Weak coupling $d$-wave BCS superconductivity and unpaired electrons in overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystals

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The low-temperature specific heat (SH) of overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystals ($0.178 \leq x \leq 0.290$) has been measured. For the superconducting samples ($0.178 \leq x \leq 0.238$), the derived gap values (without any adjusting parameters) approach closely onto the theoretical prediction $\Delta_0 = 2.14k_BT_c$ for the weak-coupling $d$-wave BCS superconductivity. In addition, the residual term $\gamma(0)$ of SH at $H = 0$ increases with $x$ dramatically when beyond $x \sim 0.22$, and finally evolves into the value of a complete normal metallic state at higher doping levels, indicating growing amount of unpaired electrons. We argue that this large $\gamma(0)$ cannot be simply attributed to the pair breaking induced by the impurity scattering, instead the phase separation is possible.

PACS numbers: 74.25.Bt, 74.20.Rp, 74.25.Dw, 74.72.Dn

I. INTRODUCTION

For hole-doped cuprates, it is now generally perceived that the superconducting state has robust $d$-wave symmetry. In the underdoped region, due to the presence of the pseudogap and other possible competing orders, 

the measured quasiparticle gap may not reflect the real superconducting gap. In contrast, in the overdoped region, the normal state properties can be described reasonably well by the Fermi liquid picture although still with electronic correlation to some extent. Under this circumstance, one may think that the overdoped cuprate provides a clean gateway to the intrinsic high-$T_c$ superconducting state. To accumulate experimentally accessible parameters, such as the superconducting gap, and compare with the mean field BCS prediction in this very region is thus expected to be particularly valuable.

Another puzzling point in the overdoped cuprates is that the superfluid density $\rho_s$, determined by muon spin relaxation ($\mu$SR) technique decreases just as the transition temperature $T_c$, when beyond a critical doping point $p_c \sim 0.1\text{ }^{6,7,8}$ This is actually not demanded by the BCS theory. The decrease of $\rho_s$, first reported in $\text{TI}_2\text{Ba}_2\text{CuO}_6$ ($\text{TI}2201$) and subsequently confirmed in other families of cuprates, was attributed to the unpaired carriers at $T \rightarrow 0$ in overdoped cuprates. Similar conclusion was also drawn from studies of the optical conductivity and magnetization. Recently, the Meissner volume fraction was revealed to decrease as $T_c$ with increasing doping in overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) and the result was suggested to be consistent with the occurrence of a phase separation into superconducting and normal-state regions. It is thus highly desired to use the specific heat (SH) which is very sensitive to the quasiparticle density of states (DOS) at the Fermi level to directly probe these unpaired charge carriers.

In this paper we shall address these two issues by the low-temperature SH which has established its importance to identify the pairing symmetry in high-$T_c$ cuprates over the past decade. Recently, the quantitative analysis shows that it provides a bulk way to obtain the magnitude of the superconducting gap. By analyzing the field-induced SH, it is found that the pairing symmetry in the overdoped regime (up to $x = 0.238$) is still $d$-wave and the derived gap values $\Delta_0$ approach closely onto the theoretical prediction of the weak-coupling $d$-wave BCS superconductivity. Our data also reveal a quick growing of the residual term $\gamma(0)$ of SH at $T \rightarrow 0$ with increasing doping, which cannot be simply attributed to the pair breaking induced by the impurity scattering.

II. EXPERIMENT

Single crystals of LSCO were grown by the traveling-solvent floating-zone method. Details of the sample preparation have been given elsewhere. The Sr content of the sample, $x$, taken as the hole concentration $p$, was determined from the inductively coupled plasma measurement. Figure 1(a) shows the dc magnetization curves measured in 10 Oe after the zero-field cooling (ZFC) mode using a SQUID magnetometer, where the onset of the diamagnetic signal was defined as the critical temperature $T_c$. Six samples have been measured, with $x = 0.178$, 0.202, 0.218, 0.238, 0.259, 0.290 and $T_c = 36$, 30.5, 25, 19.5, 6.5, and below 1.7 K, respectively. As shown in Fig. 1(b), the $T_c$ can be described well by the empirical formula $T_c/T_{\text{c max}} = 1 − 82.6(x − 0.16)^2$ with $T_{\text{c max}} = 38$ K. The SH measurements were performed on an Oxford Maglab cryogenic system using the thermal relaxation technique, as described in detail previously. The temperature was down to 1.9 K and the magnetic field was applied parallel to $c$-axis in the measurements.
III. RESULTS AND DISCUSSION

