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Anomalous behavior of the complex conductivity of $Y_{1-x}Pr_xBa_2Cu_3O_7$ observed with THz spectroscopy

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We have measured the complex conductivity of $Y_{1-x}Pr_xBa_2Cu_3O_7$ single-crystal thin films using coherent THz spectroscopy. We obtain directly the London penetration depth, the plasma frequency ω_p, and the quasiparticle scattering rate $1/\tau$. We find that $1/\tau$ drops rapidly with temperature below T_c in *all* the superconducting samples, implying that this is a *signature* of high-T_c superconductivity. ω_p decreases with increasing x, indicating that Pr takes mobile carriers from the CuO planes. Both the THz and dc conductivity yield evidence for the opening of a spin gap *above* T_c.

The large body of vital spectroscopic data on the high-T_c superconducting compound $YBa_2Cu_3O_{7-\delta}$ (YBCO) measured in the far infrared (FIR) as well as the GHz region has revealed many interesting features. Among them are: the presence of one[1] or more[2] energy gaps in the superconducting state, a temperature-dependent penetration depth that is indicative of d-wave pairing,[3] and a quasiparticle scattering rate which is proportional to frequency in the normal state[1] and which drops by four orders of magnitude at T_c.[4]

The technique of THz-time-domain spectroscopy *bridges* the gap between the FIR and the GHz regime. THz measurements of YBCO display a peak in the temperature dependence of σ_1 below T_c, which appears to be related to a temperature-dependent scattering rate $1/\tau$ rather than to BCS coherence effects.[5] Other experiments using the same technique have revealed that the penetration depth λ_L, has a temperature dependence inconsistent with BCS theory.[6]

Here we report results of a THz investigation into the $Y_{1-x}Pr_xBa_2Cu_3O_7$ (YPrBCO) system. These measurements are of great interest because samples covering a wide range of critical temperatures can be obtained simply by varying the Y/Pr ratio.[7] Also, because YPrBCO is fully stoichiometric in the oxygen content, it is more homogeneous than oxygen-depleted YBCO and does not change from an orthorhombic to a tetragonal lattice upon decreasing T_c. Several mechanisms have been proposed for the T_c suppression, including magnetic pair breaking[8] and depletion of holes in the CuO_2 planes.[9]

Recently, the opening of a spin gap at temperatures above T_c in oxygen-deficient YBCO has been deduced from various experiments, e.g., dc resistivity and Hall coefficient,[10,11] neutron scattering,[12] and NMR measurements.[13] However, until now only few electromagnetic measurements on underdoped YBCO have been linked to the presence of a spin gap.[1,14] In this paper, we report evidence for a spin gap obtained from measurements *both* at dc *and* at THz frequencies in YPrBCO, which is consistent with Pr depleting holes from the CuO planes.[9]

Our spectroscopic technique involves a coherent time-domain measurement of a ps microwave impulse $E(t)$ transmitted through the sample.[15] A Fourier transform yields the complex transmission spectrum $t(\omega)$ and the complex conductivity $\sigma(\omega)$, without the use of Kramers-Kronig analysis. The London penetration depth $\lambda_L(T)$, the plasma frequency ω_p in the clean limit, and the scattering time $\tau(T)$ are obtained with the aid of a two-fluid model.

The microwave source is a biased 30 μm transmitting antenna fabricated on low-temperature-grown GaAs, triggered with $\sim$100 fs optical pulses from a colliding-pulse mode-locked dye laser. The emitted microwave pulses have spectral components spanning the 0.1–1.0 THz spectral region which is difficult to access with conventional electronics.[16] The receiver is a 30 μm antenna, fabricated on ion-implanted silicon-on-sapphire and gated with a second pulse from the laser. The receiver photocurrent is proportional to the incident microwave field.

