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Photo-excitation of single crystals of $\text{La}_2\text{CuO}_{4+\delta}$ near the metal–insulator transition

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Transient photoconductivity (σ_{ph}) experiments have been carried out in single crystals of insulating $\text{La}_2\text{CuO}_{4+\delta}$ near the metal–insulator transition ($\delta \approx 1\text{--}2\%$). The time evolution of the σ_{ph} changes dramatically with light intensity (I_L). At low I_L , σ_{ph} is characterized by power law time decay, $t^{-\alpha}$, in the nanosecond time regime, and the exponent, α , decreases significantly with increasing I_L . As I_L increases to 5×10^{15} photons/cm², σ_{ph} reaches ~ 15 S/cm, and the lifetime of the conducting state is enhanced by more than two orders of magnitude: σ_{ph} exhibits a delayed peak centered at approximately 30 ns, followed by exponential decay with time constant of ~ 360 ns. The data reveal a continuous distribution of localized electronic states above the (hole) mobility edge: the M–I transition is achieved when the Fermi level is shifted away from the localized states and across the mobility edge either by chemical doping or by photo-excitation. The time evolution of σ_{ph} at high I_L implies the formation of metastable metallic droplets after photo-excitation.

1. Introduction

In the Cu–oxide materials which exhibit high temperature superconductivity (HTSC), the antiferromagnetic (AF) transition, the metal–insulator (M–I) transition and the superconducting (SC) transition are closely correlated with the density of charge carriers on CuO_2 layers [1]. Photo-excitation provides an alternative method to vary the carrier density on the CuO_2 planes without the accompanying changes in structure and the formation of localized defect states, etc., that are inherent to chemical doping. Moreover, photo-excitation and the measurement of transient photo-induced conductivity provide a special opportunity to probe the dynamics of the non-equilibrium response of the HTSC systems as a function of charge-carrier density.

Recent transient σ_{ph} experiments in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

demonstrated that the metallic/superconducting state can be achieved in the nanosecond regime by means of photo-excitation from samples in the insulating phase pre-doped to be near the metal–insulator transition ($\delta > 0.6$) [2,3]. The magnitude of the peak photo-induced conductivity (which is time-delayed with respect to the excitation) was found to increase superlinearly at high pumping intensities, I_L . The temperature dependence of σ_{ph} following successively higher levels of excitation corresponds to that of the dark conductivity at successively higher oxygen levels, implying “photo-doping” with carriers injected onto the CuO_2 planes. The M–I transition was achieved in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at $I_L \sim 5 \times 10^{15}$ photons/cm²; at higher levels the data were interpreted in terms of the formation of metallic droplets which become locally superconducting at temperatures below approximately 90 K.

In this paper, we present the results of an experimental study of the transient photo-induced conductivity in single crystals of $\text{La}_2\text{CuO}_{4+\delta}$ with δ near

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that required for the M–I transition ($\delta \approx 1.3\%$). The time evolution of the transient photo-induced conductivity changes dramatically with I_L . For low I_L (about 10^{14} photons/cm² and below), σ_{ph} decays within a few nanoseconds following a power law, $t^{-\alpha}$, where $\alpha \approx 1$. As I_L increases, the initial σ_{ph} increases toward the minimum metallic conductivity, σ_{min} , and the exponent of the power law decay decreases significantly. Following photo-excitation at high I_L , a metastable conducting state is formed; at $I_L \approx 5 \times 10^{15}$ photons/cm², σ_{ph} reaches ~ 15 S/cm, exhibits a delayed peak centered at approximately 30 ns, and subsequently decays exponentially with time constant $\tau \approx 360$ ns.

