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Far-infrared absorptivity of single-domain $YBa_2Cu_3O_7$

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Measurements on detwinned single crystals for radiation polarized along the **a** axis at 2 K give an approximately 0.5% absorptivity for frequencies between $\cong 100$ and 400 cm^{-1} and a strong onset at $\cong 450$ cm^{-1}. Anisotropy is observed between the **a**- and **b**-axis polarization absorptivities. The conductivity function deduced from a Kramers-Kronig analysis of the **a**-axis data shows low-frequency absorption bands of electronic strength.

The infrared response of superconductors played an important role in the development of the BCS theory. The observation of a gap for optical excitations as predicted by the theory was important early confirmation of the theory.[1] The high-temperature superconductors have also been vigorously studied by infrared spectroscopy for clues to the physics of the superconductivity in these materials. So far the results are not well understood. Concentrating on $YBa_2Cu_3O_{7-x}$, which is the most studied material, a clear optical edge is observed at $\nu_0 \cong 500$ $cm^{-1} \cong 60$ meV.[2-5] For $x \cong 0$ the corresponding gap frequency $2\Delta \cong 8kT_c$. However, ν_0 has been found[3,6] to have little dependence on T_c (i.e., x) or T, which is in striking contrast to the predictions of BCS theory. The theoretical ideas being advanced for the high-T_c superconductors have not yet explained these discrepancies. Consequently, the identification of the 500-cm^{-1} edge as the superconducting energy gap has been challenged.[3,4,7] Also, although the reflectance of the superconducting materials is high at low frequencies, it has not yet been established if they are essentially lossless as expected from BCS theory and has been observed in the conventional superconductors.[8] In single domain $YBa_2Cu_3O_7$ crystals the reflectance is found to be anisotropic for light polarized in the *ab* plane. The reflectance below 500 cm^{-1} is higher for light polarized along the **a** axis than for the **b** axis polarization.[2] The increased absorption for the **b** polarization is thought to be due to excitations associated with the CuO chains. Although the **a** polarization reflectance is high ($\cong 100\%$) and flat for $\nu \lesssim 500$ cm^{-1}, its deviation from unity cannot be ascertained to better than $\cong 1\%$ because of systematic errors in the reflectance measurements for the small detwinned crystals.

The studies reported in this paper address the question of optical absorption below the 500-cm^{-1} edge in detwinned $YBa_2Cu_3O_7$.

The samples are single-crystal $YBa_2Cu_3O_{7-x}$ (typically $0.7 \times 1.0 \times 0.2$ mm^3 grown by the flux method and oxygen annealed[9] and then detwinned by annealing under uniaxial stress.[10] T_c's determined by dc susceptibility measurements were typically 93 K and the transition width was typically 1 K. The resistivity at 100 K was typically $\rho \cong 100$–200 $\mu\Omega$ cm.[11]

The far-infrared measurements are made using a low-temperature bolometric technique, which directly measures the absorptivity, $A = 1 - R$, of the sample at $T \cong 2$ K. The basic design of the apparatus was described in an earlier paper.[12] In the present apparatus there are three bolometric systems simultaneously illuminated by the IR beam: the $YBa_2Cu_3O_7$ sample, a brass reference sample, and a silicon composite bolometer for absolute reference. The relative absorptivity of the sample is obtained by taking the ratio of the sample to the reference spectra. Absolute absorptivity is obtained by a calibration of the detectors. With this system we measure absolute absorption to within 20% error.

A wire-grid polarized (polyethylene substrate) which can be rotated *in situ* is mounted $\cong 10$ mm in front of the bolometer array. The extinction coefficient $k = T_\perp / T_\parallel$ for the polarizer has been measured and is found to vary approximately linearly from $k \cong 0$ at $\nu \cong 0$ to $k \cong 0.06$ at 600 cm^{-1}. The data presented here has been corrected for the polarization leakage. These corrections are very small on the scale of the observed anisotropy. Another correction comes from the small amount of remaining twinning in the samples (typically less than 5%). These effects lead to less than 0.1% error in A at $\nu \cong 400$ cm^{-1} where the error is maximum.

