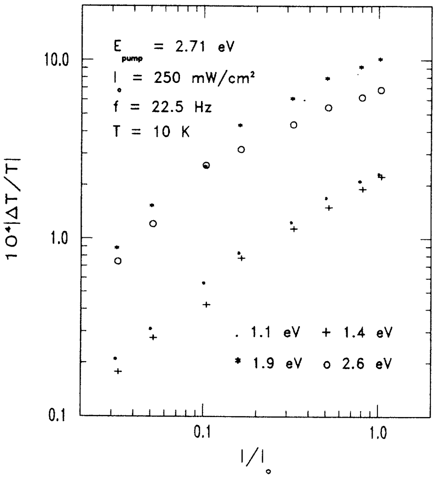

FIG. 4. Power dependence of each of the peaks of $\mathrm{YBa_2Cu_3O_{6.3}}$ at a chopper frequency of 22.5 Hz and temperature of 10 K.

similar power law, with $|\Delta T|/T \propto I^{0.6}$ for relative weak pump intensity (≤ 40 mW/cm^2). However, with increased laser intensity, the slope decreases to ~ 0.5.

We note that we experienced sample-to-sample variations and sample-surface degradation in studying this material. Sample surfaces were apparently subject to degradation even when the samples were kept in a dessicator. For example, when pumped by light on the external surface side of the films, the photoinduced-absorption spectra of the samples showed significant changes after the samples were kept in the dessicator for approximately 3 months. However, when we performed the photoinduced-absorption experiment by pumping into the substrate side of the samples, the photoinduced-absorption spectra show the same results as obtained 3 months earlier. This result demonstrates that the degradation occurred predominately in the external surface of the samples, which is in agreement with the optical photoemission results obtained by Arko *et al.* for superconducting samples.[30] The data presented here are typical of freshly prepared samples and the substrate side of aged samples.

IV. DISCUSSION

A. Direct-absorption spectra

The interpretation of the 0.5-eV direct-absorption peak is controversial. Kamarás *et al.* observed this peak in superconducting $YBa_2Cu_3O_{6+x}$, but reported it absent in the semiconducting form.[1] Orenstein and Rapkine argued that this peak for metallic samples comes from the Drude term distorted for an ensemble of small grains that have different orientations (small-particle resonance).[2] Geserich *et al.*[23] and Romberg *et al.*,[24] however, reported a 0.5-eV peak in semiconducting as well as superconducting $YBa_2Cu_3O_{6+x}$. Since in semiconducting samples the Drude form does not apply, we can rule out the small-particle resonance effect for our semiconducting sample. Geserich *et al.* assigned the peak to a Cu *d-d* transition, though they pointed out the unexpectedly large oscillator strength of the peak. For example, in NiO the *d-d* transition intensities are usually weak, with the absorbance normally on the order of 10^2-10^3 cm^{-1} due to symmetry reasons (most *d-d* transitions are dipole forbidden).[31] In the high-T_c parent materials, the absorbance is of order 10^5 cm^{-1}. Since $d_{xz(yz)}$ to d_{xy} and $d_{xz(yz)}$ to $d_{x^2-y^2}$ orbital transitions are dipole allowed, and there is hole admixture in these orbitals as observed by x-ray photoemission and electron-energy-loss spectroscopies,[3,32] the large oscillator strength is reasonable. We note here that this *d-d* transition led Weber to propose a different pairing mechanism,[33] which was later more completely examined by Jarrell, Krishnamurthy, and Cox.[34] An alternative origin of the large *d-d* transition oscillator strength is the proposed role of virtual electric quadrupole fluctuations.[35]

The peak at ~ 1.7 eV in the absorption spectra of $YBa_2Cu_3O_{6+x}$ for $x = 0.0$ and 0.3 is assigned to the optical transitions of the charge-transfer gap from the oxygen $p\sigma_x, p\sigma_y$ band to the copper $d_{x^2-y^2}$ band ($pd\sigma$) in the copper oxide planes. Several arguments led us to this conclusion. First, a theoretical study shows that the charge-transfer gap of $YBa_2Cu_3O_{6+x}$ is around 2–3 eV.[17] Second, ellipsometry studies show the 1.7-eV peak present only in the nonmetallic state of $YBa_2Cu_3O_{6+x}$.[18–22] This peak also vanishes for optical measurements polarized along the *c* axis.[36,37] Geserich *et al.*[23] and Romberg *et al.*[24] also reported this peak in their absorption spectra and assigned it as the charge-transfer gap. In the next section, the correspondence of the 1.9-eV photoinduced-bleaching peak with the ~ 1.7-eV peak of the direct-absorbance measurements will be shown, which strongly suggests that this 1.9-eV bleaching peak is the band-gap photoexcitation from the oxygen *p* band to the copper *d* band. This assignment is in accord with recent photoconductivity experiments.[38] The 3.0-eV direct-absorption peak is independent of oxygen composition.[18,19] This peak is also absent in the optical measurements polarized in the *c* direction.[36,37] We assign this peak to in-plane O $p\pi_{x,y}$ to Cu $d_{x^2-y^2}$ and/or out-of-plane O $p\pi_z$ to Cu $d_{3z^2-r^2}$ transitions in the Cu-O plane. We expect that the contribution from the latter transition is less significant, since only $\sim 15\%$ of holes go into Cu $d_{3z^2-r^2}$ orbitals.[32] The strong peak at 4.3 eV has been assigned to a highly localized O—Cu—O complex in the Cu-O chain.[18] Alternatively, this peak has been assigned to localized O—Cu—O units with some contributions of Ba-O interband transitions.[19,20] Our data show a lack of dependence of this peak on oxygen doping for $0.0 \leq x \leq 0.3$, consistent with the results of Garriga *et al.*[20] supporting the conclusion that this peak originates from Ba-O interband transitions. The shift of the highest-energy peak from 4.8 eV (for $x = 0.0$) to 5.2 eV (for $x = 0.3$) strongly suggests that this peak comes from a localized transition around the O—Cu—O complex in the Cu-O chain.

