Persistence of the Superconducting Condensate Far above the Critical Temperature of $\mathrm{YBa_2(Cu,Zn)_3O_y}$ Revealed by *c*-Axis Optical Conductivity Measurements for Several Zn Concentrations and Carrier Doping Levels

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The superconductivity precursor phenomena in high temperature cuprate superconductors is studied by direct measurements of the superconducting condensate with the use of the c-axis optical conductivity of $\mathrm{YBa_2(Cu_{1-x}Zn_x)_3O_y}$ for several doping levels (p) as well as for several Zn concentrations. Both the real and imaginary parts of the optical conductivity clearly show that the superconducting carriers persist up to the high temperatures T_p that is higher than the critical temperature T_c but lower than the pseudogap temperature T^*. T_p increases with reducing doping level like T^*, but decreases with Zn substitution unlike T^*.

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Precursor superconductivity is one of the subjects that currently attracts a lot of attention in the research of high temperature superconducting cuprates [1–6]. Despite the number of reports presented so far, this problem is still controversial. One common observation is that the superconducting fluctuation regime can be described in a temperature range between T_c (superconducting critical temperature) and T^* (pseudogap temperature). However, the carrier-doping dependence and the temperature range show significant differences among the different probes. Some experiments like the Nernst effect [1], diamagnetism measurements [2] reported the superconducting fluctuation regime at temperatures as high as 3–4 T_c with a doping dependence different from that of T_c. On the other hand, microwave experiments [5] showed that the temperature range of the superconducting fluctuation is only 10–20 K above T_c with a doping dependence similar to the T_c dome.

Here we report the observation of a superconducting condensate above T_c through the c-axis optical spectra of Zn-doped $\mathrm{YBa_2Cu_3O_y}$ (YBCO) single crystals for several doping levels (p) in a wide energy range (2.5 meV–40 eV). The doping level p in YBCO varies with the oxygen concentration [7], and the maximum T_c is achieved at $p = 0.16$ (optimum doping). In the c-axis optical conductivity, we can clearly distinguish the pseudogap and the superconducting gap, while in many probes it is difficult to distinguish these two gaps. YBCO has high conductivity along the c-axis, compared to many other cuprates, which allows us to detect small changes in conductivity. Zn substitution, on the other hand, is useful to resolve the superconductivity related responses. Temperature dependent reflectivity measurements are performed on $\mathrm{YBa_2(Cu_{1-x}Zn_x)_3O_y}$ single crystals. The details regarding the samples are described in the Supplemental Material [8].

The c-axis optical conductivity is suppressed at low energies both by the pseudogap and the superconducting gap, while the direction of the spectral weight (SW) transfer is opposite in these two gaps. The lost SW is transferred to the high energy region for the pseudogap, while it is redistributed at δ-function at zero frequency for the superconducting gap. We determined the pseudogap opening temperature T^* by tracing the suppression of the low energy optical conductivity (at 20 $\mathrm{cm^{-1}}$), as shown in Fig. 1. When the temperature decreases from room temperature, the low energy optical conductivity gradually increases due to the metallic response of the system, and below T^*, it begins to decrease. The metallic behavior is weakened and the turning point—T^*—increases with underdoping. The pseudogap issue has been discussed in many experiments [9]. Our T^* values for the Zn-free samples are in good agreement with those by the other methods such as the measurements of the ^{89}Y nuclear magnetic resonance (NMR) Knight shift [10] and resistivity [11]. Moreover, as has been pointed out by many research groups [12–15], the pseudogap temperature does not change significantly with Zn substitution [see Figs. 1(b) and 1(c)].

The optical probe is also very sensitive to the superconducting carrier response. The imaginary part of the optical conductivity $[\sigma_2(\omega)]$ is directly related to the superfluid density $[4\pi\omega\sigma_2(\omega) = \omega_{ps}^2 = 4\pi n_s/m^*]$. Another way to

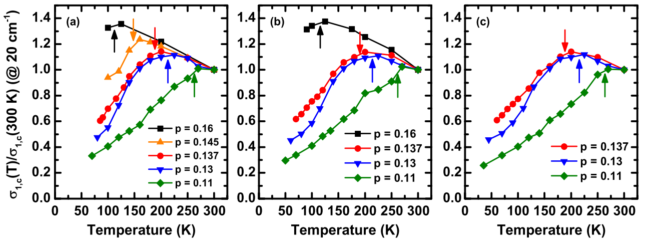

FIG. 1 (color online). T dependence of low energy optical conductivity for various p with Zn content $x = 0$ (a), $x = 0.007$ (b), and $x = 0.012$ (c). The arrows indicate the pseudogap temperature, T^*. All the values are normalized to the room temperature value.

