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Infrared absorptivity of $YBa_2Cu_3O_{7-x}$ crystals

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Measurements on twinned single crystals at 2 K show a smooth, approximately ω^2, absorptivity for frequencies between 80 and 400 cm^{-1}. Analysis of the data with a simple model conductivity suggests a constant lossy conductivity contribution in the bulk superconductor. Superimposed on the ω^2 background are absorption features corresponding to optically active phonons, plus a broad feature ($\Delta A \cong 0.2\%$) near $\hbar\omega = 3.5kT_c$. This feature is discussed in terms of possible $\cong 3.5kT_c$ gap excitations.

Despite prodigious research efforts the high-temperature superconductors remain mysterious, not only in their superconducting properties but also in their normal state. There have been extensive measurements reported in the literature relating to the nature of the low-frequency excitations and a possible energy gap in the superconducting state, including infrared reflectance,[1–5] tunneling,[6] photoemission,[7] and Raman scattering.[8] Even the measurements on the best single-crystal (twinned) materials available have not yet led to a clear picture of the superconducting ground state. In particular, there is controversy not only over the width of the superconducting energy gap but even over its existence. This unsatisfactory situation arises, in part, from material problems inherent in these ceramic oxides: sensitivity of results to granularity, anisotropy, twinning planes, nonstoichiometry—and in the case of tunneling—surface defects together with the short coherence lengths. These problems add to the difficulty of interpreting data.[9] Another problem in the IR measurements is purely experimental. The absolute IR reflectivity R of high-quality $YBa_2Cu_3O_{7-x}$ single crystals in the far-infrared, where the superconducting gap may be expected to be observed ($\nu \lesssim 400$ cm^{-1}), is very close to unity ($R \geq 98\%$).[1–5] Since the measurements of R are subject to detector noise and normalization errors the accuracy of the measurements is limited to $\cong 1\%$. This gives a severe limitation to the detection of low-lying excitations of the superconducting state by reflectance measurements in these highly reflecting materials. We report here far-infrared measurements using an alternative approach, the absorptivity technique,[10–13] which directly determines the absorptivity, $A = 1 - R$, of the sample. It has inherently high accuracy (0.05%) and therefore provides a sensitive probe of the excitation spectrum of the superconducting state. In particular, this measurement determines directly whether or not the superconducting samples are lossless over some frequency range. We have investigated the far-infrared absorptivity of $YBa_2Cu_3O_{7-x}$ twinned crystals in the range of frequencies corresponding to the BCS gap ($0.8 \leq h\nu \leq 5.4kT_c$). We report our preliminary results in this Rapid Communication.

We have studied several $YBa_2Cu_3O_{7-x}$ crystals with qualitatively similar results. The samples were microtwinned crystals $\cong 2\times2\times0.1$ mm^3. T_c determined from ac susceptibility measurements before and after the IR studies were typically 93 ± 0.2 K. The dc resistivities near T_c are about 100 $\mu\Omega$ cm. We focus here on the crystal that was most thoroughly studied.

The apparatus for the measurement of the absolute absorptivity is shown in Fig. 1. Radiation from a step-scan far-infrared Fourier transform spectrometer (Specac) is directed into the $T = 2$ K sample holder through a Cu plate (Ap) which has two apertures ($\simeq 1$ mm diam). One aperture opens onto a sample detector and the other onto the reference detector. The sample detector (S) consists of a thin silicon substrate with a doped-silicon thermistor epoxied to its back surface to monitor the temperature rise upon absorption of radiation. The Y-Ba-Cu-O sample (Sa) is held down onto the silicon substrate by thermal grease (Apezion N). Similarly, the reference detector (R) is a silicon substrate-thermistor pair in which the silicon substrate has a layer of Nichrome deposited on the back surface to provide a large and uniform absorptivity. The far-infrared radiation is chopped and the detector signal is measured using phase-sensitive amplifiers. The relative absorptivity of the sample is obtained by taking the ratio of the sample to reference spectra. Absolute absorptivity is obtained by a calibration of the two detectors.

