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Specific-Heat Measurement of a Residual Superconducting State in the Normal State of Underdoped $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ Cuprate Superconductors

Hai-Hu Wen, Gang Mu, Huiqian Luo, Huan Yang, Lei Shan, Cong Ren, Peng Cheng, Jing Yan, and Lei Fang

National Laboratory for Superconductivity, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, People's Republic of China

We have measured the magnetic field and temperature dependence of specific heat on $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ single crystals in wide doping and temperature regions. The superconductivity related specific-heat coefficient γ_{sc} and entropy S_{sc} are determined. It is found that γ_{sc} has a humplike anomaly at T_c and behaves as a long tail which persists far into the normal state for the underdoped samples, but for the heavily overdoped samples the anomaly ends sharply just near T_c. Interestingly, we found that the entropy associated with superconductivity is roughly conserved when and only when the long tail part in the normal state is taken into account for the underdoped samples, indicating the residual superconductivity above T_c.

One of the most important issues in cuprate superconductors is the existence of a pseudogap above T_c in the underdoped region [1]. It appears in close relationship with many anomalous properties in the normal state and thus receives heavy debate about its nature. One scenario assumes that the pseudogap reflects only a competing or coexisting order of superconductivity and it may have nothing to do with the pairing. However, other pictures, such as the Anderson's resonating-valence-bond (RVB) model [2] and related models [3,4], regard the pseudogap as due to the spin-singlet pairing in the spin liquid state, and it has a close relationship with Cooper pairing for superconductivity. Experimentally, some evidence for fluctuating superconductivity in the normal state of underdoped samples has been inferred in the measurements of the Nernst effect [5,6], diamagnetization [7], time-domain optical conductivity [8] and thermal expansion [9], etc. The evidence from specific heat (or entropy) for this residual superconductivity in the normal state is, however, still lacking.

By using the differential heat capacity technique, Loram *et al.* [10] successfully measured the electronic specific heat (SH) of cuprate superconductors (most of the time at zero field). The advantage of this technique made it possible to observe the SH anomaly near T_c and the suppression to the electronic SH coefficient γ_e below T^* in underdoped region. It remains, however, unresolved whether this suppression to γ_e below T^* is due to the preformed pairing or induced solely by the competing order [11]. In addition, for a superconductor within the BCS scenario, the superconductivity related entropy (SRE) is conserved at just above T_c. We are thus also curious to know whether the SRE is conserved in very underdoped samples. Answering this question casts a big challenge since the SRE is difficult to determine in cuprate superconductors. One way to reach this goal is to measure the

difference of heat capacity between the superconducting state and a normal state background which is normally achieved by using a high magnetic field to suppress the superconductivity. The heat capacity under magnetic fields has been measured near T_c by Junod, Erb, and Renner on YBCO, Bi-2212, and Bi-2223 single crystals [12]. Because of the very high critical field in those samples, the relatively low magnetic field (about 10 T) in the usual laboratory cannot suppress the bulk superconductivity completely. It is thus highly desired to do the field-dependent SH measurement on some single crystals with low T_c; in such a case, a magnetic field in the scale of 10 T can suppress the bulk superconductivity. As far as we know, no such investigations on SH on systematic doped cuprate samples have been reported. In this Letter, we present the SH data measured on high quality $Bi_2Sr_{2-x}La_xCuO_6$ (Bi-2201) single crystals [13] in a wide temperature and doping regime, and the superconductivity is tuned by the magnetic field. The evidence for residual superconductivity far above T_c has been found based on the analysis of entropy conservation in underdoped samples.

