No Far-Infrared-Spectroscopic Gap in Clean and Dirty High-T_c Superconductors

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We report far-infrared transmission measurements on single crystal samples derived from $Bi_2Sr_2CaCu_2O_8$. The impurity scattering rate of the samples was varied by electron-beam irradiation, 50 MeV $^{16}O^{+6}$ ion irradiation, heat treatment in vacuum, and Y doping. Although substantial changes in the infrared spectra were produced, in no case was a feature observed that could be associated with the superconducting energy gap. These results all but rule out "clean limit" explanations for the absence of the spectroscopic gap in this material, and provide evidence that the superconductivity in $Bi_2Sr_2CaCu_2O_8$ is gapless.

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The existence of a superconducting energy gap in the high-T_c superconductors has been hotly debated. A simple s-wave BCS model has a complete gap of width 2Δ around the Fermi energy with $2\Delta/k_BT_c = 3.5$ for weak coupling or higher for stronger coupling. This energy gap is evident in the far-infrared–microwave range for low-T_c superconductors [1]. Infrared studies [2–7] on high-T_c materials reveal a feature at $\sim$(8–12)k_BT_c, originally thought to be the gap. However, there is increasing evidence to the contrary [7]. In high-T_c superconductors the gap might not show up in the infrared spectrum for several reasons. First, the scattering rate of the charge carriers may be low relative to the superconducting energy gap ($1/\tau << 2\Delta$), and the infrared spectroscopy cannot distinguish between a near perfect conductor and a true superconductor [3]. Second, there seems to be a temperature independent contribution to the oscillator strength in this frequency range, overlapping and possibly masking the weak gap feature. Third, the gap feature may be broad, either due to anisotropy or lifetime effects. It is also possible that the description of the superconducting state cannot be put in a BCS framework.

We can experimentally test the first possibility by enhancing the impurity scattering rate to produce optimum circumstances for the observation of the spectroscopic gap. In this Letter, we present far-infrared data on ultrathin single crystals of the $Bi_2Sr_2CaCu_2O_8$ family. We first measured the "pure" samples' far-infrared transmission spectra. The samples were then made "dirty" by electron-beam irradiation, 50 MeV $^{16}O^{+6}$ ion irradiation, or heat treatment in vacuum to drive out oxygen. The infrared measurements were then repeated and compared with the "pure" measurements. In another set of experiments we looked at Y-doped samples of composition $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$, with x = 0.0–0.35. In spite of the enhanced scattering rate, the results from all samples show no spectroscopic gap. We present a simple analysis and conclude that an s-wave BCS gap should lead to significant features in the infrared spectrum.

The far-infrared measurements were made at beamline U4IR at the National Synchrotron Light Source, Brookhaven National Laboratory [8]. The samples were mounted on the cold finger of an LT-3-110A Heli-Tran liquid transfer refrigeration system and were maintained at various temperatures. A Nicolet 20F rapid scan FTIR spectrometer with a helium cooled Si bolometer detector recorded the spectra. The samples used in this study were typically 2000 Å thick with a diameter of 0.6 mm, and had initial ("clean state") transition temperatures of $T_c \sim 84$ K. Prior to the infrared study the samples were characterized with electron microscopy and dc transport measurements as described elsewhere [9].

The electron-beam irradiation was done for 20 h in the JEOL electron microscope at the Earth and Space Sciences Department at Stony Brook. Although the resistivity of the sample increased, the critical temperature was suppressed by less than 1 K. The 50 MeV $^{16}O^{+6}$ ion irradiation was done at the +30° beam line of the Tandem Van de Graaf accelerator operated by the Nuclear Structure Laboratory at Stony Brook [10]. Approximately 6×10^{15} ions/cm^2 went through the sample and the T_c was lowered by $\sim$ 4 K. The increase of the critical current reported earlier [11] also demonstrated the presence of lattice damage. The heat treatment was done with a microfurnace while the sample was under vacuum in the spectrometer. The sample was heated to $\sim$ 650 °C to drive out oxygen. The critical temperature, as determined from dc resistivity measurement, was reduced by $\sim$ 20 K. The Y doping is described in previously published studies [12,13]. At the highest doping level discussed here ($x = 0.35$) the critical temperature was about 60 K.

