Bulk Evidence for s-Wave Pairing Symmetry in the n-Type Infinite-Layer Cuprate $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$

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The pairing symmetry is one of the essential points in clarifying the underlying physics of high temperature superconductors (HTS), since it is supposed to be related to the pairing mechanism in these materials. In the hole doped side, the pairing symmetry of the cuprate is widely believed to be $d_{x^2-r^2}$. This has been supported by tremendous experiments$^{[1]}$ both from surface detection$^{[2, 3, 4, 5, 6]}$ and bulk measurements$^{[7, 8, 9, 10]}$. For the electron doped systems, the symmetry of the order parameter remains highly controversial. Angle-resolved photoemission spectroscopy (ARPES)$^{[11]}$ and phase-sensitive scanning SQUID measurements$^{[12]}$ indicate a d-wave symmetry in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (NCCO) and $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (PCCO). In addition, Raman scattering shows a nonmonotonic d-wave order parameter$^{[13]}$. Specific heat measurement on PCCO reveal also lines of nodes on the gap function$^{[14]}$. However, this has been contrasted by tunnelling$^{[15]}$ and penetration depth measurement$^{[16, 17]}$. It has been recently argued that there may be a crossover from d-wave to s-wave symmetries by changing the doped electron concentration$^{[18, 19]}$. Recently Chen et al.$^{[15]}$ reported evidence of strongly correlated s-wave pairing in the infinite-layer superconductor $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ by tunnelling spectroscopy. This conclusion can also be correlated indirectly by the stronger suppression of $T_c$ by magnetic quantum impurities $\text{Ni}$ than non-magnetic ones $\text{Zn}$,$^{[20]}$ which is the same as observed in conventional s-wave superconductors. Since tunnelling technique relies on the surface situation, a bulk evidence is thus strongly desirable for the pairing symmetry in this material. It is well known that the specific heat is one of the important means to explore the low energy excitations which reflect the bulk properties$^{[21]}$. In this Letter we present magnetic field dependent specific heat of $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ in low temperature region. The magnetic field induced quasiparticle DOS have been found to be well consistent with a s-wave pairing symmetry. We further conclude that the vortex cores contribute the dominant part of DOS in this n-type cuprate. This is in sharp contrast to the observations in p-type cuprates.

The sample studied in this work is high-density granular material of $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$.$^{[22]}$ X-ray diffraction (XRD) patterns show no any trace of a second phase in the sample. The ac susceptibility measured with $H_{ac} = 10e$ and $f = 333Hz$ is shown in the inset of Fig.1, and one can see that the sample has a sharp transition at a temperature of $T_c = 43K$. A piece about 23.13 mg in mass, $2.3 \times 2.0 \times 0.8mm^3$ in dimensions, was chosen for the specific heat (SH) measurement. The heat capacity data presented here were taken with the relaxation method based on an Oxford cryogenic system Maglab. The heat capacity is determined by a direct measurement of the thermal time constant, $\tau = (C + C_{add})/\kappa_w$, where $C$ and $C_{add}$ are the heat capacity of the sample and addenda (including a small sapphire substrate, small printed film heater, tiny Cernox temperature sensor, $\phi 25 \mu m$ gold wire leads, Wakefield thermal conducting grease (100µg)) respectively, where $\kappa_w$ is the thermal conductance between the chip and a thermal link. The value $C_{add}$ has been measured and subtracted from the total heat capacity, thus $C$ value reported here is only the heat capacity of the sample. We have also checked the field dependence of $C_{add}$ and found that the change (if any) of $C_{add}$ under 12 T is in the same order of the noise background (20 nJ/K at 5 K and 40 nJ/K at 20 K). The influence of the magnetic field (12 T) on the readout of the thermometer is below 0.02 K and can be neglected. During the measurement, the sample was cooled to the lowest temperature under a magnetic field ($H||c$) (field-cooling) followed by data acquisition in the warming up process.

Fig.1 shows the SH coefficient $C/T$ vs. $T^2$ at magnetic fields ranging from 0 to 12 T. The separation be-
tween each field can be well determined. In low temperature region the curves are upturned below 4 T, and gradually a slight but broad hump appears for higher magnetic fields, these are due to the Schottky anomaly of free spins which will be discussed later. Beside the Schottky anomaly, the curve at zero field extrapolates to a finite value \( \gamma_0 \approx 1.2mJ/molK^2 \) at 0 K, which is about 3 to 5 times smaller than that observed in p-type cuprate superconductors. If the sample has the d-wave symmetry, this can be interpreted as potential scattering near the node of \( d_{x^2-y^2} \) gap function due to small amount impurities. However, if the sample has a typical s-wave symmetry, this term should be very weak if the scatterers are non-magnetic. The small but finite value of \( \gamma_0 \) observed here may be still explained as due to impurity scattering with strong correlation effect in the present sample although it is s-wave.

