No Far–Infrared–Spectroscopic Gap in Clean and Dirty High-T$_C$ Superconductors

D. Mandrus$^1$, Michael C. Martin$^1$, C. Kendziora$^1$, D. Koller$^1$, L. Forro$^2$, and L. Mihaly$^3$

$^1$Department of Physics, SUNY at Stony Brook, Stony Brook, NY 11794–3800
$^2$Department of Physics, Ecole Polytechnique Federale de Lausanne, 1015 Lausanne, Switzerland
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We report far infrared transmission measurements on single crystal samples derived from Bi$_2$Sr$_2$CaCu$_2$O$_8$. The impurity scattering rate of the samples was varied by electron-beam irradiation, $50\text{MeV}^{16}\text{O}^{+6}$ 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$_2$Sr$_2$CaCu$_2$O$_8$ 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 2$\Delta$ 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] on high-T$_C$ materials reveal a feature at $\sim 8–12k_BT_C$, originally thought to be the gap. However there is increasing evidence to the contrary [3]. 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 ($1/\tau \ll 2\Delta$), and the infrared spectroscopy can not distinguish between a near perfect conductor and a true superconductor [4]. 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$_2$Sr$_2$CaCu$_2$O$_8$ family. We first measured the “pure” samples’ far infrared transmission spectra. The samples were then made “dirty” by electron-beam irradiation, $50\text{MeV}^{16}\text{O}^{+6}$ 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$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_8$, 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 [5]. The samples were mounted on the cold-finger of an LT$-3–110\text{A}$ 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 2000A thick with a diameter of 0.6mm, and had initial (“clean state”) transition temperatures of $T_C \sim 84\text{K}$. Prior to the infrared study the samples were characterized with electron microscopy and dc transport measurements as described elsewhere [6].

The electron-beam irradiation was done for 20 hours 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 1K. The $50\text{MeV}^{16}\text{O}^{+6}$ ion irradiation was done at the $+30^\circ$ beam line of the Tandem Van de Graaf accelerator operated by the Nuclear Structure Laboratory at Stony Brook [7]. Approximately $6 \times 10^{15}$ ions/cm$^2$ went through the sample and the $T_C$ was lowered by $\sim 4\text{K}$. The increase of the critical current, reported earlier [8], also demonstrated the presence of lattice damage. The heat treatment was done with a micro-furnace while the sample was under vacuum in the spectrometer. The sample was heated to $\sim 650\text{C}$ to drive out oxygen. The critical temperature, as determined from dc resistivity measurement, was reduced by $\sim 20\text{K}$. The Y-doping is described in previously published studies [8][9][10]. At the highest doping level discussed here ($x = 0.35$) the critical temperature was about 60K.

A simple, universal indicator of the lattice damage in all samples is the room temperature resistivity ratio, $\alpha = \rho\text{dirty}/\rho\text{clean}$. The infrared data can be self consistently used to calculate this quantity. As we established earlier [10], for low transmission samples the low frequency limit of the transmission is $t = \rho^2d^2(c/2\pi)^2$, where $\rho$ is the dc resistivity, and $d$ is the sample thickness. Therefore, for the samples where direct resistivity measurements were not performed, we used $\alpha = \{t(300\text{K})/t(300\text{K})\text{pure}\}^{1/2} = \rho\text{dirty}/\rho\text{pure}$.

To verify that our samples are not inhomogeneous, a Meisner fraction measurement would be optimal. How-
ever the very small and ultra-thin dimensions of our samples make this measurement unfeasable. 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 non-superconducting portion the transmission would have a non-zero 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 \( \omega = 2\Delta/h \) \([10]\). For high-\( T_C \) superconductors, this frequency is expected to fall within the 400 – 800 \( \text{cm}^{-1} \) range, depending on the gap value.

Figure 1(a) shows the infrared transmission spectra obtained at 13K, 100K, and 300K 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 13K 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 \( \text{cm}^{-1} \).

The 50MeV \(^{16}\text{O}^{+6}\) ion irradiated sample’s spectra are shown in figure 1(b). Again the dotted curves display spectra taken before irradiation and the solid lines were measured after. Data were obtained at 5K, 100K, and 300K. 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 (5K) spectra. The 100K spectra were fit to a simple Drude model with a mid-infrared absorption as was done previously \([2]\). The increase of a gap in the superconducting (5K) spectra. The transmission increased at all temperatures, indicative of a higher scattering rate and/or reduced carrier density. The increase of scattering rate in this approximately follows Matthiessen rule \([14,15]\). 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 100K is increased by a factor of 6 relative to the pure sample, suggesting a relaxation rate in the range of 1, 200 \( \text{cm}^{-1} \). This number may decrease by as much as 50% if the changes in carrier concentration are taken into account [see figures 1 and 2 of ref. [2]]. Nevertheless, the normal state relaxation rate corresponds to \( 1/\tau \approx 2\Delta \), and the high relaxation rate is expected to survive in the superconducting state. Figure 2 illustrates that no peak is seen for any of the impure samples.

