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Low temperature specific heat studies on the pairing states of high-T_c superconductors: a brief review

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Abstract

Low temperature specific heat (LTSH) data on a variety of high-T_c superconductors, such as $YBa_2Cu_3O_7$, $La_{1-x}Sr_xCuO_4$, $Bi_2Sr_2CaCu_2O_8$, and $Ba_{0.6}K_{0.4}BiO_3$ are reviewed. The agreement between the experimental data and theoretical predictions, such as T^2-dependence of specific heat at zero magnetic field and $H^{1/2}$-dependence of electronic specific heat is widely discussed within the scenario of *d*-wave superconductivity. Impurity scattering effects and scaling model on *d*-wave superconductivity are verified using Zn- and Ni-doped $La_{1-x}Sr_xCuO_4$. The low energy quasiparticle density of states $N(E) = N(0) + E^{1/2}$ are deduced from dirty *d*-wave superconductors. Absence of paramagnetic contribution to LTSH is found both in superconducting and non-superconducting underdoped samples suggesting that a mechanism beyond Kondo screening model maybe required to explain its magnetic property.

1. Introduction

Since the high-temperature superconductivity (HTSC) in cuprates was discovered in 1986, searching the mechanism responsible for HTSC has been one of the most exciting subjects of condensed-matter physics. The determination of the order-parameter symmetry is a crucial first step in identifying the pairing mechanism and the subsequent development of a microscopic theory for high-temperature superconductors (HTSCs). After many efforts made to clarify the pairing symmetry in HTSCs, a growing consensus has emerged in recent years that the symmetry of hole-doped HTSCs is *d*-wave [1]. It is noted that the tunneling and angle-resolved photoemission experiments are sensitive to either the interface of the junction or surface of the sample [2]. This has been one of the reasons to take such a long time settling this issue. However, the low-temperature specific heat (LTSH) is insensitive to the phase of order parameter and thought to be one of the unique experiments which provides bulk information on the behavior of the density of states [DOS, $N(E)$] near the Fermi level E_F. In *d*-wave superconductors, at zero magnetic field $H = 0$, the electronic specific heat C_e is expected to be proportional to T^2 rather than $\exp(-\Delta/k_BT)$ as in conventional *s*-wave superconductors, where Δ is the superconducting gap. In magnetic fields, $C_e = \gamma(H)T$ at low temperatures with γ proportional to $H^{1/2}$, as first proposed by Volovik [3]. Subsequently, the scaling behavior of the electronic specific heat contribution $C_e(T,H)$ has been predicted by theory [4,5]. Unfortunately, in earlier LTSH experiments, evidence of the T^2 term was either ambiguous or had to be identified through sophisticated fit [6–10]. This is that most of LTSH measurements on cuprates usually suffer an upturn in C/T at low temperatures. This upturn hinders the investigation of the low-temperature electronic contribution to specific heat and is presumably due to either a hyperfine contribution or a local magnetic moment, both of which are probably associated with defects in samples. Since a small impurity scattering rate can cause disappearance of the T^2 term, comparisons of $C(T,H)$ between the nominally clean and impurity-doped samples may generate fruitful implication on the existing puzzles. Moreover, the very recent non-linear sigma model field theory (NLSMFT) and related numerical calculations [11–16] predicted that the quasiparticle density of states $N(E)$ shows a pronounced dip below a small energy scale

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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.

To shed light on all these theoretical characteristics of d-wave superconductivity, we present and discuss mainly the magnetic field dependent LTSH on good-quality polycrystalline samples $La_{2-x}Sr_xCu_{1-y}M_yO_4$ ($x = 0.10$, 0.16 and 0.22; M = Ni and Zn; $y = 0$, 0.01 and 0.02) [17–20]. In this article, we first briefly describe the related theoretical predictions of LTSH on s- and d-wave superconductivity. Next, the experimental LTSH results on $YBa_2Cu_3O_7$(YBCO), $La_{2-x}Sr_xCuO_4$(LSCO), $Bi_2Sr_2CaCu_2O_8$(BSCCO), and $Ba_{0.6}K_{0.4}BiO_3$(BKBO) will be shortly reviewed. We then discuss several issues which are related to the data analysis with different materials. Finally, some comments are made for currently on going subjects.

2. Theoretical predictions

The LTSH probes the low energy excitation and thus can provide valuable information of quasiparticle density of states $N(E)$ near $E = 0$. In this section, we present a concise theoretical back ground for C and $N(E)$ of s- and d-wave superconductors. The results both at the zero magnetic field $H = 0$ and in the vortex state will be mentioned. Current theoretical studies of C and $N(E)$ for d-wave superconductors in the vortex state are mainly based on the semi-classical approach. The detailed context of the semi-classical approach and discussions of its legitimacy can be found in Ref. [21]. Beyond the semi-classical model, the band structure of quasiparticles has been studies by introducing a gauge transformation [22].

2.1. s-wave superconductors

For a fully gapped superconductor, the electronic specific heat:

$$C_e \propto e^{-\frac{\Delta}{k_B T}} \quad (1)$$

is exponentially small for $T \ll T_c$ at $H = 0$, where Δ is the superconducting energy gap and k_B is the Boltzmann's constant. For a Type II superconductor in the vortex state, the vortex core has an energy level spacing $\epsilon_0 \approx \Delta^2/E_F$, where E_F is the Fermi energy [23]. This energy spacing originates from the confinement of the quasiparticles in the normal core. It is noted that ϵ_0 is small for conventional s-wave superconductors and for almost all practical experiments $k_B T \gg \epsilon_0$. Therefore, the cores behave like normal metal and contribute to C_e in proportion to the numbers of the cores. It can be written as $C_e = \gamma(H)T$ with:

$$\gamma(H) \approx \gamma_n \frac{H}{H_{c2}} \quad (2)$$

where γ_n is the coefficient of the linear T term in the normal state and H_{c2} is the upper critical field. Eq. (2) is valid when H is much larger than the lower critical field H_{c1}, since the approximation $B \approx H$ does not hold when H is close to H_{c1} [24]. By this context, C_e of s-wave superconductors mainly comes from the cores, and the region outside the vortex cores does not play a significant role for C_e contribution. However, this long-believed scenario has been challenged in several s-wave superconductivity cases recently, as we shall discuss later in Section 5.

