Infrared Probe of Transition from Superconductor to Nonmetal in $YBa_2(Cu_{1-x}Zn_x)_4O_8$

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(Received 8 April 1997)

We report on a study of the optical conductivity of single crystals of the high-T_c superconductor $YBa_2Cu_4O_8$ in which superconductivity is suppressed by random substitution of Cu with Zn. The a-axis infrared spectrum, which is a direct measure of the charge dynamics in the CuO_2 planes, is dominated by a bound state at ≈ 120 cm^{-1}. This indicates that the low-energy electronic states are on the verge of localization driven by the Zn impurities. [S0031-9007(98)07061-6]

PACS numbers: 74.25.Gz, 74.25.Nf

The interplay and competition between Anderson localization and superconductivity in disordered superconductors is a subject of continued interest [1–3]. Transport and tunneling experiments have thrown light on some generic trends in the degradation of superconductivity in a variety of disordered substances [2]. However, not much is known about the *dynamic* properties of systems in which defects suppress superconductivity. In order to explore the dynamic behavior of a disordered superconductor we use infrared spectroscopy on $YBa_2Cu_4O_8$ (Y124) cuprate high-T_c material in which up to 3.5% of Cu atoms were substituted with Zn. This allowed us to probe the evolution with disorder of the superfluid density as well as of the characteristic energy scales in the system.

Among the high-T_c cuprates the $YBa_2Cu_4O_8$ system is special in many respects. Most notably, Y124 is a *stoichiometric* compound unlike the majority of cuprates. This is important for the study of impurity effects since pure crystals of this material (those without substitution of Zn) are presumably better ordered than most other cuprates. Also, Y124 crystals are *naturally untwinned*, which allows one to probe the genuine response of the CuO_2 planes with light polarized in the "a" direction, normal to the double chains.

We obtained the complex conductivity $\sigma_1(\omega) + i\sigma_2(\omega)$ from a Kramers-Kronig analysis of the reflectance measured over a broad energy range (40–20 000 cm^{-1}) in polarized light. As a high frequency extrapolation we used ellipsometry data [4]. Single crystals of $YBa_2(Cu_{1-x}Zn_x)_4O_8$ were grown under high pressure of oxygen. The Zn content of the single crystals was determined using microprobe analysis. The pure sample had T_{c0} of 82 K. With increasing Zn content T_c was suppressed and vanished in the sample with $x = 0.035$. Structural studies performed on the closely related $YBa_2Cu_3O_y$ (Y123) compounds demonstrate that Zn preferentially occupies Cu sites in the CuO_2 planes [5].

In Fig. 1 we plot the real part of the in-plane conductivity $\sigma_a(\omega)$ for the crystals with $x = 0$, 0.007, 0.014, and 0.035. The insets display raw reflectance data in far infrared. The $\sigma_a(\omega)$ spectra at $T = 300$ K are similar in all samples: the conductivity shows metallic behavior (a broad peak centered at $\omega = 0$). However, the falloff of the $\sigma_a(\omega)$ with increasing ω is slower than is expected within a simple Drude model [6,7]. As the temperature is reduced, the pure sample behaves in a fashion typical of other cuprates: the width of the Drude-like feature narrows so that the dc conductivity σ_{dc} is enhanced [8,9].