B. Photoinduced-absorption spectra

It is well known that photoinduced-absorption peaks are related to the photoexcitations of intrinsic defect states of the materials, such as the solitons and polarons or bipolarons of conducting polymers. In this experiment, broad photoinduced-absorption peaks are observed at 1.1 and 1.4 eV. Sharper photoinduced-bleaching peaks are observed at 1.9 and 2.6 eV. The photoinduced-bleaching peaks correspond closely to direct-absorption peaks at 1.7 and 3.0 eV, although they are much sharper than the direct-absorption peaks. Hence we propose that the 1.9-eV bleaching peak arises from a reduction in the oscillator strength of the in-plane O $p\sigma$ to Cu $d_{x^2-y^2}$ transition and the 2.6-eV bleaching peak arises from a reduction in the oscillator strength of the in-plane O $p\pi_{x,y}$ to Cu $d_{x^2-y^2}$ and/or out-of-plane O $p\pi_z$ to Cu $d_{3z^2-r^2}$ transitions, respectively, due to formation of localized defect states (see below).

Recently, several models have been proposed to explain the possible origin of doping and photoexcited defect states.[16,17,39–44] Bound states for oxygen holes were proposed and calculated for $YBa_2Cu_3O_7$ (Ref. 16) and doped La_2CuO_4 (Ref. 17) within the Anderson impurity model. The results calculated by Eskes and Sawatzky[16] show that in the metallic state of $YBa_2Cu_3O_7$, the excess holes of the CuO plane upon oxygen doping form a singlet bound state. Annett *et al.* found two competing states for holes introduced by hole doping, with primarily in-plane O $p\sigma$ and out-of-plane O $p\pi_z$ character.[17] Rice and Wang proposed that positive and negative polarons can be formed upon charge-transfer excitation.[39] The positive polaron was suggested to be self-trapped at the O^{2-} sites. Later, the hole-defect state was described as a self-localized polaron related to the distortion of the antiferromagnetic spin background in the *t-J* model.[40,41] The formation of a localized "polaronic" state in $YBa_2Cu_3O_{6.3}$ upon photoexcitation was suggested, based on the observation of 0.13-eV "electronic" photoinduced-absorption peak.[6,7,43] However, recent studies of photoinduced ir absorption of semiconducting $YBa_2Cu_3O_{6+x}$ of powder form showed that the details of the "electronic" photoexcitation spectrum varied systematically with oxygen content.[10] In the companion work of Ye *et al.*, this ~0.13-eV defect state is proposed as the anionic D^- localized states trapped in Cu-O-Cu chain segments.

We suggest here that the 1.1-eV photoinduced-absorption peak comes from a low-lying O *p* band to a photoexcited *intrinsic* self-localized hole polaron state in the gap. It is noted that the actual polaron level may lie substantially closer to the valence-band edge as the 1.1 and 1.4-eV photoinduced absorptions include the effects of Coulomb repulsion for inserting a second charge in the polaron level. Several possibilities exist for an interpretation of the 1.4-eV peak. One speculation is that this peak is associated with transitions from an in-plane O $p\pi_{x,y}$ band to the same polaron level. Since photoinduced-bleaching peaks demonstrate that the in-plane O $p\pi_{x,y}$ and O $p\sigma$ bands are separated in energy by 0.7 eV, the corresponding photoinduced-absorption peaks should be separated in energy by approximately the same amount, somewhat larger than the observed 0.3-eV splitting between these two peaks. The chopper-frequency dependence of the 1.4-eV PA peak gives evidence that this peak contains contributions from both photoinduced absorption and bleaching. At low frequencies, the magnitudes of the photoinduced-bleaching peaks decrease with a greater rate than the magnitudes of the photoinduced-absorption peaks with increase of chopper frequency. This photoinduced-absorption peak may be distorted by the tail of the adjacent photoinduced-bleaching peak, narrowing the apparent splitting between these two photoinduced-absorption peaks.