A simple, universal indicator of the lattice damage in all samples is the room temperature resistivity ratio, $\alpha = \rho_{\rm dirty}/\rho_{\rm clean}$. The infrared data can be self-consistently used to calculate this quantity. As we established earlier [2], for low transmission samples the low frequency limit of the transmission is $t = \rho^2 d^2 (c/2\pi)^2$, where ρ is the dc resistivity, and d is the sample thickness. Therefore, for the samples where direct resistivity measurements were not performed, we used $\alpha = \{t(300\ {\rm K})_{\rm dirty}/t(300\ {\rm K})_{\rm pure}\}^{1/2} = \rho_{\rm dirty}/\rho_{\rm pure}$.

To verify that our samples are not inhomogeneous, a Meissner fraction measurement would be optimal. However, the very small and ultrathin dimensions of our samples make this measurement unfeasible. Fortunately, the absolute value of the transmission at zero frequency is another good measure of the homogeneity of our crystals. If a sample has a nonsuperconducting portion the transmission would have a nonzero intercept. Since we do observe in all cases that our samples' superconducting transmissions extrapolate to zero at zero frequency, we can assert that there are no normal state windows in the samples.

In s-wave BCS superconductors the frequency dependence of the transmission coefficient of electromagnetic radiation exhibits a peak at a frequency somewhat above (but close to) the gap frequency $\omega = 2\Delta/\hbar$ [14]. For high-T_c superconductors, this frequency is expected to fall within the 400–800 cm^{-1} range, depending on the gap value.

Figure 1(a) shows the infrared transmission spectra obtained at 13 K, 100 K, and 300 K for the electron-beam irradiated sample. The dotted and solid curves were obtained before and after the irradiation, respectively. It is clear that for the irradiated sample the infrared transmission has increased at all temperatures, indicative of a higher scattering rate and/or reduced carrier density. Looking at the 13 K spectra where the sample is well below T_c, we see no features representative of a gap appearing in the irradiated sample up to 700 cm^{-1}.

The 50 MeV $^{16}O^{+6}$ ion irradiated sample's spectra are shown in Fig. 1(b). Again the dotted curves display spectra taken before irradiation and the solid lines were measured after. Data were obtained at 5 K, 100 K, and 300 K. The transmission increased significantly more for samples irradiated this way, showing that we are doing far more damage to the sample than the electron-beam irradiation did. This "dirtier" sample again shows no evidence of a gap in the superconducting (5 K) spectra. The 100 K spectra were fitted to a simple Drude model with a midinfrared absorption as was done previously [2]. The fit produced the following numerical results: Before irradiation, $1/\tau = 170$ cm^{-1}, $\omega_p = 9100$ cm^{-1}; after irradiation, $1/\tau = 230$ cm^{-1}, $\omega_p = 6600$ cm^{-1}. The Drude plasma frequency (ω_p) decreased by about 40%, corresponding to a decrease of carrier density. The increase of the Drude scattering rate ($1/\tau$) indicates that we are indeed moving away from the "clean limit." If we associate the increase of the scattering rate with impurities, we obtain $1/\tau_0 = 60$ cm^{-1} for the impurity scattering rate.

The infrared transmission of the reduced oxygen sample due to heat treatment in vacuum is shown in Fig. 1(c). The transmission increased at all temperatures (6 K, 100 K, and 300 K) as a result of the heat treatment. As in the previous cases, we do not observe any feature indicative of a superconducting energy gap.

