Infrared synchrotron-radiation transmission measurements on $YBa_2Cu_3O_{7-\delta}$ in the gap and supercurrent regions

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We report infrared synchrotron-radiation transmission measurements on ~1-μm-thick films of high-T_c $YBa_2Cu_3O_{7-\delta}$ from 40 to 290 cm^{-1} (5 to 36 meV). The films were deposited onto MgO substrates and showed resistive superconducting transitions with an onset at 83 K. Spectra below T_c show superconducting behavior, including the characteristic $1/\omega$ supercurrent dependence for frequencies below 100 cm^{-1}. The entire spectrum can be fit when a Mattis-Bardeen-type conductivity is included identifying increasing absorption beginning at a photon energy of 23 meV. However, a substantial residual absorption persists to the lowest measured frequencies. In addition, the appearance of phonons, some attributable to c-axis vibrations, suggests we are sampling a mixture of both a-b-plane and c-axis properties.

We report infrared transmission measurements made on a partially oriented, high-T_c $YBa_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O) film in the region where superconducting effects should appear. Other experimental techniques used to date (tunneling, infrared reflectivity, Raman scattering, and photoemission) are highly surface sensitive. However, the surfaces of these materials are prone to oxygen depletion and degradation, and so may not represent bulk properties. In contrast, a transmission measurement probes the entire film thickness, and is potentially more sensitive to small changes in absorption. Our transmission measurements were made possible by a new high-intensity infrared beam line operating at the National Synchrotron Light Source at Brookhaven National Laboratory,[1,2] combined with experimental and analytical techniques developed at Emory University for thin superconducting films.[3,4] A main purpose here is to show the value of infrared transmission spectroscopy, as opposed to the widely used reflection method, for superconductor analysis.

The interpretation of far-infrared reflectivity spectra[5,6] for the high-T_c materials is complicated by their high reflectance and sensitivity to dispersive as well as absorptive effects. As a result, it is difficult to identify a superconducting absorption edge, even with Kramers-Kronig analysis.[7] To illustrate the problems, although the work of Thomas *et al.*[8] shows for the first time a low-frequency reflectivity consistent with superconductivity (i.e., $R=1$ for $\omega<\omega_g$, the gap frequency), the change in R upon entering the superconducting state is still no greater than the measurement accuracy. Nevertheless our data will be seen to be consistent with the results of reflectance measurements.

Other techniques for detecting an energy gap have not conclusively proved its existence. Raman studies show reduced scattering intensity for frequency shifts less than $\sim 3.5 k_B T_c$, consistent with the transformation of normal carriers into superconducting ones.[9,10] Anisotropy effects have also been discussed. High-resolution photoemission by Imer and co-workers[11] yields an energy gap in Bi-Sr-Ca-Cu-O single crystals of $2\Delta/k_B T_c \cong 8$, suggesting very strong coupling. Onellion *et al.*[12] reported similar results on the same materials, although at lower resolution. Tunneling measurements have provided the widest range of gap values, illustrating the sensitivity of this technique to surface preparation, contamination, and possibly anisotropy.[13]

Infrared transmission spectroscopy potentially overcomes many of these problems. Transmitted radiation probes the entire sample, not only the surface, and is often more sensitive to absorptive processes, changing by large factors between the superconducting and normal states. The difficulty is that the transmission coefficients are small and the flux available from conventional blackbody sources is low at the frequencies where superconducting behavior is expected. This problem, as well as limitations due to small sample size, was solved by utilizing synchrotron radiation as a source.

Transmission measurements through high-T_c films are also hampered by the lack of infrared transmitting substrates which are suitable for film growth. Commonly used lattice-matched materials such as $SrTiO_3$, $LaGaO_3$, and $LaAlO_3$ used for depositing epitaxial films, transmit poorly. Highly transmitting Al_2O_3 or Si substrates are unsuitable because of the heating needed for further processing generates undesirable reactions. We deposited our films onto MgO substrates which transmit reasonably well up to 300 cm^{-1} at low temperatures, but with spectral complications which we discuss later.

