Large Dielectric Constants and Massive Carriers in La_2CuO_4

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We report measurements of the conductivity and dielectric constant as a function of frequency and temperature on samples of La_2CuO_4 from dc to 100 GHz. An analysis of the frequency dependence of the complex conductivity indicates that the high-frequency dielectric constant is large ($\simeq 50$) and weakly temperature dependent. The dc charge carriers are massive ($1100m_e$), weakly damped, and partially pinned.

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The discovery[1] of superconductivity in $La_{2-x}Sr_xCuO_4$ by Bednorz and Müller has led to extensive studies of these materials. They and others have proposed[2] that $La_{2-x}Sr_xCuO_4$ is similar to $Pb_{1-x}Ba_xBiO$, a perovskite with a superconducting transition temperature larger than expected from the carrier density, and that both are likely candidates for bipolaronic superconductivity. To test this we have made extensive measurements of the frequency-dependent conductivity and dielectric constant in single crystals of semiconducting La_2CuO_4. We find a high dielectric constant of 50–75 and extremely massive ($m^* = 1100m_e$) charge carriers. We show that these results are consistent with theories of bipolaronic transport.

All of the measurements reported here were performed on crystals of La_2CuO_4 grown from a CuO flux. The samples were annealed in N_2 at 650 °C, slowly cooled, and then polished to eliminate all the flux and off-stoichiometric surface layers. In the *a-b* plane of one sample we made the 34-GHz measurements, applied four-probe contacts, measured the dc conductivity, polished off the contacts, and finally made the 60-GHz, 94-GHZ, and microwave bridge measurements. A second sample was used only for 10-kHz capacitance bridge measurements of the anisotropic dielectric constant.

The millimeter-wave conductivity measurements were performed with a bridge technique extensively discussed and tested in an earlier publication.[3] The bridges operate on an interferometer principle with precision attenuators and phase shifters used to null the output of an arm containing a sample against that of a reference arm. Here we only discuss the equivalent circuit for the termination admittance

$$Y = [Z_{\rm inf} + Z_\sigma]^{-1}, \tag{1}$$

where $Z_{\rm inf}$ is the impedance of an infinitely conducting object with dimensions and position identical to the sample and Z_σ is the part of the impedance that depends on the conductivity. Schwinger and Saxon[4] have calculated $Z_{\rm inf}$ and $Z_\sigma \propto 1/\sigma$ for a small sample aligned with the electric field of the TE_{011} mode and extending between plates of a continuous section of waveguide. Here we use a section of waveguide with a hole for the sample a distance $3\lambda_g/4$ from a terminating plate, where λ_g is the guided wavelength. Tests with quartz rods verified that the expression for Z_σ is accurate with $\sim 20\%$ corrections. We find that $Z_{\rm inf} = i\omega L$, where $L = (l\mu_0/2\pi)\ln(r'/r) = 0.6$ nH with l the sample length and r' the radius of the hole. The effective radius $r = (A/\pi)^{1/2} = 0.1$ mm is determined from the sample cross section A.

The measurements in the microwave regime were performed with a bridge operating in the range 3–15 GHz. The bridge operates on the same principle as the millimeter-wave bridges, except that it is implemented with coaxial transmission lines. The sample is placed between the center conductor, which is terminated as a flat surface perpendicular to the axis of the coaxial line, and the outer conductor, which extends on as a circular waveguide beyond cutoff. The admittance of this termination is

$$Y = i\omega C_e + \frac{1}{i\omega L - i/\omega C_c + Z_\sigma}, \tag{2}$$

where C_e is the capacitance from the end of the inner conductor to the outer conductor, L is the inductance of the sample, C_c is the contact capacitance, and $Z_\sigma = l/A\sigma$ is the sample impedance. We tested the validity of this description with separate experiments for each term. For the first term in Eq. (2) we machined a Teflon cylinder which precisely fit the interior dimension of the outer conductor and touched the end of the inner conductor. The frequency dependence of the phase shift was such that a capacitance $C_e = 25$ fF was an appropriate description. We estimated the inductance to be $(l'\mu_0/2\pi)\ln(\alpha l'/A^{1/2})$, where l' is the distance between outer and inner conductors and α is a constant of order unity. We evaluated α by measuring the frequency-dependent phase shift of a Pt wire silver painted across the end of the coaxial line and established that $\alpha = 1.33$ and that the termination was a nearly pure inductance, with a small end-capacitance correction and no apparent