2. Experimental

The apparatus used for these experiments is similar to that described in our previous publications on $YBa_2Cu_3O_{7-\delta}$ [2,3]. The excitation source was either a N_2 laser (PRA LN1000) with 600 ps pulsewidth at 3.7 eV or a 30 ps dye laser (PRA LN105A) at 2.6 eV. The repetition rate was set at about 3 pulses per second. The gatewidth of the sampling head in the boxcar integrator (EG&G PRAC 4400 system) could be varied from 25 ps to tens of microseconds. Suitable gatewidths were chosen (25 ps in the time-range less than 10 ns and 2 ns in the time-range from 10 ns up to 1 μ s) to obtain the desired time resolution and the necessary sensitivity. Signal averaging was necessary (5 to 20 pulses per point, depending on signal magnitudes) to obtain an acceptable signal-to-noise ratio.

The samples for transient photo-induced conductivity were cut from a larger crystal into platelets with approximate dimensions $1 \times 1 \times 0.6$ mm and mounted onto Auston switch transmission lines [4] such that current flow would be in the ab -plane (CuO_2 plane) with the light beam incident perpendicular to the ab -plane. In this configuration, the carriers were excited and transported in the CuO_2 planes. For all experiments, the bias field strength was relatively small, in range of 10–250 V/cm. The Auston switch was loaded in a sample holder mounted at the tip of a cold-finger, allowing measurements at temperatures from 300 K to 20 K. All measurements were carried out in vacuum of less than 10^{-4} Torr.

Details of the experimental arrangements can be found in earlier publications [2,3].

Single crystals of $La_2CuO_{4+\delta}$ were grown by the flux method from a CuO -rich La_2O_3 – CuO melt in a platinum crucible, followed by annealing either in Ar (or in air) from 600°C to 350°C over 12 h. The excess oxygen is known to be difficult to remove completely from $La_2CuO_{4+\delta}$ even after post-synthesis annealing in a high-flow of Ar [6]. It has been confirmed that the extra oxygen atoms occupy the O(4) sites in the lattice [7], locally distorting the lattice structure and inducing carriers (holes) onto the CuO_2 planes. This excess oxygen doping causes changes in electronic structure which are similar to those caused by substitution of Sr for La: the doping destroys the AF order, induces a M–I transition and finally makes the material a superconductor ($T_c = 38$ K) at $\delta \approx 0.04$ [8].

The samples used for our photo-excitation measurements were in the insulating phase, but near the M–I transition. The temperature (T) dependence of the dark-conductivity in ab -plane, $\sigma(T)$, is thermally-activated, $\sigma(T) = \sigma_0 \exp(-E_a/k_B T)$, from 300 K to 50 K. Conductivity measurements yielded $E_a \approx 18$ meV with variations of ± 4 meV from sample to sample. The δ value is estimated to be about 1.3% by comparing the activation energy with the data in the literature [9]. The Néel temperature T_N at this doping level is in the range of 260 K–280 K [9,10]. The room temperature conductivity of the samples was 5–10 S/cm (two probe measurement). Extrapolation of the dark $\sigma(T)$ to the high temperature limit gives the pre-factor σ_0 (corresponding to the minimum metallic conductivity [2,3], σ_{min}) in this material $\sigma_{min} \approx 10$ –20 S/cm, comparable with the value measured by other groups [9,10] and with that in $MBa_2Cu_3O_{7-\delta}$ ($M=Y, Dy$) [3,11]. No strong anomalies were observed in the $\sigma(T)$, consistent with the fact that T_N is larger than 250 K [10].

For T near 300 K ($k_B T = 26$ meV), the dark $\sigma(T)$ is so high that the transient σ_{ph} could not be detected above the dark conductivity background; Joule heating of the highly conducting samples limits the electric-field strength and the attainable signal/noise ratio. At $k_B T \ll E_a$, σ_{ph} becomes detectable; consequently, the σ_{ph} data in this paper were taken at 25 K.

