Depression of Quasiparticle Density of States at Zero Energy in $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$

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We have measured low-temperature specific heat $C(T, H)$ of $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$ ($x = 0$, 0.01, and 0.02) in both zero and applied magnetic fields. A pronounced dip of C/T below 2 K was observed in Zn-doped samples, which is absent in the nominally clean one. If the origin of the dip in C/T is electronic, the quasiparticle density of states $N(E)$ in Zn-doped samples may be depressed below a small energy scale E_0. The present data can be well described by the model $N(E) = N(0) + \alpha E^{1/2}$, with a nonzero $N(0)$ and positive α. Magnetic fields depress $N(0)$ and lead to an increase in E_0, while leaving the energy dependence of $N(E)$ unchanged. This novel depression of $N(E)$ below E_0 in impurity-doped cuprates cannot be reconciled with the semiclassical self-consistent approximation model. Discussions in the framework based on the nonlinear sigma model field theory and other possible explanations are presented.

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The issue of quasiparticles in unconventional superconductors has attracted considerable new attention from various directions. There are now at least two controversial questions remaining. One is the extended quasiparticle states and quasiparticle transport in the mixed state [1–3], which has been intensively studied by methods such as thermal conductivity [4,5] and specific heat [6–9]. The other is the quasiparticle density of states in the presence of impurities or disorders. Early theoretical work based on self-consistent approximation gave a general conclusion that the impurity scattering generated a residual density of states $N(E)$ at zero quasiparticle energy ($E = 0$) [10–13]. Especially, the unitary scattering could lead to a nearly constant $N(E)$ near $E = 0$, which was qualitatively verified by experiments [14–16]. Very recently, this scenario has been reexamined by the technique of the nonlinear sigma model field theory (NLSMFT) and related numerical calculations [17–19]. This new theoretical treatment brings in a new phase transition between thermal (spin) "metals" and "insulators" in disordered d-wave superconductors. One of the important predictions is that $N(E)$ will show a pronounced dip below a small energy scale E_0. In the quasiparticle localized phase, $N(E)$ is argued to vanish as E or E^2, depending on whether the time reversal is a good symmetry or not.

In principle, the low-temperature specific heat (LTSH) $C(T)$ is a powerful probe of $N(E)$ of the quasiparticle low-energy excitation. Nevertheless, previous LTSH experiments in impurity-doped (especially Zn-doped) [14,15,20] cuprates usually suffered an upturn in C/T at low temperatures. This upturn hinders the investigation of the low-temperature electronic contribution in C, and is presumably due to either a hyperfine contribution or the local magnetic moment, both of which are probably associated with defects in samples. To shed light on the issue of the low-energy quasiparticle $N(E)$, we have carefully prepared Zn- and Ni-doped $La_{1.9}Sr_{0.1}CuO_4$. These samples show no upturn in C/T down to the lowest experiment temperature 0.6 K. Therefore, LTSH can be readily used to probe $N(E)$ and provide valuable information. In the following, since both Zn- and Ni-doped samples reveal the same information, the results from more intensively studied $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$ are reported.

Polycrystalline samples of $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$ with $x = 0$, 0.01, and 0.02 were carefully prepared from La_2O_3, $SrCO_3$, and CuO powder of 99.999% purity. Details of the preparation were described in [7] and references therein. The powder x-ray-diffraction patterns of all samples used in the experiments show a single T phase with no detection of impurity phases. The transition temperature T_c is 33 and 14 K for $x = 0$ and 0.01. The $x = 0.02$ sample is not superconducting down to 2 K. The transition width (90% to 10% by the resistivity drop) of T_c is 3 and 4 K for $x = 0$ and 0.01, respectively, suggesting a decent homogeneity of the samples. $C(T)$ was measured from 0.6 to 8 K with a ^{3}He thermal relaxation calorimeter using the heat-pulse technique. The precision of the measurement in the temperature range is about 1%. Details of the calorimeter calibrations by a standard copper sample can be found in [7]. The scatter of data in different magnetic fields is about 3% or better.

