PHYSICAL REVIEW B VOLUME 40, NUMBER 16 1 DECEMBER 1989

Properties of optical features in $YBa_2Cu_3O_{7-\delta}$

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(Received 27 June 1989; revised manuscript received 21 August 1989)

Characteristic optical features in the far-infrared conductivity of $YBa_2Cu_3O_{7-\delta}$ crystals have been studied as a function of doping. We focus particularly on a reflectivity "edge" near 435 cm^{-1} which we find to be both insensitive to carrier concentration (i.e., T_c), and present in the normal state of some samples. These results place tight constraints on possible interpretations of this feature.

Far-infrared studies of the high-T_c superconductor $YBa_2Cu_3O_7$ have been principally motivated by a desire to study both the superconducting energy gap and the low-frequency excitations that mediate superconductivity in this compound. Unfortunately, while recent far-infrared studies of this compound are now in uniform agreement that a distinct knee in the superconducting-state reflectivity is present near 435 cm^{-1}, interpretations of this feature have not reached a similar consensus. For example, this feature has been variously attributed to normal-state particle-hole excitations across a band edge,[1-4] free-carrier scattering from excitations having an onset near 435 cm^{-1},[4] and a large BCS superconducting energy gap ($2\Delta/k_BT_c \sim 8$).[5-7] To further complicate interpretations of $YBa_2Cu_3O_7$'s far-infrared properties, there have been reports of an additional onset of absorption near 150 cm^{-1} in the superconducting state that appears to exhibit features characteristic of a BCS gap.[3,4,6]

In view of the uncertainties confronting interpretations of these data, we have studied the optical reflectivity of $YBa_2Cu_3O_{7-\delta}$ as a function of δ (and consequently, T_c) in order to elucidate the nature of both far-infrared features. Evidence is presented that, within the large error bars characteristic of this high reflectivity region, the low-frequency feature scales with T_c in a manner consistent with BCS theory. By contrast, the higher-frequency onset of absorption near 435 cm^{-1} exhibits properties which make it unlikely to be due to either a conventional superconducting gap or a band edge.

The single-bounce reflectivity results in this study were performed on numerous crystals (microtwinned in the *a-b* plane) having a variety of T_c's. The $T_c = 90$ K crystals used in this study showed full diamagnetism and a large Meissner fraction. Furthermore, other crystals from the same batches maintained high surface conductances,[8] sharp superconducting onsets in microwave absorption,[9] instrumentally limited channeling ($x_{\min} = 3\%-5\%$) in Rutherford backscattering,[10] and immeasurably small *c*-axis misalignment in x-ray scattering[11] and electron microscopy.[12] The crystals with lower-T_c values were obtained by controlled annealing of $YBa_2Cu_3O_{7-\delta}$ in O_2,[13] which changes the carrier concentration by altering the O concentration in the sample. The 30-K sample was obtained by first substituting $\sim 10\%$ Al on Cu chain sites, then annealing the sample. All the low-T_c samples exhibited high values of reflectivity, which is the standard that we use to define good crystals.[14] Although the resistive transitions of the lower-T_c crystals are broader than those having $T_c = 90$ K, the estimates of magnetism and crystallographic alignment are otherwise similar to the 90-K samples. This indicates that the lower-T_c samples are not mixed phase crystals, but rather bulk superconductors having disordered oxygen. In particular, there is no evidence of phases with higher-T_c values in the conductivity,[8] magnetic susceptibility,[15] or microwave absorption[9] of these low-T_c crystals. Far-infrared measurements (at frequencies < 700 cm^{-1}) were performed using a Michelson interferometer, with light directed at the samples via a light pipe. An external manipulator was used to position either sample or Au reference in the beam path. Reflectivity data at higher frequencies (> 500 cm^{-1}) were obtained using a rapid-scanning interferometer, with incident and reflected beams focused by mirror optics. The estimated errors associated with these measurements are less than 1%.