3. Results and discussion

Since the photo-conductive response in La_2CuO_4 follows the optical absorption in the vicinity of the interband transition [12], the photon energy used for photo-excitation experiments should be larger than 2 eV. In fig. 1, we show the time dependence (log-log scales) of the transient σ_{ph} obtained from $\text{La}_2\text{CuO}_{4+\delta}$ ($E_g \approx 20$ meV) at 25 K at several different I_L in the range below 6×10^{14} photons/cm². The excitation source used in this measurement was the N_2 laser (600 ps, 3.7 eV). The magnitude of σ_{ph} was estimated by assuming that the photo-induced current is carried in a layer with thickness equal to the optical absorption depth, which is about 400 Å (as inferred from measurements of the optical constants) [13]. The data show that σ_{ph} follows a power law decay, $t^{-\alpha}$, with the exponent α decreasing in magnitude as I_L increases. For the lowest two curves in fig. 1, the power law is characterized by $\alpha \approx 1$, while for the highest curve, $\alpha \approx 0.62$.

Figure 2 shows semi-log plots of $\sigma_{\text{ph}}(t)$ following successively higher I_L (pumped with the N_2 laser) for times out to 500 ns. A significant change in the time evolution of $\sigma_{\text{ph}}(t)$ was observed when I_L reached the level of 10^{15} photons/cm². For $I_L \approx 5 \times 10^{15}$ photons/cm², $\sigma_{\text{ph}}(0) \approx 15$ S/cm (corresponding to 2×10^{-6} S/sheet), which is comparable with the σ_{mm} in this material. At these high levels of photo-excitation, the photo-induced conductivity

Fig. 1. Transient photoconductivity, $\sigma_{\text{ph}}(t)$, plotted on log-log scales at low light intensities at 25 K. (●) 6.3×10^{14} photons/cm², (■) 2.8×10^{14} photons/cm², (◆) 1.3×10^{14} photons/cm², (▲) 7.2×10^{13} photons/cm².

Fig. 2. Transient photoconductivity, $\sigma_{\text{ph}}(t)$, plotted on semi-log scales at higher light intensities at 25 K. (□) 5.1×10^{15} photons/cm², (○) 3.8×10^{15} photons/cm², (△) 2.6×10^{15} photons/cm², (■) 1.5×10^{15} photons/cm², (●) 6.3×10^{14} photons/cm².

Fig. 3. Transient photoconductivity, $\sigma_{\text{ph}}(t)$, during the initial 40 ns after photo-excitation. The symbols and the corresponding I_L are the same as those in the fig. 1 and fig. 2.

persists to long times with a gentle maximum at about 30 ns followed by an exponential decay with time constant of approximately 360 ns.

The dependence of $\sigma_{\text{ph}}(t)$ during the initial 40 ns following photo-excitation is shown in fig. 3; the data were obtained with the N_2 laser, $\hbar\omega = 3.7$ eV with pulsedwidth of 600 ps. The evolution of σ_{ph} from the power law decay at low I_L to persistence at high I_L are clearly shown. The data in figs. 2 and 3 dem-

onstrate that at the lowest I_L , σ_{ph} decays one order of magnitude in a few nanoseconds; while at $I_L > 10^{15}$ photons/cm², several hundred nanoseconds is required for σ_{ph} to decay by an order of magnitude. Thus, the decay time (10%–90%) increases by more than two orders of magnitude. Similar results have been obtained following excitation by the dye laser ($\hbar\omega = 2.6$ eV, pulsewidth of 30 ps): both the magnitude and the delay of σ_{ph} are nearly independent of the pulse widths and the photon energies (for $\hbar\omega > E_g$), and are mainly determined by the total number of photons per pulse.

Similar to the phenomena observed earlier in $YBa_2Cu_3O_{7-\delta}$ [3,11], the σ_{ph} data following pulsed excitation at successively higher I_L can be understood in the context of an Anderson disorder-induced M–I transition [14]. The random occupation of the excess oxygen on the O(4) sites in the lattice results in a broad distribution of localized electronic states within the bandgap on the CuO_2 planes as characterized by absorption throughout the infrared [15].

We assume the existence of a mobility edge, E_c , which separates extended electronic states from localized states. The insulating phase is the so-called Fermi glass state [16] with Fermi energy, E_F , lying within the region of localized electronic states. Within this model, the M–I transition occurs when E_F moves across E_c into the region of extended states [14]. A schematic diagram of the two situations is shown in fig. 4.