The $C(T, H = 0)$ data of the samples with $x = 0$, 0.01, and 0.02 are shown in Fig. 1. By comparing these data, it is found that (i) the data of the $x = 0$ sample can be well fitted to $C(T, 0) = \gamma(0)T + C_{lattice}$, where $C_{lattice} = \beta T^3 + \delta T^5$ represents the phonon contribution, with $\gamma(0) = 1.54$ mJ/mol K^2, $\beta = 0.164$ mJ/mol K^4, and $\delta = 0.00065$ mJ/mol K^6. (ii) Plotted as C/T vs T^2 in Fig. 1, the data of both $x = 0.01$ and 0.02 samples are parallel to those of $x = 0$ at high temperatures. Actually, fits of the data of both samples from 5 to 7 K yield almost identical $C_{lattice}$ to that of the $x = 0$ sample. This is expected, as the small Zn doping should not considerably change the phonon contribution. (iii) Extrapolated from
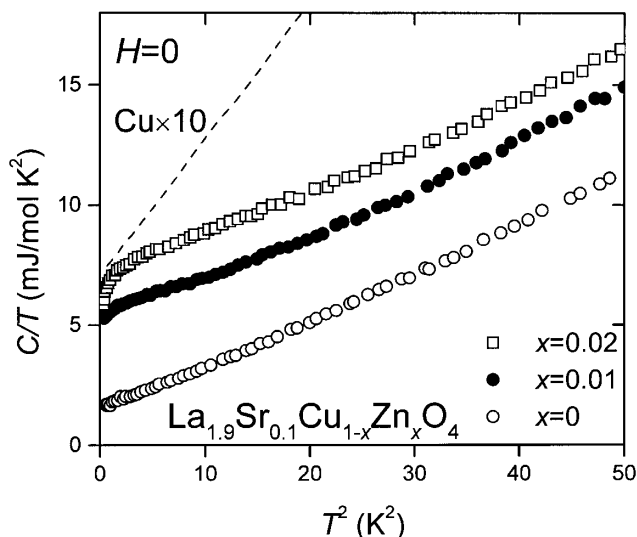
FIG. 1. C/T vs T^2 of $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$. The specific heat of copper is included as the dashed line to contrast with the low-temperature dips in both Zn-doped samples.

the high-temperature part, the intersection γ increases significantly with increasing Zn doping. (iv) Intriguingly, the C/T of both Zn-doped samples shows a dip at low temperatures, most evidently below 2 K, while this dip is absent in the $x = 0$ sample.

The present LTSH data are usually considered in the context of d-wave pairing symmetry in cuprates [3,6–9]. For clean d-wave superconductors, the electronic contribution is expected to be proportional to T^2 at $H = 0$. Indeed, this T^2 term has been clearly identified in overdoped $La_{1.78}Sr_{0.22}CuO_4$ [7,21]. The T^2 term leads to a downward curve at low temperatures in the plot of C/T vs T^2, which becomes a straight line in small magnetic fields [7], in contrast to the persistent dip of C/T in strong magnetic fields as observed in $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$ for $x \neq 0$ (see the following paragraph). It is very likely that the absence of the T^2 term in the nominally clean $La_{1.9}Sr_{0.1}CuO_4$ is due to either an intrinsically small T^2 term or a small amount of impurities or defects in CuO_2 planes, as discussed in Refs. [7] and [21]. The impurity scattering may cause the disappearance of the T^2 term and generate a small but nonzero $N(0)$, which leads to at least part of $\gamma(0)T$ in LTSH. This scenario is further supported by the recent thermal conductivity measurements which show that there exists a small impurity scattering rate Γ even in nominally pure $YBa_2Cu_3O_{6.9}$ single crystals [4]. With increasing Zn doping, pair breaking due to larger Γ generates larger $N(0)$ which leads to an increase in γ. In the unitary limit (which is widely assumed and supported by experimental results [4,22,23]), the electronic specific heat due to the quasiparticle states should have a linear T dependence. Therefore, the dip of C/T in both Zn-doped samples is certainly extraordinary. To show how peculiar the dip is, LTSH of Cu was plotted as the dashed line in Fig. 1. LTSH of Cu is known to come from a constant $N(E)$ near the Fermi

energy and the phonon contribution. As expected, C/T of Cu shows a straight line in this temperature range.