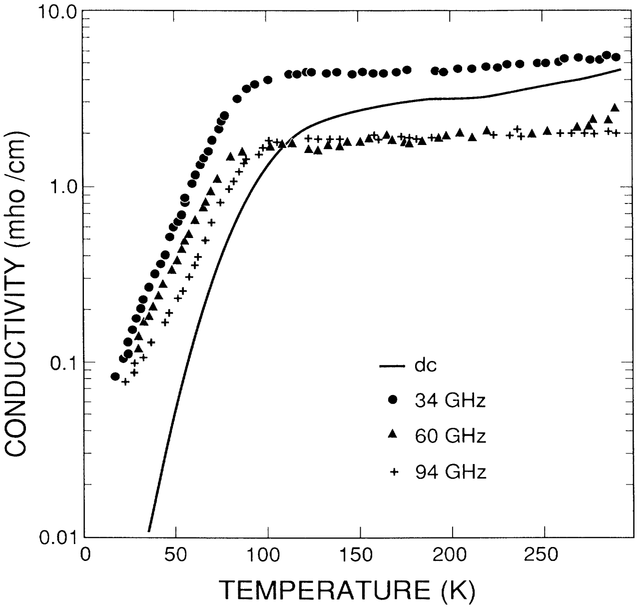

FIG. 1. The conductivity of La_2CuO_4 at dc, 34, 60, and 94 GHz.

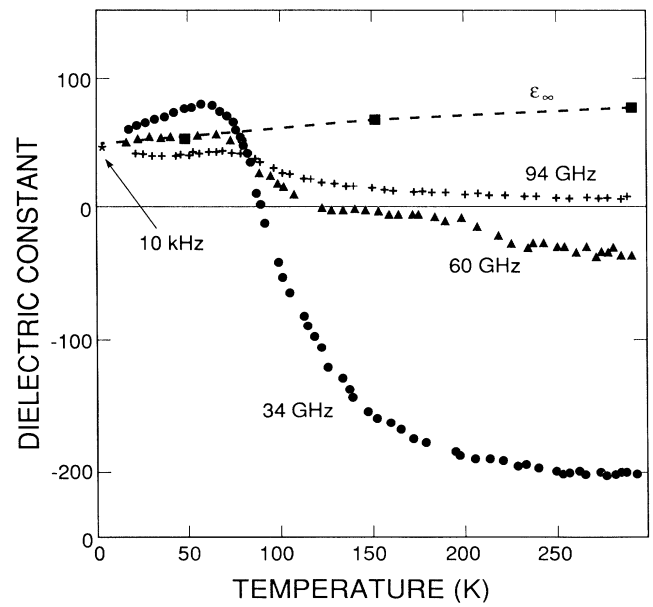

FIG. 2. The dielectric constant of La_2CuO_4 at 34, 60, and 94 GHz together with ϵ_∞ deduced from the fits by Eq. (3).

contact impedance. We used the same inductance formula to calculate an inductance of 0.75 nH for the La_2CuO_4 sample.

Further tests of the microwave bridge were made by studying the less pure La_2CuO_4 crystals grown from a PbO flux (by J. P. Remeika). The real part of their frequency-dependent conductivity displays a peak. These samples, however, had an impedance less than 50 Ω, the characteristic impedance of the coaxial line, and the conductivity resonance appeared in the loss measurements as a *minimum*. The samples prepared from a CuO flux, however, have an impedance greater than 50 Ω and the conductivity resonance appears as a *maximum* in the measured loss. This confirms that no systematic error in loss measurements could produce the resonance reported here.

The temperature-dependent conductivity measurements at dc, 34, 60, and 94 GHz are displayed in Fig. 1. The largest conductivities are at 34 GHz with lower conductivities at other frequencies. Thus a maximum exists between dc and 60 GHz.

The dielectric constants at 34, 60, and 94 GHz are shown in Fig. 2. At low temperatures the dielectric constants at the three frequencies are nearly equal and all the results extrapolate to a dielectric constant of 50 at zero temperature. At temperatures above 50 K the dielectric constants decrease and then plateau at lower or negative values. We also measured the dielectric constant at 0 kHz and 4.2 K and found $\epsilon = 45 \pm 5$ in the *a-b* plane (displayed in Fig. 2) and $\epsilon = 23 \pm 3$ along the *c* axis.