Figure 1 shows reflectivity data in both the superconducting ($T \sim 20$ K) and normal ($T \sim 100$ K) states for three $T_c = 90$-K ($YBa_2Cu_3O_7$) samples. The error bars show an estimate of the combined random error and systematic uncertainty in absolute reflectivity; the relative error near the middle of the frequency range is smaller as indicated by the data scatter. The solid curves in the normal-state data represent a Drude form, illustrating the severe deviation of the data from Drude behavior [$\rho_N(100$ K$) = 30$ $\mu\Omega$ cm] above ~ 350 cm^{-1}. As we will discuss below, this deviation betrays the presence of an anomalous midinfrared absorption band in the conductivity. These data also illustrate the large changes in reflectivity occurring between the normal and superconducting states of $YBa_2Cu_3O_7$. The biggest difference between normal- and superconducting-state spectra in Fig. 1 is the appearance of a "knee" in reflectivity below T_c (arrow), representing a sudden onset of absorption near 435 cm^{-1} in the superconducting states of these samples. However, whether this absorption edge is present only in the superconducting state, or simply obscured in the normal state by increases in the scattering rate with temperature, cannot be discerned from these data alone.

More detailed information about the far-infrared region can be determined from studies of this region as a func-

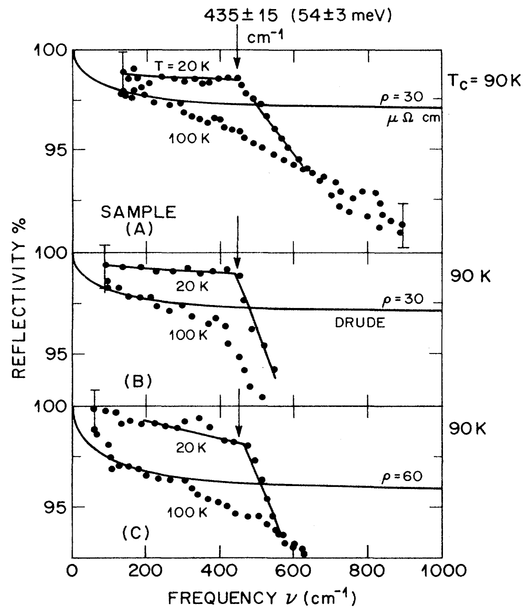

FIG. 1. Reflectivity R as a function of frequency ν for three crystals (A, B, and C) of $YBa_2Cu_3O_7$. The upper solid circles in each section are data taken in the superconducting state at $T=20$ K, and the solid lines through these points are guides to the eye. The arrows indicate the knee in the data near $\nu=435$ cm^{-1}. The lower solid circles are data in the normal state at $T=100$ K and the solid lines are estimates of the low ν resistivity using the Hagen-Rubens approximation. These fits yield ρ_N values of 30–60 $\mu\Omega$ cm and illustrate the slight down turn in reflectivity near the energy of the knee.

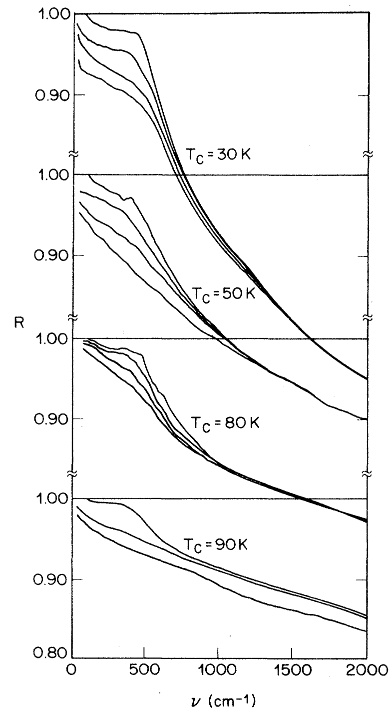

FIG. 2. Reflectivity vs frequency curves for crystals with $T_c=30$, 50, 80, and 90 K. For each sample, curves at different temperatures are shown with values: $(T_c:T\ldots)=$(30 K: 10, 100, 150, 250 K), (50 K: 10, 100, 150, 250 K), (80 K: 10, 40, 80, 150 K), (90 K: 20, 100, 200 K). Lower-energy features, at which R deviates from one within our experimental uncertainty, can also be seen.