calculate the superfluid density from optical spectra is to estimate the missing area in the real part of the optical conductivity $[\sigma_1(\omega)]$. Since we found that the spectral weight of $\sigma_1(\omega)$ is conserved below 5000 cm^{-1} in our previous study [15], the missing area was estimated from the deviation from this conserved value for each sample. In Fig. 2, we plot the temperature dependence of ω_{ps}^2 determined from the missing area in $\sigma_1(\omega)$ (red circles) and from $\sigma_2(\omega)$ (black squares) for various doping levels and Zn contents. Details of the data analysis can be found in the Supplemental Material [8]. The results of both methods are qualitatively the same: zero values at high temperatures, followed by a rapid increase at T_c due to the superconducting transition. A closer look at each figure (the insets) revealed a finite value of the superfluid densities (ω_{ps}^2) at a certain temperature higher than T_c. We name this temperature the precursor superconductivity temperature T_p. For the underdoped Zn-free sample ($p = 0.11$), this value is as high as 160 K. With decreasing temperature, ω_{ps}^2 gradually increases and the slope of increase suddenly becomes steeper at the temperature near T_c. Hereafter, we refer to this temperature as T_c'. From all the figures, we can find that the superconducting carriers persist up to much higher temperatures than T_c, although its fraction is very small (less than a few % of the total ω_{ps}^2 at $T = 0$).

