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Determination of the energy gap for charged excitations in insulating La_2CuO_4

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Measurements are reported of the photoconductivity (PC) in reduced, undoped, single-crystal La_2CuO_4. The spectral dependence of the PC shows a threshold at 2.0 ± 0.1 eV, corresponding to the minimum energy for the creation of charged excitations. Transient measurements indicate that the PC is surprisingly persistent: the average recombination time is longer than 10 s at room temperature.

Many models[1] for high-T_c superconductivity depend on the strong correlations in the motion of electrons in the two-dimensional CuO_2 layers. These same correlations result in an antiferromagnetic insulating state[2] when there is one hole per Cu ion, as in La_2CuO_4, whereas one finds a superconductor[3] with T_c near 40 K when there are 1.15 holes per Cu, in $La_{1.85}Sr_{0.15}CuO_4$. Because the excess holes induced by doping reside primarily on the oxygen ions,[4] it is believed that the lowest-energy charged excitation in the insulator corresponds to the transfer of an electron from states on the oxygen ions to states on the Cu ions. The size of this charge-transfer energy figures prominently in various theoretical descriptions[5] of the superconducting state as well.

Reflectivity measurements on undoped La_2CuO_4 yield optical conductivity[6] with a threshold below 2 eV. However, from optical experiments alone it is not possible to determine whether the threshold is that for charged excitations or for neutral ones, such as excitons. In this paper we report measurements of photoconductivity, using both pulsed and continuous photoexcitation, in insulating single crystals of La_2CuO_4. We observe a dramatic increase of the photoconductivity as a function of photon energy above 2.0 ± 0.1 eV, showing that this is, indeed, the threshold for charged excitations. The decay of the photoconductivity after pulsed excitation is very slow, corresponding to a recombination time longer than 10 s at room temperature.

Large ($\sim$ cm^3) single crystals of La_2CuO_4 were grown in air by the top-seeded solution growth method using CuO flux.[7] Brick-shaped samples, a few mm in each direction, were cut from the crystals and annealed at 900°C for 30 min in a vacuum of better than 10^{-5} torr. This procedure yielded highly insulating samples with a minimal oxygen content, in which the Néel temperature was $T_N = 325$ K, as determined from the sharp peak in the magnetic susceptibility.[8] The surfaces of the sample were polished using Meller Al_2O_3 powder (to 0.3 μm grit size) and a Buehler mixture of oil and water as the grinding fluid. Since the polishing introduces damage and annealing causes nonstoichiometry to 1 μm below the surface,[9] the samples were subsequently etched for 5 min in a solution of 1 vol. % Br in methanol. Auger measurements indicated that, after this treatment, the sample surface was stoichiometric.

Indium contacts were soldered onto two opposite faces of the sample. Although we measured the photoconductivity (PC) in two-probe geometry, comparison with four-probe measurements showed that the contact resistance was small compared to the sample resistance. The sample was placed in a variable-temperature optical cryostate, with the exciting light incident on a tetragonal (100) face. The continuous illumination was provided by a 75 W tungsten lamp dispersed by a Perkin-Elmer prism monochromator. The power incident on the sample was measured with a pyroelectric detector. The light was switched on and off using a shutter operated at 50% duty cycle with a cycling time of 10–200 s. The current as a function of time was averaged over several cycles using a Nicolet digital recorder. To measure the transient PC, the sample was excited with 10 ns pulses from an yttrium aluminum garnet laser which pumps a dye laser which, in turn, pumps a Raman shifter. The voltage across a load resistor was averaged and recorded on the digital recorder.