2.2. Clean d-wave superconductors

For quasiparticles in a clean d-wave superconductor, at $H = 0$:

$$N(E, H = 0)\alpha E. \quad (3)$$

Accordingly:

$$C_e = aT^2, \quad (4)$$

where $\alpha \approx \gamma_n/T_c$ is a constant. This is in contrast with the exponential behavior for s-wave superconductivity.

In the vortex state, the supercurrent surrounding the vortex core induces a Doppler energy shift of E by $\boldsymbol{v}_s \cdot \hbar\boldsymbol{k}$, where $\boldsymbol{v}_s$ is the supercurrent velocity. By Eq. (3), this Doppler shift leads to a local $N(0)\alpha v_s$. For a single vortex core:

$$N_{single}\,\alpha \int_{\xi}^{R} v_s 2\pi r \mathrm{d}r, \quad (5)$$

where ξ is the coherence length and R is the inter-vortex distance. Note that the core contribution is neglected. In Eq. (5), $R\alpha H^{-1/2}$ and $v_s = \hbar/m^* r$ where m^* is the mass of a Cooper pair and $r$is the distance from the center of the core. Therefore, $N_{single}\alpha H^{-1/2}$ for $H \ll H_{c2}$ (i.e. $\xi \ll R$). However, the number of the vortex cores is proportional to H. Totally:

$$N(E = 0, H) \propto H^{1/2}, \quad (6)$$

and $C_e(T,H) = \gamma(H)T$ with:

$$\gamma(H) \approx \gamma_n \sqrt{\frac{H}{H_{c2}}}. \quad (7)$$

In the literatures, the importance of the Doppler shift to d-wave superconductivity was first raised by Yip and Sauls [25]. Eq. (7) was first shown by Volovik [3] and later by Won and Maki [26]. Moreover, it can be further shown that the contribution to $N(0)$ and C_e outside the cores dominates that from the cores themselves [3].

$C_e \alpha TH^{1/2}$ is valid only when $T/H^{1/2} \ll T_c/H_{c2}^{1/2}$. It is found that, for the full ranges of T and H:

$$C_e(T, H)/TH^{1/2} = F(T/H^{1/2}), \quad (8)$$

where $F(x)$ is a scaling function [4,5]. The exact form of $F(x)$ is still not well established at present [21].

2.3. d-wave superconductors with impurities

In the presence of impurities, at $H = 0$:

$$N(E,H=0) \approx N_{\text{res}}(1 + E^2/\Gamma^2)^{1/2}, \tag{9}$$

where $N_{\text{res}} \equiv N(E=0,H=0)$ is the residual DOS due to impurity scattering and Γ is the impurity scattering rate. Note that Eq. (9) reverts to Eq. (3) in the clean limit. Near the zero energy, Eq. (9) becomes:

$$N(E,H=0) \approx N_{\text{res}}(1 + 1/2E^2/\Gamma^2). \tag{10}$$

The zero field C_e is no longer proportional to T^2. Instead,

$$C(T,H=0) = \gamma(0)T. \tag{11}$$

In the vortex state, with the Doppler shift, the additional zero energy DOS due to a single vortex is:

$$N_{\text{single}} \propto \int_{\xi}^{R} v_s^2 2\pi r \mathrm{d}r \propto \ln\frac{R}{\xi}. \tag{12}$$

Note that $x = (\Phi_0/2\pi H_{c2})^{1/2}$ where Φ_0 is the magnetic flux quantum. The total DOS in the vortex state now is:

$$N(E=0,H) = N_{\text{res}} + K\frac{H}{H_{c2}}\ln\left(\frac{H_{c2}}{H}\right), \tag{13}$$

where K is a constant related to Γ. Eq. (13) was first proposed again by Volovik [27], and later calculated in detail by others [28–30]. $C_e = \gamma(H)T$ in the vortex state, with:

$$\gamma(H) = \gamma(0)\left(1 + D\frac{H}{H_{c2}}\ln\frac{H_{c2}}{H}\right), \tag{14}$$

where $D \approx \Delta_0/32\Gamma$ and Δ_0 is the superconducting gap in the absence of impurity scattering.

Furthermore, it was pointed out by Kübert and Hirschfeld that the strong impurity scattering leads to breakdown of the scaling of Eq. (8) [28,29]. This dramatic effect is shown in Fig. 1 according to the numerical calculations.

3. Experimental results

3.1. s-wave superconductors

As an example, measured C/T vs T^2 of $Lu_5Ir_4Si_{10}$, which is an intermetallic compound with $T_c = 3.7$ K, is plotted in Fig. 2(a). The unextrapolated $(\otimes C/T_c)/\gamma_n = 1.33$ (1.41 by BCS weak coupling limit) indicates that $Lu_5Ir_4Si_{10}$ is a weak-limit superconductor. Fig. 2(b) shows that $C_e = C - C_{\text{lattice}}$, where C_{lattice} is the phonon contribution, in the superconducting state is an exponential form following Eq. (1) below $0.5\,T_c$. This result suggests that $Lu_5Ir_4Si_{10}$ is a fully gaped superconductor. Above $0.5\,T_c$, the energy gap Δ rapidly decreases, and Eq. (1) no longer holds. The coefficient 1.51 of T_c/T in the exponent is also close to 1.44 in the weak coupling limit. Another example of Ga showing the exponential behavior of Eq. (1) can be found in Ref. [31].

