# Optical Conductivity of $c$ Axis Oriented $YBa_2Cu_3O_{6.70}$: Evidence for a Pseudogap

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The $c$ axis reflectance of high-quality single crystals of $YBa_2Cu_3O_{6+x}$ has been measured over a wide range of temperatures and frequencies. The $x = 0.70$ crystal has a pseudogap in the conductivity at 200 $cm^{-1}$ which is present at room temperature. The gap deepens gradually as the temperature is lowered to 10 K with no discontinuity at $T_c$. In contrast, crystals with $x = 0.95$ show no gap in the normal state and their superconducting state is characterized by low-lying states. These observations are consistent with phase diagrams proposed to explain NMR and neutron data.

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The central question in high-temperature superconductivity is the nature of the normal state from which superconductivity condenses. In ordinary superconductors this state is a Fermi liquid, but it was suggested early on that in the copper oxides the normal-state electrons are correlated, leading to exotic behavior such as a zero-intercept linear resistivity [1]. Another important observation is the closeness of the magnetic-insulator phase at low doping levels. Both NMR [2] and neutron [3–5] measurements suggest that magnetic correlations are important, leading to a spin pseudogap (a gap where the conductivity is finite at all frequencies) in the normal state and that, in the underdoped case, the superconducting state condenses from such a gapped normal state [6–9]. The hypothesis of a gap in the normal state has been questioned and the data have been interpreted in terms of enhanced scattering [10]. Optical conductivity measurements have been used to observe gaps in spin-density-wave (SDW) systems [11]. In the $ab$-plane optical conductivity of the high-$T_c$ superconductors there are features that have been found to persist in the normal state [12–14]. They have been interpreted as spin gaps [13,14] and $c$ axis polarized optical phonons to be coupled to the $ab$-plane conductivity by a symmetry-breaking process [15].

Here we present the first results on the temperature dependence of $c$ axis optical conductivity of high-quality oxygen-reduced single crystals of YBCO. As several previous studies of polarized $c$ axis reflectance on single crystals [16] show, a gaplike depression appears in the optical conductivity, made visible by the incoherent transport in this direction, in contrast to the $ab$ plane where the materials appear to be in the clean limit [17]. We find that in the oxygen-reduced crystals a pseudogap begins to form well above $T_c$; for comparison we also show $c$ axis optical conductivity data on a fully oxygenated crystal, where instead of a pseudogap, a gap consistent with nodes in the gap function is seen.

Measurements were done on a total of three crystals, with $x$ = 0.6, 0.7, 0.8, 0.85, 0.9, and 0.95, grown by a flux method [18]. Data for an oxygen-reduced crystal, $YBa_2Cu_3O_{6.70}$, with $T_c$=63 K and $\delta T_c$ = 3.0 K determined by magnetic susceptibility and a fully oxygenated one, $YBa_2Cu_3O_{6.95}$, with $T_c$=93.2 K and $\delta T_c$ = 0.25 K determined by dc resistivity, will be shown here; results for other concentrations will be given in a future publication. The properties at other doping levels interpolate between the ones shown. The $c$ axis dc resistivity of a typical sample from the same batch was 4.6 m$\Omega$ cm at 100 K dropping slightly to 4.5 m$\Omega$ cm at 140 K, to rise to 5.6 m$\Omega$ cm at 300 K.

Cleaved, flat faces on twinned crystals between 0.5 and 0.9 mm in thickness in the $c$ direction and between 1 and 2 mm long in the $ab$ direction were used. To correct for the sample size and any remaining irregularities, the sample surface was overcoated with gold *in situ* and all the measurements were repeated on the gold-coated sample which was used as the reference [19]. We estimate the overall absolute accuracy of the reflectance to be ±1%.

Figure 1 shows the reflectance in the low-frequency region of the $YBa_2Cu_3O_{6.70}$ crystal at six temperatures. The structure at 150 $cm^{-1}$ and higher is due to transverse optic phonons. Of particular interest is the metallic behavior at low frequency, demonstrated by the negative slope of the reflectance with frequency. As the temperature is lowered the material becomes more insulating but remains metallic down to 70 K, just above the superconducting transition. The onset of superconductivity is signaled by the appearance of a plasma edge caused by the zero crossing of the real part of the dielectric function [20].