tion of doping. In Fig. 2, for example, the optical reflectivity of $YBa_2Cu_3O_{7-\delta}$ is illustrated below 2000 cm^{-1} as a function of temperature for samples with different carrier concentrations (values of T_c). In all samples presented, the knee is observed at roughly the same energy, ~435 cm^{-1} (54 meV), in spite of the fact that both T_c and the free-carrier concentration[13,16] change by approximately a factor of 3. Furthermore, this edge is apparent at higher temperatures in samples with lower carrier concentrations, and indeed is clearly present in the normal state of samples having T_c's of 30 and 50 K. As we shall discuss below, these results question the interpretation of the 435-cm^{-1} knee in reflectivity as either a band-structure edge or a BCS superconducting gap. In addition to the prominent reflectivity edge near 435 cm^{-1} in Fig. 2, there is an additional onset of absorption between 100 and 200 cm^{-1} that corresponds to a deviation from unity reflectivity.[3,4,6,15–17] This feature disappears in normal-state reflectivity data in all of our samples. Notably, in the superconducting state, the high values of reflectivity in the energy range of this feature hinder a determination of its properties as a function of doping.

Figure 3 illustrates the normal and superconducting conductivities of the reflectivities shown in Fig. 2, obtained from a Kramers-Kronig transformation of the data. These results afford insight into the low-frequency optical properties of $YBa_2Cu_3O_{7-\delta}$, as well as the 100–200- and 435-cm^{-1} far-infrared features. For example, Fig. 3 shows that the normal-state conductivity in $YBa_2Cu_3O_{7-\delta}$ has both a narrow Drude-like contribution and a broad absorption band above ~400 cm^{-1}, as observed in previous results.[1,2,4,14,18] Our doping studies (Fig. 3) illustrate that both contributions to the conductivity below 3000 cm^{-1} increase with increased doping, suggesting that the free carriers contribute to the conductivities in both the Drude-like and higher-frequency components. This conclusion is also supported by estimates that the weight in the Drude contribution is insufficient to exhaust the total free-carrier spectral weight.[16] In addition, the reflectivity edge present in the normal-state reflectivities of low-T_c samples (Fig. 2) manifests itself as a weak minimum near 435 cm^{-1} in the conductivities of Fig. 3. Notably, the 435-cm^{-1} conductivity minimum becomes more conspicuous as carrier concentration is decreased. An explanation for this is provided by the results of Fig. 3, which suggest that in higher T_c samples with a larger Drude-like component, the 435-cm^{-1} feature is obscured by the overlap between Drude and higher-frequency contributions. As the temperature is lowered, the Drude-like part narrows and the 435-cm^{-1} edge is resolved, giving the appearance of a BCS-like temperature dependence in 90-K crystals.[5,7] Thus, these data suggest that the temperature at which this feature disappears is not related to T_c,

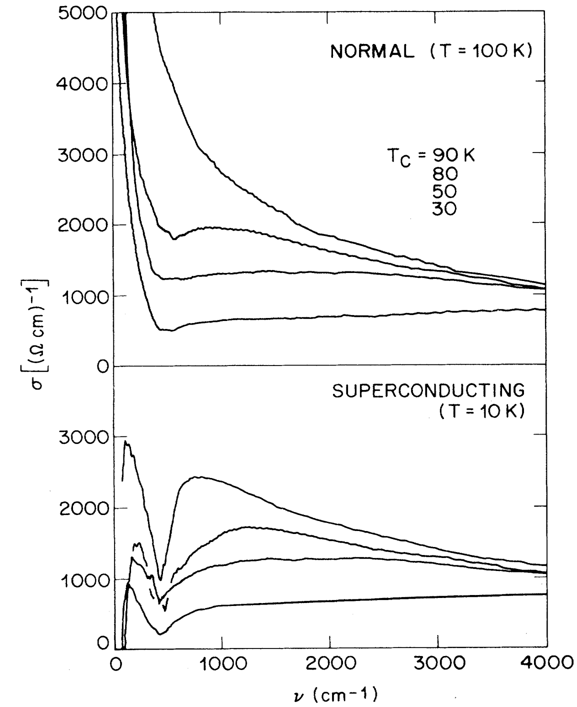

FIG. 3. Conductivity as a function of frequency for the crystals whose reflectivities are presented in Figs. 1 and 2 in both the normal (top) and superconducting (bottom) states. The values of T_c for the four curves are 90, 80, 50, and 30 K.

