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Infrared observation of two-fluid superconductivity in $YBa_2Cu_3O_{7-x}$

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We observe critical behavior near T_c in the infrared reflectivity of c-axis-oriented $Y_1Ba_2Cu_3O_{7-x}$ films prepared with pulsed *in situ* laser deposition. From comparison with theoretical spectra we show that the observed behavior is in excellent agreement with a phenomenological two-fluid model and in strong disagreement with standard BCS theory. We demonstrate that the superconducting charge carrier density is the relevant order parameter with a temperature-independent in-plane gap parameter.

Right from the beginning of the era of cuprate high-T_c superconductivity[1] attempts have been made to observe a superconducting gap with infrared reflectivity measurements. So far no clear picture of the gap has emerged. In particular, whether or not there exists a BCS gap at around 500 cm^{-1} has been subject of a debate that has not been settled yet.[2,3] Some authors[3] have attributed the failure of the many attempts to observe the expected BCS gap behavior in the cuprate superconductors to the fact that these materials are presumably in the clean limit of superconductivity, where the Mattis-Bardeen formula[4] is inapplicable.

At the heart of these debates lies the problem that experimentalists have so far tried to interprete the data using the concept of a gap having a temperature dependence characteristic for weak- and strong-coupling versions of BCS theory. This need not *a priori* be the case in the cuprate high-T_c superconductors, and in this paper we show that the qualitatively different concept of a temperature-*independent* in-plane gap parameter and a temperature-dependent superconducting density gives an accurate ansatz for the interpretation of gap investigations of cuprated high-T_c superconductors.

c-axis-oriented thin films with thicknesses of about 3000 Å were prepared using the pulsed laser deposition technique set up for *in situ* Y-Ba-Cu-O thin film growth. Experimental details have been published elsewhere.[5] Characterization of the films using scanning electron microscopy, optical microscopy, and x-ray diffraction revealed, that the films are single phase and c-axis oriented with an extremely smooth surface. We report on two samples deposited on the (100) surfaces of $SrTiO_3$ (sample A) and $LaAlO_3$ (sample B). Transmission electron microscopic measurements demonstrated a well-defined substrate-film interface on an atomic scale. Resistivity and susceptibility measurements with a superconducting quantum interference device (SQUID) magnetometer revealed a sharp superconducting transition between 88 and 90 K. Infrared measurements were carried out in a Fourier transform spectrometer with a variable temperature cryostat. Two overlapping spectral ranges were joined at 640 cm^{-1}. The reflectivity measurements were calibrated against an Al mirror where we took care to have identical experimental conditions, including temperature and elapsed time during cooldown, for the measurement of the mirror and the samples. The infrared spectra were measured at 5-K intervals in the temperature range between 150 and 20 K. In Fig. 1 we display the reflectivity of both samples. The peaks at 188, 429, and 670 cm^{-1} in sample B are transverse-optical phonons of the $LaAlO_3$ substrate, as revealed by a separate reflectivity measurement. The remaining wiggles are smaller than 0.5 % and are mostly of instrumental origin, with the possible exception of a tiny peak at 315 cm^{-1}, which coincides with a phonon that dominates the spectra of ceramic samples. We observe a kink in the temperature dependency of the reflectivity curves at T_c. There is a crossover at about 570 cm^{-1} from an upward to a downward kink, which reaches its deepest point between 700 and 800 cm^{-1}. The temperature dependence of the reflectivity of sample B is presented in Fig. 2(a). In Fig. 3(a) we display the optical conductivity of sample A obtained from Kramers-Kronig analysis. There is an absorption edge at about 400 cm^{-1} that bears some similarity to a BCS energy gap. Agreement of the shape of the spectra with previously published results[2,3] is excellent. However, the present dense sampling through T_c allows us to make a much more detailed analysis of the temperature dependence of the spectra.

We now compare these results to theoretical plots, where we assume standard BCS behavior of the gap with $2\Delta_0 = 3.52k_BT_c$, using the expressions for the dielectric constant in the superconducting phase and the normal phase based on the full solution of the Mattis-Bardeen equations[4] covering both the dirty and clean limits.[6] The parameters used are a temperature-independent bulk plasma frequency and a temperature-dependent relaxation time τ. (We assume τ proportional to $1/T$, with a saturation at about 60 K. The parameters correspond to those obtained on single crystals in Ref. 7.) For sample B the dielectric constants of the substrate material and of the superconducting films were inserted in the appropri-