The optical conductivity, shown in Fig. 2(a), has been calculated by a Kramers-Kronig transformation of the reflectance. Six strong phonons dominate the conductivity. The four phonons at 153, 195, 287, and 314 $cm^{-1}$ have symmetric line shapes, while the two at 557 and 630 $cm^{-1}$ appear to interact with the electronic background and acquire dispersionlike line shapes as the oxygen doping is

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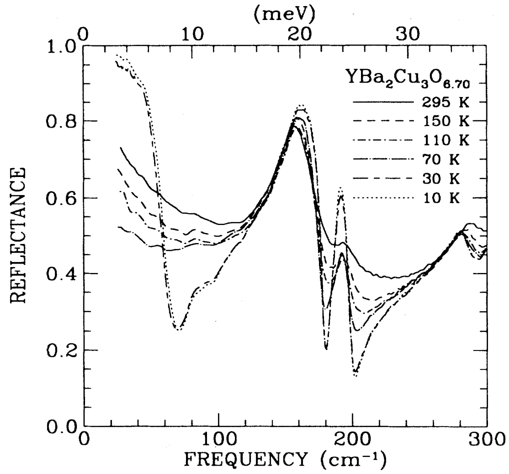


FIG. 1. The reflectance of $YBa_2Cu_3O_{6.70}$ along the $c$ axis from $\approx 25$ to 300 $cm^{-1}$, above and below $T_c$ (63 K). At room temperature (solid line), the reflectance displays a metallic response; just above $T_c$, the weak upturn in the reflectance indicates an unusual type of metallic behavior, but the material is not an insulator ($\sigma_{dc} \neq 0$). Below $T_c$, the condensation of the carriers into a zero-frequency mode is clearly shown by the plasma edge in the reflectance.

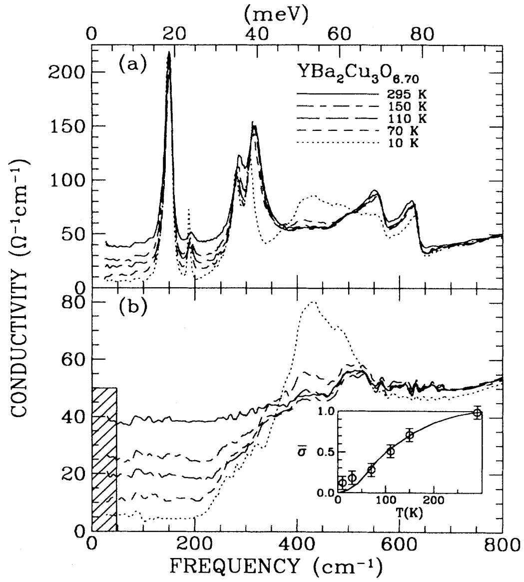


FIG. 2. The optical conductivity of $YBa_2Cu_3O_{6.70}$ along the $c$ axis from $\approx 25$ to 800 $cm^{-1}$ obtained by a Kramers-Kronig analysis of the reflectance with (a) the phonons at 150, 192, 286, 317, 557, and 630 $cm^{-1}$ present and (b) subtracted to yield the electronic background. Note that the formation of a pseudogap is clearly visible well above $T_c$ (63 K). The shaded area represents the spectral weight of the condensate (305 $cm^{-1}$) for $T \ll T_c$. Inset: The conductivity at 50 $cm^{-1}$ normalized with respect to the room temperature conductivity (open circles), compared to the normalized Knight shift for Cu(2) (solid line) in $YBa_2Cu_3O_{6.63}$ (after Ref. [2]).

decreased.

We treat the phonons as a separate channel of conductivity and subtract their contribution from the spectrum. This is done by a least-squares fit by a Lorentzian profile (except for the two high-frequency lines where an asymmetric Fano-like [21] line shape was used), and the broad phonon centered at 450 $cm^{-1}$ which we have not been able to subtract out in an unambiguous way. The total spectral weight from 250 to 650 $cm^{-1}$ does not change much with temperature despite the dramatic changes to the phonons. Figure 2(b) shows the conductivity with all the phonon lines except the one at 450 $cm^{-1}$ removed.

