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Far-infrared absorption by bulk high-T_c superconductors using an optically pumped CH_3OH laser

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We have developed a far-infrared-absorption-measurement method using an optically pumped far-infrared laser. The temperature dependence of the light absorption by high-T_c superconductors has been investigated for the photon energy between 7.6 and 17.6 meV in the temperature region between 12 and 160 K. A well-defined transition temperature was obtained from the absorption measurement. With decreasing temperature, the absorption decreased, but did not reach zero even at sufficiently low temperatures.

I. INTRODUCTION

One of the controversial problems in high-T_c superconductors is whether or not the far-infrared (FIR) reflectivity should be 100% for the photon energy below the superconducting gap energy at sufficiently low temperatures. Most studies of FIR reflection have been principally motivated by a desire to investigate the superconducting energy gap and the low-energy spin and/or charge excitations. There have been extensive measurements reported in the literature relating to the possible energy gap, but a clear picture of the gap has not been obtained yet. For example, in the superconducting-state reflectivity of $YBa_2Cu_3O_7$ (Y-Ba-Cu-O), a distinct knee is present near 54 meV. Schlesinger *et al.*[1] have suggested that this feature should be attributed to a large BCS superconducting energy gap $[2\Delta(0)/k_BT_c \simeq 8]$. In contrast, Cooper *et al.*[2] have proposed another criterion to extract a superconducting gap from FIR data. They defined the gap $[2\Delta(T) = h\nu]$ as the frequency (ν) at which the reflectivity begins to deviate from 100% with increasing frequency. Applying this criterion to numerous $YBa_2Cu_3O_{7-x}$ crystals having a variety of T_c's, they have reported evidence for a BCS-size gap $[2\Delta(0)/k_BT_c \sim 3.5]$. In addition to these reflectance measurements, there have been transmission measurements and absorption measurements in the FIR studies of the high-T_c superconductors. The FIR transmission spectra for $Bi_2Sr_2CaCu_2O_y$ superconductors have been measured for temperatures above and below T_c with high-T_c films deposited on Mg0 by Hughes *et al.*[3] and by Williams *et al.*[4] and with free-standing single crystals by Forro *et al.*[5] The latter has the advantage of high sensitivity to bulk properties. These FIR transmission spectra show that, in the superconducting state, the transmission drops at low frequencies but remains finite even at sufficiently low frequencies and that there is no indication of a transmission peak which characterizes a superconducting gap in the optical conductivity. These results are different from the results demonstrated by the classic experiments of Glover and Tinkham.[6] There have been several measurements[7-9] relating to FIR absorption using a calorimetric method, which is a measurement of the increment of the temperature as a result of the absorption of light. These measurements have been made in the superconducting state of high-T_c superconductors around 4.2 K with conventional infrared sources and spectrometers. Gershenzon *et al.*[7] have reported that the value is $2\Delta(0)/k_BT_c = 0.6$. But Lee *et al.*[8] and Pham *et al.*[9] have reported that the value is

$$2\Delta(0)/k_BT_c = 3.2 \simeq 3.5$$

and, moreover, that the most striking feature is the presence of finite absorption over the whole measured spectral range (down to ~ 5 cm^{-1}) in contrast to the expectations from BCS theory which predicts zero absorptivity for frequencies below the gap at $T=0$.

Another problem in the FIR studies is purely experimental. In the reflectance measurements, the absolute reflectivity (R) of Y-Ba-Cu-O in the FIR region, where the superconducting gap may be expected to be observed (< 70 meV), is very close to unity ($R \geq 98\%$).[1,2] However, the measurement accuracy of the reflectivity is usually about 1% (Refs. 1 and 2) because it is restricted by detector noises and normalization errors. This gives a severe limitation to the detection of low-energy excitations in the superconducting state by reflectance measurements. In the calorimetric absorption measurements, a large improvement in the signal-to-noise ratio is expected by using a high-power light source. The reason is that a strong light source compensates for the decrease in the light-absorption-induced temperature change of the specimen, which is caused by the increase of the specific heat with increasing temperature. In contrast, a strong light source has little effect on the improvement in the signal-to-noise ratio in the traditional reflectance and transmission measurements.

We have developed absorption measurements with a FIR laser, a far-infrared-laser calorimetric method (FILC). Using a high-power optically pumped FIR laser[10] enabled us to measure the light absorption at any temperature below 300 K. In this paper, we report direct measurements of the absorption of photon energy between 7.6 and 124 meV in the temperature region between 12 and 160 K.