Our Y-Ba-Cu-O films (thickness 0.1–1 μm) were deposited on (100) MgO by thermal coevaporation of Y, Cu, and BaF, and then annealed at 1020 K for 30 min each in wet oxygen and dry oxygen. The low annealing temperature minimized the strong reaction of MgO with Y-Ba-Cu-O above 1175 K. The resulting polycrystalline films were mainly composed of regions with their c axis perpendicular to the substrate, as shown by x-ray diffraction. All the films showed resistive transitions such as that shown in the inset to Fig. 1, which plots resistance versus temperature for the film described here, with T_c(onset)=83 K. Similar methods were used to deposit DyBaCuO films on Al_2O_3. These had broader resistive transitions and much higher room-temperature resistivities than the Y-Ba-Cu-O films.

Transmission spectra were measured at the 750-MeV electron storage ring located at the National Synchrotron Light Source, where a new infrared beam line[1,2] provides radiation 100–1000 times brighter than that from a conventional blackbody mercury arc source over 10–1000 cm^{-1}. The synchrotron light was collimated and analyzed with a modified commercial rapid-scan Michelson interferometer. After passing through the sample, mounted on a liquid-helium cold finger within an $f/3.5$ sample cell equipped with polyethylene windows, the radiation was detected by a liquid-helium-cooled silicon bolometer (Noise equivalent power=1.3×10^{-13} $W/Hz^{0.5}$) with suitable filters. Because of the low sample transmissivities, special care was taken to keep stray light away from the detector. We found that the light leakage never exceeded 1% of our measured radiation.

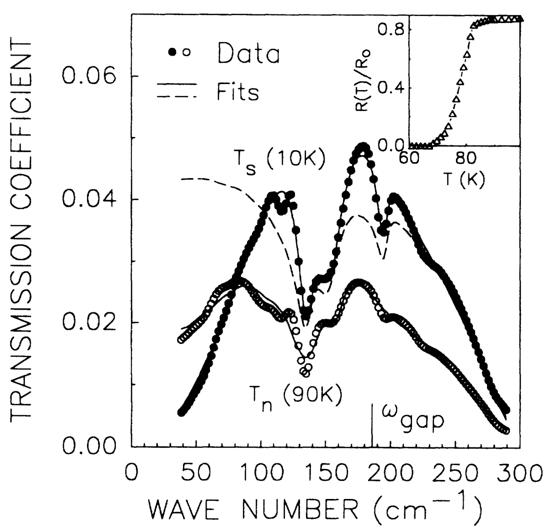

FIG. 1. Measured and fitted transmission coefficients T_s and T_n at 10 and 90 K, respectively, for 0.65-μm-thick sample of Y-Ba-Cu-O evaporated on MgO. Data from synchrotron measurements. At 90 K, the solid fitted curve includes contributions from normal-state carriers, Y-Ba-Cu-O phonons, and the MgO substrate. At 10 K, the solid fitted curve includes the same types of contributions and an added BCS-based Mattis-Bardeen superconducting term with ω_g=186 cm^{-1}. The dashed curve omits the superconducting term, showing that superconductivity is responsible for a 20% increase in the transmission (over the 90-K value) near the gap. For other details see text. Inset: Resistance (normalized to its value at 224 K) vs temperature for the same sample, showing the superconducting transition T_c (midpoint)=78 K.

To test the entire system, we measured the superconducting and normal transmissions T_s and T_n through a 100-nm-thick Nb_3Ge film on Al_2O_3. This yielded results identical to those obtained for the same film by Cook and Perkowitz,[4] who used a mercury arc source and a Michelson interferometer. The Nb_3Ge data help to interpret our high-T_c result.

We could measure a full spectrum in 3 min with run-to-run discrepancies <1% despite transmission coefficients as low as 0.1%. This rapid turnaround time was crucial, allowing us to scan many samples. We report here on the Y-Ba-Cu-O film exhibiting the largest change in transmission upon entering the superconducting state. Other Y-Ba-Cu-O films showed similar spectra and will be described elsewhere. The DyBaCuO films on Al_2O_3 did not show a substantial decrease in absorption associated with superconductivity.