The raw data of SH for all six samples in various $H$ at $T < 7$ K are shown in Fig. 2. To separate the electronic SH from other contributions, the data are fit to $C(T, H) = \gamma T + C_{ph}T + C_{Sch}(T, H)$, where $C_{ph}T = \beta T^3$ is the phonon SH. $C_{Sch}(T, H)$ is the two-level Schottky anomaly with the form $D/T^2$ in $H = 0$ and $f(x^2e^{x^2} + 1 + e^{x^2})$ in $H \neq 0$, where $\mu_B$ is the Bohr magneton, $g$ the Landé factor, and $f$ the concentration of spin-1/2 particles. The first linear-$T$ term, $\gamma T$, contains the electronic SH and resides in the heart of the present study. As demonstrated by the solid lines in Fig. 2(a)-(c), all data sets can be described reasonably well by the above expression. For $C_{ph}$ and the Debye temperature $\Theta_D$ the values derived here are in consistent with previous reports on the sample at similar doping level.\cite{24} For $C_{Sch}$, the yielded $f$ is relatively constant at high fields with an averaged value = 3 mJmol$^{-1}$K$^{-1}$ for different samples. This low $f$ reflects the small contribution of $C_{Sch}$ to the total SH and assures the reliable determination of $\gamma$.

In zero-field, after removing the Schottky term $C_{Sch}$ and by doing a linear extrapolation to the data shown in Fig. 2(f) to $T = 0$ K we can determine the residual term $\gamma(0)$ of SH. By increasing $H$, an increase in $\gamma$ is observed for $0.178 \leq x \leq 0.238$, as shown in Fig. 2(a)-(d), corresponding to $\gamma = \gamma(0) + \gamma(H)$ with $\gamma(H)$ the coefficient of the field-induced SH. For $d$-wave superconductors, it was theoretically pointed out that the $\gamma(H)$ is proportional to $\sqrt{H}$ due to line nodes of the gap,\cite{25} which has been confirmed in several experiments.\cite{14} Figure 3 summarizes the field dependence of the $\gamma(H)$ for the overdoped LSCO. It is clear that for all four samples, the $\gamma(H)$ is well described by $A \sqrt{H}$ with $A$ a doping-dependent constant, as exemplified by the solid lines in Fig. 3. This indicates that in overdoped LSCO the gap remains robust $d$-wave symmetry.

Next one can further obtain the gap magnitude by investigating $\gamma(H)$ quantitatively. Fundamentally, $\gamma(H)$ arises from the Doppler shift of the quasiparticle spectrum near the nodes due to the supercurrent flowing around vortices and thus directly relates to the slope of the gap at the node, $v_{\Delta} = 2\Delta_0/\hbar k_F$ with $\Delta_0$ the $d$-wave maximum gap in the gap function $\Delta = \Delta_0 \cos(2\phi)$, $k_F$ the Fermi vector near nodes (taking $-0.7$ Å$^{-1}$ as observed from ARPES).\cite{26} Explicitly, the relation between $v_{\Delta}$ and the prefactor $A$ is given by

$$A = \frac{4k_B^2}{3\hbar} \sqrt{\frac{\pi}{\Phi_0}} \frac{nV_{mol}a}{d} v_{\Delta} \quad (1)$$