The power law decay of the transient σ_{ph} at low I_L can be understood in the context of the theory of dispersive transport of charge carriers in disordered systems [17]. Since the unoccupied localized states act as traps, charge transport takes place via a sequence of trapping-and-release steps among the localized states in the presence of an applied electric field [18]. Due to the disorder, the transfer time becomes a random variable, and the accumulated sequence of all transfer events in the motion of a charge carrier can be viewed as a continuous-time random walk. As a result, the mobility becomes time dependent, and σ_{ph} follows a power law dependence with time, $t^{-(1-\beta)}$, where the parameter β is related to the exponent α in the form of $\alpha = (1-\beta)$. In the simplified model of an exponential distribution of trap (localized state) density, β can be written as $\beta = T/T_0$

Fig. 4. Schematic diagram of the electronic structures of the insulating phase and the metallic phase in a disordered system. (This diagram, which applies to electrons, can be altered in the obvious way to describe the holes).

T_0 , where T is temperature and $k_B T_0$ specifies an energy range over which the localized trap states can be filled [17].

In the insulating $La_2CuO_{4+\delta}$ crystals used for our σ_{ph} measurements, $k_B T_0$ corresponds to the energy between the highest occupied electronic states and E_c as shown in fig. 4(a). At low I_L , when the density of photoinduced carriers is small compared to the density of states near the E_F , the value for $k_B T_0$ obtained from σ_{ph} measurements is just the thermal activation energy, E_a , observed in the dark conductivity measurement. Using the experimental conditions, $T = 25$ K (2 meV), and $T_0 = E_a \approx 236$ K (20 meV), one obtains $\beta \approx 0.1$ and $\alpha \approx 0.9$, in agreement with the results (the lowest curve in fig. 1).

Since the σ_{ph} experiments as a function of I_L were taken at a fixed temperature ($T = 25$ K), the change of β with increasing I_L shown in fig. 1 indicates a shift of the effective E_F (the energy level separating the occupied states from the unoccupied states) toward E_c , caused by filling the localized states with photo-

excited charge carriers. Since the total time a carrier spends in traps far exceeds the total transit time in the extended band states, the localized states can be filled at high I_L , resulting in a shift of E_F towards E_c , thus causing the system to approach the M-I transition by photo-excitation. This is consistent with the fact that $\sigma_{ph}(0)$ approaches σ_{min} at the same levels of I_L . We have observed similar effects in $YBa_2Cu_3O_{7-\delta}$ and in other HTSC cuprates in the insulating phase [19].

The density of the localized states near E_c can be estimated from the data shown in fig. 1. Assuming the quantum efficiency to be approximately 1, a value of the order of $10^{22} \text{ (cm}^3 \text{ eV)}^{-1}$ is obtained from the intensity dependence of the power law decay, $\propto(I_L)$. Taking a more realistic quantum efficiency (a value well below 1 is suggested by the photo-induced absorption experiments in $YBa_2Cu_3O_{7-\delta}$ [20]), this number could be reduced by a factor of 10–50, in reasonable agreement with the $N(E_F) \approx 10^{21} \text{ (cm}^3 \text{ eV)}^{-1}$ obtained from analysis of the AC conductivity data for insulating $La_2CuO_{4+\delta}$ with $T_N \approx 285 \text{ K}$ [21].

The σ_{ph} measurements at successive I_L reveal the existence of a relatively high density of localized electronic states. In fact, the density of localized states is comparable with the density of states in the extended state regime. In the metallic phase with optimized T_C , $N(E_F) \approx 10^{22} \text{ (cm}^3 \text{ eV)}^{-1}$ as determined by measurements of the spin susceptibility and the specific heat [22].

We note that the localized charge states continue to exist below the Fermi energy, and that the density of such localized states appears to be enhanced (as indicated by the mid-infrared spectral feature) at relatively low energies below E_F when the system is switched into the metallic and superconducting phase by oxygen doping or Sr substitution. Perhaps, therefore, more attention should be paid to the effective interaction between the localized charges and the quasi-particles at E_F for an understanding of the origin of superconductivity in the HTSC cuprates.