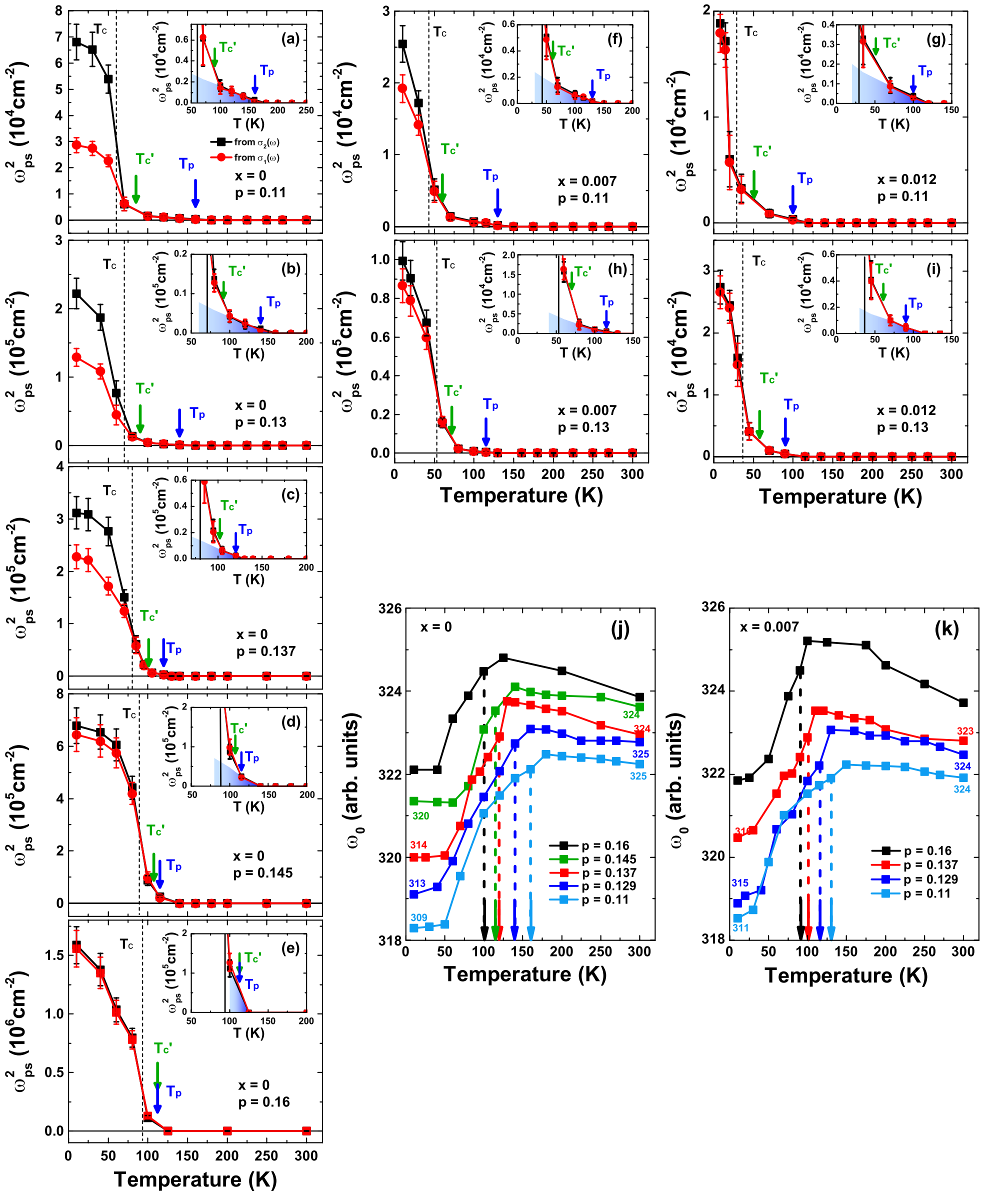

FIG. 2 (color online). Determination of the precursor superconducting state. (a)–(g) are the temperature dependences of ω_{ps}^2 obtained from the missing area in $\sigma_1(\omega)$ (red circles) and from $\sigma_2(\omega)$ (black squares). Insets are the expanded figures near T_p. Figures (a) to (e) demonstrate the doping dependent behavior for $x = 0$, while in Figs. (a), (f), and (g) and Figs. (b), (h), and (i) we can see the x dependence at $p = 0.11$ and 0.13, respectively. (j) and (k) The resonance frequencies of the oxygen bending mode for $x = 0$ and 0.007, respectively. Error bars in these figures are discussed in the Supplemental Material [8].

It is interesting that the doping dependences of T'_c and T_p are different [Figs. 2(a)–2(e)]. T'_c is always 10–20 K above T_c and, thus, follows the T_c change, whereas T_p increases with decreasing doping levels (p) and reaches much higher temperatures than T'_c. T'_c and T_p are almost merged at the optimum doping $p = 0.16$ [Fig. 2(e)]. Although these two temperature scales (T_p and T'_c) show different doping dependences, the Zn dependences are similar [Figs. 2(a), 2(f), 2(g) for $p = 0.11$ and Figs. 2(b), 2(h), 2(i) for $p = 0.13$]. Namely, as Zn content increases, both T_p and T'_c decrease just like T_c [16].

The transverse Josephson plasma (TJP) resonance mode [17] might be used as a measure of superconductivity, as well. A broad conductivity peak starts to appear weakly above T_c in the far-infrared region, and significantly grows below T_c. Meanwhile, it strongly couples with the oxygen bending mode phonon at ~320 cm^{-1}, which results in the change in the SW and the resonance frequency of this phonon mode. Therefore, by tracing the phonon frequency (ω_0) of the oxygen bending mode, we can identify the temperature at which the TJP mode starts to evolve. Dubroka *et al.* attributed the appearance of the TJP resonance mode above T_c to the precursor superconductivity effect [6]. We also plot ω_0 to estimate the onset temperature of precursor superconductivity, assuming that the TJP mode is an indication of superconductivity. From the temperature dependence of ω_0 [Figs. 2(j) and 2(k)], we can estimate the values of T_p at which ω_0 starts to decrease. In both the pure ($x = 0$) and the Zn-doped ($x = 0.007$) samples, for all the doping levels, T_p values obtained from the TJP resonance mode coincide with those estimated from $\sigma_2(\omega)$ and $\sigma_1(\omega)$. The fact that the three independent methods give the same T_p values confirms that our observation of superconductivity up to T_p is real.

We plot all the temperatures T^*, T_p, T'_c, and T_c for various doping levels and Zn contents in Fig. 3(a), where for each Zn content (x) T_c is normalized by the value at $p = 0.16$ (namely, the normalized T_c equals 1 at $p = 0.16$) and T'_c, T_p, and T^* are multiplied by the same normalization factor for each x. It turns out that T'_c and T_p, for different x samples, form a single curve, which indicates that both of these temperatures change with x, scaling with T_c, unlike the pseudogap temperatures (T^* does not change with x). The Zn dependence of T_p and T'_c gives further evidence that we really observe the superconducting signature above T_c. It is natural to consider that T'_c corresponds to a conventional superconducting fluctuation temperature described by the Ginzburg-Landau formalism [18], but T_p indicates the unusual phenomenon due to the superconductivity precursor. These systematic Zn-and doping-dependent behaviors prove that our observation of precursor superconductivity is due neither to the sample inhomogeneity nor the measurement errors.

The other new finding in the present study is that the difference of ω_{ps}^2 estimated from $\sigma_2(\omega)$ and the missing area in $\sigma_1(\omega)$ diminishes with Zn substitution. As we see in Fig. 2, for the Zn-free samples, although the temperature dependences of ω_{ps}^2 are similar, the two estimation methods give significantly different values of ω_{ps}^2 in the underdoped regime. This discrepancy has been previously pointed out [19], and attributed to the kinetic energy reduction [20]. In this scenario, not only the low energy SW but also the high energy SW in the visible region are condensed into a delta function at $\omega = 0$.