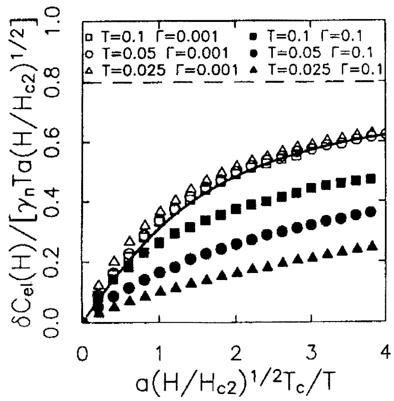

Fig. 1. Normalized vortex contribution to specific heat for fixed T and scattering rate (as shown. Unit of energy T_{c0}. Asymptotic large x limit $(2/\pi)^{1/2}$ (dashed line) [28].

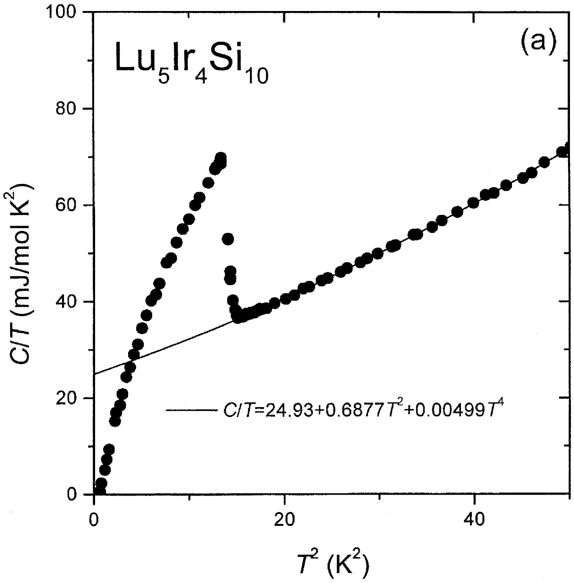

Fig. 2. (a) C of $Lu_5Ir_4Si_{10}$ in the superconducting state. $C_{\text{Lattice}}(T) = 0.6877\,T^3 + 0.00499\,T^5$ is emperically deduced from $T > T_c$. (b) $C_e = C - C_{\text{lattice}}$ in the superconducting state is plotted on a log scale vs T/T_c. The exponential dependence on $1/T$ is evident below $T_c/2$.

The case of C_e in the vortex states, supposed to follow Eq. (2), will be discussed in the Section 5.

3.2. Nominally clean d-wave superconductors

Most specific heat experiments to search for bulk evidence of *d*-wave superconductivity were carried out in the hole-doped cuprates. Among cuprates, $YBa_2Cu_3O_{7-\delta}$ (YBCO) and $La_{2-x}Sr_xCuO_4$ (LSCO) are intensively studied, though reports on $Bi_2Sr_2CaCu_2O_{8-\delta}$ can also be found [32].

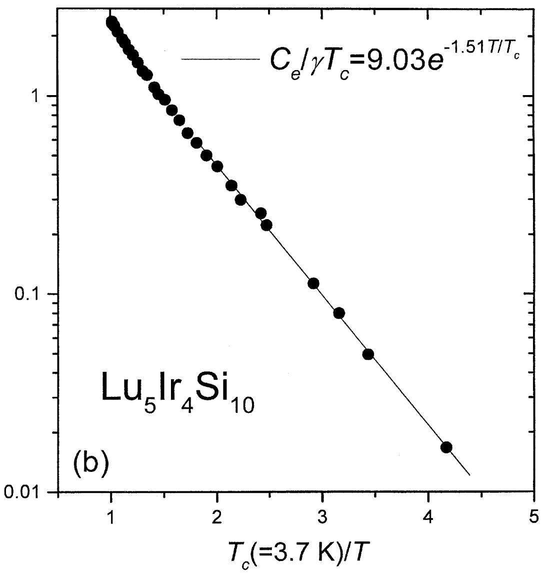

Fig. 2. (*continued*)

In this paper, mainly the results from YBCO and LSCO are discussed. Most YBCO samples studied are optimally or slightly over-doped, while LSCO ones of all doping regimes have been investigated.

The measured specific heat is believed to consist of three sources:

$$C(T,H) = C_e(T,H) + C_{mag}(T,H) + C_{lattice}(T). \quad (15)$$

$C_{lattice}$ is the phonon contribution, and usually written as:

$$C_{lattice} = \beta T^3 + \delta T^5 + \ldots \quad (16)$$

C_{mag} represents the magnetic contribution from the paramagnetic centers (PC's), nuclear hyperfine interaction and so on. Conventionally, PC's are considered as spin-1/2 moments, probably due to Cu^{+2}. Very recently, the existence and importance of spin-2 PC's has been proposed [18,33]. For $S = 1/2$, $C_{mag}(T,H) = nC_{Schottky}(g\mu H/k_B T)$ can be used, where:

$$C_{Schottky}(x) = x^2 e^x/(1 + e^x)^2 \quad (17)$$

is a two-level Schottky anomaly and n is the concentration of PC's. For $S = 2$, the effective Hamiltonian and numerical calculations have been used to obtain $C_{S=2}(T,H)$ in the literatures. It is generally supposed that spin-1/2 PC's are closely related to the oxygen vacancies in the CuO chains and the spin-2 PC's are associated with the CuO_2 planes. However, there is some doubts about the relation between spin-1/2 PC's and the CuO chains [33]. For the same amounts of PC's, $C_{Schottky}$ and $C_{S=2}$ have about the same magnitude but different temperature dependences. To obtain C_e from C by Eq. (15), C_{mag} contributes most of the uncertainty in data analysis. To avoid this difficulty, there have been attempts [9,34,35] to directly observe C_e in high quality YBCO single crystals by:

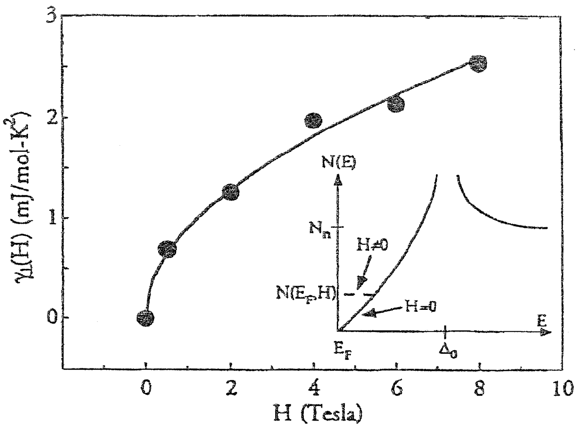

Fig. 3. $\gamma_\perp \equiv \gamma(H)$-$\gamma(0)$ of $YBa_2Cu_3O_{7-y}$ is fit to $\gamma_\perp \propto H^{1/2}$ as shown by the solid line. Inset: $N(E)$ for $H = 0$ and in the vortex state.

$$C_e(T,H) = C(T,H) - C(T,0). \quad (18)$$

Nevertheless, corrections to the magnetic contribution are still indispensable for quantitative analysis [35].

The main purposes of the experiments are to test the predictions of Eqs. (4) and (7), which are significantly different from the *s*-wave results and manifest the new physics due to the node lines in *d*-wave superconductivity. Very recently, the predicted scaling behavior of Eq. (8) has also attracted much interest of research.

Moler et al. were among the first who claimed to observe evidence of Eqs. (4) and (7) in YBCO [6,7]. The results of a non-linear $\gamma(H) = AH^{1/2}$, where A is a constant, are shown in Fig. 3 [6]. A non-linear H dependence of γ(H) was evident and confirmed later by other reports [8–10,34,35]. In contrast to $\gamma(H)$, the existence of αT^2 could only be suggested from tricky global fit [6], and by no mean evident from the raw data. Therefore, the existence of αT^2 was once questioned [8,36]. Later experiments with better samples, and improved data analysis (including the use of Eq. (18)) finally agreed on the existence of αT^2 in YBCO [10,34,35]. Nevertheless, αT^2 term was still not obvious by data themselves even in some of the best YBCO single crystals (Fig. 4(a) in Ref. [35]). The difficulty in searching for αT^2 in YBCO was likely due to the mask of C_{mag} at low temperatures. At present, it seems that all studies reach an agreement on both $\gamma(H) = AH^{1/2}$ and the existence of αT^2, however, with slightly different values of A and α. Some of the values of $A$and α from different reports are listed in Table 1, together with the crude estimates derived from Eqs. (4) and (7). The different values of A could be reconciled under a scenario that A increases with a more ordered vortex lattice, and thus is sensitive to the quality of samples [21]. For the present, there is no apparent explanation of the various values of α in different reports.

In contrast to YBCO, LSCO samples usually have

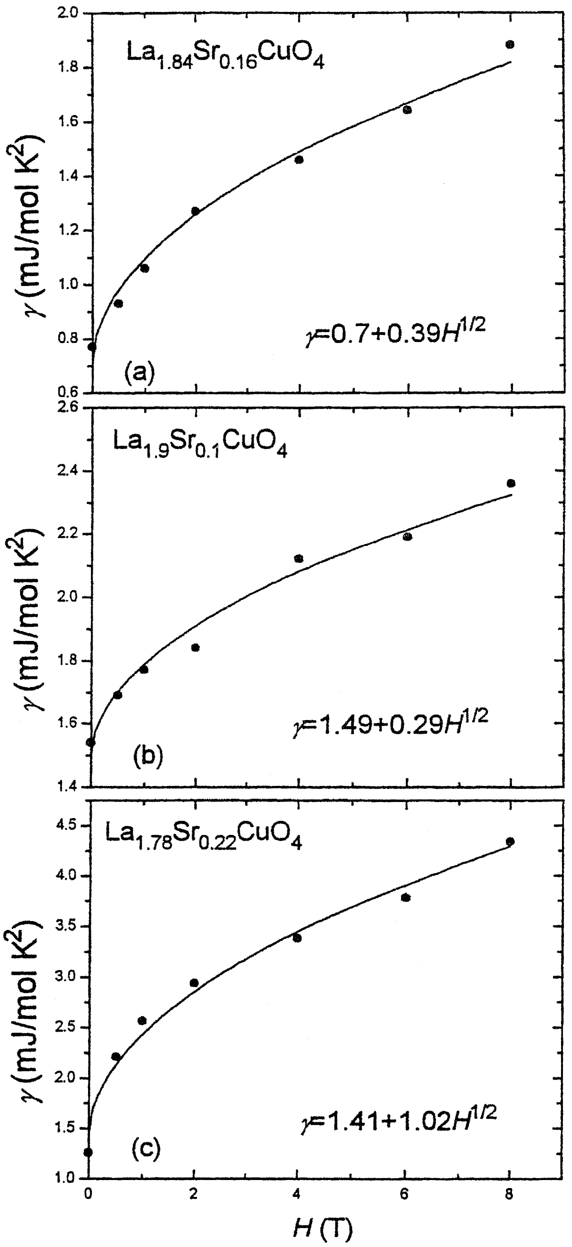

Fig. 4. Coefficient of the linear-T term γ for $La_{2-x}Sr_xCuO_4$ samples. The solid lines represent the fits of $\gamma = \gamma(0) + AH^{1/2}$.