A step scan Fourier-transform spectrometer is used to disperse the far-infrared radiation. The useful spectral range of the instrument is from $\cong 10$ to 700 cm^{-1}. We have tested the optical system by measuring the transmission of an irtran-4 filter. This filter has zero transmission at low frequencies and an onset of transmission at $\nu \simeq 450$ cm^{-1} where it rises to about 70% at 600 cm^{-1}, therefore simulating the ideal lossless response of a large gap superconductor. Our measured spectrum gave zero transmission below 450 cm^{-1} with a random noise level of 0.2%. Since $A(\nu) \cong 5\%$ at 600 cm^{-1} for $YBa_2Cu_3O_7$ for the **a**-axis polarization we can place a 0.02% uncertainty in the zero of $A(\nu)$ for our data. At low frequencies the accuracy of our measurements is limited by leakage of the IR radiation around the small samples where it can be directly absorbed by the thermistor. Careful adjustment of reflecting apertures in front of the samples can reduce this leakage.[12] Also, to further diminish the leakage signal, the cavity behind the sample is lined with IR absorbing materials. At low frequencies, however, these absorbers become less effective and the leakage signal typically reaches a level comparable with the observed absorption signal (in the **a** polarization) at $\nu \cong 100$ cm^{-1}. Although we can subtract this leakage signal with some success,[12] it gradually reduces the reliability of the data below $\simeq 150$ cm^{-1} and we do not trust our results below $\simeq 80$ cm^{-1}.

We have also tested the system by measuring the absorptivity of a small brass sample mounted in the same way as the $YBa_2Cu_3O_7$ crystal. The brass spectrum presented in Fig. 1 is seen to increase smoothly from $\nu \cong 20$ to 650 cm^{-1}. The dashed curve is a $\nu^{1/2}$ curve scaled, according to the normal skin effect. The corresponding ac resistivity agrees to within calibration errors to the measured dc resistivity of the brass sample. There is less leakage signal for the brass sample because it is possible to scallop the edges of the brass sheet and the aperture in order to reflect back more of the stray light.

Also shown in Fig. 1 is the measured absorptivity spectra for a detwinned $YBa_2Cu_3O_7$ crystal for radiation polarized along the **a** and the **b** axes. The absorptivity is seen to be anisotropic with a larger value for the **b** polarization than for the **a** polarization. The absorptivity rises strongly in both polarizations for $\nu \gtrsim 450$ cm^{-1} consistent with reflectance measurements reported in the literature.[2-5] Our absorptivity at 650 cm^{-1} is in good agreement with the reflectance on similar samples.[2] We note that the edge at 500 cm^{-1} is not as sharp in our **a** polarized absorptivity measurements as was found in the polarized reflectivity measurements on some samples.[2] However, the discrepancy is not significantly outside the random noise (0.5%) of the reflectance measurement. The **a** polarization absorptivity is seen to be finite at all frequencies down to $\cong 80$ cm^{-1} (our low-frequency cutoff). In the 100–400 cm^{-1} range $A(\nu)$ is $\cong 0.5\%$, which is too small to be detected in the reflectance measurements. Because of the leakage problem we have not succeeded in determining how rapidly $A(\nu)$ approaches zero at zero frequency. Measurements on larger twinned crystals[3,12] indicate, however, that $A(\nu)$ must approach zero fairly rapidly. We also observe structure in $A(\nu)$ on the scale of a few tenths of a percent, which is qualitatively reproducible from run to run and for different samples as seen in Figs. 1 and 2. There have been numerous reports of a feature at $\cong 140$ cm^{-1} in reflectance measurements on twinned crystals where it appears as an onset of absorption.[3-5] This feature has also been seen in thin films in reflectance.[3,5] In Figs. 1 and 2 this feature appears larger, but with roughly the same width as was found in our absorptivity measurements on twinned crystals.[12]