Figure 1 shows T_s (at 10 K) and T_n (at 90 K) vs ω for a 0.65-μm-thick Y-Ba-Cu-O film. T_s and T_n are each absolute transmission coefficients, defined as intensity transmitted through sample/intensity transmitted with sample removed. These curves illustrate the complexity of the effects. The dips near 150 and 200 cm^{-1} are phonon modes in the film, which are well known from early infrared work in Y-Ba-Cu-O and other rare-earth superconductors.[6,14] We note that these phonons are associated with unscreened modes along the c axis, indicating that we are not sensing solely a-b–plane response (a-b–plane phonons[15] near 110 and 220 cm^{-1} are reasonably well screened by free carriers and therefore less visible). The impact of this on the analysis is addressed later. Other structure, and some of the roll off above 150 cm^{-1}, comes from the complex MgO spectrum. However, two features in T_s suggest the presence of superconductivity: its rapid approach to zero as ω which approaches zero, which indicates supercurrent screening; and the increased transmission above 150 cm^{-1} relative to T_n, which is similar to what is seen in films of Nb_3Ge and other metallic superconductors in which an energy gap forms in the excitation spectrum.

Because of the complex behavior, we analyzed these data with no optical approximations. Our computer program calculates the infrared transmission of an absorbing film on an absorbing substrate, including multiple internal reflections and without any assumptions about layer thickness. The routine can simultaneously optimize many fitting parameters in the highly nonlinear optical expression to give the best least-squares fit to data.

To model the MgO layer, we carefully measured the substrate transmission versus temperature and frequency. We noted that from 90 to 10 K and below 100 cm^{-1}, MgO has negligible absorption and a constant refractive index of n=2.8. Above 100 cm^{-1}, the transmission dropped with ω and showed peak structure. We modeled this to within ~1% by using known phonon oscillators. Further details on these fits are forthcoming.

We first fitted T_n at 90 K, with the MgO parameters fixed at the values from our independent analysis. The film dielectric function ϵ was calculated assuming Drudelike free carriers and Lorentzian phonon oscillators. We allowed the Y-Ba-Cu-O phonon parameters to vary, but these did not change much from values in earlier analyses except for an oscillator at 135 cm^{-1} which may be due to incomplete reaction of some of the starting materials. Thus our excellent best fit, shown in Fig. 1, comes mainly from free variation in normal-state carrier density and mobility only. The best-fit values also give a sheet resistance of 18 Ω/sq, which agrees with the measured dc result of 16 Ω/sq within the experimental error. This corresponds to a conductivity of approximately 1000 $\Omega\,cm^{-1}$, about an order of magnitude below the *a*-*b*-plane conductivity value observed in good quality films and crystals, but still larger than the *c*-axis conductivity if one assumes an anisotropy ratio between 50 and 100. We speculate that the short duration, low-temperature anneal left regions of the film with reduced oxygen content, granularity, or incomplete *a*-*b*-plane orientation. This accounts for the somewhat suppressed and broadened resistive transition, and also its dirty-limit character.

To fit T_s at 10 K, we again set the MgO parameters to their appropriate values. The film phonon parameters were allowed to vary, but did not change much from the values for 90 K. The additional superconducting contribution to ϵ was found from the BCS-based Mattis-Bardeen[16] frequency-dependent conductivity σ_s at 0 K. This is described by the gap energy ω_g, which we allowed to vary freely in the fitting.

Extensive analysis showed that we could not fit T_s without including both superconducting and normal (absorbing) carriers. The incomplete conversion of normal to superconducting carriers, even far below T_c, has been encountered before in sintered high-T_c material.[6] The final best fit (Fig. 1) gives $\omega_g = 186$ cm^{-1} ($2\Delta = 23$ meV), while approximately 70% of the conductivity which existed above 90 K remains normal below T_c. Therefore, we caution against overinterpretation of the 23-meV value, considering the sizable residual absorption and the likelihood that we are sampling a mixture of both *a*-*b*-plane and *c*-axis responses.

