Transient terahertz photoconductivity of insulating cuprates

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We establish a detailed phenomenology of photocarrier transport in the copper oxide plane by studying the transient terahertz photoconductivity of Sr$_2$CuO$_2$Cl$_2$ and YBa$_2$Cu$_3$O$_6$. We identify and measure the intrinsic mobility of the photocarriers at early times, and characterize their evolution into a state characterized by thermal hopping.

How does a charge carrier move in an antiferromagnetic insulator? Since Brinkman and Rice posed this deceptively simple question over forty years ago [1], it has become a canonical problem in condensed matter physics and is widely thought to be at the heart of high-temperature superconductivity [2]. More recent attention has turned to optical excitations in correlated insulators [3–5], which can be studied now in real time with pulsed lasers [6, 7]. Interest in these states extends from their microscopic properties to their role in photoinduced transitions between distinct structural, magnetic, conducting, and superconducting phases [8–10]. Here, we measure the transient terahertz photoconductivity (THz-PC) of insulating antiferromagnetic copper oxides, and characterize its dependence on time, frequency, excitation density, and temperature. We find that photocarriers evolve from a nonequilibrium state of relatively high mobility to a thermalized state characterized by hopping conduction. These measurements provide a benchmark for future research on optical and single-particle excitations in magnetic solids.

In many correlated insulators, photoexcitation can liberate carriers by melting an ordered state that inhibits their conduction in equilibrium [7]. We focus here on photocarriers created instead through direct excitation across the correlation gap [8, 11–13]. Our approach complements photoemission, which provides access to individual hole states in insulating cuprates, but not to their transport properties [14–16]. Our experiments also offer guidance to the growing theoretical interest in the nonequilibrium properties of Mott insulators [17].

The infrared absorption spectrum of photoexcited copper oxides shows similarities with chemically doped compounds [8, 9, 18–20]. Uncertainties limit the extrapolation to the zero-frequency limit, but evidence exists at $\hbar \omega \gtrsim 0.1$ eV for short-lived Drude conductivity [8]. At lower frequencies, photoconductivity measurements have been limited to nanosecond timescales and are dominated by impurity band conductivity [21]. With its picosecond time resolution, THz-PC provides a method to probe the intrinsic low-frequency charge dynamics of photocarriers in the copper oxide plane [1, 22].

We studied two prototypical insulating cuprates, Sr$_2$CuO$_2$Cl$_2$ (SCOC) and YBa$_2$Cu$_3$O$_6$ (YBCO). SCOC crystals were grown by cooling the melt from 1110° C to 1075° C at a rate of 3° C/hr in an alumina crucible [22]. YBCO crystals were fabricated by a top-seeded melt growth technique [24]. The oxygen content of 6.00–6.01 in YBCO crystal is achieved by annealing at 700° C under $5 \times 10^{-7}$ torr oxygen pressure for 10 days. We saw no significant changes in the optical response during weeks of continuous experiments on the same samples, indicating the absence of photoinduced structural changes.

Fig. 1(a) shows the optical conductivity of SCOC [25], and Fig. 2 shows a simplified picture of the photoexcitation process. Insulating CuO$_2$ compounds share a common optical absorption spectrum [27, 28]. The ground state is an antiferromagnetic charge-transfer insulator with an optical gap near 2 eV [29]. Optical excitation above the gap transfers a hole from a Cu(3$d_{x^2-y^2}$) orbital to a nearby O(2$p$) orbital, whereupon it binds to an adjacent copper hole to form a spinless Zhang-Rice singlet [30]. Although the spatial structure of the 3$d^9$ L Zhang-Rice singlet is dramatically different from its spinless $d^{10}$ partner, in practice they share remarkably similar electronic properties [31]. Antiferromagnetic spin excitations couple strongly to the motion of both charge excitations, as illustrated in Fig. 2(b). Excitonic correlations should result both from this magnetic coupling and the usual Coulomb interaction, but their significance remains uncertain [32–34]. Strong temperature dependence in both the optical and single-particle photoemission spectra indicates that phonon interactions are also important [13, 16, 24, 32–34].

The inset to Fig. 1(a) shows a schematic of our measurement process. We create photocarriers by illuminating the sample with 100 fs, 3.10 eV pump pulses from a frequency-doubled laser amplifier. We probe their transient THz response with ZnTe using standard nonlinear optical methods [22]. To determine the time-dependent photoconductivity, we mechanically chop the pump beam to measure $\Delta E(t, \tau)$, the change in the THz probe field as a function of THz measurement time $t$ and pump delay $\tau$, and compare this to a reference THz field $E(t)$ transmitted through the unexcited sample. The terahertz beam diameter is 1.1 mm or less throughout our 2–4 meV measurement bandwidth, so our 5 mm pump beam diameter provides uniform illumination.