The spectrum of the oxygen-reduced sample is dominated by a pseudogap extending from 30 $cm^{-1}$, our lowest measured frequency, to 200 $cm^{-1}$ at low temperature. The inset in the diagram is the magnitude of the normalized conductivity in the flat gap region as a function of temperature plotted as open circles.

Added to the finite-frequency conductivity is the delta function response of the superconducting condensate at zero frequency. The area under this singularity can be found in two ways: by plotting $\epsilon_1$ as a function of $\omega^2$, [17] or by using a sum rule for the conductivity [22]. The two methods yield the same spectral weight indicated by the shaded area in Fig. 2(b). Expressed as a plasma frequency through $\int \sigma(\omega) d\omega = \omega_p/8$, the spectral weight is 305 $cm^{-1}$ ($\lambda_L = 5.2$ $\mu$m). Above the superconducting transition, as the pseudogap deepens, the spectral weight between 50 and 800 $cm^{-1}$ is decreasing in a roughly linear fashion without a break at $T_c$. In the superconducting state, the spectral weight is transferred to the delta function, in contrast to above $T_c$, where it appears to go to higher-frequency regions of the spectrum.

The behavior of the fully doped sample with the phonons subtracted is shown in Fig. 3. The major change in the phonon structure in the fully doped sample compared to the $x = 0.70$ sample is that the doublet centered at $\approx 600$ $cm^{-1}$ is replaced by a single, more symmetric peak at 567 $cm^{-1}$. The electronic continuum in the fully doped sample shows no evidence of a pseudogap in the normal state above the limit of our data at 100 $cm^{-1}$. The conductivity is flat at room temperature and *increases* slightly as the temperature is lowered, consistent with the dc conductivity which also increases as the temperature is lowered. There is a slight downturn of dc conductivity just before the superconducting transition in our sample.

In the superconducting state, in the fully oxygenated sample, a gaplike depression of conductivity develops as the temperature is lowered. However, both the frequency and temperature dependence differ from BCS dirty-limit behavior. There is no evidence for a true gap in the conductivity at low frequency. The 10 K conductivity

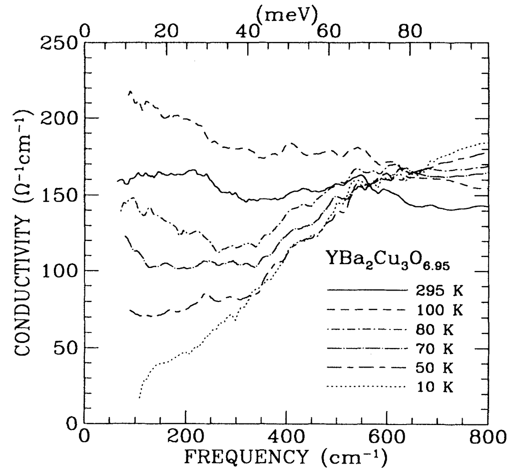


FIG. 3. The optical conductivity of $YBa_2Cu_3O_{6.95}$, along the $c$ axis from $\approx$90 to 800 cm$^{-1}$, above and below $T_c$ (93 K), with the phonons normally present at 153, 195, 287, 313, and 567 cm$^{-1}$ removed to show the electronic background. The normal-state behavior is metallic. Below $T_c$ a gaplike depression appears in the conductivity, but shifts to zero frequency with decreasing temperature, leaving residual conductivity at $\approx$10 K (dotted line) down to the lowest measured frequency point $\approx$ 100 cm$^{-1}$.