The absorptivity spectra of our Y-Ba-Cu-O crystal are shown in Fig. 2. The most notable observation is an approximately ω^2 ($\omega = 2\pi c\nu$) dependent background absorption over the entire measurement range (up to 400 cm^{-1}). In addition there appears several absorption features superimposed on the background with well-defined peaks at 142, 187, 263, 292, 332, and 351 cm^{-1},

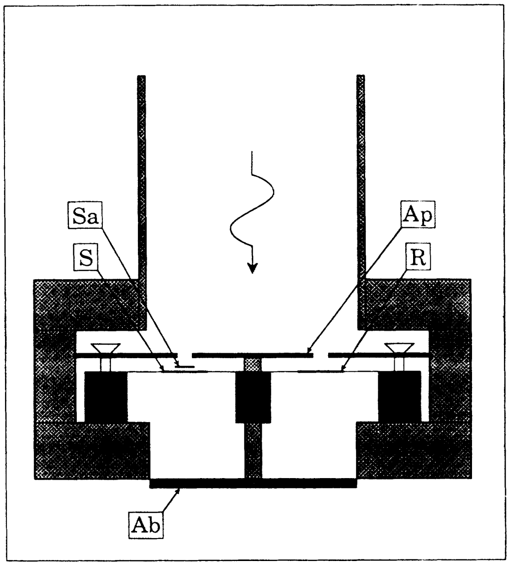

FIG. 1. Bolometric absorptivity apparatus. The fir radiation passes through an aperture plate (Ap) onto a reference (R) detector and a Y-Ba-Cu-O sample (Sa) mounted on top of a sample (S) detector. An absorber (Ab) reduces the reflection of transmitted radiation back to the detectors.

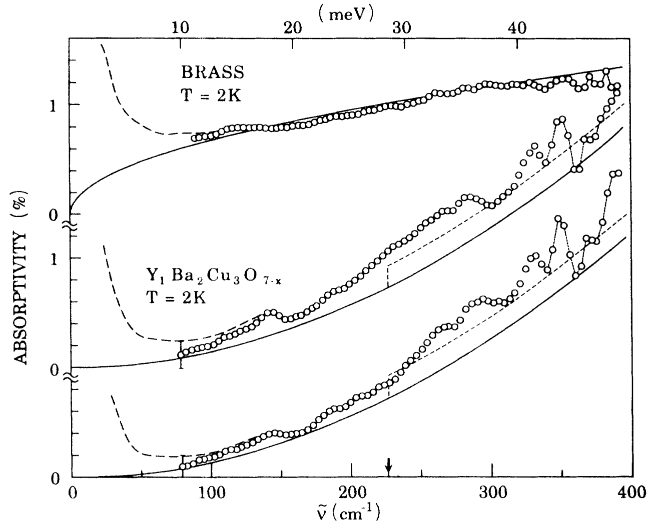

FIG. 2. Top: Measured (open circle) and calculated (solid curve) normal skin-effect absorptivity of brass. Bottom: Measured (open circle) superconducting absorptivity of two sides of a $T_c \simeq 93$ K crystal. The estimated ω^2 background absorptivity of the superconductor, in the absence of the phonon contribution, is indicated by the solid curve. The dashed curves show the leakage signal. The dash-dotted curve represents a clean-limit BCS contribution to A. The error bars represent the estimated combined systematic and statistical errors. The arrow marks the BCS gap frequency $\nu = 3.5kT_c$ ($\simeq 227$ cm^{-1}).

and a broad feature starting around 230 cm^{-1}. The data above $\simeq 370$ cm^{-1} are less precise due to reduced modulation efficiency of the wire grid beam splitter of the spectrometer. The absolute scale of the absorptivity agrees with published reflectance data,[1-5] within the calibration errors of our measurements. On the other hand, the essentially continuous (within 0.1%) absorptivity observed from near 80 to 360 cm^{-1} differs from earlier $T_c < 90$ K crystal reflectivity[1] and more recent $T_c > 90$ K thin-film reflectivity[2] studies in which a sharp energy gap below $\simeq 130$ cm^{-1} is reported. The background observed in our absorptivity measurements is consistent with recent $T_c > 90$ K crystal reflectivity studies.[3-5] An ω^2 frequency dependence has also been reported in microwave absorption[14] of ceramic $YBa_2Cu_3O_7$ at low temperature, $T = 2$ K. Their coefficient of ω^2, however, is thirty times larger than the value that we find.