We investigated five YPrBCO samples having Pr composition x = 0.0, 0.2, 0.3, 0.4, and 1.0. The films are grown by pulsed laser deposition[17] onto $NdGaO_3$ substrates. The film thicknesses are approximately 150 nm (Table I). $NdGaO_3$ is the ideal substrate because it remains transparent and nondispersive over the entire spectral bandwidth of our pulses, as well as over the entire range of temperatures investigated here. The excellent lattice match of $NdGaO_3$ to YPrBCO is a prerequisite for a low density of misfit dislocations on the film-substrate interfaces. The substrates have a (001) orientation, yielding $\hat{c}$-oriented, twinned films. The critical temperatures T_c^{dc} (Table I) are determined from the temperature-dependent resistivity, as measured with a four-point probe.

TABLE I. Film thickness d, London penetration depth $\lambda_L(0)$, plasma frequency ω_p, dc-transition temperature T_c^{dc}, and ac-transition temperature T_c^{ac} for $Y_{1-x}Pr_xBa_2Cu_3O_7$ with x= 0, 0.2, 0.3, and 0.4.

x	d (nm)	$\lambda_L(0)$ (nm)	ω_p (cm^{-1})	T_c^{dc} (K) (4-point probe)	T_c^{ac} (K) (microwave)
0.0	155	170 ± 10	9500	93	92
0.2	134	350 ± 10	4560	68	72
0.3	170	375 ± 7	4244	53	59
0.4	170	590 ± 15	2693	40	41

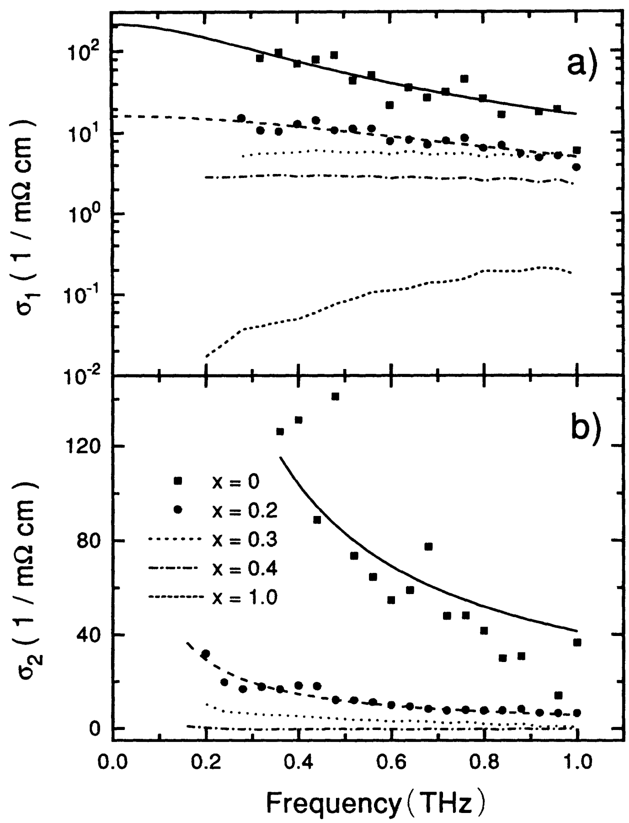

FIG. 1. (a) $\sigma_1(\nu)$ and (b) $\sigma_2(\nu)$ for $Y_{1-x}Pr_xBa_2Cu_3O_7$ at $T=50$ K. The solid and dashed uppermost curves are fits (a) to a Drude form, and (b) to $1/\omega$ (see text).