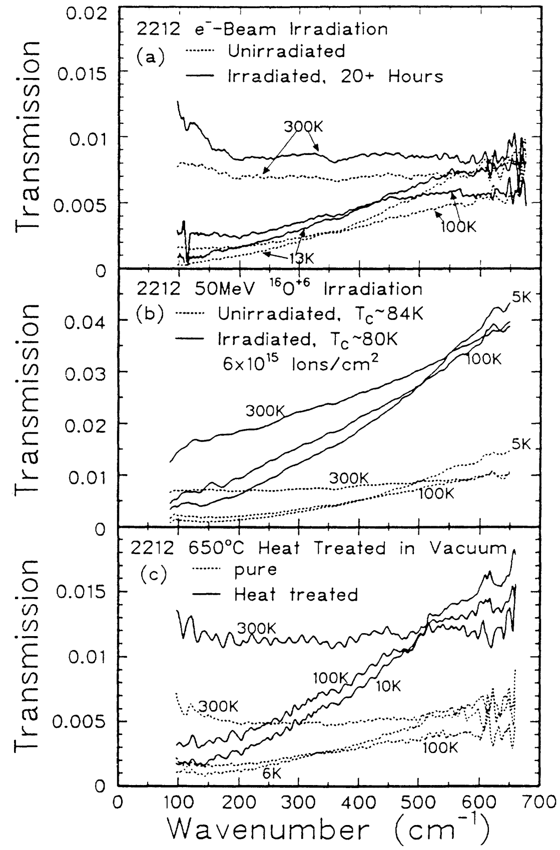

FIG. 1. Infrared transmission of pure (dotted line) and "dirty" (solid line) samples. (a) Sample before and after electron-beam irradiation. Spectra for three temperatures are shown. (b) Spectra for a 50 MeV $^{16}O^{+6}$ ion irradiated sample for three temperatures. The sample was irradiated with 6×10^{15} $ions/cm^2$. (c) Infrared transmission for a pure and heat treated in vacuum sample for three temperatures.

In Fig. 2, we show the ratio of the transmission in the superconducting state (taken at the lowest temperature) to the nonsuperconducting spectra (taken at 100 K) for all samples in this study, including the Y-doped samples [15]. The investigation of the electrical transport properties of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ indicated that the increase of scattering rate in this approximately follows the Matthiessen rule [12,13]. Therefore we have reason to believe that impurity scattering acts as a temperature independent additive contribution to the relaxation rate. For a sample at $x = 0.38$ the resistivity at 100 K is increased by a factor of 6 relative to the pure sample, suggesting a relaxation rate in the range of 1200 cm^{-1}. This number may decrease by as much as 50% if the changes in carrier concentration are taken into account (see Figs. 1 and 2 of Ref. [13]). Nevertheless, the normal state relaxation rate corresponds to $1/\tau \gtrsim 2\Delta$, and the high relaxation rate is expected to survive in the superconducting state. Figure 2 illustrates that no peak is

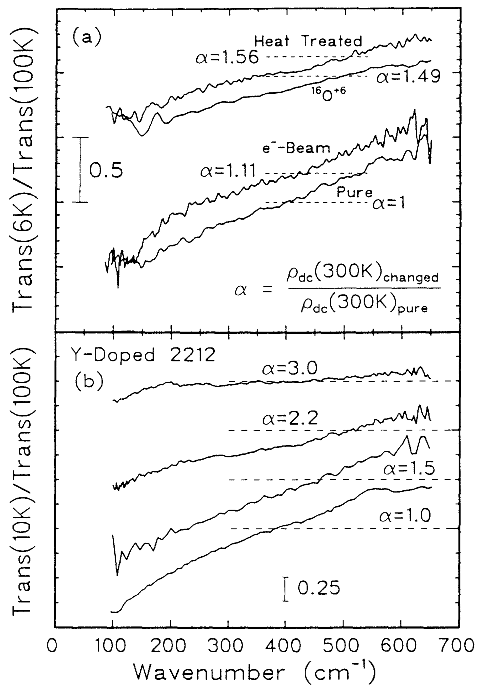

FIG. 2. Ratios of superconducting transmission (low temperature) to nonsuperconducting transmission (100 K). The curves are offset for clarity, and the dashed line represents the transmission ratio equal to unity for each curve. The top panel (a) was obtained from the results presented in Fig. 1; the lower panel (b) shows the results for four $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ samples (x ranging from 0 to 0.35). The vertical scale is indicated separately on each panel. The quantity α is a measure of sample purity, as discussed in the text ($\alpha = 1$ corresponds to pure sample).

seen for any of the impure samples.

Earlier IR data [2–6] saw evidence for a gap feature at ~ 700 cm^{-1}. However, since this feature does not have a temperature dependence, or disappear above T_c when T_c is significantly reduced, many (including us) argue that it is not the superconducting gap [7]. We also argue that the gap is not hidden by the clean state of the sample as originally suggested by Kamaras *et al.* [3]. Even if the relaxation rate of the normal component drops further in the superconducting state (as proposed by Romero *et al.* [16]), the impurity scattering rate of our samples would be significant enough to expose the gap feature. In this respect our work is in contradiction to Brunel *et al.* [17] who observed a gap feature in the reflectivity of dirty $Bi_2Sr_2CaCu_2O_8$ films.