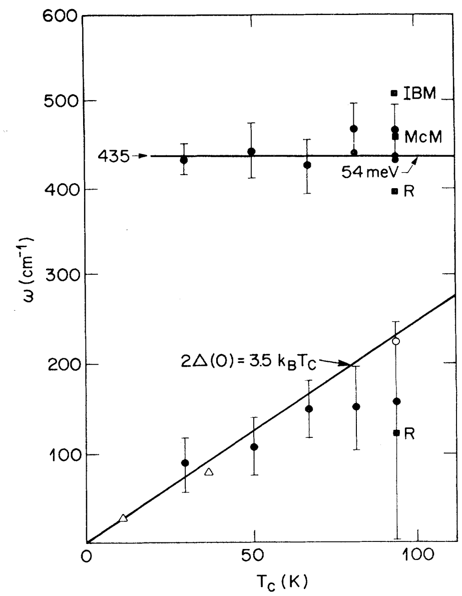

FIG. 4. A summary of the frequency of the knee and lower-energy feature as a function of T_c. The results from Figs. 1 and 2 are shown as solid circles and two additional points are plotted from similar crystals with $T_c = 80$ and 70 K. Results from other groups are plotted as solid squares labeled IBM (Refs. 5 and 7), McM (Ref. 2), and R (Ref. 6). The solid triangles and open circles are results for other materials (Refs. 29 and 30) and pressed pellets (Ref. 31). The line through the upper data set represents a T_c independence of the 435-cm^{-1} reflectivity edge, while the lower line is the prediction of weak-coupling BCS theory for the superconducting gap energy.

but rather to the breadth, $\Gamma(T)$, and weight of the Drude-like conductivity.

In the superconducting state, the conductivities of all samples exhibit a loss of spectral weight relative to the normal state. For each sample, this "lost" spectral weight goes into δ function at $\omega = 0$, further exposing the 435-cm^{-1} conductivity minimum. The magnitude of the missing spectral weight in the superconducting state corresponds to the spectral weight in the superfluid condensate, and indeed our data corroborates London penetration-depth measurements of the superfluid weight ($\lambda \sim 1400$ Å) in $T_c = 90$ crystals.[19] The superconducting-state conductivities of Fig. 3 also indicate a feature at lower frequencies which appears to increase in energy somewhat with increased doping. By contrast, the 435-cm^{-1} onset of absorption does not shift with T_c.

Figure 4 summarizes the energies of the two far-infrared features as a function of doping (and T_c). In lower T_c samples, the low-frequency absorption threshold appears to vary with T_c in a manner consistent with BCS theory. However, as shown in Fig. 4, this scaling does not extend to $T_c = 90$-K samples, in agreement with other results (solid square).[3,6] It is important to stress that the properties of this lower energy feature with doping are difficult to ascertain, since the errors associated with measuring differences in high reflectivities are large. Figure 4 also reiterates that the $\sim$435-cm^{-1} edge (solid circles) does not shift as a function of T_c. For comparison, other groups' results on $T_c = 90$-K crystals are also shown (solid squares).[2,5,6]

The above results present significant constraints on interpretations of the 435-cm^{-1} optical feature. Indeed, it appears that a number of interpretations may be ruled out by this study: (i) a band-structure feature. The observation that the reflectivity knee does not shift with doping suggests that it is unlikely to arise from an onset of absorption in band structure, as the energy of such an onset would be sensitive to filling; (ii) a conventional superconducting gap. Although this feature has an apparent BCS temperature dependence,[1,4,5,7] the absence of a shift with T_c, and the appearance of this feature in the normal state of lower T_c samples, argues that the knee cannot be a BCS gap; and (iii) scattering of carriers from an excitation whose characteristic energy is $\sim$435 cm^{-1}, independent of carrier density. In a strong scattering interpretation, the absorption onset should shift by 2Δ in the superconducting state as a gap opens to the free carriers.[20] Figure 3 illustrates that, except for small values of 2Δ, our results are not consistent with such a shift.