II. EXPERIMENTAL DETAILS

We investigated three types of the fully oxygenated high-T_c superconductors, which were sintered $YBa_2Cu_3O_Y$, sintered and single-crystal $Bi_2Sr_2CaCu_2O_Y$ (Bi-Sr-Ca-Cu-O). The resistances, measured by the standard four-probe method, are shown in Fig. 1. These curves are normalized at 120 K for convenience. A typical size of the specimen was $2\times2\times0.1$ mm^3 for the FILC measurement.

The experimental setup is schematically shown in Fig. 2. Three types of excitation light sources were used. One was an optically pumped CH_3OH laser which gave a choice of monochromatic photons with energies between 7.6 and 17.6 meV [$<2\Delta(0)$]. Another was a CO_2 laser which gave photons with 124 meV [$>2\Delta(0)$]. The other was a tungsten lamp which was used as a white light source. We used lines of a CH_3OH laser with the power levels above 10 mW. The intensity of the laser beam in the cryostat was estimated to be about 1 mW due to losses caused by air, optical windows, and so on. The light was chopped at 1.6 Hz and was focused with a lens onto the 2×2 mm^2 surface of the specimen. A typical size of the spot was 2 mm in diameter. Thermocouples (Chromel-Alumel) and a copper wire were silver pasted on the rear surface of the specimen. These wires provided mechanical support and thermal connection to the sample holder. Using the thermocouples, we measured the temperature variation which was induced by the chopped light. The average light intensity falling on the specimen caused its average temperature to rise (ΔT_{dc}), which was measured by a digital multimeter. The amplitude of temperature oscillation (ΔT_{ac}) was measured by a phase-sensitive lock-in amplifier. The temperature of the sample holder (T_b) was monitored with a chromel-gold–0.07 at % iron thermocouple. The sample temperature (T_s) was the sum of T_b and ΔT_{dc}.

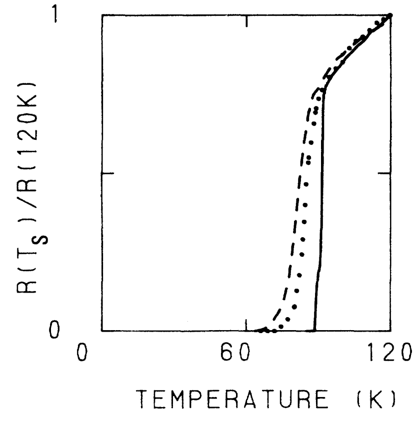

FIG. 1. Normalized dc resistance vs temperature. Solid line, sintered $YBa_2Cu_3O_y$, dotted line, sintered $Bi_2Sr_2CaCu_2O_y$, and dashed line, single-crystal $Bi_2Sr_2CaCu_2O_y$.

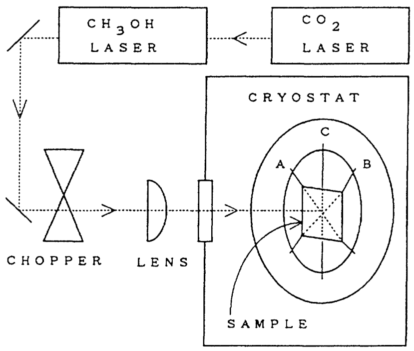

FIG. 2. Block diagram of the optical arrangement for a FILC method. A and B, thermocouple, and C, copper wire.

III. RESULTS

We made two kinds of experiments in order to investigate the temperature dependence of the infrared absorption by high-T_c superconductors. First, we irradiated the specimen with lasers in order to measure the amplitude of temperature oscillation (ΔT_{ac}) in the region of the photon energy between 7.6 and 124 meV. Next, we coated the front surface of the same specimen with graphitic paint to keep absorptivity constant and irradiated its surface with a tungsten lamp in order to measure the ΔT_{ac}. The latter is the same technique as a well-known light-irradiated ac calorimetric measurement. By combining the results from the two experiments, as we describe later, we can estimate the infrared absorption even if we have no information on the heat capacity and the thermal conductances. Figure 3 represents the ΔT_{ac} as a function of temperature. These curves are normalized at 105 K for convenience. Open circles and open triangles represent the ΔT_{ac}'s obtained from Y-Ba-Cu-O specimen irradiated at 7.6 and 17.6 meV, respectively. When we turned off the laser at the temperature of 12, 28, and 155 K, the ΔT_{ac}'s became zero as shown by solid circles. There were two striking features in the open circles and triangles. First, they dropped abruptly just below T_c

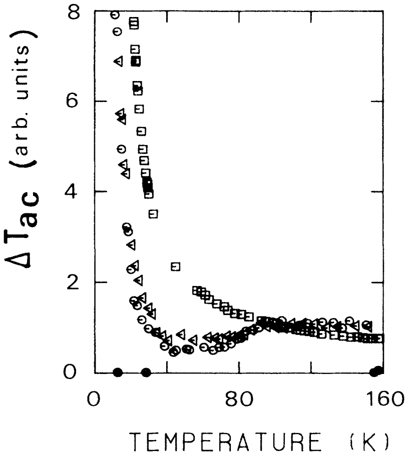

FIG. 3. Amplitude of temperature oscillation, ΔT_{ac}, vs temperature. Open circles and open triangles, $YBa_2Cu_3O_y$ sample irradiated at 7.6 and 17.6 meV, respectively. Open rectangles, painted $YBa_2Cu_3O_Y$ sample irradiated with a tungsten lamp.