To elucidate what the lack of a peak in our data implies, we numerically fabricated several $\sigma_1(\omega)$ functions [Fig. 3(a)] and calculated the resulting transmission ratio [Fig. 3(b)]. The model parameters were chosen to represent a homogeneous, dirty sample (using numbers generated by our fits to the $^{16}O^{+6}$ irradiated sample).

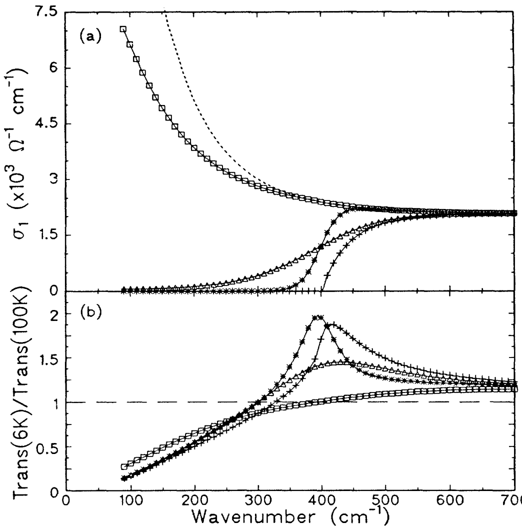

FIG. 3. Calculations of the superconducting to nonsuperconducting transmission ratio expected for various, arbitrary cutoffs at low frequency in $\sigma_1(\omega)$. The upper panel (a) shows the nonsuperconducting $\sigma_1(\omega)$ (dashed line) and the different cutoffs we fabricated. The lower panel (b) shows the transmission ratios calculated from the $\sigma_1(\omega)$ of the same symbol.

First we simulated the optical conductivity at 100 K as a sum of a Drude term with $1/\tau = 230$ cm^{-1}, $\omega_p = 6600$ cm^{-1} and a broad midinfrared resonance with $\Gamma = 25\,000$ cm^{-1}, $\Omega_p = 25\,500$ cm^{-1}, and $\omega_0 = 3000$ cm^{-1} [Fig. 3(a), dashed line]. We emphasize that in the investigated frequency range the resulting optical conductivity $\sigma_1(\omega)$ cannot be distinguished from that obtained by the assumption of a single carrier with frequency dependent relaxation rate, as discussed by Schlesinger *et al.* [4], so the particular choice of mathematical representation does not restrict our arguments.

Next, we created a hypothetical nonsuperconducting low-temperature conductivity, by using $1/\tau_0 = 60$ cm^{-1} [18]. To represent superconductivity we introduced various, somewhat arbitrary cutoffs to $\sigma_1(\omega)$ at low frequencies. The missing area was calculated, a Kramers-Krönig transformation was performed to provide $\sigma_2(\omega)$, the superconducting condensate was represented by the appropriate $1/\omega$ contribution, and finally the transmission in the superconducting and nonsuperconducting cases was calculated and ratioed. The first σ_1 function (plus signs) has a complete gap. This type of optical conductivity is expected in the "single carrier model," where the normal state relaxation rate is frequency dependent, there is no extra midinfrared absorption, and the superconducting gap is complete. We also tried a smooth drop in σ_1 where no complete gap opens. When the slope at 2Δ is large (asterisks), a pronounced peak still results. If the transition is very gradual (triangles), a peak is still visible, but it is broadened significantly. A ratio without a peak is observed when we assume a gapless optical conductivity in the superconducting state (squares) which smoothly approaches the nonsuperconducting $\sigma_1(\omega)$ at higher frequency. This gapless calculated ratio certainly best matches our data.

The general conclusions we can draw are that gapless spectra do fit our data, and if a gap feature does exist, it must be much smoother than predicted by the BCS theory. This result is consistent with a recent reflectivity study on Ni-doped $YBa_2Cu_3O_{7-\delta}$ films [19]. The absence of a fully developed s-wave gap is in accordance with the results of tunneling studies on the same material [20]. The results of photoemission spectroscopy are compatible with the absence of an s-wave BCS gap [21]. The strongest argument for a fully developed gap came from early penetration depth studies, but recent precision measurements by Hardy *et al.* [22] provide evidence for nodes in the gap function. The anisotropy of the NMR relaxation rate [23] and the nonvanishing low frequency Raman absorption [24] point in a similar direction. Our data are another piece of a growing amount of evidence that the low-temperature density of states in the high-T_c materials is profoundly different from conventional superconductors.

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