There appears to be some variation in the amplitude of the absorptivity for sample to sample in the 100–200 cm^{-1} range. For example, our earlier measurements[12] on a twinned single crystal gave a smaller $A(\nu)$ at 140 cm^{-1} than some of the detwinned crystals reported here. This variation may be correlated to sample quality. For example, the 140-cm^{-1} absorptivity was found to increase after several cyclings of the sample to low temperatures. This can be seen by comparing runs 1 and 2 of sample 2 in Fig. 2. Run 1 was approximately one month earlier than run 2. We note that this region of variability is at low frequencies where there is some uncertainty due to the leakage problem. Our assessment, however, is that the variation at $\nu \cong 140$ cm^{-1} is much larger than the leakage errors at this frequency. This implies an extrinsic aspect of the absorptivity at low frequencies; e.g., it may depend on the defect density. On the other hand, the absorptivity in the 200–650 cm^{-1} frequency range appears nearly sample independent.

In Fig. 3 we present the optical conductivity σ_1 for the **a**-axis data as determined from a Kramers-Kronig analysis of the absorptivity data. The results are for sample 2, run 1; this is our lowest absorptivity data on detwinned crystals. For frequencies above our 650-cm^{-1} limit we have used the published reflectance data from detwinned crystals[2] (which come from the same source). For the low-frequency extrapolations (below 100 cm^{-1}) we assume that $A(\nu) \to 0$ as $\nu \to 0$. We have examined

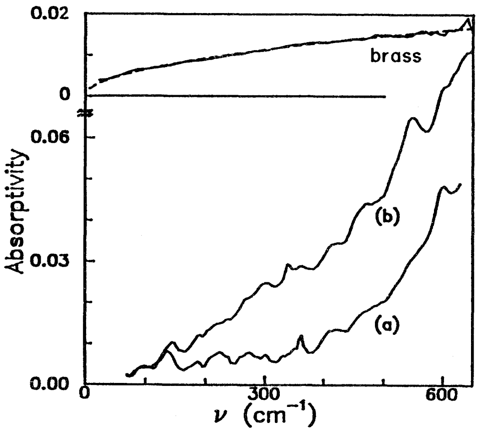

FIG. 1. Absorptivity of $YBa_2Cu_3O_7$ sample 2, run 2 for **a** and **b** polarized light. Also shown is the absorptivity of a brass reference sample (solid curve) and the calculated absorptivity based on its dc resistivity (dashed curve). The sample temperatures are 2 K.

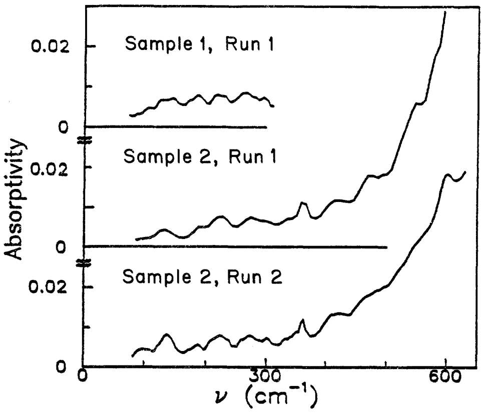

FIG. 2. Absorptivity of two samples of $YBa_2Cu_3O_7$ for **a** polarized light as a function of frequency. The resolution of the top and bottom curves are 4 cm^{-1}, and 8 cm^{-1} for the middle curve. The sample temperatures are 2 K.

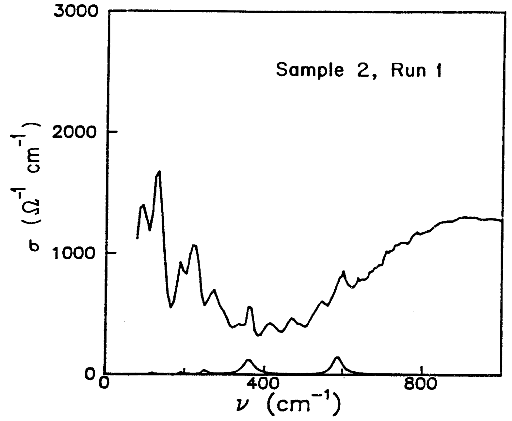

FIG. 3. Optical conductivity of sample 2, run 1 determined by Kramers-Kronig analysis of the absorptivity data. Also shown is the optical conducivity of insulating $YBa_2Cu_3O_6$ as deduced from Ref. 14.

