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Far-infrared reflectivity of $La_{2-x}Sr_xCuO_4$

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We have measured and modeled the far-infrared reflectivity of $La_{2-x}Sr_xCuO_4$ for $x=0.175$ in the normal and superconducting states in the frequency range 20 to 350 cm^{-1}. We find a much stronger drop of the reflectivity with increasing frequency below 100 cm^{-1} than is implied by the dc conductivity. In addition, we observe a resonance of large spectral weight at $\omega \approx 250$ cm^{-1}, which is absent or much weaker in the insulating $x=0$ compound. Below the superconducting temperature of the $x=0.175$ sample we observe an additional sharp feature at ≈ 80 cm^{-1}, which can be accounted for in terms of the unusual normal-state properties of the material.

The $La_{2-x}Sr_xCuO_4$ system has been the subject of intense investigation in recent months since the discovery[1] of superconducting transition temperatures T_c in excess of 30 K for $x \sim 0.15-0.18$. In this paper we report measurements and modeling of the far-infrared (FIR) reflectivity below 350 cm^{-1} for a sample with $x=0.175$ and $T_c \approx 36$ K in both normal and superconducting states. We present evidence for a resonance of large spectral weight centered at a frequency of about 250 cm^{-1} in the normal state (by contrast, an insulating $LaCuO_4$ sample showed no feature of comparable strength in our frequency range). The resonance remains essentially unaltered in the superconducting state, and, as seen in earlier measurements,[2] a sharp dip in the reflectivity appears below T_c around 80 cm^{-1}.

We model the reflectivity in the $x=0.175$ system in the normal state in terms of a Drude model plus an oscillator, and below T_c in terms of the conventional Mattis-Bardeen approach for normal BCS superconductors. We show that the unusual normal-state reflectivity in this system leads to the observed sharp "phononlike" dip without postulating a low-frequency phonon alluded to in a previous analysis of FIR measurements.[2] Within our model the real part of the dielectric function $\epsilon(\omega)$ turns out to be *positive* at low frequencies in the normal state (unlike a conventional metal). The superconducting state, on the other hand, is characterized by a *negative* real part of $\epsilon(\omega) \sim \omega^{-2}$. Consequently, the real part of $\epsilon(\omega)$ crosses zero at a frequency of the order of the gap, implying a plasmonlike collective mode due to the onset of superconductivity. However, the precise location of the resonance depends sensitively on materials parameters, and a more detailed study is required for quantitative extraction of the superconducting gap.

Our measurements were made using a Michelson interferometer with a single, near normal (angle of incidence $\approx 15°$) reflection from the sample. The source light intensity was reduced to a fraction of a percent with irises and filters to ensure linear response of the detector, a composite bolometer cooled to 0.3 K using charcoal-pumped liquid ^3He. The temperature (T) was varied over the range 10–160 K.

A thick layer of the pressed pellet samples was removed using dry emery paper, and then polished to produce a smooth surface. Some pits were present in all samples, but the appearance was otherwise uniform. Reflectivity curves were measured in comparison with a polished brass reference at the same T, which could be moved into the light path in place of the sample.

Figure 1 shows the measured reflectivity of one of the samples in the normal state (R_N) at $T=42$ K, just above the superconducting temperature (solid circles), as well as at a low temperature, $T=10$ K, in the superconducting state (R_S, open circles). In the normal state, the reflectivity R_N departs rapidly with increasing frequency (ω) from the expected metallic value of unity at $\omega=0$, goes through a minimum, and exhibits a pronounced maximum around 250 cm^{-1}. The exact magnitude (and to a lesser extent the location) of the maximum differs from sample to sample, but is virtually temperature independent up to 160 K for each sample.