In this experiment, we have selected six high quality crystals grown by the traveling solvent floating zone technique [13]; five of them are from $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ with $x = 0.8$ (underdoped, $p \approx 0.11$, $T_c = 11$ K), $x = 0.7$ (underdoped, $p \approx 0.123$, $T_c = 18.5$ K), $x = 0.6$ (underdoped, $p \approx 0.131$, $T_c = 22$ K), $x = 0.4$ (optimally doped, $p \approx 0.16$, $T_c = 30$ K), and $x = 0.1$ (overdoped, $p \approx 0.20$, $T_c = 17.6$ K), and one of $Bi_{1.74}Sr_{1.88}Pb_{0.38}CuO_{6+\delta}$ (overdoped, $p \approx 0.22$, $T_c = 9.4$ K). For simplicity, they are denoted as UD11K, UD18.5K, UD22K, OP30K, OD17.6K, and OD9.4K, respectively. In Fig. 1, we present the ac susceptibility of two underdoped samples in (a) and (b) and one overdoped sample (with Pb doping) in (c). For the underdoped samples [see, for example, Fig. 1(b)], a
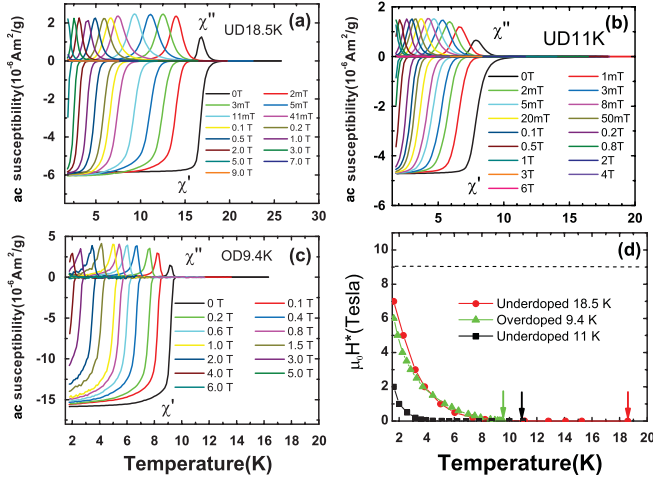
FIG. 1 (color). ac susceptibility for three single crystals of (a) UD18.5K, (b) UD11K, and (c) OD9.4K. The measurements were done with an ac field of 0.1 Oe and an oscillating frequency of 333 Hz. The critical field H^* for bulk superconductivity (see text) is shown in (d). The arrows indicate the positions of the bulk superconducting transitions at zero field for the three samples. In this study, all measurements were done with the magnetic field parallel to the c axis of the crystals.

FIG. 2 (color online). The subtracted specific heat for four samples: (a) UD18.5K, (b) UD11K, (c) OD9.4K, and (d) Nb with $T_c = 9.3$ K (using 2 T as the background). In (a) and (b) the dashed lines mark the positions of T_c.

very small magnetic field can suppress the superconducting transition quickly manifesting a very fragile superfluid density. If we take the point where both the real part susceptibility χ' and the imaginary part χ'' merge into the flattened normal state background (actually buried in the noise level) as the criterion for bulk superconductivity, the critical field $H^*(T)$ is obtained and shown in Fig. 1(d). One can see that, when the field is beyond 9 T, no bulk superconductivity can be detected above 2 K. This allows us to use the data at 9 T as the appropriate background for the state without bulk superconductivity above 2 K [14]. Thus we define the superconductivity related SH as $\gamma_{sc} = [C(H) - C(9\text{ T})]/T$, where $C(H)$ and $C(9\text{ T})$ are the total heat capacity measured at the magnetic field H and 9 T, respectively. This treatment naturally removes the phonon contribution since it is field-independent.