Figure 1 shows the photoconductance per square of photoexcited surface normalized to the continuous incident photon flux as a function of excitation energy E_x at $T = 132$ K. For these measurements, the intensity of the incident light was reduced until the PC became linear; at the higher photon energies and at higher intensities it was sublinear. The incident light was polarized parallel (open circles) and perpendicular (solid squares) to the CuO_2 planes, but the applied electric field was in the CuO_2 plane for both measurements. From $E_x = 1.0$ eV to 2.2 eV, $\Delta g_{\square}/F$ increases by nearly 4 orders of magnitude. The approximately exponential rise just below 2 eV has a slope (60 meV) that corresponds to an energy only slightly larger than the spectral resolution for the data shown. However, we checked that the edge does not sharpen appreciably with higher resolution. Above $E_x \sim 2.4$ eV, $\Delta g_{\square}/F$ varies slowly with E_x, but the precise dependence varies with surface preparation. Figure 2 shows the photoconductance normalized to incident photon flux on a linear scale. Least-squares fits of power laws to the data for a number of samples gives exponents of about 1 and thresholds of 2.0 ± 0.1 eV. Yu *et al.* have reported[10] a threshold for photocurrent in $YBa_2CuO_{6.3}$, also near 2 eV. However, the onset is more gradual than that in Fig. 2, with an exponential tail of about 0.4 eV width, compared to our 60 meV.

The PC depends on the polarization of the exciting light, but the anisotropy, like the high-energy spectrum, is sensitive to surface preparation and is only a factor ~ 2–3 at the highest excitation energies. A possible explanation

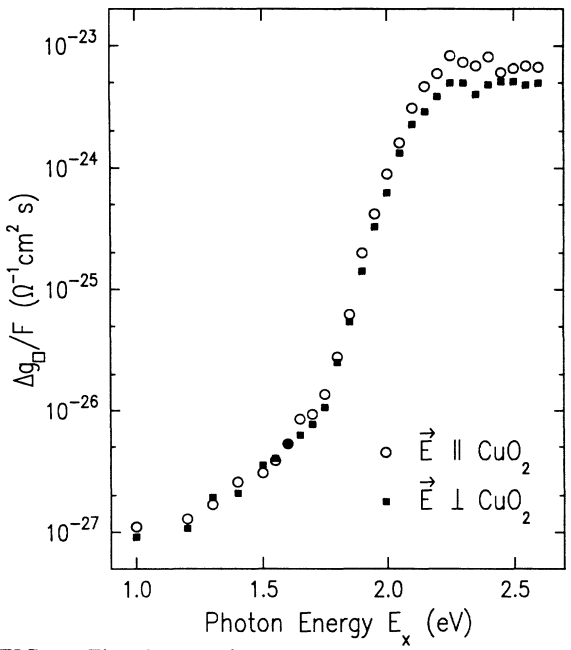

FIG. 1. The photoconductance per square $\Delta g_\square$ normalized to the incident photon flux F as a function of photon energy E_x for light polarized parallel (open circles) and perpendicular (solid squares) to the CuO_2 plane. The chopper cycle time was 40 s, and $T=132$ K. F was reduced until $\Delta g_\square$ was proportional to F for each E_x.

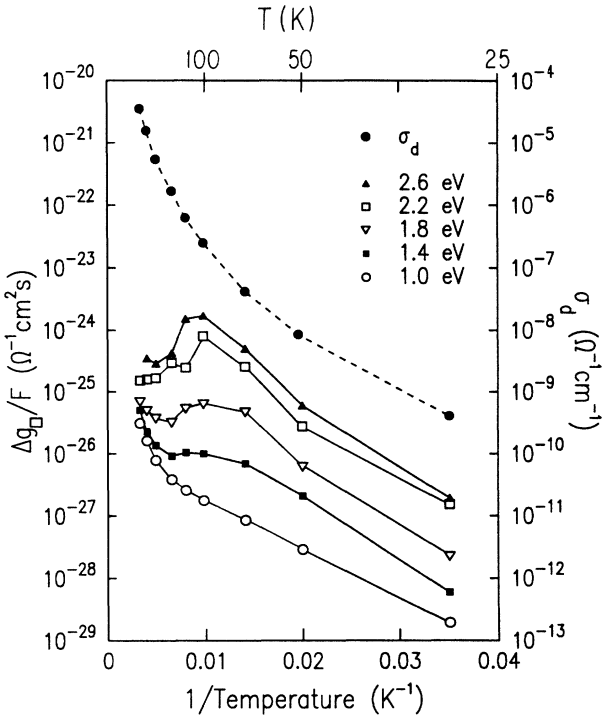

FIG. 3. $\Delta g_\square/F$ as a function of temperature for various E_x (left-hand-side scale). The dark conductivity σ_d is shown for comparison (right-hand-side scale).

of the small polarization is discussed below. To within experimental error we observe no polarization dependence for $E_x < 1.8$ eV.