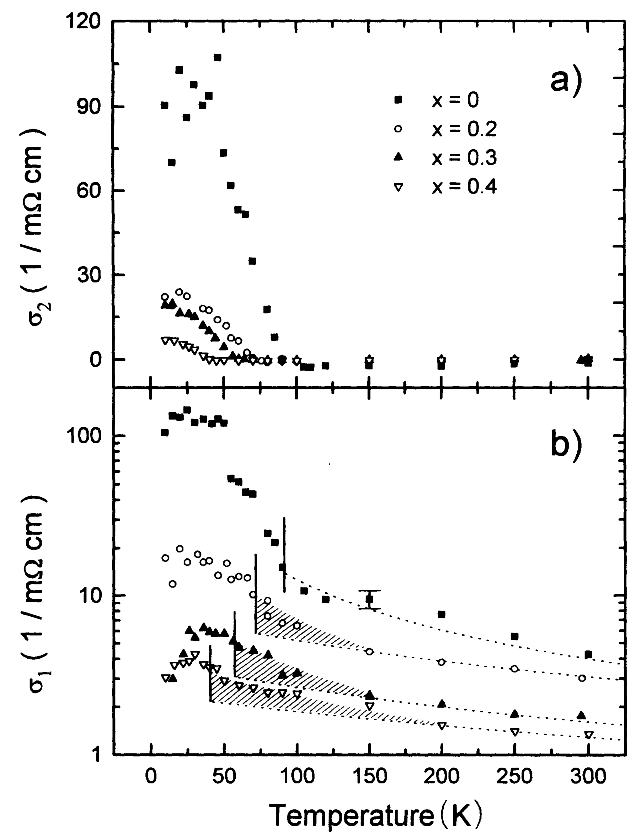

FIG. 2. (a) $\sigma_2(T)$ and (b) $\sigma_1(T)$ for $Y_{1-x}Pr_xBa_2Cu_3O_7$ at 480 GHz. The dashed curves in (b) show $1/\rho^*$ (see text). The vertical lines indicate T_c^{ac}. For clarity, the data for $x=0.3$ in (b) have been multiplied by 1.5. The error bars for the alloys with $x>0$ are comparable to the symbol size.

The transition width (90–10%) varied from 0.3 K for $x=0$ to 3 K for $x=0.4$. X-ray diffraction showed the presence of sharp $(00l)$ peaks only; no traces of other orientations and/or phases could be detected. Critical currents of samples with $x=0$ are typically 6×10^7 A/cm^2 at 4.2 K and $>10^6$ A/cm^2 at 77 K.

To calculate the conductivity, we make use of the multiple reflection formula for the field transmitted through a layer of (complex) index n_2, thickness d, bounded by media of index n_1 and n_3:

$$t(\omega)=\frac{t_{12}t_{23}\exp[in_2(\omega/c)d]}{1+r_{12}r_{23}\exp[2in_2(\omega/c)d]}\,, \qquad (1)$$

where $t_{ij}=2n_i/(n_i+n_j)$ is the field transmission coefficient at the ijth interface, and $r_{ij}=(n_i-n_j)/(n_i+n_j)$ is the field reflection coefficient. In our geometry, n_1 represents vacuum, $n_2=\sqrt{1+i\sigma(\omega)/(\epsilon_0\omega)}$ is the index of the superconducting layer, and n_3 is the measured index of the substrate. As $n_2(\omega/c)d\ll1$, and $n_2\gg n_3>1$ in our samples, Eq. (1) reduces to

$$t(\omega)=\frac{1+n_3}{1+n_3+Z_0\sigma(\omega)d}\,, \qquad (2)$$

where Z_0 is the impedance of free space.

The effect of varying Pr content x (hereafter [Pr]) on the conductivity spectra $\sigma(\omega)$ at $T=50$ K is similar to the effect of varying the temperature for a given alloy (Fig. 1). The addition of Pr has at least two interrelated effects: (a) The suppression of T_c changes the partitioning between normal and superconducting carriers. (b) The total number of carriers N (or their mobility) may be reduced. To the extent that the superconducting carriers make the largest contribution to σ_2, both factors (a) and (b) lead one to expect that at a given temperature, pure YBCO would have the largest σ_2, and it does. Samples with 20% and 30% Pr have smaller values of σ_2, since they are only slightly below their T_c. The sample with 40% Pr has $\sigma_2\approx0$ because it is above T_c at 50 K.