Figure 2 presents the temperature dependence of γ_{sc} for the corresponding samples shown in Fig. 1. The heat capacity was measured by using the relaxation method based on a physical property measurement system (Quantum Design) with the latest upgraded puck. For the underdoped samples, one can easily draw the following interesting conclusions: (1) In the zero temperature approach, the magnetic field always enhances γ_{sc}, leading to a finite quasiparticle density of states. This is consistent with the results in La$_{2-x}$Sr$_x$CuO$_4$ and other systems [15,16]. Our results support also the conclusion of a Fermi surface in the normal state revealed by recent quantum oscillation measurements [17]. (2) What surprises us is that there is *no* steplike SH anomaly at T_c for the underdoped samples; instead, it shows a broad humplike peak at
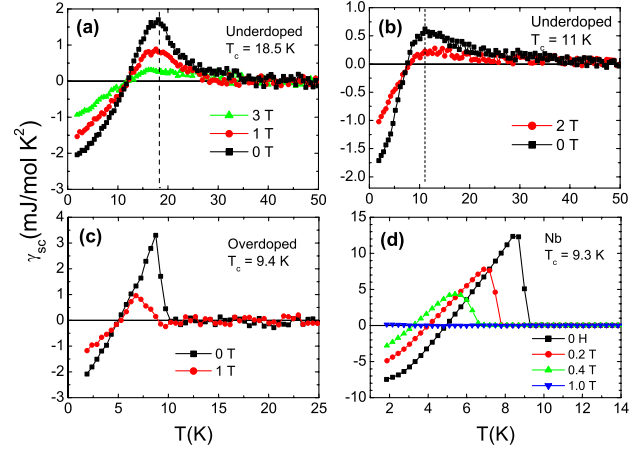
about T_c and remains as a long tail of $\gamma_{sc}(T)$ far above T_c. For example, for the underdoped sample with $T_c = 11$ K, this long tail can last up to about 42 ± 5 K, where the signal is buried in the noise background. (3) In a BCS superconductor, when the superconductivity is suppressed by a magnetic field, the peak height of the SH anomaly is suppressed and the transition temperature is lowered due to the field induced pair breaking [see an example in Fig. 2(d) for a conventional BCS superconductor Nb]. However, as shown in Figs. 2(a) and 2(b), for the underdoped samples, one can see that the position of the SH peak remains unchanged but the height is suppressed greatly by the magnetic field. Very surprisingly, the onset for bulk superconductivity as measured by the ac susceptibility shifts quickly with the magnetic field. This indicates that the bulk superconductivity is not determined by the position of the SH anomaly. Regarding the long tail of $\gamma_{sc}(T)$ extending up to high temperatures, we conclude that there is residual superconductivity far above T_c. In order to check whether this is a special property for the underdoped samples, in Fig. 2(c), we present the data for a heavily overdoped sample in the same system. It is easy to see that the $\gamma_{sc}(T)$ data show only a steplike BCS mean field transition with the absence of the long tail in the normal state.

To further illustrate the difference between the underdoped and overdoped samples, we present the $\gamma_{sc}(T)$ data in Figs. 3(a) and 3(b). For underdoped samples, the long tail of $\gamma_{sc}(T)$ extends to the temperature region between 35 and 45 K. In addition, towards underdoping, the SH peak is strongly suppressed leading to a humplike anomaly. For the strongly underdoped sample UD11K, the ratio of $\Delta C/\gamma_n T_c = 0.25$ determined here is far below the value expected by the BCS theory ($\Delta C/\gamma_n T_c = 1.43$ for an s-wave gap and higher for a d-wave gap), where we take $-\gamma_{sc}(0)$ as $\gamma_n(0)$ and $\Delta C = \gamma_{sc}(T_c)T_c$. When the hole
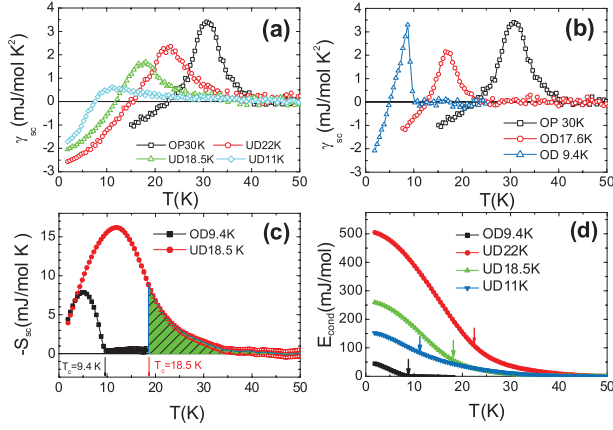
FIG. 3 (color). A collection of $\gamma_{sc}(T)$ at zero field for three underdoped samples and one optimally doped sample in (a) and two overdoped samples and one optimally doped sample in (b). (c) Temperature dependence of the superconductivity related entropy calculated by integrating $\gamma_{sc}(T)$ in a wide temperature region. (d) The condensation energy calculated through integrating the entropy (see text). The arrows mark the temperatures of the bulk superconducting transition.