The conductivity and dielectric constants are plotted with the microwave bridge results in Fig. 3 at $T = 293$ and 50 K. The real part of the dielectric constant is presented as the imaginary part of the complex conductivity. The curves in Fig. 3 are fits with a harmonic-oscillator model

$$\sigma(\omega) = \frac{ne^2\tau}{m^*} \frac{i\omega}{i\omega + \tau(\omega_0^2 - \omega^2)} + \frac{i\omega\epsilon_\infty}{4\pi}, \tag{3}$$

where the solid curve is $\mathrm{Re}(\sigma)$, the dashed curve is $\mathrm{Im}(\sigma)$, and the fit parameters are displayed in Table I. The high-frequency dielectric constant ϵ_∞ contains contributions from phonons, bound impurity states, and all other higher-frequency polarizabilities. For a typical semiconductor the first term in Eq. (3) is constant below 100 GHz and given by $ne^2\tau/m^*$, where n is the carrier density, m^* is the effective mass, and τ is the carrier lifetime. Here, however, the peak in $\mathrm{Re}(\sigma)$ and the negative values of $\mathrm{Im}(\sigma)$ imply a long lifetime τ and a pinning frequency ω_0 for the carriers. Equation (3) is then the simplest model which can qualitatively fit our data. Models which include a dc conductivity and have several additional parameters provide better fits than seen in Fig. 3, particularly at low frequencies, but do not provide additional insight.

Figure 2 displays the values of ϵ_∞ deduced from the fits by Eq. (3). If we assign all the spectral weight of 10^{22} electrons/cm^3 to the $\hbar\omega_0' = 1.7$ eV gap[5] then the contribution to the dielectric constant at low frequencies is $\epsilon = 4\pi ne^2/m_e\omega_0'^2 \simeq 5$. Optical reflectance measurements[5] indicate a dielectric constant of 6 at frequencies between the gap and optical-phonon modes, in excellent

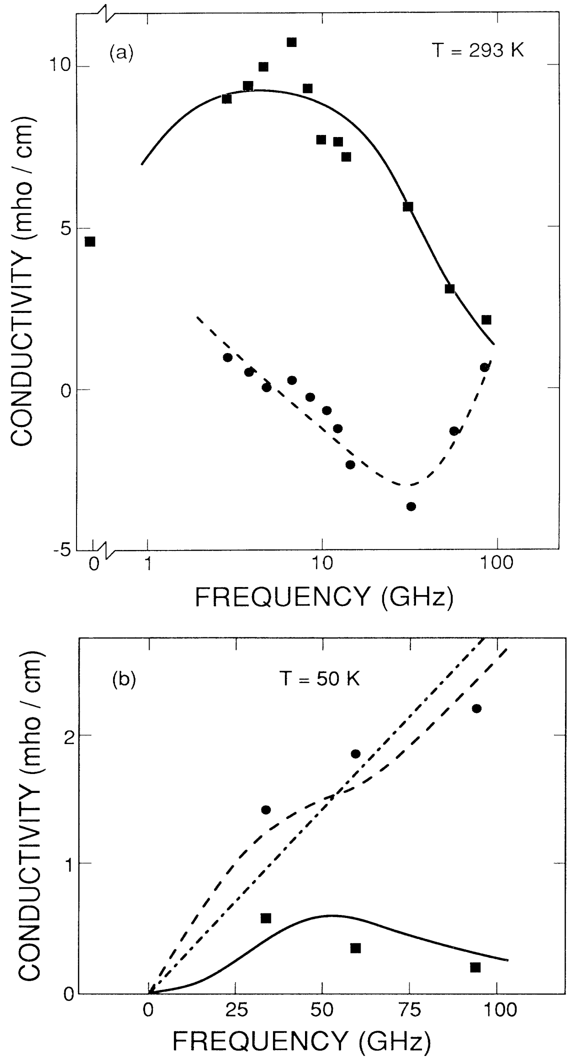

FIG. 3. The real and imaginary parts of the frequency-dependent conductivity of La_2CuO_4 at (a) $T=293$ K and (b) $T=50$ K. The solid and dashed lines are fits by the real and imaginary parts of Eq. (3), respectively, with parameters discussed in the text. The dot-dashed line in (b) is $\omega\epsilon_\infty/4\pi$.

agreement with this estimate. Other studies[6] of reflectance at 40 cm^{-1} (below many of the phonon lines) imply $\epsilon_\infty=51$ in the *a-b* plane and $\epsilon=23$ perpendicular to the *a-b* plane, in excellent agreement with our results. Samples of La_2CuO_4 prepared with our techniques typically have a carrier density $n=10^{19}/cm^3$ at room temperature and a dc conductivity activation energy $\hbar\omega_0/k_B \simeq 100$ K. If these carriers are bound to impurity sites at low temperature then their contribution to ϵ_∞ could be significant. This would decrease at $T>100$ K when the carriers are thermally ionized, an effect we do not observe. The most likely source of the dielectric constant is the low-lying phonon modes,[5,6] suggesting that the material is near a ferroelectric instability. This large dielectric constant will screen electron-electron interactions, an important effect in the superconducting material.