Another approach to analyzing the spectra uses the fact that MgO absorbs negligibly below 100 cm^{-1}. Then our data could be described by Tinkham's result[17] for the transmission of a film into a nonabsorbing substrate of refractive index n

$$T = \frac{4n}{(n+1+y_1)^2 + y_2^2}, \tag{1}$$

where $y_1 + iy_2$ is the film's complex surface admittance $4\pi/c(\sigma d)$, with σ the complex film conductivity $\sigma_1 + i\sigma_2$ and d the film thickness. Equation (1) is a good approximation when $d \ll \delta$ (penetration depth), the case here.

A striking feature of superconducting electrodynamics is that σ_s takes on the same form ($\sigma_1 = 0$ and $\sigma_2 = A/\omega$, where A is a constant) both in the London and the Mattis-Bardeen theories for $\omega \ll \omega_g$.[18] This is very different from the Drude normal-state conductivity, unless $\omega\tau \gg 1$, where τ is the relaxation time. A careful analysis, using Eq. (1), shows that our measured T_s (Fig. 1) does not arise from σ_{Drude} (neither the infrared data nor the temperature-dependent dc resistivity data give a sufficiently large value of τ), but is characteristic of σ_s. Figure 2, inset, displays σ_2 for $\omega < 100^{-1}$ as derived directly from T_s and Eq. (1). The result, at frequencies far from the Y-Ba-Cu-O phonons and from substrate effects, closely follows the predicted $1/\omega$ inductive behavior, evidence that superconductivity appears in the spectrum. The very small deviation from the prediction (see figure) may represent the Drude contribution from the normal carriers remaining below T_c.

In addition to the significant $1/\omega$ frequency dependence, the value of the constant A is important because it equals $\pi\omega_g/2$ in Mattis-Bardeen theory. Our fit value $A = 272$ cm^{-1} yields $\omega_g = 173$ cm^{-1}, within 7% of the result (186 cm^{-1}) from our full fit.

More insight into the superconducting film is given in Fig. 2, which shows the approximate ratio T_s/T_n that would be seen if transmission were measured through the Y-Ba-Cu-O film only with no distorting substrate. T_s/T_n was generated from the fit parameters used in Fig. 1, with the MgO layer omitted. For comparison, we show the T_s/T_n curve we measured for Nb_3Ge, with its clear peak near the gap.[4]

Although the T_s/T_n ratio for Y-Ba-Cu-O is affected by its strong phonon modes, there appears to be an underlying peak structure similar to that predicted and observed for Nb_3Ge and other superconducting films. The curve added schematically in the figure gives a peak frequency nearly 3 times that for the Nb_3Ge film.

Though our analysis using the Mattis-Bardeen conductivity provides a value for a superconducting energy gap, we emphasize that our data do not show a true gap frequency, as our conductivity retains a substantial portion

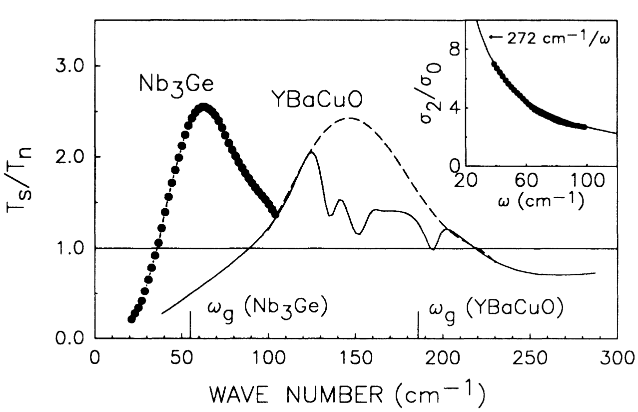

FIG. 2. T_s/T_n for Y-Ba-Cu-O and Nb_3Ge. The solid curve for Y-Ba-Cu-O comes only from the fit parameters (Fig. 1), with the MgO substrate omitted. The structures near 150 and 200 cm^{-1} are Y-Ba-Cu-O phonons. The dashed line is a projected peak in T_s/T_n without the phonons, to be compared to the peak for Nb_3Ge, with $T_c = 21$ K and $\omega_g = 55$ cm^{-1}. The much higher peak frequency for Y-Ba-Cu-O is consistent with its much higher T_c and gap, although the exact value is not meaningful in this projection. Inset: The imaginary part σ_2 of the conductivity in the superconducting state (divided by the normal-state dc conductivity σ_0), from measured T_s (Fig. 1) and Eq. (1). The expected $1/\omega$ behavior of the pure inductive supercurrent response is apparent.