concentration increases, the ratio is getting larger, but for all underdoped samples, this ratio is significantly below the expected BCS value. Since the applied magnetic field is not high enough to suppress the bulk superconductivity for the optimally doped sample, the data were shown only above 15 K, and the $\gamma_{sc}(T)$ tail extends to about 42 K, which is close to the upper boundary of the Nernst signal in this sample [6]. It is interesting to note that the SH anomaly near T_c is not sharp-step-like for the optimally doped sample; rather, it shows a symmetric peak. This is consistent with the observation by Junod, Erb, and Renner in optimally doped Bi-2212 and Bi-2223 [18]. For overdoped samples, this tail becomes much shorter: For sample OD17.6K, it ends at about 23 K, and for the very overdoped OD9.4K, it vanishes at 10 K being very close to $T_c =$ 9.4 K. In Fig. 3(c), we present the temperature dependence of the entropy calculated by $S_{sc} = \int_0^T \gamma_{sc}(T')dT'$; here the data of $\gamma_{sc}(T)$ at $T = 0$ K were obtained by doing the linear extrapolation of the low temperature data. For the overdoped sample OD9.4K, the entropy is conserved at just $T_c = 9.4$ K. The slight nonzero entropy above T_c is induced by the uncertainty in deriving the value of $\gamma_{sc}(T)$ at $T = 0$ K. The condensation energy calculated by integrating the entropy, i.e., $E_{cond} = - \int_0^{T_c} S_{sc}(T')dT'$, is about 48 ± 5 mJ/mol for sample OD9.4K. For the underdoped sample UD18.5K, the entropy is obviously not conserved by integrating $\gamma_{sc}(T)$ just up to T_c, but, surprisingly, it becomes roughly conserved when the long tail part of $\gamma_{sc}(T)$ in the normal state is taken into account as shown by the red circles in Fig. 3(c). As stressed previously [19,20], in underdoped cuprates, the term "condensation energy" may have a different meaning as compared to a

conventional superconductor since the pairing in the normal state certainly contributes a significant part to the total condensation energy, but the bulk superconducting transition at T_c saves extra energy. By integrating the entropy from T to 50 K, namely, $E_{cond} = - \int_T^{50 \text{ K}} S_{sc}(T')dT'$, we derived the temperature dependence of the condensation energy E_{cond} for three underdoped samples UD11K, UD18.5K, and UD22K and the heavily overdoped sample OD9.4K (integral from T to 18 K). The results are shown in Fig. 3(d). For sample UD18.5K the total condensation energy at $T = 0$ K is about 263 ± 10 mJ/mol, while the normal state contributes an energy savings of about 52 ± 5 mJ/mol; this gives a portion of about 20% of the total condensation energy. An estimate for the more underdoped sample UD11K finds that the normal state contribution to the total condensation energy can be as large as 54%, as shown by the blue triangles in Fig. 3(d). This large ratio of the normal state contribution to the condensation energy makes it almost impossible to attribute the residual superconductivity above T_c to the Gaussian fluctuation. It also clearly prohibits us from understanding the superconducting transition in underdoped samples within the BCS scenario.