the effects of various smooth low-frequency $A(\nu)$ extrapolations. The resulting conductivity below 100 cm^{-1} is sensitive to these extrapolations, but the conductivity above $\nu \cong 100$ cm^{-1} is not. For $\sigma_1(\nu)$ at low frequencies to be constant or approach zero at $\nu = 0$ it is necessary for $A(\nu)$ to approach zero with a power equal to or greater than 2. While the data on twinned crystals suggest[3,12] that this is the case, better low-frequency data is needed to verify this.

In Fig. 3 the **a** axis σ_1 below 400 cm^{-1} is seen to consist of structures of increasing strength as the frequency decreases. The peak in σ_1 at 130 cm^{-1} follows directly from the corresponding peak in $A(\nu)$ which is seen in all the spectra. The σ_1 peak at 90 cm^{-1} is due to the much smaller feature seen in $A(\nu)$ in Fig. 1. From the data of Fig. 2 we see that the presence of this feature is not so clear. Since it falls in the range where there is greater uncertainty due to the leakage signal we must consider its existence only tentative at this point. If, instead, it is assumed that the $A(\nu)$ spectra falls off sharply below 100 cm^{-1}, then the peak at 140 cm^{-1} is the lowest absorption feature in the spectra.

It is interesting to compare the spectral weight associated with the low-frequency absorption bands with the total spectral weight. For electronic absorption processes the conductivity sum rule gives $\int_0^\infty \sigma_1 d\omega = \pi n e^2/2m^*$ where n is the carrier density and m^* is the mass (we take $m^* = m_e$ for reference). The contribution to the sum rule of the absorption above the edge at 500 cm^{-1} is $n_h \cong 0.4$ carriers/unit cell.[2] The δ-function conductivity at zero frequency due to the superconducting condensate contributes $n_s \cong 0.2$/unit cell as deduced from the measured London penetration depth (1500 Å) and/or σ_2 determined from the Kramers-Kronig analysis of the absorptivity data. Integrating σ_1 from $\nu \cong 80$ to 500 cm^{-1} for our data we find $n_l = 0.03 \pm 0.01$ holes/unit cell. Therefore, n_l is small compared with the other contributions to the sum rule.

In discussing these data we first consider the contribution of optical phonons to σ. The a-b plane phonon spectrum has been measured in the insulating $YBa_2Cu_3O_6$ crystals by Crawford, Burns, and Holtzberg.[13] We have plotted the corresponding σ_1 for these phonons in Fig. 3. The features in the $YBa_2Cu_3O_7$ spectrum at 550 cm^{-1} (600 cm^{-1}) and 340 cm^{-1} (360 cm^{-1}) are seen to correspond to **b** (**a**) axes polarized zone-center phonons.[13,14] The $YBa_2Cu_3O_6$ phonons at lower frequencies are too weak to be seen in our data. That is, the observed absorption is much stronger than that expected from phonons. Although there will be additional phonon modes associated with the CuO chains,[14] there is no reason to expect that they would be many orders of magnitude stronger than the $YBCO_6$ phonon modes. The essential point is that the spectral weight associated with the phonons is much smaller than that for electrons because the sum rule involves the ion masses.[15]

There has been much discussion of the renormalization of phonons by the interaction with the electrons.[16,17] Shifts in phonon frequencies and broadening of phonons have been observed in Raman-scattering measurements on high-T_c superconductors as the sample temperatures are lowered below T_c.[17] Although it is possible, in principle, to obtain giant phonon shifts if the electron-phonon coupling is very large and, therefore, pile up phonon modes at low frequencies, this mechanism would not transfer oscillator strength from the electron system to the phonon system.[18]