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After passing through the sample, the terahertz waveform $E(t)$ is measured in the time domain by repetitive sampling of the electric field at the terahertz measurement time $t$; the red marker indicates the point associated with $t = 2.3$ ps. We measure the change in $E(t)$ in response to a pump pulse that precedes the measured field point by a time delay $\tau$, to determine $\Delta E(t, \tau)$. (b) Measurements of $\Delta E(t, \tau)$ for $\tau = 1.3, 4.0, 16.0$, and 75.4 ps, together with the reference field $E(t)$ transmitted through the sample without pump excitation. The pump fluence is $F = 245$ $\mu$J/cm$^2$. All curves are normalized to the peak value of $E(t)$, with different vertical scales for $\Delta E(t, \tau)$ (left) and $E(t)$ (right), as indicated by the arrows.

Fig. 1(b) shows $E(t)$ together with $\Delta E(t, \tau)$ at various values of $\tau$, all for SCOC in units normalized to the peak of the reference field at $t = t_p$. Results for YBCO are qualitatively similar, with quantitative differences that we discuss below. Dividing the difference signal by the reference in the frequency domain gives $\Delta E(\omega, \tau)/E(\omega)$, the fractional change in the THz transmission spectrum. The optical penetration depth is much shorter than the THz penetration depth, so we treat the photoexcited material as an optically thin conducting film on an insulating substrate. In the small signal limit, and for time delays greater than the photocarrier momentum relaxation time, the THz-PC is $\sigma(\omega, \tau) \approx -(1+n)(\Delta E(\omega, \tau)/E(\omega))/\delta Z_0$, where $Z_0$ is the impedance of free space, $n$ the THz refractive index of the sample, and $\delta$ its optical penetration depth.

The inset of Fig. 3 shows the real part of the THz-PC, $\sigma_1(\omega, \tau)$, obtained from the data in Fig. 1(b). Our results for the imaginary part, $\sigma_2(\omega, \tau)$, are consistent with zero within our measurement uncertainty. We find that $\sigma_1(\omega, \tau)$ is approximately constant across our measurement bandwidth and remains so as it decays with increasing $\tau$. The spectra clearly extrapolate to a nonzero $\sigma_1$ at DC, indicating the existence of free, mobile carriers.

The lack of dispersion in $\sigma_1(\omega, \tau)$ allows us to focus on the time dependence by relating the THz-PC to the difference signal at the peak of the THz field. We define $\sigma_1(\tau) \equiv -(1+n)\Delta E(t_p, \tau)/\delta Z_0 \approx \langle \sigma_1(\omega, \tau) \rangle_\omega$, and show $-\Delta E(t_p, \tau)$ in the main panel of Fig. 3. The THz-PC develops promptly upon photoexcitation, then decays on multiple picosecond timescales. Qualitatively similar behavior is observed in the photoinduced absorption spectrum at mid-infrared frequencies.

We can estimate the photocarrier mobility by examining the peak THz-PC, $\sigma_{1p} \equiv \sigma_1(\tau = 0)$, as a function...
Assuming excitation density is saturating, not the carrier mobility. Absorption at the charge-transfer gap, indicating that the observed similar fluence dependence in the photoinduced transient currents, and the Gaussian pump pulse shape, \( g(\tau) = \Theta(t)(a_1e^{-t/T_1} + a_2e^{-t/T_2} + a_3) \), with best-fit parameters \( T_1 = 2 \) ps and \( T_2 = 40 \) ps. Markers identify \( \tau = 13 \) (○), \( 4.0 \) (○), \( 16.0 \) (△), and \( 75.4 \) (□) ps, as in Fig. 3(b). Inset: Room temperature photoconductivity spectra obtained from Fig. 4(b). Solid lines indicate mean values.

In Fig. 3, (color online). Room temperature fractional change \(-\Delta E\) in the peak THz field amplitude transmitted through SCOC after photoexcitation with \( F = 245 \) \( \mu \)J/cm\(^2\). Each point represents an average over \( N > 300 \) individual measurements, and the error bars show the standard deviation of the mean. The solid line depicts a model of multiple exponential decays convolved with the Gaussian pump pulse shape, \( y(\tau) = [f \ast g](\tau) \) with \( f(t) = e^{-t^2/(2\omega_p^2)/(\sqrt{2\pi}\omega_p)} \) and \( g(t) = \Theta(t)(a_1e^{-t/T_1} + a_2e^{-t/T_2} + a_3) \), with best-fit parameters \( T_1 = 2 \) ps and \( T_2 = 40 \) ps. Markers identify \( \tau = 13 \) (○), \( 4.0 \) (○), \( 16.0 \) (△), and \( 75.4 \) (□) ps, as in Fig. 3(b). Inset: Room temperature photoconductivity spectra obtained from Fig. 4(b). Solid lines indicate mean values.