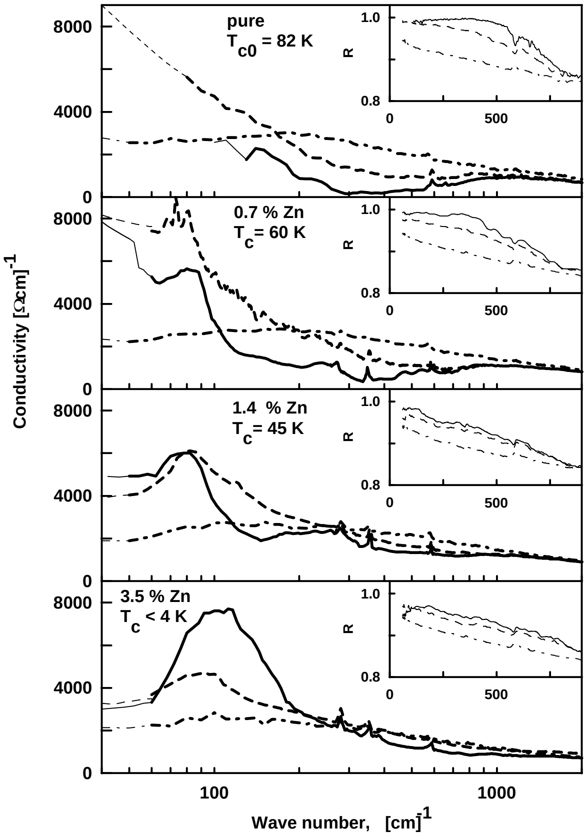

FIG. 1. The real part of the optical conductivity along the a axis in $YBa_2(Cu_{1-x}Zn_x)_4O_8$. Dash dotted lines—300 K spectra; dashed lines—spectra at $T \simeq T_c$; solid lines—10 K spectra. Nonsuperconducting crystal: dash dotted line—300 K; dashed line—75 K, solid line—10 K.

At frequencies $\omega > 300\ \mathrm{cm}^{-1}$ the low-temperature behavior of the conductivity in both pure and in Zn-substituted crystals is nearly the same. However, distinctions become prominent at lower energies, where the Drude peak centered at $\omega = 0$ in the pure crystal changes into a peak positioned at *finite* frequency in disordered samples. In the crystal with $x = 0.007$ the Drude-like response still persists, and the peak at finite frequency produces only a weak feature on top of the Drude background. At higher concentrations of Zn the peak acquires progressively more of the spectral weight and its center frequency shifts from 70 to 120 cm^{-1}. The $x = 0.035$ crystal with vanishing T_c still remains a conductor (not an insulator) since $\sigma_1(\omega \rightarrow 0)$ extrapolates to *finite* value at all T. However, the low temperature spectra shown in the bottom frame of Fig. 1 do not even remotely resemble those of metals.

A peak in the $\sigma_1(\omega)$ centered at finite frequency is characteristic of the response of *bound carriers,* whereas the conductivity for free electrons is a Lorentzian centered at $\omega = 0$. Signatures of a nonmetallic response are also visible in the raw reflectance data: in disordered samples the low-frequency reflectance shows a downturn at low energies which corresponds to the peak in the conductivity. The results displayed in Fig. 1 suggest that Zn substitution induces a transition of Y124 crystal from superconductor to a nonmetal but not to an insulator.

The spectral weight of a peak in Fig. 1 develops at the expense of "free-carrier" excitation at $\omega = 0$. The total infrared spectral weight is not diminished by the Zn substitution. This can be seen from the integration of the conductivity spectra up to 1 eV, which yields the effective spectral weight $N_{\mathrm{eff}} = \frac{120}{\pi} \int_0^{1\ \mathrm{eV}} d\omega\, \sigma_a(\omega)$. The magnitude of $\sqrt{N_{\mathrm{eff}}}$ which has the dimensions of frequency, is the same (16 000 cm^{-1}) within 12% in all the samples studied. Since the peak in the conductivity is brought on by disorder and its spectral weight emerges from the Drude-like feature seen in the clean crystals, it is reasonable to attribute this bound state to the response of *localized carriers* produced by random substitution of Cu with Zn. Indeed, a finite frequency peak is a generic feature of disordered conductors at the verge of the metal-insulator transition [10]. If we choose the position of the peak ω_{peak} to characterize the energy scale associated with localization in Zn-substituted Y124, then this scale E_c does not exceed 120 cm^{-1}.

The finite frequency peak in the *ab*-plane spectra is a feature seen in many cuprates which are intrinsically disordered including $\mathrm{Pb_2Sr_2(Y/Ca)Cu_3O_{8+\delta}}$ [11], $\mathrm{Tl_2Ba_2CuO_{6+d}}$ [12], and $\mathrm{Bi_2Sr_{2-x}La_xCuO_6}$ [13]. The conductivity peak was also seen in the response of a high-purity $\mathrm{YBa_2Cu_3O_{6.95}}$ single crystal after low energy $\mathrm{He^+}$ ion irradiation [14]. However, the latter study was performed on twinned samples; therefore it was not possible to conclude unambiguously that the peak was associated with the properties of the $\mathrm{CuO_2}$ planes and not with one-dimensional Cu-O chains. With our untwinned samples, we are able to attribute the peak to the response of the $\mathrm{CuO_2}$ planes, deliberately disordered by Zn.