The existence of a low-lying electronic absorption band in $YBa_2Cu_3O_7$ suggests several possibilities. First, we consider defect-induced absorption mechanisms. Oxygen depletion, especially near the surface, is one defect expected in this materials. The presence of a nonsuperconducting metallic or insulating layer was discussed in an earlier report.[12] In the low-frequency limit, a layer of thickness d and conductivity σ_L gives rise to an absorptivity $A = 64\pi^3\lambda_L^2\nu^2c^{-1}\sigma_{L1}d$, where λ_L is the London penetration depth. Therefore, a layer with a ν independent conductivity (corresponding to a dirty metal) would lead to a $A \propto \nu^2$ dependence. Indeed, the approximately $A \propto \nu^2$ observed in the **b** axis polarization appears to be due to the metallic response of CuO chains. A clean Drude metal ($1/\tau \lesssim 100$ cm^{-1}) would give rise to an approximately constant absorptivity. If we assume a layer of low x material, similar to the oxygen-depleted twinned $YBa_2Cu_3O_{7-x}$ recently studied by far-infrared spectroscopy, it would take $d \gtrsim 1000$ Å to produce an absorptivity of 0.005. It is unreasonable for the low x material to extend in this deep. Moreover, this interpretation does not explain the structure observed in $A(\nu)$. Defect-induced coupling to the **c** or **b** axis excitations can also be considered. The existing data indicate that the electronic conductances in these directions are constant[2,12] (**b**) or increasing with frequency[19] (**c**). Therefore, the observed σ_1 behavior would have to come from the details of the coupling mechanism. Much more work will be necessary in order to determine the effects of defects on the low-frequency absorption.

An interesting possibility for the low-frequency absorption is low-lying electronic modes of the condensate. Gapless superconductivity seems to be ruled out by the temperature dependence of the London penetration depth.[20,21]

However, Raman measurements on untwinned crystals show a broadband of electronic scattering centered at $\nu \cong 400$ cm^{-1} that extends to low frequencies.[22]

We will discuss our results in terms of excitonic modes which are an example of low-lying excitations that have been considered within BCS theory.[23] These modes can be thought of as excited states of the Cooper pair. For the case of an isotropic system the modes can be labeled according to the angular momentum quantum number l. Exchange symmetry then requires that the odd l states must be spin triplets. The optical transitions to these modes would then require a spin flip. The even l modes would be spin singlets, but transitions to them from the $l=0$ ground state would not be dipole allowed. We note that dipole selection rules apply in these materials because the coherence length is much shorter than the penetration depth and therefore the electrodynamics is local. Breakdown of the dipole selection rule could arise from the lattice asymmetry, impurities, or phonons. The variation in the 140-cm^{-1} absorption may then arise from domination of defect-induced coupling at low frequencies while phonon-induced coupling may dominate at higher frequencies (for the phonon coupling the absorption is shifted by the phonon frequency). The structure observed in the spectra could arise either from a frequency-dependent relaxation rate τ^{-1} of these excitations due to phonon emission as they decay back to the ground state or from a spectrum of excitonic modes.[24] An analysis of the data in terms of a conductivity function with a frequency dependent τ^{-1} gives a $\tau^{-1}(\nu)$ spectrum that correlates with the c-axis phonons at 120, 150, and 190 cm^{-1}.[25] At higher frequencies the shifting of the excitonic modes because of the phonon coupling could account for some of the structure. For example, the $A(\nu)$ structures between 400 and 550 cm^{-1} occur in a frequency range where there are no direct IR active phonon modes. Some support for an interpretation of the low-frequency absorption in terms of low-lying electronic excitations also comes from recent high-resolution measurements of the London penetration depth.[21] From the temperature dependence of λ_L they deduce an activation energy of $\cong 140$ cm^{-1} this is consistent with the spectral data reported here if it is assumed that 130-cm^{-1} peak is the lowest spectral feature.

In summary, finite absorption has been observed in **a**-axis polarized far-infrared measurements on $YBa_2Cu_3O_7$ at all frequencies down to $\cong 80$ cm^{-1}. Conductivity sum-rule arguments indicate that this absorption is electronic. Although extrinsic effects cannot be ruled out and do appear to play a role in some of the spectral features, this low-frequency absorption provides some evidence for low-lying excitations in superconducting $YBa_2Cu_3O_7$.

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