It is known that different gap symmetries give rise to different quasiparticle DOS \( N_F \) near the Fermi level. Conventional low-\( T_c \) superconductors show an s-wave gap symmetry in which the electronic SH has an exponential temperature dependence, \( C_{el} \propto T_e^{-\Delta/k_BT} \), where \( \Delta \) is the energy gap. For present sample, \( \Delta \) is about 13 meV, thus \( C_{el} \) can be negligible at temperatures considered here (\( T \leq 7K \)). For a clean d-wave superconductor with nodes, since \( N_F \propto E \) near the Fermi level, this leads to the relation \( C_{el} \propto T^4 \). Therefore we fit the zero field SH data with Eq.(1) and Eq.(2) according to d-wave and s-wave (when \( k_BT \ll \Delta \)) respectively,

\[
C(T, 0) = \Theta/T^2 + \gamma_0 T + \alpha T^2 + \beta T^3 \quad (1)
\]

\[
C(T, 0) = \Theta/T^2 + \gamma_0 T + \beta T^3 \quad (2)
\]

where \( \Theta/T^2 \) is the zero field Schottky anomaly due to the effective internal field, \( \beta T^3 \) is the phonon term, \( \gamma_0 T \) is the zero field linear term as discussed above, and the \( \alpha T^2 \) term is due to the excitations with lines of nodes in d-wave case. The fit results of the zero field data to Eq.(1), with the phonon coefficient \( \beta \) to be free and to be fixed as the average of the fit results of the high fields, 0.118mJ/molK^4, are shown in Table I.

### Table I. Zero-field specific heat fit to Eq.(1).

| H    | \( \Theta \) | \( \gamma_0 \) | \( \alpha \) | \( \beta \) |
|------|--------------|----------------|--------------|------------|
| 0.0  | 1.68 ± 0.28  | 1.29 ± 0.07    | -0.10 ± 0.03 | 0.123 ± 0.003 |
| 0.0  | 2.0 ± 0.1    | 1.18 ± 0.02    | -0.054 ± 0.003 | 0.118   |

From table I, one can see that the zero field data can not produce reasonable \( \alpha \) both with free \( \beta \) and with the fixed \( \beta \). This indicates that the zero field DOS of the sample does not have the term \( \alpha T^2 \). So we use Eq.(2), the case of s-wave when \( k_BT \ll \Delta \), to fit the zero field data and deduce the reasonable value of \( \beta \). The absence of the \( \alpha T^2 \) may indicate preliminarily that the pairing symmetry of present sample is not clean d-wave like.

Then we take a general fit to the SH data at different fields. No matter the sample has a s-wave or d-wave symmetry, at a fixed magnetic field, in low temperature region the fit formulae can be written as,

\[
C(T, H) = C_{Sch}(T, H) + \gamma(H)T + \beta T^3 \quad (3)
\]

\[
C_{Sch}(T, H) = n\left(\frac{g\mu_B H}{k_BT}\right)^2 \frac{e^{g\mu_B H/k_BT}}{(1 + e^{g\mu_B H/k_BT})^2} \quad (4)
\]

where \( C_{Sch}(T, H) \) is the Schottky anomaly under a magnetic field; \( n \) is related to the concentration of spin-1/2 particles; and \( \gamma(H)T \) is the sum of the zero field linear term and the magnetic field induced linear contribution, \( \Delta\gamma = \gamma(H) - \gamma_0 \propto H \) for s-wave and \( \propto \sqrt{H} \) for d-wave. All data are fit with a Landé \( g \) factor of \( g = 2.0 \) and the fit results are shown in Table II.

### Table II. Fit of specific heat at fixed magnetic fields to Eq.(3)

from 2-7K. (Units are mJ, K, and T)

| H    | \( \gamma \) | \( \beta \) | \( n \) |
|------|--------------|----------|------|
| 0.0  | 1.04 ± 0.01  | 0.1126 ± 0.0004 |
| 0.5  | 1.13 ± 0.02  | 0.1136 ± 0.0006 33.3 ± 2.1 |
| 1.0  | 1.21 ± 0.02  | 0.1139 ± 0.0006 11.3 ± 0.6 |
| 2.0  | 1.34 ± 0.02  | 0.1158 ± 0.0006 4.5 ± 0.2 |
| 4.0  | 1.59 ± 0.04  | 0.1186 ± 0.0010 2.8 ± 0.2 |
| 6.0  | 1.77 ± 0.11  | 0.1195 ± 0.0022 3.1 ± 0.7 |
| 8.0  | 2.09 ± 0.05  | 0.1199 ± 0.0007 2.1 ± 0.5 |
| 10.0 | 2.25 ± 0.02  | 0.1214 ± 0.0004 2.7 ± 0.3 |
| 12.0 | 2.41 ± 0.01  | 0.1215 ± 0.0004 3.1 ± 0.3 |