We have also studied the magnetic field dependence of $C(T, H)$ of all of these samples. For $x = 0$, the increase in γ is proportional to $H^{1/2}$ as reported in [7], consistent with Volovik's predictions. For the $x = 0.01$ sample, an increase in γ due to applied magnetic fields was observed above 3 K. Below 3 K, however, the increase in C/T due to H becomes less significant, as shown in Fig. 2(a). Indeed, $C/T(H = 4 \text{ T})$ tends to be smaller than $C/T(H = 0)$ at very low temperatures [see inset of Fig. 2(a)]. This plot shows that, with increasing H, depression of LTSH at low temperatures becomes more significant, and the temperature T_0, below which the depression occurs, increases. Applied magnetic fields lead to similar effects on $C(T, H)$ of the $x = 0.02$ sample, as shown in Fig. 2(b). The low-temperature depression of C/T due
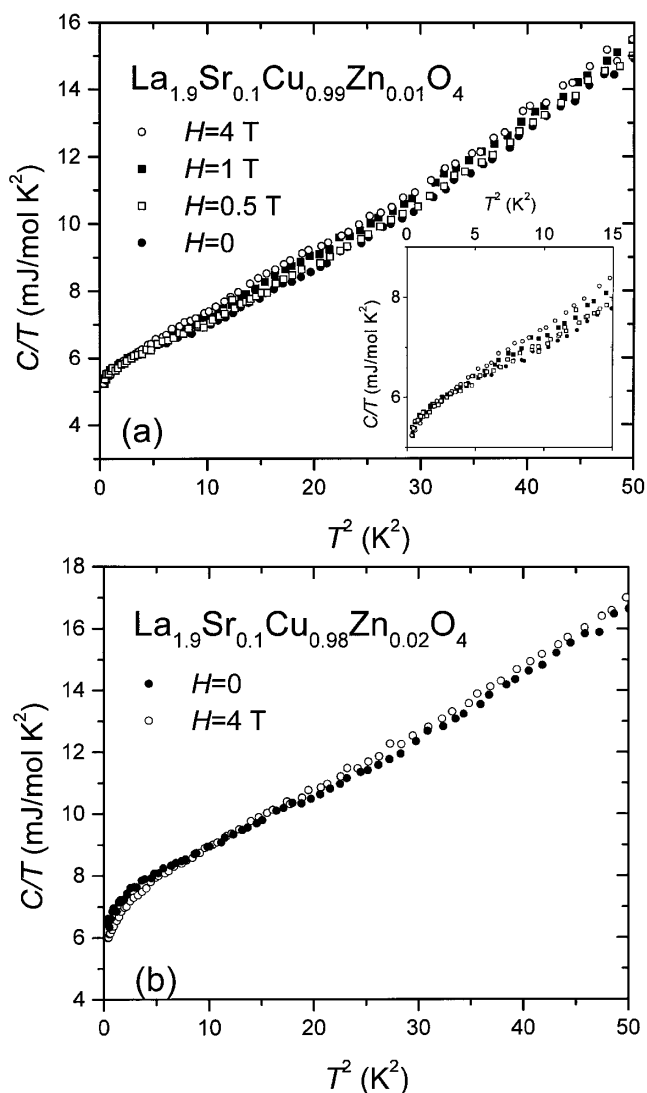

FIG. 2. (a) The effects of magnetic fields on $C(T, H)$ of the $x = 0.01$ sample. Inset: The enlargement of the low-temperature part. (b) $C(T, H)$ of the $x = 0.02$ sample.

to H is even more obvious since H does not lead to a significant increase in γ for the nonsuperconducting sample, in contrast to the $x = 0.01$ sample.

One of the possible origins of the dip in C/T of the Zn-doped samples is the depression of $N(E)$ below E_0. It is noted that this possibility cannot be reconciled with previous theoretical works based on semiclassical self-consistent approximation, which is general leads to a constant $N(E)$ [10–12]. Very recently works on the NLSMFT and the related numerical calculations on the dirty high-temperature superconductors, however, reveal a vanishing $N(E)$ among other things, such as the localization of the quasiparticles [13,16–18]. In this framework, quasiparticles are always localized in the two-dimensional dirty d-wave system, if quasiparticle interactions can be ignored. Furthermore, $N(E)$ vanishes as E or E^2 depending on whether the time is a good symmetry or not.