The temperature dependence of the PC under continuous excitation for 40 s and for $E_x = 1.0$, 1.4, 1.8, 2.2, and 2.6 eV is shown in Fig. 3. For $E_x \geq 1.8$ eV and $T > 150$ K both the magnitude and the temperature dependence of the PC vary from sample to sample and, for the same sample, from day to day. From past experience, we believe that this results from absorption of oxygen near the sample surface. At low T, and for low E_x at all T, the steady-state PC is much more reproducible. Nevertheless, for all except the lowest E_x, the PC displays a peak near 100 K. For comparison the dark conductivity σ_d of the sample is also shown. It is clear that below ~ 100 K the PC is remarkably parallel to the dark conductivity for all E_x.

Figure 4 is a log-log plot of the time dependence of the photoconductance per square divided by incident photons per square, $\Delta g_\square/N_\square$, in a short laser pulse with $E_x = 2.20$ eV. Note that this plot covers eight decades of time. Transients look qualitatively similar at all photon energies and temperatures. The more rapidly decaying component

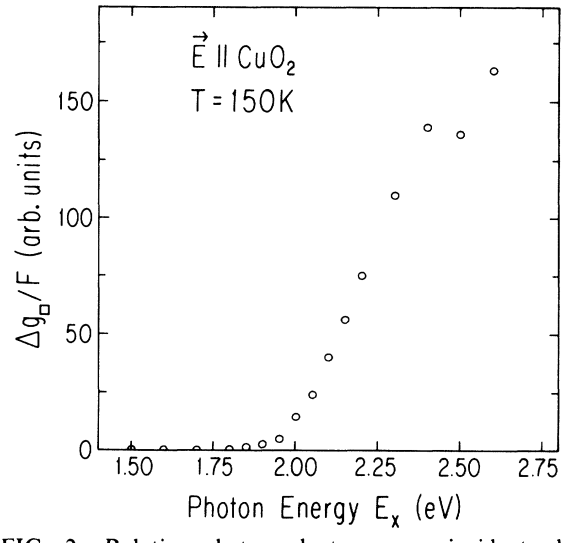

FIG. 2. Relative photoconductance per incident photon. When fit to a power law, these data and those for other sample all give threshold energies of $2.0 = -0.1$ eV. These data were for a sample different from those in Fig. 1, and only the relative, but not the absolute, photon flux was measured.

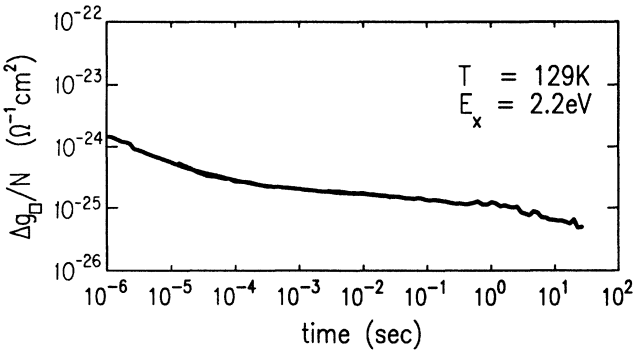

FIG. 4. Time dependence of the transient photoconductance per square normalized to the number of photons incident per unit area in a 10 ns pulse.

seen at the shortest times becomes relatively larger in magnitude at low photon energies and at high temperatures. As discussed below, we believe this to be a bolometric (heating) effect. The true PC decays very slowly with time. There appears to be some steepening of the decay near ~ 10 s for the temperature of the measurement in Fig. 4. For higher temperatures we sometimes observe such steepening at shorter times, although this, like the magnitude of the PC is not reproducible. However, the decay never becomes more rapid than $t^{-0.3}$ and even at room temperature a fit to an exponential decay always gives time constants longer than 10 s.