smaller C_{mag}, probably owing to lack of the CuO chains. In LSCO, the apparent evidence of αT^2 was first reported by Momono et al. [36,37]. However, the relation of $\gamma(H) = AH^{1/2}$ was not tested in their studies. Intensive specific heat studies on LSCO from underdoped to overdoped regimes were later carried out by Chen et al. [17]. The relation of $\gamma(H) = AH^{1/2}$ was observed for all doping levels, as shown in Fig. 4. For $La_{1.78}Sr_{0.22}CuO_4$ at $H = 0$, C/T vs T^2 shows an obvious downward curve at low temperatures rather than a straight line, as marked by the arrow in Fig. 5(a). The best fit yields a significant αT^2 term. Since this αT^2 term is ~20% of total zero-field specific heat at 4 K and exceeds the γT term above this temperature, its identification is unambiguous [17]. At $H = 0.5$ T, this downward curve becomes a straight line except below 1 K where the contribution from the Schottky anomaly is important. Furthermore, in Fig. 5(b), C/T vs T of this sample shows a straight line that convincingly manifests the αT^2 term without any fitting. The existence of the αT^2 term at $H = 0$ and its disappearance in magnetic fields are both consistent with the predictions for the d-wave superconductivity. Fisher et al. reported similar results of $La_{1.85}Sr_{0.15}CuO_4$ to those of $La_{2-x}Sr_xCuO_4$ by Chen et al., though the αT^2 term of Fisher et al. was obtained from fitting [37]. The values of A and α of LSCO from some of the literatures are listed in Table 2.

The scaling behavior of $C(T,H)$ in cuprates has been studied by several groups [9,10,17,18,35]. For example, the results of YBCO and LSCO are shown in Figs. 6 and 7(a), respectively. All studies reported a scaling form of Eq. (8). However, there seems to be discrepancy in the form of $F(x \equiv T/H^{1/2})$. For the results shown in Figs. 6 and 7(a), $F(x)$ is almost constant at small x, and shows an *increase* when x is larger than a crossover x_c. On the other hand, in Refs. [9,17,35], $F(x)$ decreases when $x > x_c$. These apparently contrary results may be actually consistent with each other. As pointed out in Refs [21,39], The scaling of $C_e(T,H)$ itself would show the former behavior, and $\delta C_e \equiv C_e(T,H)$-$C_e(T,0)$ shows the latter behavior. For example, both C_e's of $La_{1.78}Sr_{0.22}CuO_4$ in Fig. 8 and $La_{1.84}Sr_{0.16}CuO_4$ in Ref. [17]were derived from

$$\Delta C_e(T,H) \equiv C(T,H) - \gamma(H=0)T - C_{lattice} - C_{mag}. \quad (19)$$

Since $C(T,0) = \gamma(0)T + \alpha T^2 + C_{lattice}$ for $La_{1.78}Sr_{0.22}CuO_4$ [17], $\Delta C_e(T,H)$ defined by Eq. (19) is $C_e(T,H)$ itself. On the other hand, $C(T,0) = \gamma(0)T + C_{lattice}$ for $La_{1.84}Sr_{0.16}CuO_4$ in Ref. [17]. Because αT^2 was not resolved in $La_{1.84}Sr_{0.16}CuO_4$, its phenomenological $\gamma(0)T$ may contain αT^2 contribution. Thus $\Delta C_e(T,H)$ of $La_{1.85}Sr_{0.16}CuO_4$ in Ref. [17] is δC_e. In this scenario, there would be reconciliated for the reported scaling results of all groups. Still, more comprehensive studies of this scaling subject are desirable.

For $Ba_{0.6}K_{0.4}BiO_3$, though sometimes classified as a high-temperature superconductor, recent $C(T,H)$ results are found to be consistent with s-wave superconductivity [40].

Several papers reported that the non-linear H dependence of γ was also observed in conventional superconductors, and raised the question whether the $H^{1/2}$ dependence of γ is indeed due to d-wave pairing. In addition, there remains controversies on the existence of the T^2 term at $H = 0$. These puzzles make the $C(T,H)$ studies of the impurity-doped cuprate superconductors

Table 1
Comparison of A and α of $YBa_2Cu_3O_{7-\delta}$ from Berkekey [10], Stanford [7], and Geneve [35] groups. Estimates of A and α are also listed from Eqs. (4) and (7) with $T_c = 92$ K, $H_{c2} = 120$ T, and $\gamma_n = 20$ mJ/mol K^2

	Berkeley group	Stanford group	Genéve group	Estimated
A (mJ/mol $K^2T^{1/2}$)	0.91	0.91	1.34	1.83
α (mJ/mol K^3)	0.06	0.11	0.21	0.22

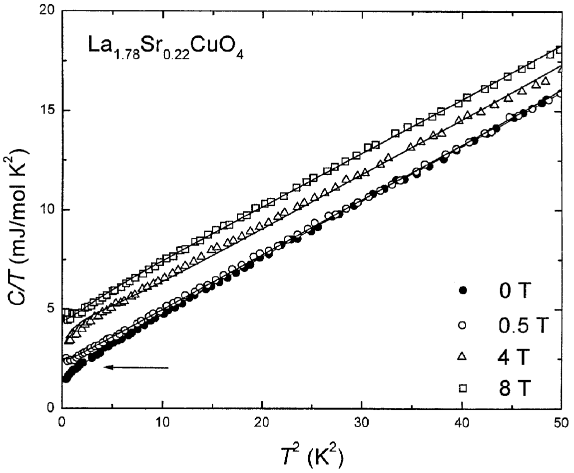

Fig. 5. (a) $C(T,H)/T$ vs T^2 of $La_{1.78}Sr_{0.22}CuO_4$. The solid lines are from the fit described in Ref. [17]. The change from $C_e = \alpha T^2$ at $H = 0$ to $C_e = \gamma T$ at $H \neq 0$ is emphasized by the arrow. (b) C/T vs T for $T < 2$ K, where the contribution from the T^2 term is apparent.