On the other hand, evidence that the optical feature may be related to a gap to some type of pair excitation is offered by photoemission[21,22] and tunneling[23,24] measurements of the single-particle density of states in $YBa_2Cu_3O_{7-\delta}$. These studies exhibit a feature at roughly half the energy of the conductivity feature near 435 cm^{-1}, as would be expected if the latter feature was related to a pair breaking energy (2Δ). Indeed, Raman scattering measurements also exhibit structure in the superconducting state that is consistent with $2\Delta \sim 500$ cm^{-1}.[25,26] Attributing the absorption onset near 435 cm^{-1} to an optical gap (2Δ) can be reconciled with the appearance of this feature in the normal state of σ (Fig. 3) if one assumes that a pairing gap exists in the normal state. Such a pseudogap would indicate strong normal-state correlations between carriers that precede the transition to bulk superconductivity (i.e., normal-state pairing). Evidence that precursor effects may be present in the normal state of high-T_c superconductors has been chiefly provided by nuclear magnetic resonance measurements $YBa_2Cu_3O_{6.7}$.[27] These data show an anomalous decrease in Cu(2) spin relaxation above T_c that has been interpreted as evidence for gap formation in the spin-excitation spectrum near $T = 100$ K. Furthermore, evidence that a gap forms in the normal-state spin-excitation spectrum of $La_{1.85}Sr_{0.15}CuO_4$ has been reported by neutron-scattering results.[28] The results of the present investigation also suggest that the 435-cm^{-1} optical feature is most consistently described as a preformed gap in the normal state, although a more thorough consideration of this interpretation requires theoretical guidance.

In conclusion, we have observed a knee in the a-b plane reflectivity of $YBa_2Cu_3O_{7-\delta}$ crystals as a function of doping. The properties of this knee differ substantially from those expected of a conventional superconducting gap or a normal-state band-structure feature. For example, this feature does not shift with carrier concentration (T_c), and it is present above T_c. A comparison with other experimental evidence suggests that this feature may indicate strong carrier correlations in the normal state.

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[1]T. Timusk and D. B. Tanner, in *The Physical Properties of High Temperature Superconductors,* edited by D. M. Ginsberg (World Scientific, Singapore, 1989), Chap. VII.

[2]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).

[3]K. Kamaras, S. L. Herr, C. D. Porter, N. Tache, D. B. Tanner, S. Etemad, T. Venkatesan, and E. Chase (unpublished).

[4]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).

[5]Z. Schlesinger, R. T. Collins, D. L. Kaiser, and F. Holtzberg, Phys. Rev. Lett. **59**, 1958 (1987).

[6]J. Schützmann, W. Ose, J. Keller, K. F. Renk, B. Roas, L. Schultz, and G. Saemann-Ischenko, Europhys. Lett. **8**, 679 (1989).

[7]R. T. Collins, Z. Schlesinger, F. Holtzberg, and C. Feild, Phys. Rev. Lett. **63**, 422 (1989).

[8]D. L. Rubin, K. Green, J. Gruschus, J. Kerchgessner, D. Moffat, H. Padamsee, J. Sears, Q. S. Shu, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. B **38**, 6538 (1989).

[9]S. H. Glarum, S. H. Marshall, and L. F. Schneemeyer, Phys. Rev. B **37**, 7491 (1988); results on reduced T_c samples are unpublished.

[10]A. E. White (private communication); A. E. White, K. T. Short, J. P. Garno, J. M. Valles, R. C. Dynes, L. F. Schneemeyer, J. V. Waszczak, A. F. J. Levi, M. Anzlower, and K. W. Baldwin, Nucl. Instrum. Methods Phys. Res., Sect. B **37/38**, 923 (1989).

[11]R. M. Fleming, L. F. Schneemeyer, P. K. Gallagher, B. Batlogg, L. W. Rupp, Jr., and J. V. Waszczak, Phys. Rev. B **37**, 7920 (1988).

[12]C. H. Chen, D. J. Werder, L. F. Schneemeyer, P. K. Gallagher, and J. V. Waszczak, Phys. Rev. B **38**, 2888 (1988).

