Specific-Heat Measurement of Residual Superconductivity in the Normal State of Underdoped Cuprate Superconductors

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We have measured the magnetic field and temperature dependence of specific heat on $Bi_2Sr_{2−x}La_xCuO_{6+δ}$ 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 hump-like 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 the long tail part in the normal state is taken into account for the underdoped samples, indicating the residual superconductivity above $T_c$.

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One of the most important issues in cuprate superconductors is the existence of a pseudogap above $T_c$ in the underdoped region. 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 and related models, 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 have been inferred in the measurements of Nernst effect, diamagnetization, time-domain optical conductivity and thermal expansion, 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. successfully measured the electronic specific heat (SH) of cuprate superconductors (most of 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. In addition, for a superconductor within the BCS scenario, the superconductivity related entropy (SRE) is conserved at just above $T_c$. It is thus also curious to know whether the SRE is conserved in very underdoped samples. Answering this question casts big challenge since the SRE is difficult to be determined 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 et al. on YBCO, Bi-2212 and Bi-2223 single crystals. Due to the very high critical field in those samples, the relatively low magnetic field (about 10 Tesla) 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 case a magnetic field in the scale of 10 Tesla 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 $Bi_2Sr_{2−x}La_xCuO_{6+δ}$ (Bi-2201) single crystals in 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, five of them are from $Bi_2Sr_{2−x}La_xCuO_{6+δ}$ with $x = 0.1$ (underdoped, $p ≈ 0.11$, $T_c = 11$ K), $x = 0.7$ (underdoped, $p ≈ 0.123$, $T_c = 18.5$ K), $x = 0.6$ (underdoped, $p ≈ 0.131$, $T_c = 22$ K), $x = 0.4$ (optimally doped, $p ≈ 0.16$, $T_c = 30$ K), $x = 0.1$ (overdoped, $p ≈ 0.20$, $T_c = 17.6$ K), and one of $Bi_1.74Sr_{1.88}Pb_{0.35}CuO_{6+δ}$ (overdoped, $p ≈ 0.22$, $T_c = 9.4$ 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), one overdoped sample (with Pb doping) in (c). For the underdoped samples, see for example Fig.1(b), a 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 Tesla, no bulk superconductivity can be detected above 2 K. This allows to use the data at 9 Tesla as the appropriate background for the state without bulk superconductivity above 2 K.\[14\] Thus we define the superconductivity related SH as \( \gamma_{sc} = [C(H) - C(9T)]/T \), here \( C(H) \) and \( C(9T) \) 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.

Fig.2 presents the temperature dependence of \( \gamma_{sc} \) for the corresponding samples shown in Fig.1. The heat capacity was measured by using the relaxation method based on a PPMS 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 \( \gamma_{sc} \), leading to a finite quasiparticle density of states (DOS). This is consistent with the results in \( La_{2-x}Sr_xCuO_4 \) and other systems.\[15\] [16] Our results support also the conclusion of a Fermi surface in the normal state that revealed by recent quantum oscillation measurements.\[17\] (2) What surprises us is that there is NO step-like SH anomaly at \( T_c \) for the underdoped samples, instead it shows a broad hump-like 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 \( \pm \) 5K 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 Fig.2 (a) and (b), for the underdoped samples, one can see that the position of the SH peak keeps 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 shows only a step-like 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 Fig.3 (a) and Fig.3 (b). For underdoped samples, the long tail of \( \gamma_{sc}(T) \) extends to the temperature region between 35 K and 45 K. In addition, towards underdoping, the SH peak is strongly suppressed leading to a hump-like anomaly. For the strongly underdoped sample, UD11K, the ratio of \( \Delta C/\gamma_nT_c = 0.25 \) determined here is far below the value expected by the BCS theory (\( \Delta C/\gamma_nT_c = 1.43 \) 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 concentration increases, the ratio is get-
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. 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 et al. in optimally doped Bi-2212 and Bi-2223.[18] For overdoped samples, this tail becomes much shorter: for sample OD17.6 K, it ends at about 23 K, and for the very overdoped one 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 $S_{sc} = \int_0^T \gamma_{sc}(T')dT'$, where the data of $\gamma_{sc}(T)$ at $T = 0$ K was 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., $E_{cond} = -\int_{T'}^T S_{sc}(T')dT'$, is about $48 \pm 5$ mJ/mol for the 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 $E_{cond} = -\int_T^{50K} S_{sc}(T')dT'$, 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 the sample UD18.5K the total condensation energy at $T = 0$ K is about $263 \pm 10$ mJ/mol, while the normal state contributes an energy-saving of about $52 \pm 5$ mJ/mol, this gives a portion 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 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 of $\gamma_{sc}(T)$ using the criterion of
0±0.15 mJ/molK², where the SRE has dropped below 0.5 mJ/molK (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.[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 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 measures the residual superconductivity, 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 the scanning tunneling microscopy.[23] These nano-scale droplet 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 $E_{coh} = \hbar \rho_s(T_c)/m^*$ given by Deutscher et al.[24] where $\rho_s$ is the superfluid density, $m^*$ is the effective mass. Below $T_c$ the quasi-particles which reside on the small Fermi surfaces in the normal state will pair up 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.[25, 26] Above $T_c$, strong phase fluctuation[24, 25] 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 hump-like 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 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.

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