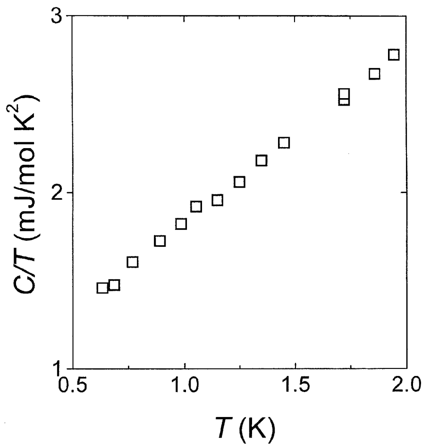

Fig. 5. (*continued*)

particularly of interest. Furthermore, since a small impurity scattering rate can cause disappearance of the T^2 term, it is desirable to know the magnetic field dependence of $C(T,H)$ in the impurity-doped cuprates. These issues mentioned in this paragraph will be further addressed in the next section.

4. Discussion

4.1. Low-T upturn in C/T and zero-field linear term γ(0) of LTSH

There are two interesting sample-dependent features, namely the low-T upturn in C/T and zero-field linear term $\gamma(0)$, in LTSH of most studied systems [6–10,17–20]. Because the estimated αT^2 term in LTSH of d-wave cuprates is less than or comparable to 5% of phonon specific heat at ~2 K, the existence of these two contributions has hindered the analysis within the d-wave scenario. For YBCO, the low-T upturn in C/T is usually attributed to a spin-1/2 [6,10] or spin-2 [10] Schottky-like anomaly. While for the existence of zero-field linear term $\gamma(0)$, which is inconsistent with clean lines of nodes if it is associated with the superconducting carriers. Because the impurity phases $BaCuO_2$ and the Cu^{2+} moments could make significant contributions to $\gamma(0)$. In addition, the Cu^{2+} moments may act as pair-breaking centers limiting the transition to the superconducting state and also producing a contribution to $\gamma(0)$. Phillips et al. [41] speculated that it may be contributed from normal-state-like excitations associated with the Cu-O chain or non-superconducting regions. This is consistent with that the low-T upturn and $\gamma(0)$ were greatly increased in Zn-doped YBCO [41,42]. Moreover, a separate origin from the excitations which gives rise to the d-wave superconductivity has been proposed [6]. On the other hand, in LSCO system, the upturn and the value of $\gamma(0)$ are strongly related to the residual resistivity [17,36] indicating that these two features depend on the sample quality. Nevertheless, there is no evidence that the $\gamma(0)$ is an intrinsic property of superconducting state for a nominally clean sample. It is noted that these two features were much more suppressed in overdoped than in optimally- and under-doped LSCO suggesting their correlation with electronic properties [17].

4.2. Impurity scattering effects on the d-wave superconductivity

Now we are going to test the Eq. (7) for clean and Eq. (14) for dirty d-wave superconductors. To compare $\gamma(H)$ of the clean sample with that of the Ni-doped ones, γ vs $H^{1/2}$ of all samples was plotted in Fig. 8. If γ has a $H^{1/2}$ dependence as expected in a clean sample, the data will follow a straight line as represented by the dashed line. Indeed, data of the sample with $x = 0$ indicate a clear $H^{1/2}$ dependence of γ

Table 2
Comparison of LTSH experimental results of $La_{2-x}Sr_xCuO_4$ with the estimates of *d*-wave model [17,38]

	$x = 0.10$	$x = 0.16$	$x = 0.22$	$x = 0.15$
T_c (K)	33	39	29	39
γ_{c2} (*T*)		~ 50		~ 50
Estimated α (mJ/mol-K^3)	0.17	0.26	0.41	0.23
Observed α (mJ/mol-K^3)	< 0.06	< 0.01	0.31 ± 0.02	0.09
Estimated *A* (mJ/mol K^2 $T^{1/2}$)		0.96		0.86
Observed *A*(mJ/mol K^2 $T^{1/2}$)	0.29	0.39	1.02	0.49

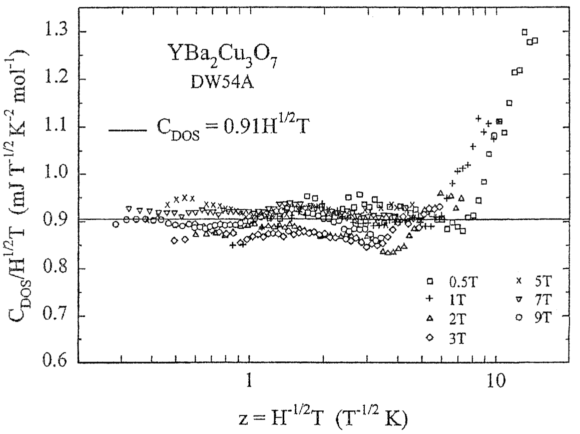

Fig. 6. The scaling behavior of $C_e(T,H)$of $YBa_2Cu_3O_{7-\delta}$ [10].