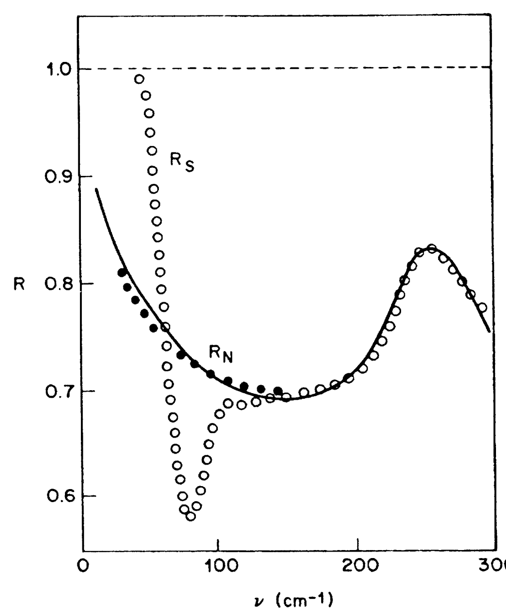

FIG. 1. Reflectivity for a sample of $La_{1.825}Sr_{0.175}CuO_4$ as a function of frequency in the normal state at $T=42$ K (solid circles) and in the superconducting state at $T=10$ K (open circles).

In the superconducting state, the reflectivity R_S is enhanced at low frequencies, qualitatively as expected in the BCS theory, due to a superconducting gap. However, many of our samples, like the one shown in Fig. 1 (open circles) show a precipitous drop followed by a sharp pronounced dip below the normal-state reflectivity around 80 cm^{-1}. We find that the magnitude of the dip for different samples is positively correlated with (a) the normal-state reflectivity R_N and (b) the enhancement $(R_S - R_N)$ at low frequency, and we suspect, therefore, with the quality of the sample. Indeed, previous reports[2-6] show variations in this feature. In the samples where the dip is most pronounced, it is sharpest and largest at low T, and broadens, reduces in magnitude, and moves to lower frequencies as T_c is approached from below, qualitatively as seen before.[5]

We model the normal-state reflectivity in our frequency range in terms of three contributions to the dielectric function $\epsilon(\omega)$: a Drude term due to the free carriers, an oscillator of adjustable spectral weight Ω and damping γ centered at a frequency ω_0, and a background dielectric constant ϵ_∞ enhanced from unity to represent effects due to excitations at energies above our range. A similar model has been applied to the $BaPb_{1-x}Bi_xO_3$ system.[7] Thus in the normal state

$$\epsilon(\omega) = \epsilon_\infty + \frac{4\pi i \sigma(\omega)}{\omega} + \frac{\Omega^2}{\omega_0^2 - \omega^2 + i\gamma\omega}, \tag{1}$$

where

$$\sigma(\omega) = \frac{\omega_p^2}{4\pi(\tau^{-1} - i\omega)} \tag{2}$$

is the normal-state Drude conductivity with plasma frequency ω_p and scattering rate τ^{-1}. The reflectivity is computed via the normal incidence formula

$$R = |(\sqrt{\epsilon} - 1)/(\sqrt{\epsilon} + 1)|^2 . \tag{3}$$

While Eq. (1) has many parameters, the striking behavior of R_N in our frequency range allows a reasonable determination of them. At low frequencies the Drude term may be approximated by the constant value $\sigma_0 = \omega_p^2 \tau / 4\pi$, which is chosen to reproduce the falloff of R_N from unity at $\omega < 100\ \mathrm{cm}^{-1}$. The position and width of the resonance determine ω_0 and γ, while the intensity and shape of the feature fix Ω and ϵ_∞. Given the limited frequency range of our fit, our fitted parameters are at best reliable to $\pm 20\%$. We find a rather good fit for the sample shown with $\sigma_0 = 720\ \mathrm{cm}^{-1}$, $\Omega = 1300\ \mathrm{cm}^{-1}$, $\omega_0 = 240\ \mathrm{cm}^{-1}$, $\gamma = 40\ \mathrm{cm}^{-1}$, and $\epsilon_\infty = 30$, and the reflectivity calculated with these parameters is shown as the solid line in Fig. 1. The large value of ϵ_∞ is supported by reflectivity measurements of Orenstein *et al.*[8] at higher frequencies, who find a resonance of large spectral weight around 0.5 eV, leading to an effective $\epsilon_\infty \sim 25$ at lower ω.