where $\Phi_0$ is the flux quantum, $n$ the number of CuO$_2$ planes per unit cell, $d$ the $c$-axis lattice constant, $V_{mol}$ the volume per mole, and $a = 0.465$ for a triangular vortex lattice.\cite{27} Inset of Fig. 3 shows the doping dependence of $A$ by fitting the data to $\gamma(H) = A \sqrt{H}$. Thus, with the known parameters for LSCO ($n = 2$, $d = 13.28$ Å, $V_{mol} = 58$ cm$^3$), the doping dependence of $\gamma(0)$ and $\Delta_0$ can be derived without any adjusting parameters according to Eq. (1). In this way we extracted the gap values $\Delta_0 = 9.2 \pm 0.7, 6.6 \pm 0.3$ and $5.6 \pm 0.3$ meV for $x = 0.178, 0.202$ and $0.218$, respectively (for $x = 0.238$, the observed $A$ should be corrected due to the volume correction which will be addressed later). It can be seen immediately that $\Delta_0$ decreases with increasing doping in the overdoped LSCO, concomitant with the decrease of $T_c$. The same trend of $T_c$ and $\Delta_0$ with overdoping implies that the suppression of superconductivity mainly comes from the decrease in the pairing gap. Figure 4 plots the doping dependence of $\Delta_0$, together with the value extracted from SH in underdoped and optimal doped LSCO single crystals.\cite{15,25} For comparison, the weak-coupling $d$-wave BCS gap relation $\Delta_0 = 2.14k_BT_c$ is also plotted as a dotted curve in Fig. 4(a) and a dotted horizontal line in Fig. 4(b),\cite{28} where $T_c$ is determined by the empirical formula described before. Remarkably, beyond $x \sim 0.19$, the experimental data approaches closely onto the theoretical prediction, revealing a strong evidence for the weak coupling $d$-wave BCS superconductivity. Previous results about $\Delta_0$ determined by scanning tunnelling spectroscopy\cite{29} and penetration depth measurements\cite{26} are in excellent quantitative agreement with our present results, which strongly supports the validity of the present analysis.

Now we examine the implication of the residual term $\gamma(0)$ in zero-field. Figure 5(a) summarizes the doping dependence of $\gamma(0)$, where the values from previous studies are also included.\cite{19,25} For comparison, the normal-state SH coefficient $\gamma_N$ in the corresponding doping region is shown together.\cite{28} We can see that the $\gamma(0)$ increases with doping up to $x = 0.259$. For the nonsuperconducting $x = 0.290$ sample, the $\gamma(0)$ is actually the $\gamma_N$, which shows good consistency with the previous value. Note that for $x = 0.259$, the $\gamma(0)$ is already close to the reported $\gamma_N$. Close to the optimal doping point
the small \( \gamma(0) \) may be attributed to the impurity scattering by which a finite DOS is generated for a \( d \)-wave superconductor. However the large \( \gamma(0) \) appearing beyond \( x \sim 0.22 \) cannot be simply attributed to this reason. This can be understood by having an estimation on the impurity scattering induced DOS \( \gamma_{\text{imp}} \) in the superconducting state, which has the relation \( \gamma_{\text{imp}}/\gamma_N = (2\gamma_0/\pi\Delta_0) \ln(\Delta_0/\gamma_0) \) with \( \gamma_0 \) the pair breaking parameter. Also in the unitarity limit, \( \gamma_0 \sim 0.6 \sqrt{\Delta_0} \) with \( \Gamma = 1/2\tau_0 \) the normal state quasiparticle scattering rate which can be estimated from the residual resistivity \( \rho_0 = m^*/ne^2\tau_0 \) and the plasma frequency \( \omega_p = \sqrt{ne^2/\epsilon_0m^*}. \) With \( \rho_0 = 26 \ \mu\Omega\text{cm} \) and \( \omega_p \approx 1.2 \text{ eV} \) for \( x = 0.238 \) one gets \( \Gamma \sim 2.5 \text{ meV}. \) Assuming \( \Delta_0 = 2.14k_BT_c, \) we obtain \( \gamma_{\text{imp}}/\gamma_N \sim 0.2 \) and therefore \( \gamma_{\text{imp}} \approx 2.9 \text{ mJmol}^{-1}\text{K}^{-2} \) for \( x = 0.238, \) which is far below the \( \gamma(0). \)

Furthermore, if the large \( \gamma(0) \) is completely induced by the impurity scattering, the field-induced \( \gamma(H) \) at low \( H \) is expected to deviate from the \( \sqrt{H} \) dependence and instead show an \( H \ln H \) behavior: \( \gamma(H) = \Lambda(H/H_c) \ln[B(H_c/H)], \) where \( \Lambda = \Delta_0\alpha^2\gamma_N/8\gamma_0 \) with \( B = \pi/2a^2. \) In Fig. 6 we present the fits to \( \gamma(H) \) for \( H \leq 4 \text{ T} \) with this function. First, we leave \( \Lambda \) and \( H_c \) as both free fitting parameters (fit1) and the best fit is shown in Fig. 6(a). As shown in Fig. 6(b), this yields the parameter \( \mu_0H_c < 4 \text{ T} \) for all samples \( 0.178 \leq x \leq 0.238. \) The rather low \( H_c \) is physically unacceptable. At the same time, from the parameter \( \Lambda, \) the coefficient of the residual specific heat \( \gamma_{\text{imp}} \) can be calculated using the expressions and the \( \gamma_N \) described above. It can be seen, for \( x \geq 0.218, \) the obtained \( \gamma_{\text{imp}}/\gamma_N \) is also inconsistent with the experiment. Secondly, we try to fit the data with \( H_c \) fixed within the values shown in the shaded region in Fig. 6(e) (fit2). The transport and Nernst effect measurements have indicated that \( \mu_0H_c \sim 1.5T_c \) (\( H_c \) in Tesla and \( T_c \) in Kelvin) for the overdoped LSCO. The current SH suggests \( \mu_0H_c > 12 \text{ T} \) for all samples. Hence, in Fig. 6(e) the lower limit of the shaded region is set to be \( \mu_0H_c = 12 \text{ T} \) and the upper limit to be \( \mu_0H_c = 2T_c. \) In this case, we could not obtain a satisfactory fit to the data, as indicated by the typical result shown in Fig. 6(d). Again, the

