Far-Infrared Transmission Study of Single-Crystal $Bi_2Sr_2Ca_1Cu_2O_x$ Superconductors

L. Forro,[1] G. L. Carr,[2] G. P. Williams,[3] D. Mandrus,[1] and L. Mihaly[1]
[1]Department of Physics, State University of New York, Stony Brook, New York 11794
[2]Department of Physics, University of Florida, Gainesville, Florida 32611
[3]National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973
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We report the infrared transmission of free-standing single crystals of the high-temperature superconductor $Bi_2Sr_2Ca_1Cu_2O_x$, at temperatures between 25 and 300 K and at frequencies covering the range of $1.5k_BT_c < \hbar\omega < 12k_BT_c$. The normal-state Drude relaxation rate follows a linear temperature dependence $\hbar/\tau = 3k_BT$. In the superconducting state there is no indication of a transmission peak which characterizes a superconducting gap in the optical conductivity. We suggest that a strong pair-breaking interaction is responsible for this null result.

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The mechanisms responsible for the behavior of the high-temperature superconductors have remained elusive, but on a phenomenological level these materials seem to be similar to the conventional superconductors. The development of an energy gap in the excitation spectrum proved to be a fundamental property of the superconducting condensate and attempts have been made to search for similar behavior in the new materials. The gap can be elegantly revealed by frequency-dependent transmission measurements as was first demonstrated by the classic experiments of Glover and Tinkham.[1] Such measurements also have the inherent advantage of high sensitivity to bulk properties.

The present infrared transmission measurements are the first to be reported on high-quality, free-standing single crystals of high-temperature superconductors. The study was made possible by the combination of recent developments in sample preparation[2] and the use of an exceptionally bright infrared source.[3] The results reported here were obtained on $Bi_2Sr_2Ca_1Cu_2O_x$ below and above the superconducting transition temperature for films with thickness on the order of 100 nm. The use of oriented single crystals with no substrate allowed measurements to be made over a wide range of energies and with a high accuracy. The frequency-dependent response in the superconducting state is expected to show a pronounced feature due to the absorption onset at the gap edge. In the normal state the characteristic time scale of the relaxation processes, estimated from the dc resistivity, falls into the measured frequency range. From an experimental point of view, transmission measurements are complementary to reflectance studies, which have been performed recently in several laboratories.[4-9]

The $Bi_2Sr_2Ca_1Cu_2O_x$ single crystals for the present study were grown from a copper-oxide-rich melt of the starting materials. Films with approximate dimensions of 150 nm×1.0 mm×1.0 mm were cleaved from the crystals, and were characterized by magnetic susceptibility, dc resistivity, transmission electron microscopy, microanalysis, and selected-area electron-diffraction measurements.[2] All the tests indicate that the samples are good-quality, twinning-free, single-crystal superconductors, with a sharp resistive phase transition. The crystallographic c axis was found to be normal to the large surface of each sheet. The thickness d of the samples was determined from the x-ray-absorption coefficient, as measured using the National Synchrotron Light Source (NSLS) x-ray microscope facility at Brookhaven National Laboratory. The thickness was found to be uniform for each film, with values for d ranging from 100 to 250 nm. The samples, which were transparent to visible light, were mounted onto platinum disks with a circular aperture (typically 0.5–0.7 mm in diameter) and thermally anchored to a helium flow refrigerator. We performed infrared studies on five samples with comparable results. Most of the data reported here were obtained on a specimen of $d = 135$ nm and $T_c = 76$ K.

The infrared transmission measurements were performed using a Nicolet 20F interferometric spectrometer in combination with an Infrared Laboratories Si:B bolometer. The infrared source was synchrotron radiation produced at beam line U4-IR of the NSLS at Brookhaven. The beam was incident perpendicular to the film so that the electric field was in the a-b plane of the crystal. The detailed description of the instrumentation, and the comparison with conventional infrared spectrometers has been published elsewhere.[3] The good collimation and high brightness of the synchrotron radiation was an essential condition for successfully measuring the transmission of the unusually small specimens.