Despite the uncertainty in our fitted parameters due to sample-to-sample variation and limited frequency range, we can make some general comments which do not depend on the precise values. First, the value of $\omega_p^2 \tau$ needed to fit R_N for $\omega \lesssim 100\ \mathrm{cm}^{-1}$ is quite small, corresponding to a resistivity $\rho = 6500\ \mu\Omega$ cm, over an order of magnitude more than the measured dc resistivity just above T_c of 500 $\mu\Omega$ cm. Indeed the reflectivity drop from unity is large for a metal, and reminiscent of results on the highly anisotropic organic conductors.[9] Second, the spectral weight in the feature near 250 cm^{-1} (which is given by $\pi\Omega^2$) is much larger than that in typical resonances due to phonons as, for example, in the feature at 550 cm^{-1} seen in previous infrared measurements.[6,10] If we write the spectral weight of an optic phonon as $4\pi N(Ze)^2/M$, where Z is the effective charge and M the mass of the atom involved, then, using the oxygen mass for M and assuming one phonon per unit cell (so $N \sim 10^{22}\ \mathrm{cm}^{-3}$), we require an effective charge $Z \gtrsim 10$. Such large values of Z have been observed for coupled electron-phonon modes associated with a structural phase transition, and a structural transition has been reported[11] in samples with our composition at $T = 130$ K. However, we find that the feature near 250 cm^{-1} remains essentially unaltered up to temperatures of 160 K. On the other hand, reflectivity data on La_2CuO_4 (Fig. 2) in the same frequency range do not show a sharp feature of comparable magnitude. Further, calculations[12] on $La_{2-x}Sr_xCuO_4$ for $x \approx 0.17$ do not show any infrared-active phonons around 250 cm^{-1} with large enough dipole matrix element to give the observed Z for the K_2NiF_4 structure. This may indicate the presence of a heretofore undetected charge-density-wave-type distortion in the doped sample.

In the superconducting state, we replace the Drude term [Eq. (2)] by the Mattis-Bardeen form in the dirty limit.[13] Our analysis allows for the possibility that a fraction f remains normal below T_c, to model possible compositional inhomogeneities. We use the effective medium approximation[14] to determine the conductivity of the mixture. Details of Mattis-Bardeen and effective medium formalism are described elsewhere,[15] where a similar analysis is carried out for the $Ba_2YCu_3O_{9-\delta}$ system.

If we use a $T = 0$ gap equal to the BCS value $2\Delta = 3.5kT_c \approx 85\ \mathrm{cm}^{-1}$ (for a T_c of 36 K), then with the other parameters unchanged we obtain at low temperatures the reflectivity curves shown in Fig. 3, $C(f = 0.1)$, $B(f = 0.5)$, and A (normal state). Besides the expected enhancement of the reflectivity at low frequencies, the most striking feature is the sharp dip in the calculated reflectivity in the vicinity of 2Δ. The dramatic drop in R_S

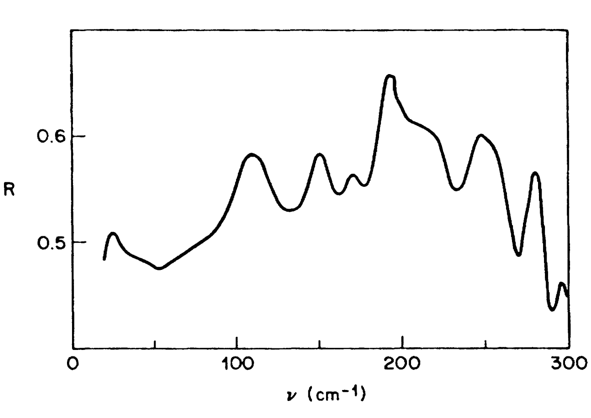

FIG. 2. Reflectivity R as a function of frequency for a sample of La_2CuO_4.