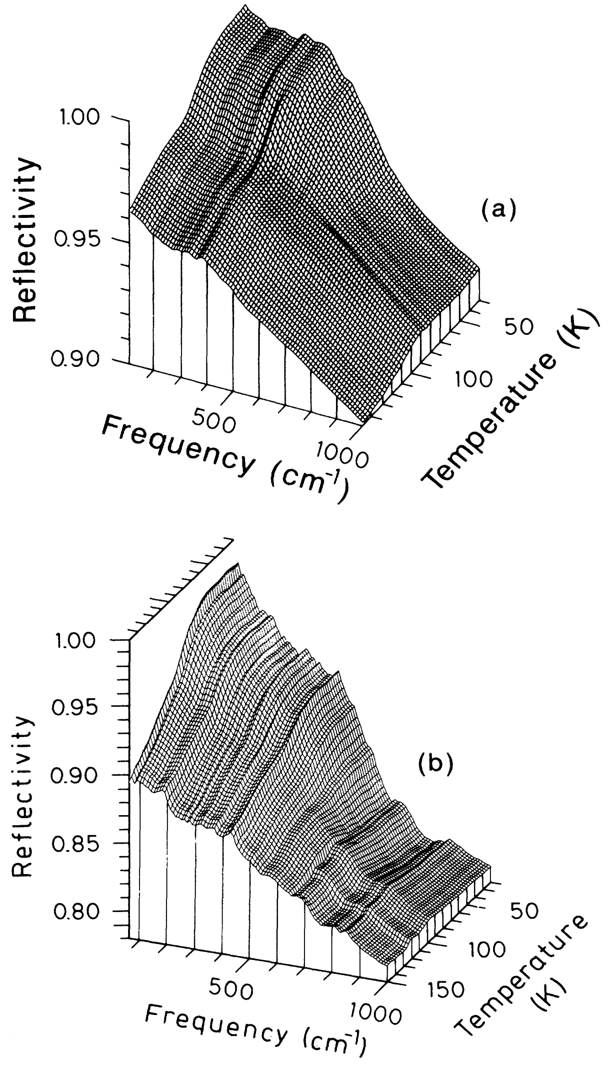

FIG. 1. Experimental reflectivity data of samples A (a) and B (b) as a function of frequency and temperature.

ate Fresnel formula for the combined substrate–thin-film system, resulting in the theoretical plot of Fig. 2(b). We clearly recognize a step at T_c in the low-frequency region, which shifts to lower temperatures as the frequency approaches $2\Delta_0$. This behavior is manifestly absent in the experimental data of Fig. 2(a). We checked that the disagreement with Fig. 2(a) cannot be removed by assuming a steeper descent near T_c in addition to assuming a larger value of Δ. In Fig. 3(b) we display the optical conductivity by assuming a distribution of Δ between 200 and 325 cm^{-1}, which results in the best low-temperature fit for both samples. On comparing to Fig. 3(a) we see that the experimental temperature dependence is quite different from regular BCS behavior, as the edge does not shift to zero frequency as T approaches T_c. In fact, the edge vanishes in an essentially different way, i.e., by "filling in" instead of closing.

Inspired by the pioneering work of Gorter and Casimir[8] we now turn to a description of our observations in terms of a two-fluid model. We do so by assuming that below T_c the free-electron part of the dielectric constant is the linear combination of two contributions:

$$\epsilon = f_s(T)\epsilon_s + [1 - f_s(T)]\epsilon_n \tag{1}$$

where ϵ_s and ϵ_n represent the dielectric functions of the superconducting and normal fractions, respectively. The former fraction approaches zero linearly for $T \rightarrow T_c$. The detailed temperature dependence of the fraction of superconducting charge carriers $f_s(T)$ should follow from a microscopic model of the two-fluid phase, which is at present not available. We also have to make assumptions about the nature of ϵ_n and ϵ_s. For the former we will assume standard Drude behavior with the same parameters for ω_p and τ as described above. For the latter we also use these Drude parameters, and, in addition, we assume a temperature-independent distribution of Δ between 200 and 325 cm^{-1} as in Fig. 3(b). In Figs. 2(c) and 3(c) we display the reflectivities taking

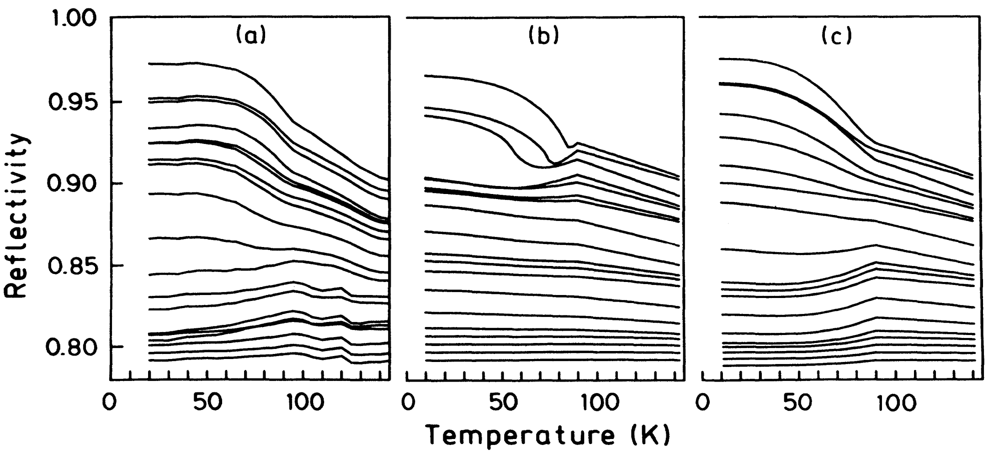

FIG. 2. (a) Reflectivity of sample B vs temperature, (b) theoretical plot using BCS theory, and (c) the same as (b) using the two-fluid model. From top to bottom: $\nu = 100$–$1000\ \text{cm}^{-1}$ in increments of 50 cm^{-1}.