To compare the data with the present theory, $C(T, H)$ below 2 K has been analyzed based on the model $N(E) = N(0) + \alpha E^\nu$. This analysis leads to a nonzero $N(0)$ which is further depressed by H. Meanwhile, it is found that $\nu = 1/2$ gives a better fit than $\nu = 1$, although both values of ν qualitatively describe the data. The fitting results for $\nu = 1/2$ are shown as the solid lines in Fig. 3. This nonzero $N(0)$ resulting from LTSH is consistent with the results of thermal conductivity
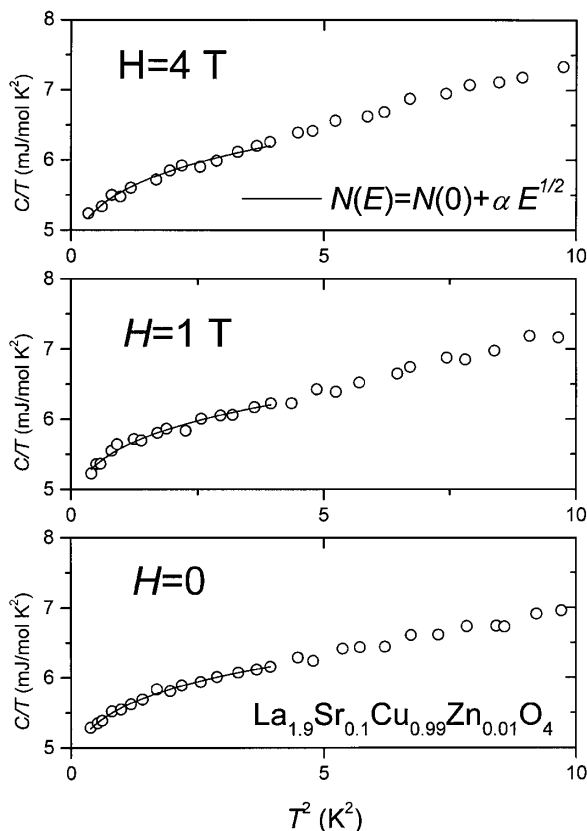
measurements in Zn-doped YBCO [4]. Interestingly, the case of a nonzero $N(0)$ with $\nu = 1/2$ coincides with the case of the "thermal metal" in NLSMFT [19]. If this is the case, it is not clear whether interactions between quasiparticles are the cause of delocalization. However, this assumption is not implausible since cuprates are known to be systems of strong correlation. Whatever the underlying mechanism, $N(E) = N(0) + \alpha E^\nu$ rather than $N(E) = N(0)$ was clearly observed, perhaps indicating a crossover from a diffusive to a localization regime of the quasiparticles in $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$. In this scenario, $C/T(T = 0)$ is proportional to $N(0)$. The fits yield $C/T(T = 0) = 4.92 \pm 0.03$, 4.90 ± 0.05, and 4.80 ± 0.03 mJ/mol K^2 for $H = 0$, 1, and 4 T, respectively. These results suggest that $N(0)$ is depressed by H. This depression effect of H on $N(0)$ can also be seen in Fig. 2(b) even without fitting. We summarize $N(E)$ of $La_{1.9}Sr_{0.1}Cu_{0.99}Zn_{0.01}O_4$ suggested from LTSH by Fig. 4. $N(E)$ dips to a nonzero $N(0)$ below the energy scale $E_0/k \sim 2$ K. In the presence of magnetic fields, $N(E)$ above E_0 increases due to the Doppler shift proposed by Volovik [3]. More importantly, magnetic fields raise E_0 and further depress $N(0)$, while the energy dependence of $N(E)$ remains unchanged.

We have measured $C(T, H)$ of $La_{1.9}Sr_{0.1}Cu_{1-x}Ni_xO_4$ and $La_{1.78}Sr_{0.22}Cu_{1-x}Ni_xO_4$. While the results of $La_{1.9}Sr_{0.1}Cu_{1-x}Ni_xO_4$ are the same as those of $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$ reported above, C/T of $La_{1.78}Sr_{0.22}Cu_{1-x}Ni_xO_4$ shows no dip. This is probably because the underdoped samples are more two dimensional than the overdoped samples. On the other hand, it is not theoretically clear whether the depression of $N(E)$ would still take place when a d-wave superconductor is impurity doped to become nonsuperconducting [24].