(Fig. 8(a)). In Ni-doped LSCO samples, the *H* dependence of γ is smaller than in the clean one, and the data show a pronounced curvature for small *H* and are better described by Eq. (14) as represented by the solid line (Fig. 8(b) and (c)). This behavior makes $\gamma(H)$ of Ni-doped samples distinct from that of the clean one. Thus, the effect of impurity scattering is clearly identified.

The most crucial test of the recent theory for a *d*-wave superconductor with impurities probably lies on the breakdown of the scaling behavior of $C_e(T,H) \equiv C(T,H)$-$\gamma(H=0)T$-βT^3-$nC_{S=2}$. For a clean *d*-wave superconductor, if $C_e/(TH^{1/2})$ vs $H^{1/2}/T$ is plotted, all data at various *T* and *H* should collapse into one scaling line according to the recent scaling theory [4,5]. This scaling of $C_e(T,H)$ has been observed in $YBa_2Cu_3O_{7-\delta}$ [8,9] and $La_{1-x}Sr_xCuO_4$ samples [17,37]. As shown in Fig. 7(a), $C_e(T,H)$ of $La_{1.78}Sr_{0.22}CuO_4$ follows this scaling. However, a recent theory predicts that strong impurity scattering can cause the breakdown of the scaling [28,29]. This dramatic effect is best illustrated in Fig. 7(b) and (c). In contrast to the scaling of $C_e(T,H)$ of the clean sample, $C_e(T,H)$ data of Ni-doped samples split into individual isothermal lines as predicted by the numerical calculations [28,29]. It is thus suggested that the unconventional features observed in $C(T,H)$ of either clean or impurity-doped cuprate superconductors are intrinsic bulk properties of *d*-wave superconductivity.

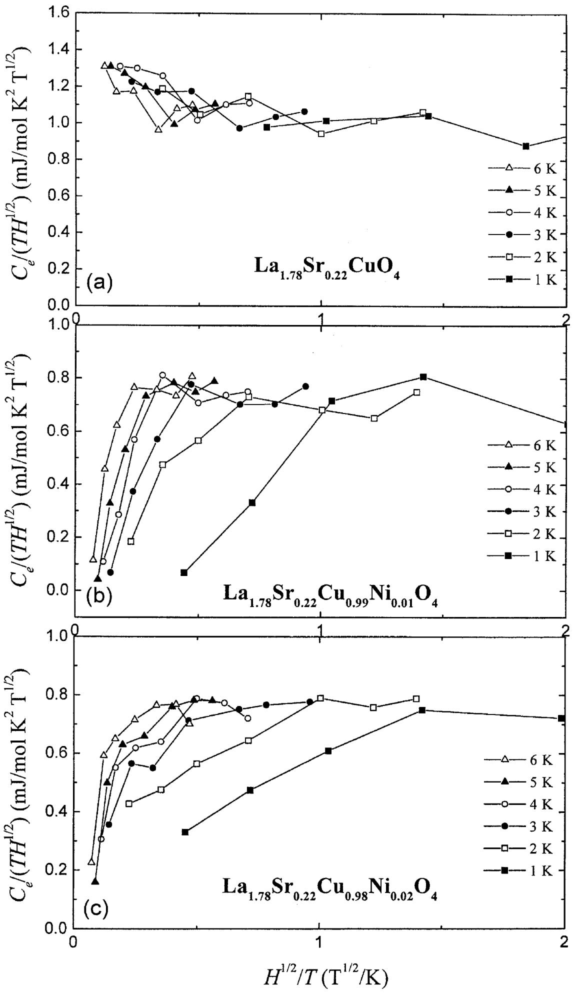

Fig. 7. Plots of $C_e/(TH^{1/2})$ vs $H^{1/2}/T$ for (a) $x = 0$, (b) $x = 0.01$, and (c) $x = 0.02$. Note that the scaling holds in (a), breaks down in (b) and (c) due to impurity scattering.

4.3. Low energy quasiparticle density of states in dirty d-wave superconductors

Fig. 9 shows the $C(T, H=0)$ data of the samples $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$ with $x = 0$ and 0.02. Intriguingly, *C*/

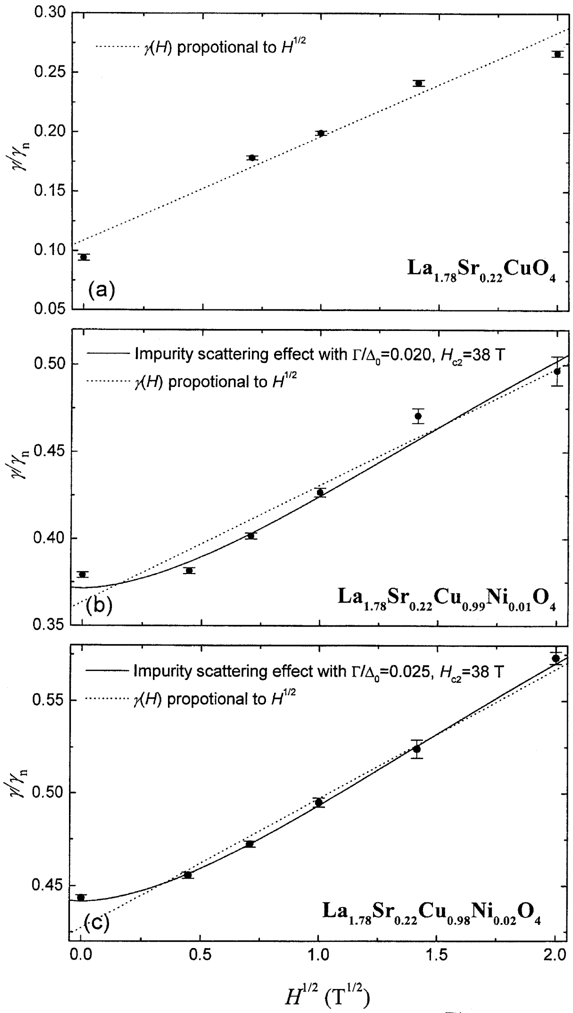

Fig. 8. Normalized $\gamma(H)$ vs $H^{1/2}$ for three $La_{1.78}Sr_{0.22}Cu_{1-x}Ni_xO_4$ samples. The solid lines are the results of the fit by Eq. (14), which includes the impurity effects on $C(T,H)$. Dashed lines represent $\gamma(H)\alpha H^{1/2}$ expected in clean d-wave superconductors. In (a) no solid line is presented since the fit by Eq. (14) gives a unrealistic value of $H_{c2} > 1000\ T$.