the phenomenological expression for the superconducting carrier density in terms of the London penetration depth $f_s(T) = [\lambda(T)/\lambda(0)]^2 = 1 - (T/T_c)^4$. We modeled the chain conductivity as a gapless wide Drude oscillater[9] corresponding to the dashed curve in Fig. 3(a). From comparing Fig. 2(c) to Fig. 2(a) and Fig. 3(c) to Fig. 3(a) we see that the phenomenological assumption of a constant gap and a temperature dependent superconducting fraction is in excellent agreement with the observed data. In particular, we observe that there is no shift of the reflectivity step as a function of frequency and temperature, which is a considerable improvement over the BCS mean field results of Figs. 2(b) and 3(b).

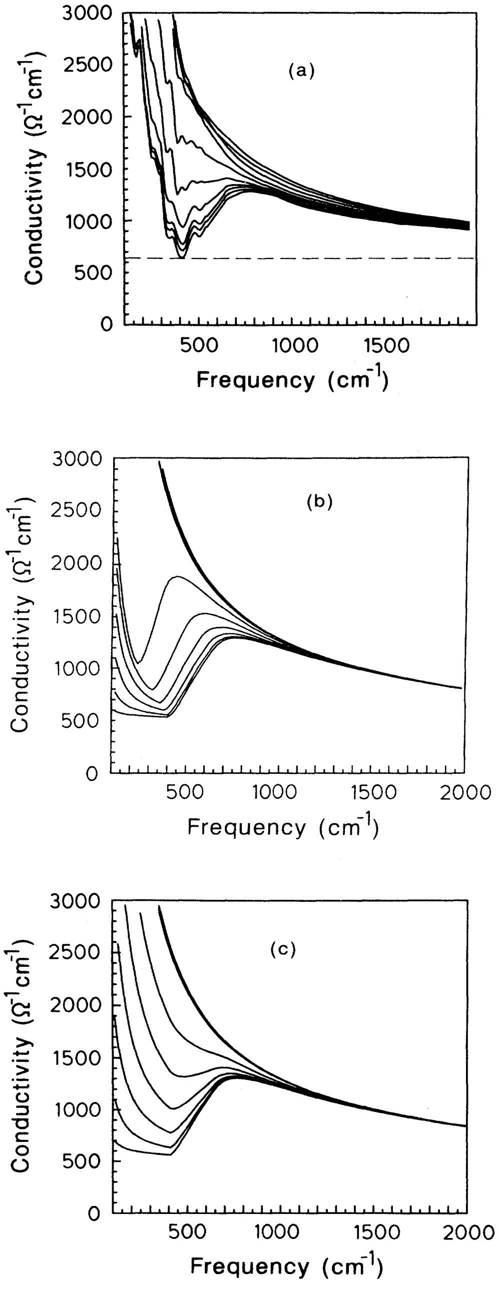

FIG. 3. (a) Experimental conductivity of sample A vs frequency, (b) theoretical plot using BCS theory, and (c) the same as (b) using the two-fluid model. From top to bottom: T = 120–30 K in increments of 10 K.

The most important implication of our observations is that $f_s(T)$ is effectively decoupled from $|\Delta|^2$ in these materials. As $f_s(T)$ is observed to be a proper order parameter with a second-order phase transition at T_c, those properties that only depend on the Ginzburg-Landau phenomenological model are not directly affected by the rather unusual behavior of the gap. All gap-related features, including the Korringa relaxation rate, are influenced. Other experimental observations of the (near) constancy and large value of Δ have been made with photo electron,[10] tunneling,[11] Raman,[12] and energy-loss[13] spectroscopies.

Why does an *ad hoc* two-fluid model with a temperature-independent gap work so well compared to weak- or strong-coupling BCS theory? The strong deviations from the mean-field behavior described above suggest that the BCS-type quasiparticles may not be the only excitations involved in the superconducting transition. One can speculate on a scenario where the phase transition takes place at a temperature much lower than the temperature where the gap would normally close. The layered two-dimensional nature of the material could play a central role here. Rather than by breaking up Cooper-pairs, the superconducting ground state would be destroyed through thermal excitation of, e.g., collective phase and/or density oscillations,[14] local pairs,[15] or pairing bag excitations.[16] Closely related to this is a recent interesting suggestion that the normal state may be a mixture of bound pairs of electrons and "free" electrons.[17] A phase transition of the type described above would follow, if the pair condensation at T_c is accompanied by the formation of additional pairs out of the free electrons. Such bound pairs would be a consequence of local nonretarded electron pairing, as discussed by Micnas *et al.*[15]

In conclusion we have observed critical behavior of the reflectivity of superconducting $Y_1Ba_2Cu_3O_7$ films, which can be understood in terms of a two-fluid model with a normal-metal component and a superconducting component with a constant gap parameter, whereas the superconducting density is proportional to the order parameter describing the second-order phase transition. A microscopic understanding of the separation in two components is as yet still lacking.

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