The bound state induced by disorder in high-T_c superconductors does not seem to lead to activated behavior of the dc conductivity. Crystals with $x = 0.7\%$ and $x = 1.4\%$ of Zn still show an enhancement of the low-temperature conductivity in the limit of $\omega \rightarrow 0$; the data for the $x = 3.5\%$ nonsuperconducting sample indicate possible suppression $\sigma_a(\omega \rightarrow 0)$ but only at $T < 90$ K. This is consistent with the studies of resistivity in disordered samples. Ion-damaged thin films or crystals with substitutions of Cu with impurity atoms usually show metallic behavior until some critical concentration of defects when superconductivity is completely suppressed. Intrinsically disordered materials mentioned above also reveal metallic resistivity despite the peak observed in the spectra of $\sigma(\omega)$ in infrared frequencies. The coexistence of a disorder-induced bound state in the spectra of $\sigma(\omega)$ with a positive (metallic) $\rho(T)$ slope, as seen here, indicates that localization affects only a certain fraction of the electronic states, whereas the rest preserve extended character. While we are not aware of any similar results obtained for doped semiconductors, a similar effect is seen for the conductivity along the Cu-O chain direction (b axis) in Y123 crystals. If Cu-O chains are disordered, they give little contribution to the dc conductivity while the spectra of $\sigma_1(\omega)$ show a peak at finite energy [8,15]. Nevertheless, the b-axis resistivity shows metallic slope in the crystals both with disordered and perfectly ordered chains.

Another remarkable feature of the crossover to nonmetallic regime in Y124 system with Zn substitution is the low characteristic energy $E_c \simeq 120\ \mathrm{cm}^{-1} = 15$ meV, much smaller than a crude estimate of the band width $D \simeq 1$ eV. The conventional picture of Anderson localization implies that electronic sates in the band tails are localized first. Therefore in a simple metal with a half-filled band one expects E_c to be of the order of D. This is not corroborated by the data in Fig. 1, which indicate that in Y124 $E_c \ll D$. Furthermore, the general trends observed through transport measurements of strongly disordered cuprates reveal a similar small energy scale. Resistivity (even when measured in strongly disordered, nonsuperconducting samples) usually shows "metallic" ($d\rho_{ab}/dT > 0$) slope at high temperatures with a crossover to negative (nonmetallic) slope only at $T < 80$–120 K [3,16].

In considering possible origins of the anomalously low energy scale associated with the nonmetallic response in disordered Y124, one may recall that in doped Mott-Hubbard insulators the Fermi energy E_F is located close to the top of the nearly filled band where the electronic states are most vulnerable to localization. A consequence of this electronic structure is that the metal-insulator transition does not require localization of the whole band (as in ordinary metals), and therefore E_c can be significantly lower than D. Thus, localization trends are expected to be more pronounced in the *underdoped cuprates* including Y124 and other lightly doped Mott insulators. This picture implies that it should be difficult or impossible to initiate localization in overdoped cuprates—those in which E_F is approaching the middle of the band. Recent analysis of disorder and doping effects in $YBa_2(Cu_{1-x}Zn_x)_3O_y$ and $La_{2-z}Sr_zCu_{1-x}Zn_xO_4$ [16] is consistent with the proposed picture. Indeed, it was observed that significantly higher impurity concentrations were required to initiate a crossover to nonmetallic behavior of the resistivity in the samples with higher carrier density than in their counterparts with a reduced number of holes. Remarkably, *overdoped* $La_{1.8}Sr_{0.2}Cu_{1-x}Zn_xO_4$ crystals show metallic resistivity at all temperatures for x up to 0.04 whereas in *underdoped* $YBa_2(Cu_{1-x}Zn_x)_3O_{6.63}$ a similar concentration of Zn results in a negative slope of $d\rho/dT$ [17].