Finally, there are other possible explanations for the depression of C/T [or $N(E)$] to be discussed. Since the dip
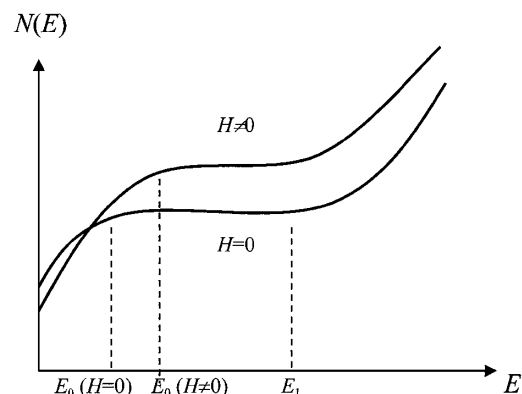
FIG. 3. The LTSH data at low temperatures can be well described based on the model $N(E) = N(0) + \alpha E^{1/2}$ (see text).

FIG. 4. The proposed quasiparticle $N(E)$ of the impurity-doped cuprates based on LTSH data. The scale of E_0 is exaggerated. In reality, $E_0/k \sim 2$ or 3 K in $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$. E_0/E_1 is of the order of 10 in the $x = 0.01$ sample, where E_1 is the energy scale above which $N(E)$ is no longer constant. The magnitude of E_1 is estimated from the results in [10] by $T_c(x = 0.01)/T_c(x = 0) = 0.42$.

of C/T is influenced by magnetic fields, the explanation of optical phonons can be ruled out [25]. By the same token, the depression of $N(E)$ due to Coulomb interactions is unlikely to be the case [26]. At low temperatures, a second superconducting phase, induced by impurity doping, could possibly develop a small gap and lead to the depression of C/T. However, this second superconducting phase, if it exists, should be suppressed rather than enhanced by applied magnetic fields [27].

Zn substitution may disturb the magnetic correlation in CuO_2 planes and induce the local moment on the four neighboring Cu sites [28]. Assuming that the local moment is spin-$1/2$, it could contribute to LTSH according to the Schottky form. However, it is found that the magnetic contribution of $4x$ paramagnetic centers (PC's) is too large to be incorporated into LTSH data of the Zn-doped samples. Very recent studies actually indicated an overwhelming screen of the Schottky anomaly in LTSH and a partial screening of the induced moment in susceptibility measurements for Zn-doped cuprates [20,29]. If the dip in C/T were attributed to the magnetic origin, an effective field of $H_0 = 4.2$ T would be required at zero applied field for the $x = 0.01$ sample. Meanwhile, the fit would lead to a PC concentration of 0.02% rather than 4%. Although this effective field is not particularly large, it has never been observed in samples with the same or larger order of PC concentration [7,20,21]. The analysis for $x = 0.02$ data in this context would lead to the same implausible results also. To further examine the possibility of the magnetic interpretation, we have fit data by $C(T, H) = \gamma(H)T + \beta T^3 + \delta T^5 + nC_{\text{Schottky}}(T, H + H_0)$, where $\gamma(H)T$ is the electronic contribution, $\beta T^3 + \delta T^5$ are the phonon contribution, and the last one is the Schottky anomaly. These fits result in a perplexing *decrease* in γ with increasing H for both samples. Furthermore, the curvature of the fitting curves does not match that of data at low temperatures, especially for large H. Thus, the magnetic interpretation is less plausible though it cannot be totally eliminated as a possible explanation.

In summary, we have carefully measured $C(T, H)$ of $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$ and found an intriguing depression of C/T at low temperatures in Zn-doped samples. If the origin of this peculiar phenomenon is electronic, the present LTSH data suggest a dip of $N(E)$ at zero energy. This novel quasiparticle density of states $N(E)$ is sensitive to the applied magnetic fields as shown in Fig. 4. It is hoped that this Letter is one of the first experimental efforts toward a full understanding of the quasiparticle states in impurity-doped cuprates.

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