FIG. 1: Specific heat coefficient \( C/T \) vs. \( T^2 \) at magnetic fields ranging from 0 to 12 T for the sample \( Sr_{0.9}La_{0.1}CuO_2 \). The inset shows the ac susceptibility of the sample.
The fit results of the phonon term $\beta$ and the Schottky term at 12 T are shown as insets of Fig. 2, where $C_{Sch} = C - \gamma(H)T - \beta T^3$. The large value $n$ in low field region may be induced by the residual effect of the internal crystal field. In order to remove the influence of the Schottky anomaly, we subtract the raw data with $C_{Sch}$ and the results are shown in the main panel of Fig. 2.

In the mixed state, there are two types of quasiparticle excitations in the bulk of a superconductor: bound states inside the vortex cores, and extended states outside the vortex cores (as predicted for d-wave$^{23}$). In conventional s-wave superconductors, the inner core bound states dominate the quasiparticle excitations; therefore, the electronic SH is proportional to the number of vortices. The number of vortices increases linearly with field, thus the magnetic field induced electronic SH is proportional to $H$,$^{23}$ i.e., $C_{core} \approx \gamma_n T H / H_{c2}(0)$. If we divide each side by $T^3$, one obtains

$$\frac{C_{core}}{T^3} = \frac{\gamma_n}{H_{c2}(0)} \left( \frac{T}{\sqrt{H}} \right)^{-2} \quad (5)$$

For a gap with lines of nodes (e.g., d-wave symmetry), the extended quasiparticles dominate the excitation spectrum in the clean limit. It has been shown that the electronic SH has a $\sqrt{H}$ dependence in the clean limit at $T = 0$,$^{23}$ and the data should obey Simon-Lee$^{24}$ scaling law

$$\frac{C_{vol}}{T^2} = f \left( \frac{T}{\sqrt{H}} \right) \quad (6)$$

Since the phonon SH is field independent and the Schottky contribution has been removed from the raw data, we can obtain the field dependent part of the electronic SH through subtracting the zero field SH from the one measured at other fields. Therefore for the s-wave symmetry, $C_{col-s} = [(C(H) - C_{Sch}(H)) - (C(H = 0) - C_{Sch}(H = 0))] / T^3 \propto \gamma(H) / H^3$, thus should scale with $T / \sqrt{H}$. For the d-wave symmetry, $C_{col-d} = [(C(H) - C_{Sch}(H)) - (C(H = 0) - C_{Sch}(H = 0))] / T^2 = C_{vol} / T^2 - \alpha$, should also scale with $T / \sqrt{H}$.

The scaling result of the magnetic field induced DOS with the s-wave condition (Eq. (5)) is presented in Fig. 3a. The scaling quality is quite good. The solid line is a theoretical curve $C_{col-s} = 0.15H / T^3$, thus $\gamma_n / H_{c2}(0) \approx 0.15 mJ / molK^2T$ according to Eq. (5). Taking $H_{c2}(0) = 50T$, $\gamma_n = 7.5 mJ / molK^2$, which is quite close to the value of optimally doped LSCO$^{23}$. Fig. 3b shows the scaling by following the d-wave condition (Eq. (6)). It is obvious that the result of the scaling for the s-wave condition is much better than the clean d-wave condition. Therefore it is tempting to conclude that the pairing symmetry of the sample is not the clean d-wave but very likely s-wave. The field induced quasiparticle DOS are contributed mainly by the vortex cores.

Further more, the zero temperature electronic DOS $\gamma(T = 0)(H)$ was obtained and shown in Fig. 4. The circles represent raw data, and the solid line is the fit using the formula $\gamma(T) = \gamma(T = 0) + AH^B$. It is known that the expected value for $B$ is 0.5 for d-wave and 1 for s-wave. The obtained $B$ is 0.85, being close to the linear condition $B = 1$. It is important to note that all SH measurements on p-type cuprates (mostly near optimal doped point) yield a value $B \approx 0.5$ giving the evidence for d-wave. Distinction from the d-wave symmetry is apparent in present sample although $B \approx 0.85$ instead of 1 is found here. Actually the curve between 1 T and 10 T is close to be linear.
It has been pointed out that when the field is relatively high, the vortex lattice effect should be considered and usually the linear $H$ dependence of the quasiparticle DOS cannot be seen for $s$-wave. In Fig.4 the dotted line is a fit to the clean d-wave superconductor with $B=1/2$. It is clear that the clean limit d-wave cannot describe the data at all. We have also used the dirty-limit relation to fit the zero temperature DOS. At the unitary limit and $T=0$, Kübert and Hirschfeld predicted that the field induced DOS for d-wave is $\delta\gamma/\gamma_0 = P_1(H/H_c)\log(P_2/H)$, where $P_1 = 0.322(\Gamma/\Delta_0)^{1/2}$, $\Delta_0$ the gap maximum, $\Gamma$ the impurity scattering rate, and $P_2 = \pi H_c/2a^2$, $a \approx 1$. Worthy of noting is that this relation is too flexible which can apparently fit to data with strong diversity. The fit to our data yields $\pi H_c/2a^2=3604$. Taking $a=1$, one has $H_{c2} = 2294T$ which is far beyond the reasonable value. So the d-wave in the dirty limit cannot be used to interpret our data either. This is in sharp contrast with what appears for the p-type cuprates. Recently SH measurements on an overdoped LSCO single crystal ($x=0.22$) revealed also a d-wave pairing symmetry and very limited contribution from the vortex cores to the electronic DOS in the mixed state. All these indicate that the features of vortex cores in present sample are very different from that in p-type ones in which a gapped electronic state may appear within the vortex cores when the superconductivity is suppressed.