One can suggest alternative interpretations of the bound state in the conductivity of disordered Y124. It has been argued that the quasiparticle description is not appropriate for cuprates and that electronic conductivity is primarily due to collective excitations [18]. According to this school of thought, a Drude-like feature in the response of clean crystal should be viewed as a collective mode. In spin- and charge-density-wave systems where collective transport is indeed observed impurities are capable of pinning these collective modes [19]. The response of a pinned mode centers at finite frequency and is qualitatively consistent with the behavior of Y124 with Zn substitution.

The major feature of the superconducting state response of Y124 is that $\sigma_a(\omega)$ remains finite in all crystals, down to the lowest frequencies. On the contrary, conventional superconductors show $\sigma_1(\omega) = 0$ at $T \ll T_c$ for ω less than the magnitude of the energy gap 2Δ. A residual conductivity is observed in all high-T_c materials for which accurate far-infrared data exist [20]. This is consistent with the view that only a fraction of the normal state spectral weight condenses into superfluid at $T < T_c$. With increasing concentration of Zn the fraction of the normal fluid ρ_n at $T = 10$ K increases, while the superfluid density ρ_s determined from model-independent sum rule as

$$\rho_s = \frac{120}{\pi}\int_0^\infty d\omega[\sigma_a(\omega, T \simeq T_c) - \sigma_a(\omega, T = 10\text{ K})] \tag{1}$$

is suppressed. This leaves the total plasma frequency $\omega_p^2 = \rho_s^2 + \rho_n^2$ nearly unchanged and shows that Zn causes a pair-breaking effect in the CuO_2 planes but does not change the carrier density [21].

In Fig. 2 (left panel) we show the T_c as a function of ρ_s in the CuO_2 planes. The data for clean Y123 and Y124 crystals are in a reasonable agreement with the linear $T_c \propto \rho_s$ plot observed in a broad variety of unconventional superconductors [24]. All Y124 samples with Zn substitution show a strong deviation from the universal plot [24]. In these disordered materials ρ_s decreases faster than T_c. Similar deviations from the universal plot are found for other disordered cuprates [11,12,14] which *all* reveal a localization peak in the $\sigma_1(\omega)$.

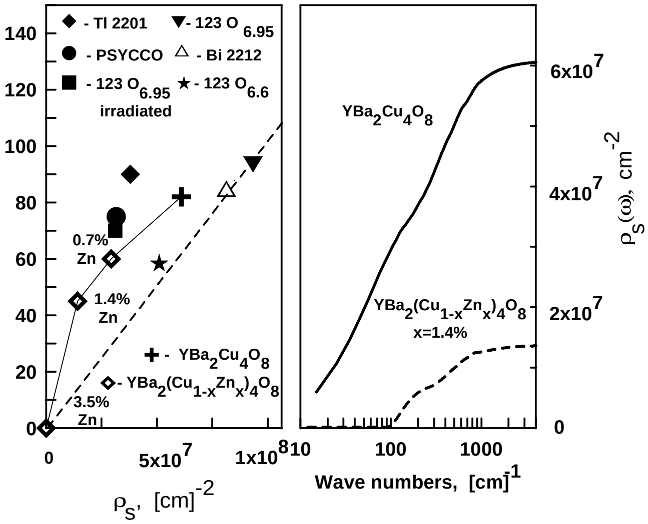

FIG. 2. Left panel: T_c as a function of the superfluid density in the CuO_2 planes determined by infrared spectroscopy. Pure $YBa_2Cu_4O_8$ (Ref. [23]); $YBa_2Cu_3O_{6.95}$ (Ref. [23]); $Bi_2Sr_2CaCu_2O_8$ (Ref. [32]); $YBa_2Cu_3O_{6.6}$ (Ref. [9]); $Tl_2Ba_2CuO_{6+\delta}$ (Ref. [12]); (Ref. [11]); $YBa_2Cu_3O_{6.95}$ (Ref. [14]). Right panel: The frequency dependent spectral weight of the superfluid $\rho_s(\omega)$ determined as described in the text.