In Fig. 4, we present a generic phase diagram derived from our data. Here we used the empirical relation $p = 0.21 - 0.18x$ to obtain the hole concentration [21]. The red squares represent the T_c values of our samples, which show very good consistency with that of Ando et al. [21]. The blue circles show the vanishing points T_{SH} of the long tail
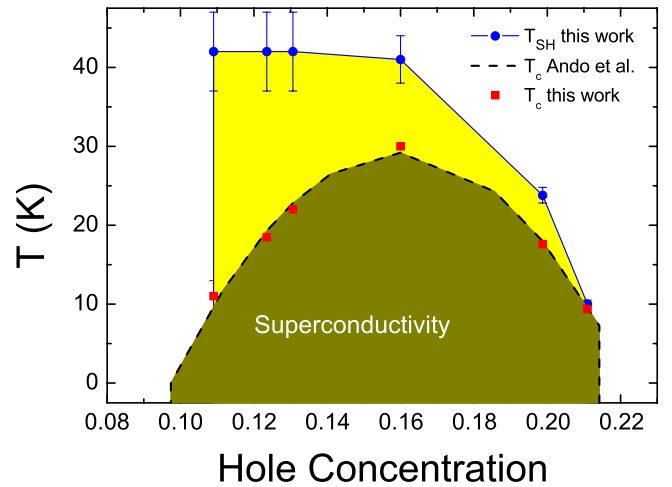

FIG. 4 (color online). A generic phase diagram plotted based on the specific-heat data. The dashed line is the T_c-p plot from Ando's group in the same system. The red squares represent the measured T_c values of our samples at the same nominal doping level. The blue circles show the temperatures T_{SH} where $\gamma_{sc}(T) = 0 \pm 0.15$ mJ/mol K^2 (within the error bars of the experiment). One can see that the gap between T_c and T_{SH} is getting monotonically larger but T_{SH} flattens out in more underdoped region.

of $\gamma_{sc}(T)$ using the criterion of 0 ± 0.15 mJ/mol K^2, where the SRE has dropped below 0.5 mJ/mol K [see Fig. 3(c)]. One can see that the difference between T_c and T_{SH} is getting monotonically larger towards underdoping. This phase diagram looks qualitatively similar to that depicted based on the Nernst measurements [6,22], but the upper limit temperatures for the Nernst signal on underdoped samples are higher than the values derived from our specific heat. There is a possible explanation about this discrepancy: It was argued by the Princeton group that the normal state Nernst signal comprises both the coherent part and the incoherent part [22]. The upper boundary of temperature for the coherent part is much lower than the incoherent one. Our data $\gamma_{sc}(T)$ here measure the residual superconductivity and thus correspond well with the coherent part of the Nernst signal. Since the entropy is naturally conserved if the normal state part of $\gamma_{sc}(T)$ is taken into account, we thus believe that there is residual superconductivity in the normal state of underdoped samples.

Our results are also qualitatively consistent with the recent observation of local pairing above T_c as seen by scanning tunneling microscopy [23]. These nanoscale droplets of Cooper pairs above T_c will certainly contribute to the condensation energy of the system and make the entropy unconserved (at T_c) unless the upper temperature for counting the entropy is beyond T_{SH} in our definition. In this sense the superconducting transition in underdoped samples means to establish the long range phase coherence [3]. Thus the thermal energy $k_B T_c$ may be equated by the phase coherence energy $E_{coh} = \hbar^2 \rho_s(T_c)/m^*$ given by Deutscher [24], where ρ_s is the superfluid density and m^* is the effective mass. Below T_c, the quasiparticles which reside on the small Fermi surfaces in the normal state [17,25] will pair up with each other and condense into the superconducting state together with the residual Cooper pairs formed above T_c. This naturally builds up a new gap on the small Fermi surfaces in the region near the nodes [26,27]. Above T_c, strong phase fluctuation [3,28] breaks up many Cooper pairs with small pairing energy [25], but some residual pairs with stronger pairing strength will exist up to a high temperature. As demonstrated by our data, the superconducting condensation in the underdoped region cannot be put into the BCS category.