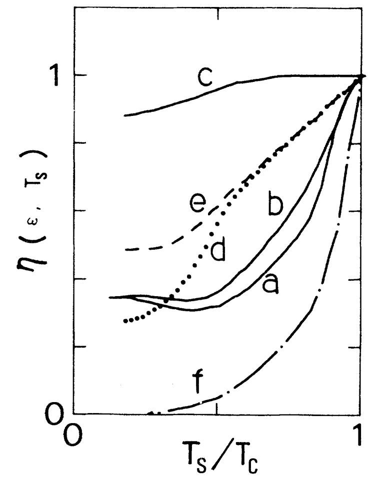

FIG. 4. Surface resistance ratio, $\eta(\varepsilon, T_s)$, between the superconducting state and the normal state vs reduced temperature $\theta(=T_s/T_c)$. a, b, and c, sintered $YBa_2Cu_3O_y$ sample irradiated at 7.6, 17.6, and 124 meV; d and e, sintered and single-crystal $Bi_2Sr_2CaCu_2O_y$ irradiated at 10.4 meV; f, σ_{1s}/σ_n derived from the Mattis and Bardeen theory (Ref. 12).

($\sim$90 K), so that we could obtain a well-defined transition temperature from the FILC measurement. Second, although the specimen was in the superconducting state, the ΔT_{ac}'s increased gradually below 30 K. These features were also observed in the sintered and the single-crystal Bi-Sr-Ca-Cu-O. Open rectangles represent the ΔT_{ac}'s obtained from the painted Y-Ba-Cu-O specimen irradiated with a tungsten lamp. The signal-to-noise ration in Fig. 3 is larger than 25.

All the ΔT_{ac}'s in Fig. 3 did not become zero even at sufficiently low temperatures. This is due to the FIR absorption by high-T_c superconductors. With decreasing temperature, the rapid increasing of ΔT_{ac}'s is not only due to the variation of the FIR absorption but also due to the decreasing of the specific heat. Here we describe the process to obtain the temperature dependence of infrared absorption by high-T_c superconductors. The infrared absorption $[\Delta Q(\varepsilon, T_s)]$ and the amplitude of temperature oscillation $[\Delta T_{ac}(\varepsilon, T_s)]$ are considered as a function of photon energy (ε) and temperature (T_s). On the other hand, in the case of the white-light irradiation, the incident light is absorbed by the paint and heat is therefore given to a specimen. The light absorption by the paint (ΔQ^0) is constant because its absorptivity is considered to be independent of the temperature, so that the amplitude of temperature oscillation $[\Delta T^0_{ac}(T_s)]$ is considered as a function of temperature only. We analyze the data based on the model of the ac-temperature calorimetry.[11] The penetration depth of the light is estimated to be about 200 nm (Ref. 1) in the FIR region. This depth is thin enough in comparison with the thickness of the specimen, so that the incident light is absorbed by the surface layer. Then the $\Delta T_{ac}(\varepsilon, T_s)$ can be expressed as

$$\Delta Q(\varepsilon, T_s) = \omega C_s \Delta T_{ac}(\varepsilon, T_s) F(\omega, C_s, K_s, K_b \cdots), \quad (1)$$

where ω is the chopping frequency, C_s and K_s are heat capacity and thermal conductance of specimen, respectively, and K_b is thermal conductance between the specimen and the sample holder. Here, the $F(\omega, C_s, K_s, K_b \cdots)$ is not a function of photon energy only. We deal with a quantity,

$$\eta(\varepsilon, T_s) = \Delta Q(\varepsilon, T_s)/\Delta Q^0 .$$

Considering Eq. (1), the $\eta(\varepsilon, T_s)$ can be obtained from the ratio of the amplitude of temperature oscillation,