of its original value below this frequency. Early data on sintered ceramic material[6] also displayed residual normal carriers. Our data do, however, indicate an increasing absorption between 150 and 200 cm^{-1}. We note that reflectivity studies of *a*-*b*-plane Y-Ba-Cu-O crystals[8] show an absorption onset at a similar frequency. If, however, this feature is indeed an energy gap, then our value will reflect some sort of average over all orientations due to incomplete *a*-*b*-plane crystalline alignment and possible gap anisotropy of the material.

Infrared transmission measurements through high-T_c films show superconducting behavior below 100 cm^{-1}. At higher frequencies, despite interference from phonons and remaining normal-state carriers, our modeling shows that nearly half the observed change in transmission is due to superconductivity, much larger than the change seen in reflectivity. Certainly samples which became more completely superconducting would enhance these effects. Another future possibility is to make simultaneous transmission and reflection measurements, as has been done for metallic superconducting films, to give a more complete picture.

We have reported what we believe is the first transmission measurement on high-T_c films, and shown how a gap can be derived from the data. We expect to apply this technique to a series of well oriented and characterized films.

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[1]G. P. Williams, P. Z. Takacs, R. W. Klaffky, and M. Shleifer, Nucl. Instrum. Methods Phys. Res. Sect. A **246**, 165 (1986).
[2]G. P. Williams, Int. J. Infrared Millimeter Waves **5**, 829 (1984).
[3]S. Perkowitz, in *Electromagnetic Waves in Matter,* edited by K. J. Button, Infrared and Millimeter Waves Vol. 8 (Academic, New York, 1983), Vol. 8, p. 71.
[4]W. B. Cook and S. Perkowitz, Phys. Rev. B **33**, 4557 (1986).
[5]For a review of infrared reflectivity studies, see T. Timusk and D. B. Tanner, in *Physical Properties of High T_c Superconductors,* edited by D. M. Ginsberg (World-Scientific, Singapore, 1989).
[6]S. Perkowitz, G. L. Carr, B. Lou, S. S. Yom, R. Sudharsanan, and D. S. Ginley, Solid State Commun. **64**, 721 (1987).
[7]T. Timusk, S. L. Herr, K. Kamaras, C. D. Porter, D. B. Tanner, D. A. Bonn, J. D. Garrett, C. V. Stager, J. E. Greedan, and M. Reedyk, Phys. Rev. B **38**, 6683 (1988).
[8]G. A. Thomas, J. Orenstein, D. H. Rapkine, M. Capizzi, A. J. Millis, R. N. Bhatt, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. Lett. **61**, 1313 (1988).
[9]S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **37**, 5920 (1988).
[10]For a review of Raman experiments, see C. Thomsen and M. Cardona, in *Physical Properties of High T_c Superconductors,* edited by D. M. Ginsberg (World-Scientific, Singapore, 1989).
[11]J.-M. Imer, F. Patthey, B. Dardel, W.-D. Schneider, Y. Baer, Y. Petroff, and A. Zettl, Phys. Rev. Lett. **62**, 336 (1989).
[12]M. Onellion, Ming Tang, Y. Chang, G. Margaritondo, J.-M. Tarascon, P. A. Morris, W. A. Bonner, and N. G. Stoffel, Phys. Rev. B **38**, 881 (1988).
[13]For a survey of tunneling results, see articles in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987).
[14]R. Sudharsanan, S. Perkowitz, B. Lou, B. R. Caldwell, and G. L. Carr, in *High Temperature Superconducting Materials,* edited by W. H. Hatfield and J. H. Miller (Marcel Dekker, New York, 1988), pp. 283–288.
[15]M. K. Crawford, W. E. Farneth, E. M. McCarron III, and R. K. Bordia, Phys. Rev. B **38**, 11 382 (1988).
[16]D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).
[17]M. Tinkham, in *Far Infrared Properties of Solids,* edited by S. S. Mitra and S. Nudelman (Plenum, New York, 1970).
[18]M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975), pp. 68–71.