In Fig. 1 we show representative transmission spectra at several temperatures. The generally parabolic shape (and finite intercept at $\omega = 0$) of the transmission is consistent with a Drude metal and finite relaxation rate. At 50 K the transmission approaches zero at low frequencies, as expected for a superconducting sample.[1] The transmission dips at 370, 480, and 590 cm^{-1} are reproducible and weakly temperature dependent. We associate these features to strongly screened phonon modes. Our results below 300 cm^{-1} are similar to those observed by Williams *et al.*[8] and Hughes *et al.*[10] who mea-

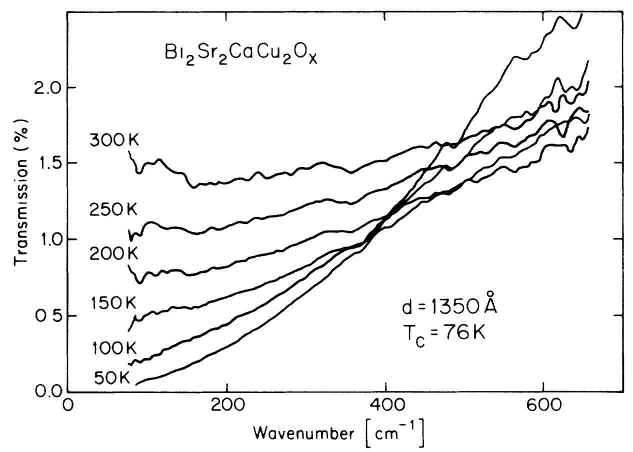

FIG. 1. Frequency-dependent infrared transmission of a $Bi_2Sr_2CaCu_2O_x$ single crystal at several temperatures. The incident light is perpendicular to the a-b plane, the electric field is in the plane. Similar spectra were obtained on other samples of $T_c = 81$ and 83 K.

sured the transmission of high-T_c films deposited on MgO. These measurements suffered from the difficulties associated with the substrate, and neither of them were made on single-crystal samples.

The transmission coefficient of a thin film of thickness d is[1]

$$t = \frac{1}{(1+\sigma_1 dZ/2)^2 + (\sigma_2 dZ/2)^2}, \quad (1)$$

where σ_1 and σ_2 are the real and imaginary parts of the conductivity and Z is 377 Ω in mksa units. First, we use this expression to compare the results with the dc resistivity measurements with no assumptions concerning the mechanism of conduction. A simple polynomial fit was used to extrapolate the infrared spectra to zero frequency and to obtain $t_0 \equiv t(\omega=0)$. In Fig. 2 we show the quantity $\rho' = Zd/[2(t_0^{-1/2} - 1)]$. In the normal state, the imaginary part of the conductivity σ_2 goes to zero as $\omega \to 0$ and according to Eq. (1), $\rho' = 1/\sigma_1(\omega=0) = \rho_{dc}$. The magnitude of ρ_{dc} at room temperature (340 $\mu\Omega$ cm) agrees well with the dc resistivity measurements on our samples.

In the superconducting state the quantity ρ' cannot be related to the dc resistivity, but it still serves as an indicator of the superconducting transition. Below T_c, σ_1 develops a δ function at $\omega=0$, and $\sigma_2 \approx 1/\omega$. Therefore the transmission will vanish at zero frequency and $\rho'=0$. The temperature dependence of ρ' indeed reaches zero between 60 and 70 K (Fig. 2). The discrepancy between this temperature and the transition temperature of our samples (obtained from the dc resistivity and magnetic susceptibility measurements) is due to the absorption at low (but nonzero) frequencies for temperatures near T_c.[1] The extrapolation of the transmission to zero at low frequencies is additional evidence that the samples were of high quality.

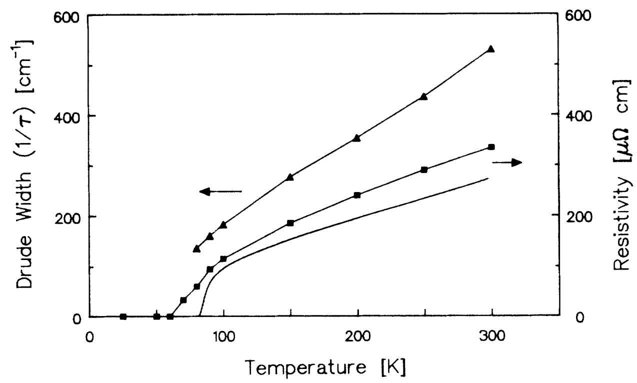

FIG. 2. Temperature dependence of the resistivity ρ' (squares) and the Drude relaxation rate $1/\tau$ (triangles). ρ' was obtained from extrapolation of the infrared transmission data to zero frequency; for comparison we show the measured dc resistivity (solid line with no symbols). The relaxation rate was calculated by fitting the parameters of Eq. (2).