The temperature and time dependences suggest that the increase of conductance under photoexcitation for $E_x \sim 1$ eV is bolometric. The dark conductivity is simply activated at high T with energy ~ 0.1 eV. This is higher than the value ~ 40 meV found in lightly oxygen doped crystals,[11] consistent with the idea that the shallowest impurities have been removed by our annealing procedure. Below ~ 100 K the conductivity crosses over to the variable-range hopping dependence[11,12] $\sigma_d \sim \exp[-(T_0/T)^{1/4}]$. Heating of the crystal by an amount ΔT would therefore cause an increase in conductivity proportional to σ_d/T^2 at high T, and to $\sigma_d/T^{5/4}$ at low T. Of course, ΔT depends on T, but since σ_d is exponential in T^{-1} or $T^{-1/4}$, the power-law variations of the prefactor are secondary, and the bolometric effect is expected to be approximately proportional to σ_d. Figure 3 shows that for $E_x = 1.0$ eV this is the case. The more rapid decay of the transient PC seen at the shortest times in Fig. 4 is the relaxation of the increased sample temperature after the laser pulse. This effect becomes more prominent at the higher tempertures because the temperature dependence of the conductivity is stronger at higher T.

When the hole concentration is high the bolometric mechanism is the only one observed.[12] However, for crystals with $T_N = 325$ K we always see the threshold behavior in Fig. 1, and we believe, for the following reasons, that it results from the creation of charged excitations. First, for the bolometric effect the photoresponse is linear in light intensity, independent of photon energy; as already mentioned, we find sublinear intensity dependence at the high photon energies in the $T_N = 325$ K crystals. Second, we find that at ~ 100 K a 1-mm-thick crystal transmits light at $E_x = 1$ eV but is opaque above ~ 1.6 eV. Since the reflectivity is less than $\sim 20\%$ this means that, in the spectral region of the edge in the PC, virtually all the light is absorbed. Therefore, the threshold is not simply one for optical absorption, and must, instead, be one for the quantum efficiency for creation of charged excitations. Last, the time decay is inconsistent with a heating effect. Using an electric current to heat the sample, we find that the thermal relaxation time is less than ~ 0.01 s, whereas the decay after photoexcitation lasts at least 10 s. Because the excitations carry current, they obviously carry a net charge, unlike excitons, for example.

When the PC is linear in light intensity and all the light is absorbed by the sample, the photoconductance per square of surface per incident photon flux is given by

$$\Delta g_{\square}/F = e\eta\mu\tau . \quad (1)$$

where e is the electronic charge, η is the quantum efficiency for charged excitations, μ is the average mobility, and τ is the average lifetime of the photocarriers or the time of exposure to the light source, whichever is shorter. The only quantity on the right of Eq. (1) that depends on the photon energy is η, so the threshold must result from the competition between creation of neutral excitations at low energy and charged excitations at high energy. The neutral species might be excitons, either excited states of the Cu ions or electrons on the Cu ions bound to holes on the oxygen ions. Alternatively, they might be excitations of defects. Presumably, the low-energy tail, between ~ 1 and 1.8 eV in Fig. 1, arises from photoionization of defects.

Because the PC is proportional to η, rather than to the absorption, it may not be surprising that its polarization dependence is small. Because of the divergence angle of the monochromator, the light is incident on the surface of the sample with angles as large as $\theta \sim 0.1$ radian. This means that even when the electric field is polarized perpendicular to the CuO_2 planes, the in-plane component is still $\sim 10\%$. Although the penetration depth of the light is then 10 times longer for the perpendular polarization if the absorption is dominated by the in-plane mechanism, the quantum efficiency will be equal for the two polarizations.