Earlier IR data \([2,9]\) saw evidence for a gap feature at \( \sim 700 \text{cm}^{-1} \). However since this feature does not have a temperature dependence, nor does it disappear above \( T_C \) when the \( T_C \) is significantly reduced, many (including us) argue that it is not the superconducting gap \([1]\). We also argue that the gap is not hidden by the clean state of the sample as originally suggested by Kambaras et.al. \([1]\). Even if the relaxation rate of the normal component drops further in the superconducting state (as proposed by Romero et. al. \([5]\)) 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. \([1]\) who observed a gap feature in the reflectivity of dirty \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8 \) films.

To elucidate what the lack of a peak in our data implies, we numerically fabricated several \( \sigma_1(\omega) \) functions (Figure 3a) and calculated the resulting transmission ratio (Figure 3b). The model parameters were chosen to represent a homogeneous, dirty sample (using numbers generated by our fits to the \(^{16}\text{O}^{+6}\) irradiated sample). First we simulated the optical conductivity at 100K as a sum of a Drude term with \( 1/\tau = 230 \text{cm}^{-1} \), \( \omega_p = 6600 \text{cm}^{-1} \) and a broad mid infrared resonance with \( \Gamma = 25000 \text{cm}^{-1} \), \( \Omega_p = 25500 \text{cm}^{-1} \) and \( \omega_p = 3000 \text{cm}^{-1} \) (Fig. 3a, dashed line). We emphasize that in the investigated frequency range the resulting optical conductivity \( \sigma_1(\omega) \) can not be distinguished from that obtained by the assumption of a single carrier with frequency dependent relaxation rate, as discussed by Schlesinger et. al. \([1]\), so the particular choice of mathematical representation does not restrict our arguments.

Next, we created a hypothetical non-superconducting low temperature conductivity, by using \( 1/\tau_0 = 60 \text{cm}^{-1} \) \([18]\). To represent superconductivity we introduced various, somewhat arbitrary cut-offs to \( \sigma_1(\omega) \) at low frequencies. The missing area was calculated, a Kramers-Kröning 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 non-superconducting cases were calculated and ratioed. The first \( \sigma_1 \) 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 mid infrared absorption, and the superconducting gap is complete. We also tried a smooth drop in $\sigma_1$ where no complete gap opens. When the slope at $2\Delta$ 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 non-superconducting $\sigma_1(\omega)$ 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$_2$Cu$_3$O$_{7-\delta}$ films [23]. The absence of fully developed $s$-wave gap is in accordance with the the results of tunneling studies on the same material [22]. The results of photoemission spectroscopy are compatible with the absence of a $s$-wave BCS gap [21]. The strongest argument for a fully developed gap came from early penetration depth studies, but recent precession measurements by Hardy et al. [23] 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 is another piece of a growing amount of evidence that the low temperature density of states in the superconducting material [20]. The results of photoemission spectroscopy are compatible with the absence of a $s$-wave BCS gap [21]. 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$_2$Cu$_3$O$_{7-\delta}$ films [23]. The absence of fully developed $s$-wave gap is in accordance with the the results of tunneling studies on the same material [22]. The results of photoemission spectroscopy are compatible with the absence of a $s$-wave BCS gap [21].

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* Present Address: Los Alamos National Laboratory, Los Alamos, New Mexico 87545.
† Permanent Address: Institute of Physics of the University, 41001 Zagreb, Croatia.
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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 50MeV $^{18}$O$^{+6}$ ion irradiated sample for three temperatures. The sample was irradiated with $6 \times 10^{15}$ ions/cm$^2$. (c) Infrared transmission for a pure and heat treated in vacuum sample for three temperatures.
FIG. 2. Ratios of superconducting transmission (low temperature) to non-superconducting transmission (100K). 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 Figure 1; the lower panel (b) shows the results for four Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_8$ samples ($x$ ranging from 0 to 0.35). The vertical scale is indicated separately on each panel. The quantity $\alpha$ is a measure of sample purity, as discussed in the text ($\alpha = 1$ corresponds to pure sample).

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