FIG. 2: (color online) Temperature and magnetic field dependence of SH in \( C/T \) vs \( T^2 \) plot. (a)-(e): Raw data for all six samples (symbols). \( \mu_0H \) varies up to \( 12 \text{ T} \) for \( 0.178 \leq x \leq 0.238 \) while up to \( 2 \text{ T} \) for \( x = 0.259 \) and 0.290. The solid lines represent the theoretical fit (see text). The fits are limited to \( T = 7, 6, 5, \) and \( 4 \text{ K} \) for \( x = 0.178, 0.202, 0.218, \) and 0.238, respectively. For \( x = 0.259 \) and 0.290, the fits are ranged to 7 \( \text{ K}. \) (f): Replot the data at \( \mu_0H = 0 \text{ T} \) for all samples (symbol: \( \square = 0.178, \circ = 0.202, \Delta = 0.218, \triangledown = 0.238, \diamond = 0.259, \odot = 0.290). The dotted lines are extrapolations of the data down to \( T = 0 \text{ K} \) with the Schottky anomaly subtracted.
FIG. 3: (color online) Coefficient of the field-induced linear-\( T \) specific heat for 0.178 \(< x < 0.238\), \( \gamma(H) = \gamma - \gamma(0) \) at \( T = 0 \) K (symbols). The solid lines are the fits to \( \gamma(H) = A \sqrt{H} \). Inset: Doping dependence of the prefactor \( A \) (mJmol\(^{-1}\)K\(^{-2}\)T\(^{-0.5}\)).

FIG. 4: (color online) Doping dependence of the superconducting gap \( \Delta \) obtained from SH measurements. (a): \( \Delta_0 \) vs \( x \). The dashed line is a guide to the eye. (b): \( \Delta_0/k_B T_c \) vs \( x \). The values from Ref. 16 (half-filled squares) and Ref. 25 (triangle) are also included. The weak-coupling d-wave BCS value, \( \Delta_0 = 2.14k_B T_c \) (\( \Delta_0/k_B T_c = 2.14 \)) is plotted as a dotted curve (horizontal line) in (a) (b). For \( x \geq 0.19 \), the experiments are consistent with the BCS prediction.

FIG. 5: (color online) (a): Doping dependence of the \( \gamma(0) \) in zero field (filled squares) and the normal state SH coefficient, \( \gamma_N \) (circles). The \( \gamma(0) \) from Ref. 19 (half-filled square) and Ref. 25 (up-triangles) are also shown. The \( \gamma_N \) is quoted from Ref. 29. (b): Doping dependence of the \( \gamma(0) \) in (a) normalized by \( \gamma_N \), \( \gamma(0)/\gamma_N \). The same for TI-2201 (diamonds) is quoted from Ref. 36. The normalized residual spin Knight shift in LSCO \( N_{res}/N_N \), is also shown for comparison (down-triangles).

obtained \( \gamma_{res}^{imp} \) is contradictory to the measurement (Note, for a given sample, one would obtain the lower \( \gamma_{res}^{imp} \) with a higher \( H_z \)) (Fig. 6(f)). Therefore, it seems that the impurity scattering effect could not account for the field dependence of the \( \gamma(H) \).