There are several sources of systematic errors that can affect the measured sample absorptivity. First, any significant absorption features coming from the reference detector can show up as spurious structures in the sample absorptivity. Therefore, to obtain a frequency independent reference absorption, the resistance of the Nichrome film is carefully tuned, to eliminate interference effects within the silicon substrate. This results in a reference absorptivity of about 50% $\pm$ 1%, from $\simeq 15$ to 1000 cm^{-1}, as inferred from separate transmission measurements. However, the reference detector can absorb more than 50% if any of the transmitted radiation ($\simeq 21\%$) is seen by the doped-silicon thermistor. Therefore, the bottom of the enclosing cavity is coated with a layer of dielectric-black paint mixture (Ab, Fig. 1) to reduce back reflection of the transmitted radiation. Because of the decreased effectiveness of the black paint at low frequencies, however, this problem limits the reliability of our measurements at low frequencies.

In addition, the silicon substrate on which the Y-Ba-Cu-O crystal is mounted can transmit radiation reflected from the bottom of the aperture plate. The top surface of the silicon substrate is, therefore, coated with an opaque gold film. The gold absorption spectra is smaller than, and has the opposite curvature from, that observed in $YBa_2Cu_3O_{7-x}$. To reduce the resulting effects of multiple reflections a coating of black paint has been applied to the bottom surface of the aperture plate. Nevertheless the low absorption efficiency of this paint at low frequencies results in a spurious divergence of A at low frequencies, as shown by the dashed lines in Fig. 2. We have corrected for this error signal by fitting the data below $\nu = 80$ cm^{-1} to a power law and subtracting this spectrum from the data. This procedure gives the open circle curves in Fig. 2.

Finally, to obtain the absolute absorptivity from these data it is necessary to determine the responsivity of the bolometer detectors at the measurement frequency ($\cong 7$ Hz). This is done by calibrating the detectors with electrical-heat sources at the measurement frequency. The slow response of our sample detector ($\tau \simeq 200$ msec) results in a relatively high uncertainty for the responsivity, therefore introducing a systematic error of about 20% into the system, i.e., $\Delta A/A \simeq 0.2$. Note, however, that this uncertainty in the electrical responsivities only contributes a multiplicative factor to the absolute absorptivity.

To check the overall system performance, the absorptivity of a similar-sized brass sample was measured, and compared with a calculated normal skin effect absorptivity (Fig. 2, top) based on the measured resistivity of brass

(3.3 $\mu\Omega$ cm) at $T=4.2$ K. The statistical noise is somewhat larger for the brass samples which were averaged for a shorter time. In summary, the black paint and the uncertainty in the responsivities determine the low- and high-frequency systematic errors, to about $\pm 0.1\%$ at 80 cm^{-1} and $\pm 0.4\%$ at 400 cm^{-1}. The problems with light leakage unabsorbed by the black paint gives a low-frequency limit to our measurements of about 80 cm^{-1}. The error due to detector noise below 300 cm^{-1} is about 0.05%.

In order to gain some insight into the implications of these data we present a simplified analysis that contains most of the important physics. At low frequencies the sample response is dominated by the supercurrent screening. Therefore we model the conductivity as consisting of two parts; an ideal London term σ_L, plus a term $\hat{\sigma}$, to describe any lossy component. For the London term $\sigma_L(\omega)=\sigma_1+i\sigma_2$, where the real part $\sigma_1(\omega)=c^2\delta(\omega)/4\lambda_L^2$ gives the infinite dc conductivity and the corresponding imaginary part is $\sigma_2(\omega)=c^2/(4\pi\lambda_L^2\omega)$ where c is the speed of light, and λ_L the London penetration depth[15,16] ($\simeq 1500$ Å). This conductivity function is that of a two-fluid model, with an infinite gap frequency for the superconducting carriers and a short mean free time $\hat{\tau}$ for the normal-state carriers. It should be valid for $\hbar\omega \ll 2\Delta$ (photon energy below the energy gap) or $\hbar\tau^{-1}\ll 2\Delta$ (clean limit), and for $\omega\hat{\tau}\ll 1$. If the conductivity $\hat{\sigma}$ is then adjusted to fit the smooth ω^2 absorptivity, a constant $\hat{\sigma}\simeq 1400$ $(\Omega\,cm)^{-1}$ accounts for the observed absorptivity. We note that the resulting $\hat{\sigma}$ satisfies $\hat{\sigma}/\sigma_2 \ll 1$ for $\nu < 400$ cm^{-1}. The contributions from infrared active phonons can be added to the above conductivity function, giving rise to absorptive features on top of the ω^2 background. A Kramers-Kronig analysis of these absorptivity data grafted onto published high-frequency reflectivity data substantiates these conclusions.[17]