Only normal carriers contribute to σ_1 for $\omega\neq0$, but now factors (a) and (b) compete. At 50 K, σ_1 decreases with [Pr], therefore the effect of a reduction in N dominates the effect of the shift in T_c which increases the fraction of normal carriers. The data for pure YBCO and 20% Pr have been fit to a frequency-dependent Drude form, and one can see that $1/\tau$ lies in our spectral range. For 30% and 40% Pr, we observe frequency-independent σ_1 and can conclude that $1/\tau$ is large compared to 1 THz. Pure PrBCO is a dielectric at 50 K, as seen by a conductivity proportional to frequency, i.e., a dielectric constant independent of frequency.

Examining σ_2 at a fixed frequency, e.g., 480 GHz (Fig. 2), we see that it is close to zero at high temperature, but rises sharply at the onset of superconductivity, thus providing

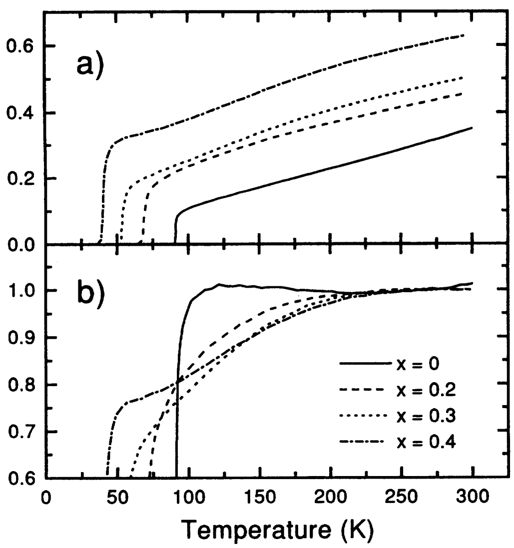

FIG. 3. (a) The dc resistivity $\rho(T)$ and (b) the normalized dc resistivity $\rho^*(T)$ for $Y_{1-x}Pr_xBa_2Cu_3O_7$.

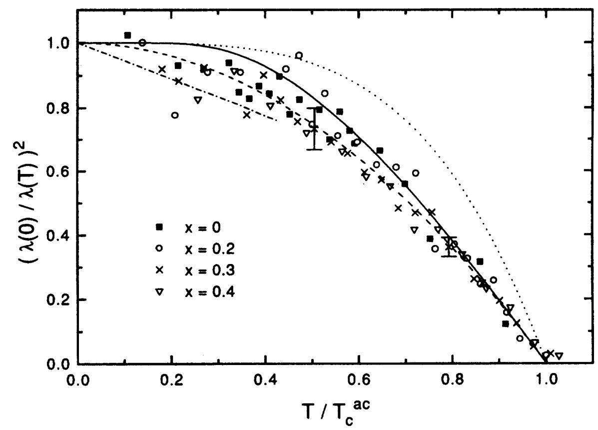

FIG. 4. Normalized London penetration depth $\lambda_L(T/T_c^{ac})$ for $Y_{1-x}Pr_xBa_2Cu_3O_7$. Also shown are curves corresponding to the predictions of BCS theory (solid line), as well as to the functional form (4) for $\alpha=1$ (dash-dotted line), 2 (dashed line), and 4 (dotted line).

an independent ac measurement of T_c (Table I). In all of the superconducting alloys, below T_c, σ_1 displays a peak, which has been previously observed only in fully oxygenated YBCO using microwave techniques[5,18] as well as by measuring the thermal conductivity.[19] It has been attributed to a sharp rise in the scattering time τ of normal carriers below T_c offsetting the decrease in the fraction of normal carriers, although coherence effects remain a possibility. For pure YBCO, the peak value is about 20 times higher than $\sigma_1(100\text{ K})$. With increasing [Pr] the peak height in σ_1 decreases but the temperature corresponding to the peak position does not shift significantly.