Using $\tau \sim 10$ s in (1) gives $\eta\mu \sim 10^{-7}$ cm^2/V s whereas the band mobility in crystals identical to the ones studied here is found, from Hall measurements,[11] to be ~ 3 cm^2/V s. Although this very small value for $\eta\mu$ might arise from a very small value of η, it is more likely that the average mobility is very low because the photoexcited carriers reside in localized states. The peak in the temperature dependence of the PC occurs at the temperature where the dark conductivity changes from hopping at low T to simply activated at high T and the PC is proportional to σ_d in the hopping regime. This, and the low value of $\eta\mu$ suggest that the PC below 100 K results from the modulation of the hopping conductivity by the addition of majority carriers, the holes.

This probably happens in the following way: Photoexcitation creates minority carriers that are trapped in localized states. The majority carriers thermalize rapidly to the Fermi energy. Quite generally, one expects[13] this thermalization to take a time $t \sim \nu_0^{-1}\exp(\Delta E/kT)$, with $\nu_0 \sim 10^{11}$–10^{13} s^{-1} and $\Delta E \sim 0.1$ eV, the high-temperature activation energy of σ_d. This is less than $\sim \mu$s at 100 K. As a result of the increased carrier density, the Fermi energy shifts slightly, and the density of states or localization length changes a little causing the conductivity to change.

Although this is a reasonable scenario for $T < 100$ K it cannot explain the decrease of the PC with temperature at higher T. The ~ 0.1-eV activation energy of σ_d is presumably the energy difference between the Fermi energy and the band edge. When the conductivity is dominated by this band conduction, one would expect an even stronger increase of the PC with increasing T if the Fermi energy shifted by the same amount, that is, if there were no recombination. It is usually the case, however, that carriers excited to the band have faster recombination

rates. From transient experiments, we find that the PC at 1 ms is proportional to σ_d for temperatures up to 275 K, much higher than for the measurements with 40 s of continuous excitation. This confirms the idea that at high T, the decrease in σ_d with increasing T comes from enhanced recombination at long times. As mentioned above, we have seen some evidence of more rapid decay at high temperatures, although it is not highly reproducible and the distribution of rates still extends to very long times. Note that a constant distribution of rates would result in a decay of t^{-1}, much more rapid than we observe.

The very long decay times are reminiscent of persistent photoconductivity, common to a wide variety of semiconductors. The long times result, in inhomogeneous systems, when the photoexcited electrons and holes are spatially separated from each other[14] or, in homogeneous systems, when the minority carrier is trapped at a defect with a very small cross section for capture of the majority carrier.[15] The latter seems a more likely explanation in the present case, since we know from studies of the orthorhombic-to-tetragonal transition that the crystals are highly homogeneous.[16] The low band mobility[11] places this system in the diffusive recombination regime[17] in which $\tau^{-1}=4\pi R n_0 \mu k T/e$, where R is the capture radius of the recombination center and n_0 is the charge carrier density in the absence of photoexcitation. From the dark conductivity we find $n_0\mu$ so we can place an upper bound on R: for $\tau > 10$ s, one has $R < 3\times 10^{-13}$ cm. Such an extraordinarily small size together with the absence of recombination to a very high T can only be explained if there is a larger barrier for capture of the majority by the minority carrier.

In conclusion, our results indicate that the threshold for charged excitations in undoped La_2CuO_4 is 2.0 ± 0.1 eV. Cooper *et al.*[6] place the optical gap at 1.8 eV, and this may be an overestimate because they use the inflection point in the graph of the imaginary part of the dielectric function versus photon energy. That the threshold for quantum efficiency is at least 0.2 eV higher than the optical gap suggests that the exciton building energy is fairly large. The photoconductivity is surprisingly persistent, lasting longer than 10 s at room temperature. Whereas persistent photoconductivity has been recently reported[18] in reduced films of $YBa_2Cu_3O_7$, other workers have reported[10,19] quite short decay times in films and single crystals.

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