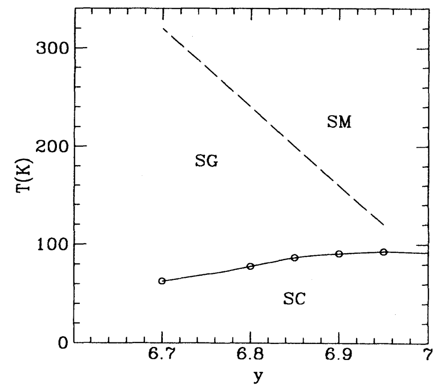


FIG. 4. The phase diagram proposed for the $t$-$J$ model for $YBa_2Cu_3O_y$ as a function of $y$, the oxygen doping, and $T$, the temperature (after Ref. [9]). The spin-gap phase (SG) exists between the dashed spinon-pairing line and the solid line, where bosons condense to form the superconducting phase (SC). We find a pseudogap in the SG region of the phase diagram, whereas at full doping the transition is directly from the "strange metal" phase (SM) to the superconducting one.

decreases monotonically with frequency down to the lowest measured frequency of $\approx$ 100 cm$^{-1}$, at which point it has reached about 5% of the normal-state conductivity. Within the experimental error we cannot rule out a possible gap below 100 cm$^{-1}$.

The temperature dependence of the conductivity also deviates from the BCS form. Figure 3 shows that as the temperature increases the position of the minimum moves to *higher* frequency with temperature in a roughly linear fashion, opposite to the BCS behavior where a minimum of conductivity occurs at the position of the temperature dependent gap starting at $2\Delta$ at $T = 0$ and moving to *lower* frequency as the temperature increases.

The striking feature of the $c$ axis conductivity in the oxygen-reduced sample is the pseudogap. Extrapolated to zero frequency it implies that the dc resistivity should change from 25 m$\Omega$ cm at room temperature to 100 m$\Omega$ cm at 70 K. This resistivity increase is consistent with published values at this doping level [23]. Thus, it appears that the temperature dependence of the $c$ axis dc resistivity in oxygen-reduced $YBa_2Cu_3O_{6+x}$ is a result of the formation of the pseudogap. Note that at frequencies well above the pseudogap the conductivity is temperature independent.

Two models of charge transport can account for the reduced conductivity in the presence of a pseudogap; a conventional Fermi liquid with a spin-density-wave gap at the Fermi surface [24], and a model with spin-charge separation where there is a gap in the spinon spectrum. We plot in Fig. 2(b) (inset) the NMR Knight shift [2] along with the optical conductivity in the low-frequency region. The excellent agreement between the two quantities can be understood in terms of both models: for the gapped Fermi liquid case, the Knight shift is proportional to the density of states at the Fermi surface as is the interplane conductivity. In the spin-charge separation picture, since the holons cannot tunnel by themselves, spinons are required to transport charge between planes [25]. The conductivity is thus proportional to the spinon density of states.

The absence of a pseudogap in the fully doped material can be understood in terms of a phase diagram proposed for the $t$-$J$ model [6–9], shown in Fig. 4. At low doping, the normal state is the spin-pseudogap phase and the superconductivity occurs through a Bose condensation of holons along the solid line. At some higher doping level the pair-formation temperature falls below the mean field Bose-condensation temperature, and the condensation into the superconducting state is a pairing transition of spinons (the dashed line). This phase diagram is in agreement with NMR data and magnetic-neutron scattering, and it also explains our data. The fully doped material is close to the crossing point of the two lines and the system enters the superconducting state directly, without the formation of the spin-gap phase.

There are several open questions. One is the nature of the superconducting state in the reduced-oxygen case. Our spectra for the fully doped crystals show evidence of low-lying states, both the presence of conductivity at low frequency and the temperature dependence [26,27]. This is consistent with either a conventional $d$-wave superconductor or $d$-wave pairing of spinons [6], although from our data we cannot rule out a gap below 100 cm$^{-1}$. In the oxygen-reduced samples there appears to be no gap structure in the superconducting state other than the 200 $\text{cm}^{-1}$ pseudogap, and were it not for the large changes in $\epsilon_1$, one could not tell that the material had become superconducting. A plot of the spectral weight between 50 and 800 $\text{cm}^{-1}$ shows a steady decrease through the transition in parallel with the low-frequency conductivity and the Knight shift. The only sign of superconductivity is the destination of this spectral weight: while above $T_c$ the spectral weight appears to go frequencies above our region of observation, below $T_c$ it goes to the condensate. This behavior is suggestive of a Bose condensation rather than a normal condensation, where large changes take place in the density of states near the Fermi surface.

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