The detailed analysis of the normal-state optical conductivity, including comparisons to the marginal Fermi-liquid model of Varma *et al.*[11] and fits with frequency-dependent relaxation rate and plasma frequency[12] (recently suggested for high-T_c superconductors by Collins *et al.*[6]), will be presented in a separate publication. Here we consider the simplest possible approach; we assume that the transmission is governed by a model dielectric function consisting of the sum of two oscillators:

$$\varepsilon = \frac{-\omega_p^2}{\omega^2 + i\omega/\tau} + \frac{\Omega_p^2/\omega_0^2}{1 - \omega^2/\omega_0^2 - i\omega/\omega'} + \varepsilon_0 . \quad (2)$$

Here ω_0 is the center frequency of the midinfrared oscillator and $\omega' = \omega_0^2/\Gamma$, where Γ is the oscillator width. The existence of excess oscillator strength in the midinfrared band has been suggested by several authors based on infrared reflectance studies[4,5,7] and Raman-scattering measurements.[13]

The calculated transmission was found to be relatively insensitive to ω_0 and ε_0, and we fixed these at 3000 cm^{-1} and 4.0, respectively, comparable to values reported by Kamaras *et al.*[5] Good-quality fits were obtained with a temperature-independent Drude plasma frequency ω_p $=9500$ cm^{-1}. The temperature variation of the relaxation rate $1/\tau$ is plotted in Fig. 2. The parameters of the midinfrared band vary between $\Omega_p^2/\omega_0^2 = 210$ and 230 and $\omega' = 500$ and 300 cm^{-1} for the temperature range of $T=100$–150 K. Above 150 K these parameters are essentially independent of temperature. The main results of this evaluation are (1) the Drude plasma frequency is independent of temperature, (2) the relaxation rate shows a linear temperature dependence with almost no intercept at $T=0$, (3) the midinfrared oscillator is overdamped (its spectral weight is large, but cannot be determined accurately from these measurements), and (4) the midinfrared conductivity exhibits a weak temperature dependence between 100 and 300 K.

The constant ω_p and linear variation of $1/\tau$ with temperature are consistent with dc resistivity measurements.[14] Their magnitudes are also consistent with values reported for other high-T_c compounds.[4,5] The large spectral weight of the midinfrared term is a typical feature of the harmonic-oscillator fits,[5] and it decreases if the Drude component is replaced by the optical conductivity of the "marginal-Fermi-liquid" charge carriers as suggested by Varma *et al.*[11] However, if we assume that the number and the mass of these charge carriers is independent of the temperature, our results cannot be interpreted without a spectral weight representing direct absorption in the midinfrared regime.

Finally, we discuss the optical response in the superconducting state. At temperatures below 60 K the temperature dependence of the transmission was found to be weak. For temperatures well below T_c and for frequencies below the gap we expect $\sigma_1 = 0$ and $\sigma_2 = c^2/4\pi\lambda^2\omega$, where λ is the *a-b* plane London penetration depth. We obtained $\lambda = 100$ nm at 25 K. Similar penetration depths have been determined for other high-temperature superconductors,[15] and λ is consistent with the assumption that the majority of the electrons are in the superconducting condensate.

In searching for evidence of a superconducting gap Δ, it has proven useful to plot the ratio of transmissions for temperatures below and above the transition temperature. Conventional superconductors exhibit a strong peak[1] at a frequency slightly greater than 2Δ, in accord with the calculated optical conductivity of Mattis and Bardeen.[16] The measured ratio of transmission at 25 and 90 K is shown in Fig. 3. There is no transmission peak in the frequency range of our measurement, which extends from $1.5k_BT_c$ to $12k_BT_c$. The smooth shoulder around 200 cm^{-1} is not evidence of an energy gap, but it is an immediate consequence of a temperature-dependent τ. The shoulder gradually disappears as we use higher-temperature data for the normal state. Since the synchrotron radiation is highly polarized and our samples are well oriented, we were able to search for the superconducting gap by rotating the crystal around the c axis. We did not find a transmission peak at any orientation. This result is in contrast to other recent works in which, using a variety of experimental techniques, a superconducting gap has been reported for $YBa_2Cu_3O_x$ (Refs. 6, 7, and 17) and $Bi_2Sr_2Ca_1Cu_2O_x$.[17-19] Considering the accuracy of our transmission data obtained on several single crystals, we have no doubts that the transmission of $Bi_2Sr_2Ca_1Cu_2O_x$ does not show evidence for a sharp spectroscopic gap in the energy range of $1.5k_BT_c$ to $12k_BT_c$.