An alternative origin for the splitting of the 1.1- and 1.4-eV PA peaks is suggested and motivated by the report of Chen and Schüttler of a numerical study of the *t-J* model in the strong-coupling limit. Their results show broad absorption features from 0.2 to 1.0 eV in the doping and photoinduced-optical-absorption spectra which may correspond to the 1.1- and 1.4-eV PA peaks.[44] They also predict that there should exist another photoinduced-absorption feature in the 4–6 eV range associated with the Zhang-Rice singlet-triplet excitation.[42,44] However, Annett *et al.*[17] calculated that the splitting between the singlet and triplet is rather small (of order 0.1 eV). Therefore, we point out as a third possibility that the splitting of the 1.1- and 1.4-eV peaks in our photoinduced-absorption spectra results from the singlet-triplet splitting in this material. If this is the case, the splitting ($2J$) can be estimated as 0.3 eV. Within this model, the antiferromagnetic exchange coupling of Cu-O, J, is estimated to be 0.15 eV, consistent with theoretical calculations.[44]

The photoinduced-bleaching peaks have stronger chopper-frequency dependence than the photoinduced-absorption peaks at low frequencies, demonstrating that the former features are longer lived than the latter. This might reflect that some of the photoinduced charges migrate to grain boundaries to form extrinsic defects, while the intrinsic hole polaronic defect state is self-localized in the Cu-O plane and the intrinsic negative defect is localized on the chain segments. As evidenced by their pump-intensity dependence, the recombination kinetics of the photoinduced-absorption and -bleaching peaks are primarily bimolecular ($I^{0.6}$). The small decrease of the slopes ($I^{0.5}$) with increasing intensity could result from saturation of photoexcited defects induced by laser pumping. Further work especially in picosecond photoinduced-absorption experiments is needed to reveal the origin of the temporal decay processes involved in photoexcitation defect states in semiconducting $YBa_2Cu_3O_{6+x}$.

V. CONCLUSION

In summary, we have studied absorption and photoinduced absorption of semiconducting $YBa_2Cu_3O_{6+x}$ thin-film samples. Absorption spectra showed five peaks for the $x=0.0$ sample at 0.5, 1.7, 3.0, 4.3, and 4.8 eV. With doping of oxygen to a level of $x=0.3$, these five peaks remain unchanged in energy except for the shift of the highest-energy peak from 4.8 to 5.2 eV. These peaks are assigned to the Cu intrasite *d-d*, O $2p\sigma$ to Cu $3d_{x^2-y^2}$ charge-transfer gap, the in-plane O $p\pi_{x,y}$ to Cu $d_{x^2-y^2}$ and/or out-of-plane O $p\pi_z$ to Cu $d_{3z^2-r^2}$ charge-transfer gap, the O 2*p* to Ba 5*d* interband, and the localized O—Cu—O complex in the Cu-O chain transitions, respectively. Photoinduced-absorption studies show two photoinduced-bleaching and two photoinduced-absorption peaks. The 1.9- and 2.6-eV bleaching peaks are proposed to correspond to 1.7- and 3.0-eV direct-absorption peaks, indicating a reduction in the available band-edge states of the Cu-O planes. Two types of defect states are proposed to exist in this material upon photoexcitation. One of the defect states proposed is a positively charged intrinsic defect D^+. The 1.1- and 1.4-eV photoinduced-absorption peaks are suggested to be the transitions from O *p* bands to this intrinsic self-localized hole polaron state within the gap. The possible origins of the splitting of the PA peaks are discussed, including the potential role of the Zhang-Rice singlet-triplet excitations. The magnitude of photoinduced-absorption and -bleaching peaks varies as $I^{0.6}$ with the pump-beam intensity, which shows that the decay channel is mainly bimolecular but mixed with some unimolecular decay process. The frequency dependence of photoinduced-absorption peaks at 1.1 and 1.4 eV is quite similar, varying with chopper frequency $f^{-0.4}$. The two bleaching peaks show similar frequency dependence $f^{-0.7}$, but different from that of the photoinduced-absorption peaks in the frequency range of 4–100 Hz. From the results of Ye *et al.*[10] we propose that there exists an intrinsic photoinduced anionic defect state. We propose that the photoexcitation of semiconducting $YBa_2Cu_3O_{6+x}$ actually leads to a hole polaron state that is 1.1 eV above the highest occupied O *p* bands of the Cu-O plane and an anionic defect state which is ~0.13 eV below the lowest unoccupied Cu *d* bands at $(O—Cu—O)^-$ segments of the Cu-O chain.

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