The normal-state behavior of our samples is particularly interesting because *underdoped* materials such as (124)YBCO and oxygen-deprived (123)YBCO undergo a phase transition associated with the opening of a spin gap at a temperature $T_D > T_c$. Evidence for the presence of a spin gap has been seen in neutron scattering,[12,20] dc resistivity measurements,[10,11] and FIR reflectivity.[14] Recent experimental[21] and theoretical[9] work confirm that YPrBCO alloys are also underdoped, i.e., superconductivity is suppressed, because holes are removed from the CuO_2 planes.

If the normal carriers couple strongly to spin fluctuations, the opening of a spin gap should be accompanied by an *increase* in the scattering time τ, giving rise to an *enhancement* in σ_1 below T_D for $\omega < 1/\tau$. For pure (optimally doped) YBCO, at 480 GHz, σ_1 shows only a single transition at T_c [Fig. 2(b)]. For the (underdoped) alloys, σ_1 has two transitions, one at T_c, the other at a higher temperature which increases with [Pr]. To accentuate the two transitions, Fig. 2(b) is shaded in the region bounded by T_c, the experimental curve, and a dashed line representing $1/(\alpha+\beta T)$ behavior.

A second, higher transition temperature in the underdoped samples is also observed in the dc resistivity [Fig. 3(a)]. The transition is manifested as a deviation from a linear T dependence. To show the deviation more clearly, the resistivity is first fit to a line $\rho = \alpha + \beta T$ between 250 and 300 K, and then the experimental values are normalized to the value determined by the line as $\rho^* = \rho/(\alpha+\beta T)$. The normalized resistivity [Fig. 3(b)] of the YPrBCO alloys shows a transition occurring at a temperature above T_c similar to that which has been observed in underdoped YBCO, and connected to the opening of a spin gap.[10,11]

For the evaluation of λ_L we are using a two-fluid model of the form

$$\sigma(\omega) = \frac{\epsilon_0 \omega_p^2 \tau}{1 - i\omega\tau} x_n + \frac{1}{\mu_0 \lambda_L^2}\left(-\pi\delta(\omega) + \frac{i}{\omega}\right) x_s, \qquad (3)$$

where ω_p is the plasma frequency, and x_n and x_s are the fractions of normal and superconducting carriers, given by $x_n + x_s = 1$. We derive the penetration depth from a fit to Eq. (3). In our frequency range, we can ignore the Drude contribution to σ_2 for temperatures which are more than a degree below T_c. As $x_n = 0$ at $T=0$ in the two-fluid scenario, we have $x_s = [\lambda_L(0)/\lambda_L(T)]^2$. Shown in Fig. 4 is the measured $[\lambda_L(0)/\lambda_L(T)]^2$ vs T/T_c^{ac} for all samples. Also plotted are theoretical curves from weak-coupling BCS theory[22] and the functional form

$$[\lambda_L(0)/\lambda_L(T)]^2 = 1 - (T/T_c)^\alpha. \qquad (4)$$

Power-law behavior in the dependence of λ_L on T for $T \to 0$ is one signature of "unconventional superconductivity," i.e., nodes in the energy gap in k space.[23] Our data are intermediate between BCS theory and $\alpha=2$, which is the exponent predicted for d-wave pairing with impurity scattering.[24] Microwave measurements at lower frequencies have indicated both $\alpha=2$ (Ref. 4) and $\alpha=1$ (in the $T\to 0$ limit) corresponding to d-wave pairing in very high-quality samples.[3,25] The Gorter-Casimir two-fluid model ($\alpha=4$),[26] as well as d-wave pairing ($\alpha=1$) are clearly inconsistent with our data.

$\lambda_L(0)$ is obtained by extrapolating $\lambda_L(T)$ to $T=0$ using a quadratic regression (Table I). Our value for pure YBCO, 170 ± 10 nm, is close to the 145 nm value typical for good samples.[4] $\lambda_L(0)$ increases with increasing [Pr] as the samples become less superconducting.