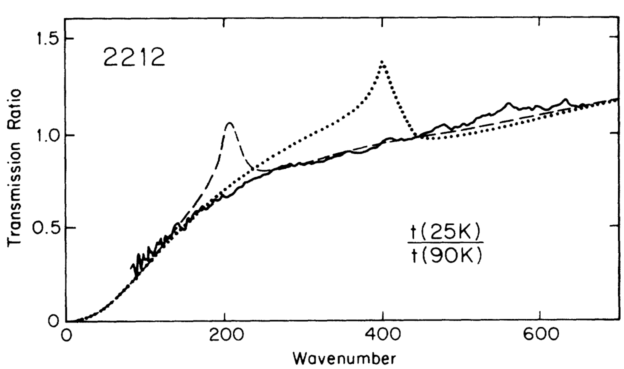

FIG. 3. Ratio of the transmissions at 25 and 90 K. The solid line represents the measured transmissions. The dashed and dotted lines were obtained from calculations of Allen (Ref. 20). We assumed a Drude relaxation rate of 50 cm^{-1} at 25 K. The BCS gap was assumed to be $2\Delta = 3.5k_BT_c = 200$ cm^{-1} and $2\Delta = 7.0k_BT_c = 400$ cm^{-1}. The calculation predicts a transmission peak even for $1/\tau < 2\Delta$; no peak is seen in the measurement.

Timusk *et al.* and Kamaras *et al.*[5] have argued qualitatively that since high-temperature superconductors are in the clean limit the Mattis-Bardeen result does not apply. Indeed, if we extrapolate our experimentally determined scattering rate for the normal state down to $T = 25$ K, we obtain a $1/\tau$ of 50 cm^{-1}, which is about a factor of 4–8 less than the expected gap frequency. However, very recently Allen has calculated the optical conductivity of a BCS-type superconductor at finite temperature and arbitrary relaxation rate.[20] These results, plotted for $2\Delta = 3.5k_BT_c$ and $2\Delta = 7k_BT_c$ in Fig. 3, predict that the gap should be seen even in the present "clean" material.

To explain the absence of the peak in the experimental data of Fig. 3 we consider three possibilities. (i) The extrapolation of the relaxation rates to lower temperatures may be incorrect, and $1/\tau \ll 50$ cm^{-1}. This would require a much faster-than-linear drop of $1/\tau$ with temperature. While this may be consistent with the Bloch-Gruneisen "T^5 law," the low-temperature, normal-state resistivities of related compounds with lower critical temperatures do not support this interpretation. (ii) A simple computer simulation shows that a distribution of gap frequencies would make the peak in the transmission broaden or totally disappear. This is due to the fact that the calculated peak in the transmission is narrow for $1/\tau < 2\Delta$. With a twinned sample or with an unpolarized infrared beam we could consider the gap anisotropy[21] as a possible source of a distribution of gap frequencies. However, since our sample is not twinned and we use polarized radiation, this argument is not valid. (iii) The third possibility is that the superconducting condensate is subjected to very strong inelastic scattering, resulting in a short lifetime which, in turn, smears the onset of the optical conductivity at 2Δ and suppresses the peak in the transmission. For conventional BCS superconductors magnetic impurities lead to this type of behavior.[22] In the high-temperature superconductors pair-breaking interactions, associated to the midinfrared band by Varma *et al.*,[11] may have a similar effect.

We believe that a strong pair-breaking interaction, leading to anomalously short lifetime of the Cooper pairs, is the most likely explanation for the absence of a peak in the experimental data of Fig. 3. This explanation is consistent with other experiments. Recent tunneling measurements on good-quality $YBa_2Cu_3O_x$ samples indicate a broad gap structure, with significant density of states down to zero energy.[23] Photoemission measurements by Olson *et al.*[18] and Petroff[19] show an increase in the density of states around the gap, but the results are compatible with some states extending to lower energies.[19] Nuclear magnetic relaxation rates[24] in $YBa_2Cu_3O_7$ do not show a "coherence peak" below T_c, and the absence of this peak was interpreted as an evidence for inelastic scattering.[25]

In conclusion, we have found that the normal-state transmission of $Bi_2Sr_2Ca_1Cu_2O_x$ can be described by a superposition of the conduction-electron response and a midinfrared band. The Drude relaxation rate follows a nearly perfect linear temperature dependence. The full spectral weight of the strongly overdamped midinfrared band is large, and transmission measurements at higher frequencies are planned for a detailed study of this part of the response. A major result of our investigation is the absence of an observable superconducting gap. Using the recent results of Allen,[20] we demonstrated that the "clean-limit" arguments of Kamaras *et al.*[5] are not sufficient to explain our results. This conclusion is further supported by our preliminary measurements on electron-irradiated samples. We proposed that an anomalously short Cooper-pair lifetime is responsible for our findings.

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