In summary, the specific-heat anomaly at T_c is strongly suppressed through underdoping leading to a humplike anomaly with the height much below the value predicted by the BCS theory. A long tail of $\gamma_{sc}(T)$ has been found far into the normal state for underdoped samples. The entropy calculated by integrating $\gamma_{sc}(T)$ to T_c is clearly not conserved, but it becomes roughly conserved when and only when the tail part in the normal state is taken into account. These results prohibit from using the BCS picture to understand the superconducting transitions in underdoped samples.

[1] T. Timusk and B. W. Statt, Rep. Prog. Phys. **62**, 61 (1999).
[2] For a review on the RVB picture, see P. W. Anderson, P. A. Lee, M. Randeria, T. M. Rice, N. Trivedi, and F. C. Zhang, J. Phys. Condens. Matter **16**, R755 (2004).
[3] S. A. Kivelson and V. J. Emery, Nature (London) **374**, 434 (1995).
[4] Z. Y. Weng, D. N. Sheng, and C. S. Ting, Phys. Rev. Lett. **80**, 5401 (1998).
[5] Z. A. Xu *et al.*, Nature (London) **406**, 486 (2000).
[6] Y. Wang, L. Li, and N. P. Ong, Phys. Rev. B **73**, 024510 (2006).
[7] Y. Wang *et al.*, Phys. Rev. Lett. **95**, 247002 (2005).
[8] J. Corson *et al.*, Nature (London) **398**, 221 (1999); A. J. Millis, Nature (London) **398**, 193 (1999).
[9] C. Meingast *et al.*, Phys. Rev. Lett. **86**, 1606 (2001).
[10] J. W. Loram *et al.*, Phys. Rev. Lett. **71**, 1740 (1993); J. Phys. Chem. Solids **62**, 59 (2001).
[11] J. L. Tallon *et al.*, J. Phys. Chem. Solids **59**, 2145 (1998).
[12] A. Junod, A. Erb, and C. Renner, Physica (Amsterdam) **317C**, 333 (1999).
[13] H. Q. Luo *et al.*, Supercond. Sci. Technol. **21**, 125024 (2008).
[14] To define a "normal state background" is a nontrivial issue for underdoped cuprate superconductors. Here we use the data measured at 9 T as a relative but appropriate background because the ac susceptibility shows no trace of bulk superconductivity above 2 K. Furthermore, we found that the difference between the specific-heat data of 9 and 8 T is almost invisible.
[15] H. H. Wen *et al.*, Phys. Rev. B **72**, 134507 (2005).
[16] H. H. Wen and X. G. Wen, Physica (Amsterdam) **460C**, 28 (2007).
[17] N. Doiron-Leyraud *et al.*, Nature (London) **447**, 565 (2007).
[18] J. W. Loram, J. L. Tallon, and W. Y. Liang, Phys. Rev. B **69**, 060502(R) (2004).
[19] S. Chakravarty, Phys. Rev. Lett. **82**, 2366 (1999); S. Chakravarty and H. Y. Kee, Phys. Rev. B **61**, 14 821 (2000).
[20] D. Van der Marel *et al.*, Phys. Rev. B **66**, 140501 (2002).
[21] Y. Ando *et al.*, Phys. Rev. B **61**, R14 956 (2000).
[22] Y. Wang, Ph.D. dissertation, Princeton University, 2004.
[23] K. K. Gomes *et al.*, Nature (London) **447**, 569 (2007).
[24] G. Deutscher, Nature (London) **397**, 410 (1999).
[25] A. Kanigel *et al.*, Phys. Rev. Lett. **99**, 157001 (2007).
[26] H. Matsui *et al.*, Phys. Rev. Lett. **90**, 217002 (2003).
[27] W. S. Lee *et al.*, Nature (London) **450**, 81 (2007).
[28] Z. Tesanovic, Phys. Rev. B **59**, 6449 (1999).