$$\Delta T_{ac}(\varepsilon, T_s)/\Delta T^0_{ac}(T_s),$$

at each T_s. Traces of $\eta(\varepsilon, T_s)$ are shown in Fig. 4 as a function of reduced temperature θ $(=T_s/T_c)$. All curves are normalized at $\theta=1$. This $\eta(\varepsilon, T_s)$ is considered to be proportional to the surface resistance ratio between the superconducting state and the normal state. The curves (a), (b), and (c) were obtained from the measurements of the Y-Ba-Cu-O specimen irradiated at 7.6, 17.6 and 124 meV, respectively. The curves (d) and (e) were obtained from the measurements of the sintered and the single-crystal Bi-Sr-Ca-Cu-O specimens at 10.4 meV, respectively. The curve (f) represents the real part of the reduced optical conductivity (σ_{1s}/σ_n) derived from the Mattis and Bardeen theory[12] (MB), where the gap energy and the photon energy are assumed to be 27.3 $[=2\Delta(0)]$ and 17.6 meV, respectively.

IV. DISCUSSION

All curves, except for curve (c), in Fig. 4 showed the abrupt decrement below $\theta=1$. The decrement became steeper as the photon energy decreased from 17.6 [(b) in Fig. 4] to 7.6 meV [(a) in Fig. 4]. Curve (c) was hardly affected by the superconducting phase transition. These results suggest that the gap energy exists in the region of the photon energy between 17.6 and 124 meV, so we can estimate that the magnitude of the gap is $1.7 < [2\Delta(0)/K_B T_c] < 10$. This wide range is due to lack of available lines from our lasers.

With decreasing temperature, the infrared absorption in all curves except for (c) decreased as expected from the MB theory.[12] However, we found, for the first time in the absorption measurement as a function of temperature, "unexpected" absorption by high-T_c superconductors. All curves stayed nonzero values of $\eta(\varepsilon, T_s)$ even at sufficiently low temperatures. As a result, the reflectivity is still below unity. From the result of Fig. 4, the reflectivity ($R = 1 - A$: R reflectivity; A, absorptivity) of the fully oxygenated Y-Ba-Cu-O specimen at sufficiently low temperatures is estimated to be 99.40±0.08% when we assume that the reflectivity in the normal state is 98% (Refs 1 and 2) just above T_c. This result represents that our FILC method provides a highly sensitive technique to observe the excitation spectrum of the superconducting state. The "unexpected" absorption is in agreement with previous absorption,[8,9] transmission,[3-5] and reflectance[1,2] experiments. The advance made in this experiment is to add information about the temperature dependence of the FIR absorption at three frequencies for Y-Ba-Cu-O and one frequency for Bi-Sr-Ca-Cu-O with higher accuracy.

We cannot attribute the "unexpected" absorption to normal electrons that are thermally excited across the gap because the curve (f) reaches zero with decreasing temperature. The phonon resonances in the Y-Ba-Cu-O had shapes with the maximum[13] at a higher photon energy than 17.6 meV, so that the absorption due to exciting phonons can be negligible. The absorption cannot be due to the polycrystalline nature such as an anisotropic energy gap because the photon energy of 7.6 meV is lower than the energy gap which has been reported.[1-13]

We can consider that the $\eta(\varepsilon, T_s)$ is the superposition of the temperature-dependent absorption on a roughly constant background absorption. The behavior of the temperature dependence of FIR absorption is similar to that of the light absorption predicted by Mattis and Bardeen theory.[12] On the other hand, the background absorption is at a level between 25 and 50% compared with the absorption in the normal state just above T_c. We cannot completely rule out the possibility that this background absorption is due to the extrinsic absorption by impurity phases or imperfections near the surface. However, this property, in common with all the specimens, suggests that much of this background should be intrinsic to the bulk high-T_c superconductors. Assuming that this background absorption is intrinsic, one possible model is gapless superconductivity over a finite area of the Fermi surface. Another possible model of the finite absorption is a low-energy excitation of spins[14] on the CuO_2 planes.

V. CONCLUSION

The far-infrared-laser calorimetric method (FILC) which we have developed has two important advantages as compared to conventional reflection measurements of high-T_c superconductors: (1) the subject to measure by the FILC method is the infrared absorption where relative change at superconducting transition considerably exceeds that of reflectance, and (2) this FILC provides a highly sensitive technique to investigate the excitation spectrum of the superconducting state. The temperature dependence of the far-infrared absorption is, for the first time, observed directly in the superconducting state of high-T_c superconductors using an optically pumped CH_3OH laser at the temperature region between 12 and 160 K. The absorption is monotonically decreasing as expected from the Mattis and Bardeen theory[12] below T_c, but the "unexpected" absorption has been observed at the lowest temperature. As a result, the reflectivity of the sintered $YBa_2Cu_3O_Y$ specimen is not unity but 99.40±0.08% at sufficiently low temperatures.

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