In summary, specific heat measurements reveal that the electronic DOS in the n-type infinite-layer superconductor $Sr_{0.9}La_{0.1}CuO_2$ are mainly contributed by the vortex cores showing a bulk evidence for the s-wave pairing symmetry. This manifests that the d-wave pairing symmetry may not be universal in cuprate superconductors, rather it depends on the specific structure and competing ground states.

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[1] C. C. Tsuei, and J. R. Kirtley, Rev. Mod. Phys. 72, 969 (2000), and references therein.
[2] C. C. Tsuei, et al. Nature 387, 481 (1997).
[3] Z.-X. Shen, et al. Park, Phys. Rev. Lett. 70, 1553 (1993); D. J. Scalapino, Phys. Rep. 250, 330 (1995).
[4] W. N. Hardy, et al. Phys. Rev. Lett. 70, 3999 (1993).
[5] A. G. Sun, et al. Phys. Rev. Lett. 72, 2267 (1994).
[6] N.-C. Yeh, et al. Phys. Rev. Lett. 87, 87003 (2001).
[7] N. Bulut and D. J. Scalapino, Phys. Rev. Lett. 68, 706 (1992). G.-q. Zheng, et al. Phys. Rev. Lett. 88, 77003 (2002).
[8] K. A. Moler, et al. Phys. Rev. Lett. 73, 2744 (1994). K. A. Moler, et al. Phys. Rev. B 55, 12753 (1997).
[9] B. Revaz, et al. Phys. Rev. Lett. 80, 3364 (1998).
[10] D. A. Wright, et al. Phys. Rev. Lett. 82, 1550 (1999).
[11] N. P. Armitage, et al., Phys. Rev. Lett. 86, 1126 (2001).
[12] C. C. Tsuei and J. R. Kirtley, Phys. Rev. Lett. 85, 182 (2000).
[13] G. Blumberg, et al., Phys. Rev. Lett. 88, 107002 (2002).
[14] H. Balci, et al., Phys. Rev. B 66, 174510 (2002).
[15] C. T. Chen, et al., Phys. Rev. Lett. 88, 227002 (2002).
[16] L. Alf, et al., Phys. Rev. Lett. 83, 2644 (1999).
[17] J. A. Skinta, T. R. Lemberger, Phys. Rev. Lett. 88, 207003 (2002).
[18] J. A. Skinta, M. S. Kim, and T. R. Lemberger, Phys. Rev. Lett. 88, 207005 (2002).
[19] A. Biswas, et al., Phys. Rev. Lett. 88, 207004 (2002).
[20] C. U. Jung, et al., Phys. Rev. B 65, 172501 (2002).
[21] For a recent review, please see N. E. Hussey, Adv. in Phys. 51, 1685 (2002).
[22] C. U. Jung, et al. Current Appl. Phys. 1, 157 (2001).
[23] G.E. Volovik, JETP Lett. 58, 469 (1993); ibid 65, 491 (1997).
[24] S. H. Simon, P. A. Lee, Phys. Rev. Lett. 57, 1548 (1997).
[25] M. Nohara, et al., J. Phys. Soc. Jpn. 69, 1602(2000).
[26] C. K"ubert, P. J. Hirschfeld, Solid State Commun. 105, 459 (1998).
[27] M. Ichioka, A. Hasegawa, and K. Machida, Phys. Rev. B, 59, 184 (1999).
[28] Z. Y. Liu, et al. Condmat: 0301366.
[29] I. Maggio-Aprile, et al., Phys. Rev. Lett. 75, 2754 (1995); Ch. Renner, et al., Phys. Rev. Lett. 80, 3606 (1998); S. H. Pan, et al., Phys. Rev. Lett. 85, 1536 (2000); B. W. Hoogenboom, et al., Phys. Rev. Lett. 87, 267001 (2001).
[30] V. F. Mitrovic, et al., Nature 413, 501 (2001).