A significant change in the σ_{ph} decay occurs at $I_L > 10^{15} \text{ photons/cm}^2$, as shown in figs. 2 and 3: one can clearly see that $\sigma_{ph}(t)$ begins to increase at $t \approx 3$ –5 ns, after an initial decay. The magnitude of σ_{ph} at this delayed maximum is about 10 S/cm, which is similar to the magnitude of $\sigma_{ph}(0)$ at the same I_L ,

and similar to σ_{min} in this material. As in photo-excitation experiments in $YBa_2Cu_3O_{8.4}$ [11], the delayed photoconductive state and its persistence to relatively long times suggests that the distribution of photoinduced carriers becomes inhomogeneous after photo-excitation, i.e., hole-rich domains (metallic droplets) are formed.

The implied phase separation of the photo-induced carriers is consistent with the results obtained from theoretical models; analysis of the t - J and t - J - V model indicate that dilute holes in a 2D antiferromagnetic system are unstable against phase separation into a pure (no-hole) phase and hole-rich phase [23]. Thus, phase separation and metallic droplet formation might be an intrinsic feature of the HTSC cuprates.

Photo-induced absorption experiments [24] indicated that the photo-induced infrared active modes in La_2CuO_4 were correlated with the infrared modes in metallic/superconducting phase rather than those in an insulating phase, consistent with phase separation and the formation of metallic droplets. Moreover, it has been demonstrated that the oxygen at O(4) sites in $La_2CuO_{4+\delta}$ is unstable in samples of $\delta \geq 3\%$; the material undergoes phase separation when cooling down, forming the stoichiometric La_2CuO_4 phase and a hole-condensed $La_2CuO_{4+\delta}$ phase at low temperatures [8a,25].

The question of interest is whether we have reached the metallic phase in the hole-rich regions following photo-excitation. The photo-induced conductivity value (10–20 S/cm; see figs. 2 and 3) at high I_L is comparable to that found in $YBa_2Cu_3O_{7-\delta}$ and characterized there as consistent with the minimum metallic sheet conductivity ($\sim e^2/h$) in two dimensions [3,11]. Moreover, the close correspondence of the photo-induced conductivity value at high I_L to the prefactor (σ_0) in $\sigma(T)$ in $La_2CuO_{4+\delta}$ is indicative of photo-excitation to metallic levels. The persistence of the σ_{ph} at the level of σ_{min} for relatively long times and the subsequent exponential decay suggest that the E_F has moved across the E_c in the hole-rich phase. Quite different from the dispersive transport behavior at low excitation levels, at $I_L = 5 \times 10^{15} \text{ photons/cm}^2$, σ_{ph} (with a magnitude of $\sim 10 \text{ S/cm}$) decays exponentially with $\tau \approx 360 \text{ ns}$ after the delayed peak. The exponential decay of $\sigma_{ph} = ne\mu$ (n is the carrier density, e is the electron charge, and μ is the carrier

mobility) suggests that the time dependence is dominated by the recombination of the carriers in extended states.

The monomolecular (exponential) decay of $\sigma_{ph}(t)$ at high I_L implies that one type of carrier dominates the transport: presumably holes. We suggest that after the initial photo-generation of electron-hole pairs, the electrons are quickly trapped, presumably at sites (associated with the excess oxygen) out of the CuO_2 planes leaving the holes to phase separate and form metallic droplets in the CuO_2 planes in the nano-second time regime.

4. Conclusion

We have studied the transient photo-induced conductivity in single crystals of insulating $\text{La}_2\text{CuO}_{4+\delta}$ with δ near the M-I transition. The time evolution of the transient σ_{ph} at low I_L is consistent with that expected for dispersive transport, indicating the existence of a relatively high density of localized states. The time evolution of σ_{ph} following photo-excitation at high levels suggests phase separation and the formation of metastable metallic droplets; the lifetime of the conducting state at high levels of excitation is enhanced by more than two orders of magnitude. The details of the transport of the photo-induced carriers suggest that the M-I transition in this system is dominated by the disorder-induced localization, similar to that in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [3,11].

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