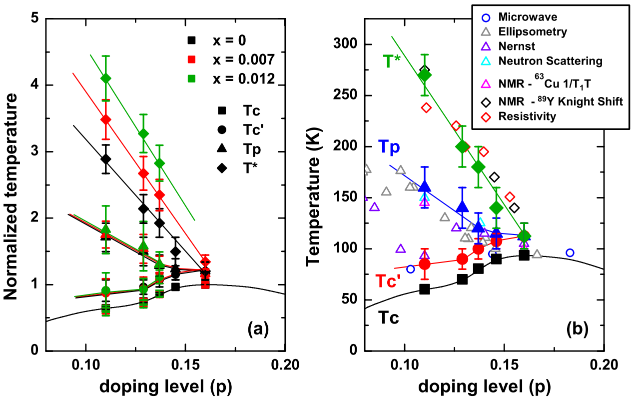

FIG. 3 (color online). Electronic phase diagram of $\mathrm{YBa_2(Cu_{1-x},Zn_x)_3O_y}$. (a) The normalized variable for T'_c (circles), T_p (triangles), and T^* (diamonds) for $x = 0$ (black symbols), $x = 0.007$ (red symbols), and $x = 0.012$ (green symbols). (b) Phase diagram of the $\mathrm{YBa_2Cu_3O_y}$ where the temperatures obtained by our measurements (solid symbols) are plotted together with the data by several other probes (Microwave [5], ellipsometry [6], the Nernst effect [28], neutron scattering [30], NMR ^{63}Cu $1/T_1T$ [31,32], NMR ^{89}Y Knight shift [10], and resistivity [11].

A similar reduction of the discrepancy in ω_{ps}^2 has been reported in the optical measurements under magnetic fields for YBCO [21]. The common effect of the magnetic field and Zn substitution is that the TJP resonance mode is suppressed in both cases. The TJP mode can be seen as a broad peak in $\sigma_1(\omega)$ below T_c, which reduces the calculated missing area [17,22]. On the other hand, the low energy $\sigma_2(\omega)$ is not affected by this mode. Therefore, we conclude that the observed difference in ω_{ps}^2 in the two methods is caused by the inappropriate estimation of the missing area, i.e., ignoring the contribution of the TJP mode to ω_{ps}^2. In other words, when the TJP mode is suppressed, the difference in ω_{ps}^2 should vanish. Note that the TJP mode above T_c is very weak [23], and thus, it does not cause an appreciable difference in ω_{ps}^2 in Fig. 2.

In Fig. 3(b), we compare our results for the Zn-free sample with the published data of YBCO determined by the other probes. Solid symbols represent our data. Our T'_c values are in good agreement with the recent results of microwave measurements on YBCO [5]. Moreover, the temperature scale of T'_c relative to T_c is also consistent with the results of THz [4,24,25] and microwave measurements [26] for the other cuprate systems, $\mathrm{La_{2-x}Sr_xCuO_4}$ and

$Bi_2Sr_2CaCu_2O_{8+\delta}$. On the other hand, neither THz nor microwave measurements detected the temperature scale T_p. This might be due to the ambiguity in determining the normal carrier component which we need to subtract in the analysis to calculate ω_{ps}^2 from $\sigma_2(\omega)$ [27].

Our T_p values are in good agreement with the temperatures observed by ellipsometry [6] and partly by the Nernst effect [28,29]. In Ref. [6], T_p was estimated only from the phonon softening related to the TJP resonance, which is not direct evidence for the superconducting condensate. Moreover, we cannot adopt this method to follow the T_p change with Zn substitution, since the TJP mode is gradually suppressed with Zn substitution. It is worth noting that T_p coincides well with the spin gap temperature reported by neutron scattering [30] and the relaxation rate T_1^{-1} of NMR [31,32].

Our results indicate that a precursor of superconductivity does exist at temperatures much higher than T_c but lower than T^*. This precursor phenomenon is clearly distinguished from the pseudogap not only because of the difference in temperature scale but also because of the fact that the electrons removed from the Fermi surface owing to the pseudogap never contribute to superconductivity [15,33]. Moreover, the observation of a superconducting condensate implies that the Cooper pairs are formed with phase coherence at T_p.

These experimental facts put a strong constraint on the theory for high-T_c superconductivity. For example, preformed pairs predicted by the mean field theory of the *t-J* model [34] do not have phase coherence, and thus, they cannot explain our observation. A microscopically phase separated state in a doped Mott insulator [35–37] is a more plausible candidate. Recently, the charge density wave (CDW) order was observed in the underdoped YBCO at a temperature close to our T_p [38,39]. The simultaneous observation of a precursor of superconductivity and the CDW order suggests microscopic phase separation. Moreover, we may expect some interplay between these two orders, although they originally compete with each other. To discuss the origin of this unusual precursor, the increase of T_p with a decreasing of the doping level is a smoking gun pointing to the importance of Mottness in the high-T_c superconductivity mechanism.

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