[13]L. F. Schneemeyer (unpublished); P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, D. W. Murphy, Mater. Res. Bull. **22**, 995 (1987). An estimate of O concentration vs T_c has been given by R. J. Cava, B. Batlogg, Ch. H. Chen, E. A. Rietman, S. M. Zahurak, and D. J. Werder, Phys. Rev. B **36**, 5719 (1987).

[14]G. A. Thomas, M. Capizzi, T. Timusk, S. L. Cooper, J. Orenstein, D. H. Rapkine, S. Martin, L. F. Schneemeyer, and J. V. Waszczak, J. Opt. Soc. Am. B **6**, 415 (1989).

[15]L. W. Rupp, Jr. and B. Batlogg (unpublished).

[16]J. Orenstein, G. A. Thomas, A. J. Millis, S. L. Cooper, D. H. Rapkine, T. Timusk, L. F. Schneemeyer, and J. V. Waszczak (unpublished).

[17]J. Orenstein, G. A. Thomas, D. H. Rapkine, A. J. Millis, L. F. Schneemeyer, and J. V. Waszczak, Physica C **153-155**, 1740 (1988).

[18]R. T. Collins, Z. Schlesinger, F. Holtzberg, P. Chaudhari, and C. Feild, Phys. Rev. B **39**, 6571 (1989).

[19]D. R. Harshman, L. F. Schneemeyer, J. V. Waszczak, G. Aeppli, R. J. Cava, B. Batlogg, L. W. Rupp, E. J. Ansaldo, and D. L. Williams, Phys. Rev. B **39**, 851 (1989).

[20]P. B. Allen, Phys. Rev. B **3**, 305 (1971).

[21]J.-M. Imer, F. Patthey, B. Dardel, W.-D. Schneider, Y. Baer, Y. Petroff, and A. Zettl, Phys. Rev. Lett. **62**, 336 (1989).

[22]C. G. Olson, R. Liu, A.-B. Yang, D. W. Lynch, A. J. Arko, R. S. List, B. W. Veal, Y. C. Chang, P. Z. Jiang, and A. P. Paulikas (unpublished).

[23]M. Gurvitch, J. M. Valles, Jr., A. M. Cucolo, R. C. Dynes, J. P. Garno, L. F. Schneemeyer, and J. V. Waszczak (unpublished).

[24]M. Lee, A. Kapitulnik, and M. R. Beasley, in *Mechanisms of High Temperature Superconductivity,* edited by H. Kaminura and A. Oshiyama (Springer-Verlag, Heidelberg, 1989).

[25]S. L. Cooper, F. Slakey, M. V. Klein, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **38**, 11934 (1988).

[26]R. Hackl, W. Gläser, P. Müller, D. Einzel, and K. Andres, Phys. Rev. B **38**, 7133 (1988).

[27]W. W. Warren, Jr., R. E. Walstedt, G. F. Brennert, R. J. Cava, R. Tycho, R. F. Bell, and G. Dabbagh, Phys. Rev. Lett. **62**, 1193 (1989).

[28]G. Shirane, R. J. Birgeneau, Y. Endoh, P. Gehring, M. A. Kastner, K. Kitazawa, H. Kojima, I. Tanaka, T. R. Thurston, and K. Yamada, Phys. Rev. Lett. **63**, 330 (1989).

[29]B. Batlogg, J. P. Remeika, R. C. Dynes, H. Barz, A. S. Cooper, and J. P. Garno, in *Superconductivity in d- and f-Band Metals,* edited by W. Buckel and W. Weber (Kernforschungszentrum Karlsruhe GmbH, Karlsruhe, 1982).

[30]G. A. Thomas, A. J. Millis, R. N. Bhatt, R. J. Cava, and E. A. Rietman, Phys. Rev. B **36**, 736 (1987).

[31]G. A. Thomas, H. K. Ng, A. J. Millis, R. N. Bhatt, R. J. Cava, E. A. Rietman, D. W. Johnson, Jr., G. P. Espinosa, and J. M. Vandenberg, Phys. Rev. B **36**, 846 (1987).