The inset to Fig. 4 shows the \( \sigma_{\text{tp}} \) dynamics is relatively independent of fluence, evidence that the photocarriers are isolated throughout our 100 ps observation time. Interactions among photoexcitations should increase the initial decay rate by opening bimolecular or Auger recombination channels at high density. At the highest measured fluence, the mean separation between excitations in both SCOC and YBCO is 2.6 nm. Using the Einstein relation, we estimate that this is more than twice the distance that a photocarrier with the measured peak mobility would diffuse in 1 ps at room temperature. While our instrumental resolution may obscure interaction effects at short times, the peak mobility would need to be 50 times larger than what we observe for the carriers to reach each other on the timescale of our 100 fs pump pulse. We conclude that the observed THz-PC is a property of an isolated electron-hole pair. Evidence for a photoinduced metallic state was obtained at comparable densities, so the excitations should have been similarly isolated [8].

The temperature dependence shown in Fig. 4 demonstrates that thermal excitations inhibit the THz-PC at early times, but enhance it at longer times. By analogy with polar semiconductors, we expect photocarriers to relax in about 100 fs from their initial 3 eV excitation energy to states near the 2 eV gap. This populates phonons and magnons preferentially at high energies, which then thermalize on picosecond timescales. Our results indicate that photocarriers move relatively freely in a nonequilibrium phonon-magnon cloud at early times, then become trapped by disorder as the cloud dissipates into a thermal distribution.
To understand the temperature dependence more quantitatively we must account for the laser pulse energy. Assuming a Debye model for the specific heat, \( C \approx \beta T^3 \), we can relate the absorbed laser energy density \( \mathcal{E} \approx F(1 - \mathcal{R})/\delta \) to a characteristic temperature \( T_e \equiv (4\mathcal{E}/\beta)^{1/4} \). A photoexcited region will then reach an effective temperature, \( T_{\text{eff}} \equiv (T^4 + T_e^4)^{1/4} \), if all of the laser energy is dissipated thermally. Assuming a Debye temperature \( \Theta_D \approx 350 \text{ K} \) \([41]\), \( T_e \approx 100 \text{ K} \). Fits with an activation model to the thermalized THz-PC, \( \sigma_{1p} \propto \sigma_0 \exp(-\epsilon_0/k_B T_{\text{eff}}) \), are shown in the insets to Fig. 5, and yield activation energies \( \epsilon_0 = 7 \pm 2 \text{ meV} \) for SCOC and \( \epsilon_0 = 12 \pm 1 \text{ meV} \) for YBCO, both with \( T_e \approx 75 \text{ K} \) and \( \sigma_0 \approx 1 \text{ (}\Omega \text{ cm})^{-1} \). These activation energies are remarkably low, much smaller than the characteristic phonon and magnon energies, and suggest hopping in a relatively weak disorder potential.

The insets to Fig. 5 also contrast the temperature dependence of \( \sigma_{1p} \) with \( \sigma_{1T} \), and indicate that the intrinsic photocarrier mobility exhibited at \( \tau = 0 \) is degraded by thermal fluctuations. The curves are fits with the phenomenological model \( \sigma_{1p}(T) = 1/(\rho_0 + A T^2) \), with \( A = 390 \pm 50 \text{ n}\Omega \text{ cm/K}^2 \) for SCOC and \( A = 910 \pm 50 \text{ n}\Omega \text{ cm/K}^2 \) for YBCO. We caution that the data may also be described by other common expressions for equilibrium scattering processes, and that while Fermi liquid theory predicts this dependence for electron-electron scattering, we have no reason to expect it to be valid in this highly nonequilibrium state. Nonetheless, the results compare favorably with measurements on underdoped cuprates that show a similar quadratic temperature dependence with \( A \propto 1/p \), where \( p \) is the doping level, and \( A \approx 33 \text{ n}\Omega \text{ cm/K}^2 \) at \( p \approx 0.03 \) \([42]\).

In summary, THz-PC demonstrates that insulating cuprates support mobile photocarriers with a common dependence on time, fluence, and temperature. We infer an intrinsic photocarrier mobility from the peak photoconductivity, and show that its temperature dependence can be associated with scattering from thermal excitations. The initial photoconductivity decay rate is independent of fluence, indicating a lack of interaction among photoexcitations. We observe a crossover with time to a thermalized regime characterized by hopping conductivity with a low activation energy. By studying the evolution of these effects with chemical doping, it may be possible to strengthen our understanding of the excitations across the phase diagram of the doped antiferromagnetic insulator.

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