TABLE I. Parameters obtained by fitting Eq. (3) to the results.

T (K)	$\omega_0/2\pi$ (GHz)	$1/2\pi\tau$ (GHz)	$ne^2\tau/m^*$ (mho/cm)	ϵ_∞
293	4.9	41	9.1	75
156	7.0	56	5.4	66
50	52	71	0.59	52

The parameters associated with the low-frequency charge transport are ω_0, $1/\tau$, and $ne^2\tau/m^*$. This transport disappears at low temperature, along with the dc conductivity. The microwave resonance must then be associated with the presence of the dc carriers and the resonant behavior indicates that the carriers are partially pinned and weakly damped. Using a mobility $e\tau/m^* \simeq 3$ cm^2/V sec, the order of magnitude deduced[7] for $La_{2-x}Sr_xCuO_4$, and the fit parameter $1/\tau$, we calculate an effective mass $m^*=1100m_e$ at $T=293$ K. Given the uncertainties in this analysis these results are in complete agreement with our earlier result[8] of $m^*=500m_e$ in Eu_2CuO_4. The effective mass is not dependent on the model; we obtain the same value from the carrier density, $n=10^{19}/cm^3$, and the integral of measured $\mathrm{Re}(\sigma)$.

There are several possible mechanisms which could enhance the dynamical mass of the carriers in La_2CuO_4. Those most commonly discussed in the literature are (i) magnetic interactions and (ii) phonon interactions.

(i) Large enhancements of the effective mass have been obtained[9] for holes in a Mott-Hubbard model. The results depend strongly on whether one considers one hole or two holes but the mass enhancements are typically $\simeq 10$ for $U/t=10$. Two-band Mott-Hubbard calculations have also been performed[10] for relevant values of the parameters and lead to mass enhancements of approximately 10.

(ii) Phonon interactions are commonly found to enhance the mass of electronic carriers. These enhancements are usually modest, except when the atoms undergo a static distortion in the response to a conduction charge. A displacement of the conduction charge then causes atomic motions which store large amounts of kinetic energy and create large mass enhancements. A typical example is the charge-density wave where mass enhancements[11] $\simeq 10^2$–10^4 occur with atomic displacements $\simeq 0.1$ Å. Similar atomic displacements are observed[12,13] in $Tl_2Ba_2CaCuO_8$ and La_2CuO_4. For a polaron with a drift velocity v_d we calculate the kinetic energy E stored in the atomic motions and define an effective mass from $E=m^*v_d^2/2$. For a drifting 2D bipolaron with maximum distortion amplitude δr at a distance R from the bipolaron center the distortion must relax in a time R/v_d. The atomic velocity is then $v_d\,\delta r/R$ and the number of atoms moving is roughly $\pi R^2/a^2$, where a is the atomic spacing. The kinetic energy sum then leads to $m^* = \pi \alpha \delta r^2$, where α is the 2D mass density. If we assume that the displacements at the O(2) sites[13] of La_2CuO_4 are caused by and follow the dopant holes, then $\alpha = 2 \times 16 \times 1800 m_e/(15\ \text{Å}^2) = 3840 m_e/\text{Å}^2$ [for O(2) only] and $\delta r = 2.4 - 2.16\ \text{Å} = 0.24\ \text{Å}$. This implies $m^* = 695 m_e$, in excellent agreement with our results.

From our measurements alone we are unable to distinguish whether the carriers are polarons or bipolarons. Recent theoretical studies,[14] however, indicate that bipolarons are stable with respect to polarons if the intrinsic ϵ_∞ is large. The dielectric constant here, $\simeq 50$, is well within the stability criteria, implying that all the measurements reported here are consistent with a bipolaron interpretation.

In conclusion, we have studied the dielectric response of La_2CuO_4 and have found that the material is not describable as a normal semiconductor. The frequency-independent portion of the dielectric constant ϵ_∞ is much larger than electronic transitions could account for, suggesting that low-energy optically active phonons are dominating the dielectric behavior of this perovskitelike structure. The surprising aspect of these measurements is the large dynamical mass, $\simeq 1100 m_e$, obtained from the analysis of the frequency-dependent conductivity. This is consistent with our earlier measurements[8] on Eu_2CuO_4, indicating that the carriers in these planar compounds are massive and self-localized. The CuO compounds which superconduct contain high densities of holes and apparently have smaller masses,[15] indicating that the mass may decrease with decreasing separation. All of these results are consistent with a bipolaronic interpretation but further investigations are required to confirm such a model.

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