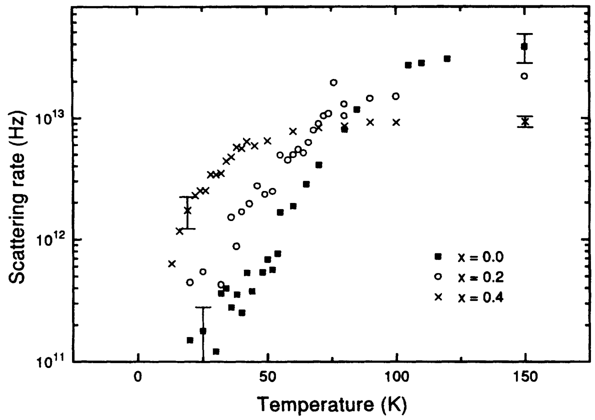

FIG. 5. Quasiparticle scattering rate $1/\tau(T)$ for $Y_{1-x}Pr_xBa_2Cu_3O_7$ at 480 GHz.

The plasma frequency ω_p (Table I) is determined with the relation $\omega_p = c/\lambda_L(0)$, which is valid in the clean limit, provided all carriers are superconducting at $T=0$. The clean limit assumption becomes less valid upon substitution of Pr, therefore the values for the alloys are only estimates. Our value of 9500 cm^{-1} in pure YBCO is close to the 12 000 cm^{-1} value indicative of good sample quality.[2]

The quasiparticle scattering rate $1/\tau$ is calculated by fitting Eq. (3) to the data for σ_1 and using, for x_n, the relation $x_n = 1 - x_s = 1 - [\lambda_L(0)/\lambda_L(T)]^2$. We find that $1/\tau$ decreases slowly with decreasing temperature until $T \approx T_c$, after which it decreases exponentially rapidly (Fig. 5), possibly reflecting the opening up of a gap in the fluctuation spectrum. Similar behavior has been reported in YBCO samples.[4] The scattering rate $1/\tau$ reveals an exponential decay below T_c by more than two orders of magnitude for all samples with different [Pr].[27] Thus we are led to conclude that this behavior is a universal feature of high-T_c superconductivity.

For $T > T_c$, we find the surprising result that $1/\tau$ decreases with [Pr] implying that alloy scattering plays a negligible role, and that depletion of carriers in the CuO_2 planes dominates the scattering. It should be noted, however, that the drop in $1/\tau$ with [Pr] may be due to an underestimate of ω_p, if the clean limit assumption breaks down for the alloys. A more precise determination of the scattering rate dependence on [Pr] above T_c is beyond the scope of this paper.

In conclusion, we have presented complex conductivity experiments in the THz range on thin films of $Y_{1-x}Pr_xBa_2Cu_3O_7$. $\sigma_1(T)$ reveals the anomalous coherence peak for all superconducting alloys. Both the conductivity in the THz region and dc resistivity measurements provide evidence for the opening of a spin gap in the excitation spectrum of the underdoped samples. $\sigma_2(\omega,T)$ yields directly the penetration depth. For the superconducting YPrBCO alloys the plasma frequency ω_p in the clean limit decreases with [Pr] above T_c due to a reduced number of carriers. The temperature-dependent quasiparticle scattering rate $1/\tau(T)$ shows an exponential drop below T_c in all the alloys. These observations fit into the picture of Pr suppressing superconductivity by reduction of the mobile carrier concentration in the superconducting CuO_2 planes.

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[27] Following O. Klein [Phys. Rev. Lett. **72**, 1390 (1994)], we cannot be certain about the exact form of $1/\tau$ near T_c, as our model, which includes no direct absorption, breaks down near T_c when the gap goes to zero. Nevertheless, our model is good outside the region right below T_c, and the magnitude of the drastic change in $1/\tau$ is still valid.