The above analysis suggests that in highly doped LSCO the \( \gamma(0) \) mainly comes from contributions other than the impurity scattering. We attribute it to the presence of nonsuperconducting metallic regions. This can be corroborated by simultaneously having a good consistency with the Volovik’s relation \( \gamma(H) = A \sqrt{H} \) and the very large ratio \( \gamma(0)/\gamma_N \) on the single sample \( x = 0.238 \). Figure 5(b) shows the ratio of \( \gamma(0)/\gamma_N \) together with the normalized residual spin Knight shift, \( N_{res}/N_N \), another probe of the residual DOS in the superconducting state. In overdoped TI-2201 the low-temperature SH has been measured by Loram et al. \( N_{res}/N_N \) is plotted together. We can see that all these quantities show a rapid increase with overdoping, indicating a generic property. Actually in LSCO previous results also showed the rapid increase of \( \gamma(0) \) with doping in highly overdoped region although those experiments were done on polycrystalline samples. One may argue, in LSCO, that there is a high-temperature tetragonal to orthorhombic structural transition near \( x \approx 0.2 \) which...
may induce the rapid increase of $\gamma(0)$. We note that, however, in Pr-doped LSCO\(^{38}\) this subtle structural transition can be tuned to much higher doping level, but the superconducting dome remains unchanged, indicating that the hole concentration rather than the slight structure distortion plays a dominant role here. Furthermore, as shown in Fig. 5, a very similar residual $\gamma(0)$ appears in Ti2201, a system without such a structural transition.

The presence of nonsuperconducting metallic phase implies immediately a decrease of the superconducting volume fraction. This can just explain the field dependence of the SH in $x = 0.238$ and 0.259 samples. For $x = 0.238$, the observed $A$ is even lower than that for $x = 0.218$, implying a significantly reduced superconducting volume fraction. Taking this into account, the $A$ used to derive the $\Delta_0$ for this sample, should be corrected roughly as $A\gamma_N/|\gamma_N - \gamma(0)|$, with the assumption that the volume ratio is similar to the DOS ratio. The gap value yielded with this correction is about 3.5 meV, which also scales with $T_c$ in $d$-wave BCS manner and is plotted in Fig. 4. For $x = 0.259$, the sample shows a large $\gamma(0)$ being close to the $\gamma_N$, indicating a rather small superconducting volume fraction.

So far, we have shown that in overdoped LSCO, the superconducting gap decreases with increasing $x$ and at high doping levels, there exist nonsuperconducting metallic regions at $T \to 0$. Let us discuss the implications of both effects. Previously it was suggested that the suppression of $T_c$ in overdoped regime may come from the increasing pair breaking effect. Our present result, however, does not support this proposal since $T_c$ is found to scale with $\Delta_0$ in good agreement with $d$-wave BCS theory, which implies that the decrease in $T_c$ should originate from an underlying reduction in the pairing strength. This point may also be helpful to elucidate the origin of the presence of nonsuperconducting metallic regions in the overdoped sample, which is yet unclear. Currently several scenarios have been proposed to account for this anomalous phenomenon. One is that the overdoped cuprate may spontaneously phase separate into the hole-poor superconducting region and the hole-rich normal Fermi liquid region due to the competition in energy between these two phases.\(^{29}\) Another scenario is associated with the microscopic hole doping state.\(^{13}\) It was speculated that in the overdoped regime the holes were doped directly into the Cu3d orbital rather 02p, which is expected to produce free Cu spins and/or disturb the antiferromagnetic correlation between Cu spins. Around these holes, the superconductivity is destroyed, forming the normal state region. Our present result seems supporting this scenario with the assumption that the superconductivity is magnetic in origin and the suppression of $\Delta_0$ originates from the disturbing of the antiferromagnetic correlation with overdoping.

IV. SUMMARY

In summary, low-temperature SH in overdoped LSCO single crystals has revealed two interesting findings: (1) The field-induced SH follows the prediction of $d$-wave symmetry yielding a gap value $\Delta_0$ approaching closely onto the weak-coupling $d$-wave BCS relation $\Delta_0 = 2.14k_BT_c$; (2) At high doping levels, the residual SH term $\gamma(0)$ rises dramatically with doping, which suggests the existence of unpaired electrons possible in association with the normal metallic regions. These discoveries may carry out a common feature in cuprate superconductors and give important clues to the high-$T_c$ pairing mechanism.

Acknowledgments

This work is supported by the National Science Foundation of China, the Ministry of Science and Technology of China (973 project No: 2006CB601000, 2006CB921802), and Chinese Academy of Sciences (Project ITSNEM).