A cursory inspection of the conductivity spectra in Fig. 1 suggests that the suppression of the ρ_s is directly related to the bound state induced by disorder. We note that according to Eq. (1) ρ_s is given by the "missing area" in $\sigma_1(\omega)$. In a pure crystal the difference between conductivities obtained above and below T_c is largest at low frequencies and at least 50% of the ρ_s is accumulated from $\omega < 150\text{ cm}^{-1}$. This is illustrated in the right panel of Fig. 2 where we plot the spectra of $\rho_s(\omega) = \frac{120}{\pi}\int_0^\omega d\Omega[\sigma_a(\Omega, T \simeq T_c) - \sigma_a(\Omega, 10\text{ K})]$. In the crystal with $x = 0.014$ the low-energy response is altered and the main feature in the low-temperature spectra is a localization peak. In this sample the conductivity spectra measured above and below T_c are nearly the same for $\omega < \omega_{\text{peak}}$, leading to a vanishing $\rho_s(\omega)$ for $\omega < \omega_{\text{peak}}$. Thus the spectral weight confined within the energy scale related to the localization problem in Zn-substituted Y124 appears to be *excluded* from condensation leading to a horizontal offset of $\rho_s(\omega)$. This suppression of superfluid density should be contrasted with what happens in conventional dirty superconductors where the largest fraction of ρ_s still originates from the lowest frequencies.

There are several possible ways in which the precursor of carrier localization may affect the T_c of disordered samples. From Figs. 1 and 2 one can conclude that the spectral weight corrupted by the localization peak in $\sigma_1(\omega)$ reduces the number of states near E_F from which the superconducting condensate can emerge. Arguments based on the role of fluctuations in low-dimensional materials suggest that in systems with low superfluid density, T_c is in fact determined by the magnitude of ρ_s [25]. The superfluid density also defines the T_c of a Bose-Einstein condensate [24]. Both of these hypotheses would lead to the decline of T_c with decreasing ρ_s.

Another possible cause of the T_c degradation may be related to the significant decrease of the low-frequency conductivity (Fig. 1) in disordered samples. Since poorly mobile carriers are nearly confined within a given spatial region, their interactions with other electrons are enhanced, leading to a decrease of the density of states in the vicinity of the Fermi level $N(0)$ [26]. This effect is in accord with tunneling experiments for disordered films of elemental superconductors [27]. Diminished far-infrared conductivity of Zn-doped Y124 (Fig. 1) is also consistent with the reduction of $N(0)$. However, the details of the evolution of the density of states with disorder are yet to be seen, because $\sigma_a(\omega \rightarrow 0)$ in Fig. 1 is still far from complete localization, a regime where one finds a direct correspondence between the fine structure of the density of states and the features of $\sigma_1(\omega)$.

Finally, we note that superconductors with a d-wave order parameter are expected to show a number of special properties as far as localization is concerned [28,29]. In a d-wave system the density of states remains finite even at $T < T_c$, and dilute concentrations of impurities may cause quasiparticle localization [28]. Resonant scattering by impurities in a d-wave scenario [30] as well as d-wave extensions of the Shiba-Rusinov resonance [31] are models that give in-gap optical excitations. These ideas are qualitatively consistent with our experiments, although signatures of localization behavior seem to be already present in the normal state.

In conclusion, we explored charge dynamics along the CuO_2 planes in disordered Y124 crystals. The data reveal a connection between quasiparticles localization and suppression of the superfluid density that is qualitatively different from the conventional dirty-limit scenario. We suggest that localization may be in part responsible for the degradation of T_c in disordered underdoped cuprates.

This work is supported by NSERC (T.T.). Work at UCSD is supported by The Alfred P. Sloan Foundation, NSF Grant No. DMR-9704299, Research Corporation, and a subcontract from Brookhaven National Laboratory. Work at NIU is supported by the NSF Science and Technology Center for Superconductivity under Grant No. DMR 91-20000.

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[17] Fukuzumi *et al.* [16] assigned the differences in the behavior of disordered cuprates in under- and overdoped regimes to the suppression of the anisotropy and the restoration of three-dimensional character in the overdoped part of the phase diagram. However, overdoped $La_{1.8}Sr_{0.2}Cu_{1-x}Zn_xO_4$ and underdoped $YBa_2(Cu_{1-x}Zn_x)_3O_{6.63}$ show *similar* anisotropy between inplane and interplane properties. Nevertheless, Zn substitution leads to profoundly different consequences for the T dependence of the resistivity ($d\rho/dT$ is negative in the latter, whereas the former sustains “metallic” dependence). Therefore it appears that reduced dimensionality is not a decisive factor in determining the properties of disordered cuprates.

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