The above analysis assumes that the low-frequency absorptivity results from losses in the bulk superconductor. It is also possible to model the ω^2 background absorptivity as a surface effect. In this case we assume a thin layer having a constant conductivity, σ_s, on top of an ideal London superconductor substrate, σ_L. If the film is much thinner than the decay length of the radiation field in the surface layer, the absorptivity approaches $16\pi\lambda_L^2\sigma_s d\omega^2/c^3$ (where d is the film thickness). Fitting the absorptivity data gives a constant resistivity $\rho_s/d=1/\sigma_s d\simeq 1$ $\mu\Omega$ cm/Å of surface layer thickness.[18]

From these model calculations the observed background absorptivity is seen to be consistent with either an intrinsic constant bulk conductivity of some origin, or an extrinsic normal-state surface layer on the superconducting sample. We note that at the measurement temperature of 2 K the contribution of thermally excited quasiparticles would be negligible in a 90 K BCS superconductor. An intrinsic constant conductivity suggests gapless (or small gap) superconductivity over a finite area of the Fermi surface, e.g., a gapless response by the CuO_2 chains. Tunneling,[6] photoemission,[7] and Raman scattering[8] experiments have also shown some indications of a continuum of states below $3.5kT_c$, although experimental artifacts and c-axis contributions have not been completely ruled out. Twinning boundaries or other defects[9] could also give rise to finite absorption for frequency below the superconducting gap.

Extrinsic effects such as prolonged ambient exposure is known to alter the surface stoichiometry[19] and photoemission data[7] on Bi-Sr-Ca-Cu-O crystals suggests that the first few layers are less superconducting than the bulk. More specifically, Auger analysis on single-crystal Y-Ba-Cu-O indicates that the stoichiometry approaches the bulk within 200 Å of the surface. The layers nearer the surface are low in Cu and O, therefore favoring insulating behavior.[19] However, taking $d=200$ Å in the above model implies $1/\sigma_s=\rho_s\cong 200$ $\mu\Omega$ cm in order to be consistent with the observed ω^2 absorptivity. Since a film of this conductivity would tend to be superconducting rather than metallic, and since Y-Ba-O compounds would tend to be insulating rather than metallic, we favor the conclusion that the background absorption is an intrinsic bulk effect. Clearly, more systematic work will be required to check this conclusion and to distinguish between intrinsic and extrinsic effects.

Absorptive peaks near 142, 187, 332, and 351 cm^{-1} are identified as infrared active phonons. In the superconducting state the phonons appear as absorptive peaks at their center frequency. We assign the 142 cm^{-1} peak to the Cu(1)-O(IV) y-axis vibrational mode, the pair 187 and 203 cm^{-1} to the Y-Cu(2)Cu(3) y- and x-axis vibrations, respectively. The 332 and 351 cm^{-1} peaks could correspond to the y and x-axis vibrations of the O(III). The weak features at 292 and possibly 263 cm^{-1} do not match with any known phonons, even for $YBa_2Cu_3O_6$ materials.[20]

In the data (Fig. 2), there also appears to be a broad extra absorption, $\Delta A\cong 0.2\%$, above the ω^2 background starting at $\nu\cong 230$ cm^{-1}. There are no phonons expected or observed in this range of frequencies, up to 300 cm^{-1}.[20] Since the weak-coupling BCS gap, $2\Delta=3.5kT_c \simeq 227$ cm^{-1} it is interesting to speculate on the possibility that this feature corresponds to the superconducting energy gap. In the clean limit of BCS theory, where the quasiparticle lifetime τ satisfies $2\Delta \gg 1/\tau$, σ_1 is proportional to $1/\omega^2\tau$ for $\omega > 2\Delta$ and this leads to a nearly constant contribution to the absorptivity for $\omega \gg 2\Delta$ (sketched in Fig. 2).[21] From the magnitude of the observed absorptive increment near 250 cm^{-1} ($\Delta A\cong 0.2\%$) we can estimate the corresponding $\tau^{-1}\cong 10$ cm^{-1} in a constant τ model.[21] The corresponding normal-state dc resistivity at 2 K would be $\cong 5$ $\mu\Omega$ cm.[22] This value is not inconsistent with the extrapolated low-temperature resistivity of these materials. If this speculation proves correct we see that the failure to observe the energy gap in the high-T_c materials in previous studies was a consequence of the clean limit behavior[4] and the obscuring effects of the background absorption and the optically active phonons.

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[22]The dc component of σ_{n1} is determined from τ and the London penetration depth.