in our model marks the point where $\mathrm{Re}\epsilon(\omega)$ crosses zero. In conventional metals $\epsilon_1 = \mathrm{Re}\epsilon$ is negative for frequencies less than the plasma frequency ω_p (which is typically $\sim 1-10$ eV), with a low-frequency limit of $\epsilon_1 = -\omega_p^2\tau^2$. In our $La_{1.825}Sr_{0.175}CuO_4$ samples, however, our fits yield a positive $\epsilon_1 \sim 50$ at low frequencies in the normal state. This is due to the large positive contributions from ϵ_∞ and the resonance around 250 cm^{-1}, as well as the low value of $\omega_p^2\tau^2$ implied by our low value of σ_0, for reasonable estimates of ω_p (>0.25 eV). We obtained reasonable fits to our data only with parameters which imply a $\epsilon_1(0)$; however, our discussion below requires only that $\epsilon_1(\omega) > 0$ in the normal state for some range of $\omega \sim 2\Delta$. Below T_c, the real part of the conductivity $\sigma(\omega)$ acquires a δ-function peak at $\omega = 0$ as a direct consequence of superconductivity. This, via the Kramers-Kronig relations yields an additional contribution to $\epsilon_1(\omega) \sim -\omega^{-2}$ at low frequencies, which in turn implies that a zero crossing of ϵ must occur as $\omega \rightarrow 0$. The precise location of this superconducting "plasmon" mode is determined by the values of Δ, the superconducting gap, as well as the dielectric function in the normal state. If the zero crossing occurs for $\omega \lesssim 2\Delta$, the imaginary part of ϵ will be small, and the plasmon will be sharp and easily visible. The feature will be sharpest for $T=0$. With increasing T, Δ decreases and $\mathrm{Im}\epsilon(\omega)$ increases for $\omega < 2\Delta$; consequently, the feature should broaden and move to lower frequencies, in qualitative accord with our experimental observations, as well as those of others.[5]

The theoretical $T=0$ curves in Fig. 3 are clearly in semiquantitative agreement with the experimental curve (open circles in Fig. 1). Better agreement may be achieved either by using a slightly lower gap or by fine tuning the normal-state parameters without significantly worsening the normal-state fit. However, we do not wish to attach, at this stage, much significance to the precise value of the gap, because of the uncertainty in determining the normal-state parameters and because we have not considered possible effects of anisotropy in the normal-state conductivity and of the gap on our pressed pellet samples. Nevertheless, our data are clearly inconsistent with a gap many times the BCS value (over most of the Fermi surface), as has been reported in some tunneling measurements,[16] because we see little difference between the normal-state and superconducting reflectivity above $\omega \approx 150$ cm^{-1}. Whether this is a consequence of materials problems, as both techniques are sensitive to the surface of the sample (our measurements probe ~ 10 μm), remains to be clarified.

In conclusion, we have measured the reflectivity of La_2CuO_4 and $La_{1.825}Sr_{0.175}CuO_4$ in the far infrared. In the latter, we have observed a feature of large oscillator strength (and, therefore, most likely with a strong electronic component) at $\omega \approx 250$ cm^{-1}, which is not seen in our frequency range in La_2CuO_4 (or, perhaps, is much weaker). The oscillator responsible for the 250-cm^{-1} feature in conjunction with a large background dielectric constant (which is likely due to a previously observed oscillator[8] at ~ 0.5 eV) also produces the sharp dip seen at ~ 80 cm^{-1} in the superconducting state. Finally, our data point to a superconducting gap of the order of the BCS value.

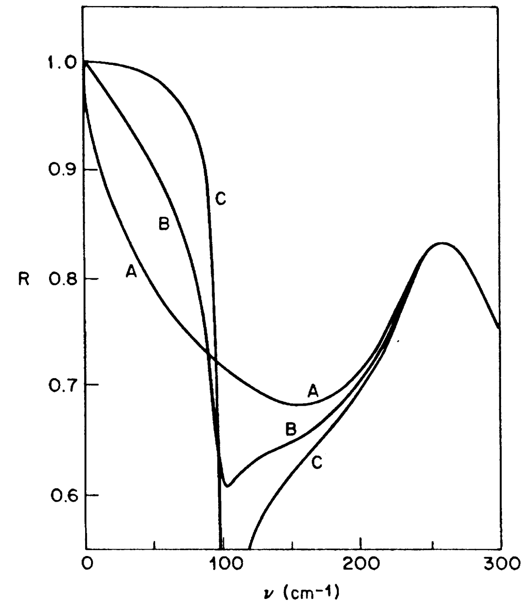

FIG. 3. Theoretical reflectivity computed as described in the text for the normal state (Curve A), as well as for the superconducting state with different fractions f of normal material ($f=0.5$ for Curve B, $f=0.1$ for Curve C).

While this manuscript was being written, we received two papers[17,18] on far-infrared studies of $La_{2-x}Sr_xCuO_4$, both of which show data in agreement with ours. One of the papers[18] also gives a similar interpretation of the reflectivity dip in the superconducting state.

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