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. Therefore, the dip of C/T in both Zn-doped samples is certainly extraordinary. 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. 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 non-zero $N(0)$ 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. We thus summarize that the $N(E)$ of $La_{1.9}Sr_{0.1}Cu_{0.99}Zn_{0.02}O_4$ suggested from LTSH exhibits a dip to a non-zero $N(0)$ below the energy scale E_0/k~2 K as shown

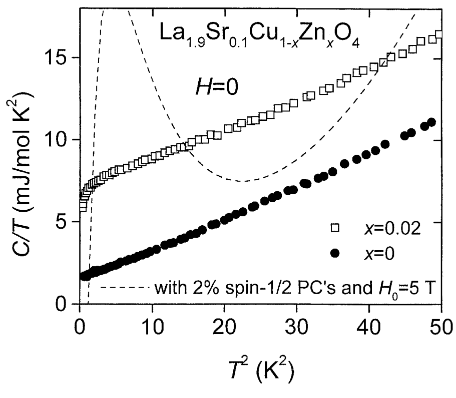

Fig. 9. C/T vs T^2 of $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$. The dashed line in the fit with 2% concentration of PC's for $x = 0.02$ data

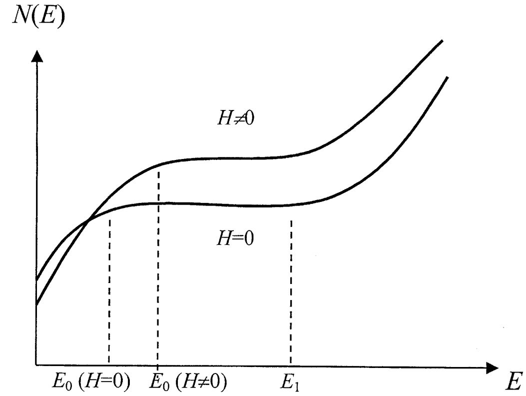

Fig. 10. The proposed quasiparticle $N(E)$ of the impurity-doped cuprates based on LTSH data. The scale of E_0 is exaggerated. In reality, E_0/k~2 or 3 K in $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$. E_0/E_1 is order of 10 in the $x = 0.02$ sample, where E_1 is the energy scale above which $N(E)$ is no longer constant.

in Fig. 10. 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 [19].

It is noted that the dip in C/T shows only in this underdoped Zn- and Ni-LSCO, while not in optimally- and overdoped ones. This is probably because the underdoped samples are more two-dimensional than the overdoped ones. On the other hand, it is not theoretically clear whether depression of $N(E)$ would still take place when a d-wave superconductor is impurity-doped to become non-superconducting.

4.4. Absence of paramagnetic contribution to the low-temperature specific heat

In the conventional s-wave superconductor, the Kondo effect is suppressed by the formation of the superconducting gap, as shown by Abrikosov and Gorkov [43]. In *d*-wave superconductors, however, there are quasiparticles in the node lines that could cause a Kondo screening. Cassanello and Fradkin calculated the thermodynamic properties of *d*-wave superconductors with magnetic impurities and predicted a screening mechanism analogous to the exchange coupling between magnetic impurities and the electrons in a Fermi liquid that causes the Kondo effect [44]. In fact, the recent LTSH of Zn-doped YBCO found an intriguing result that there was no apparent increase in the magnetic component of C associated with magnetic moments with increasing Zn doping [42]. This absence of the magnetic contribution in C can be explained within this frame work as possible Kondo screening in the superconducting state.

However, our most recent similar study on underdoped LSCO tells a little more story [20]. C/T data of samples $La_{1.9}Sr_{0.1}Cu_{1-x}Zn_xO_4$ with $x = 0$ (T_c~33 K) and 0.02 (not superconducting) are shown in Fig. 9. That there is no upturn in C/T of the $x = 0.02$ sample is surprising since each substituted Zn atoms in CuO_2 planes could at most induce four spin 1/2 local moments on the neighboring Cu sites. The dip in C/T of the $x = 0.02$ sample is likely due to depression of quasiparticle density of states rather than due to the magnetic origin [19]. To demonstrate what 2% of PC's (a conservative value) can do to C, the zero field data of $x = 0.02$ are fit with $n = 2\%$ and $H_0 = 5\ T$. As shown by the dash line in Fig. 9, the fit is catastrophic and leads to an unrealistic negative γ. As for the alternative that four spin-1/2 local moments on the neighboring Cu sites could form a composite spin-2 PC's, the same analysis would lead to $n = 0.05$ for $H = 0$ with about the same H_0 as mentioned above. Therefore, the dip is unlikely caused by the Schottky anomaly. Even if it is, n is too small compared to the concentration of Zn. Obviously, the absence of the magnetic contribution happens in both the superconducting and non-superconducting samples in a similar way. Therefore it calls for mechanisms other than Kondo screening in the superconducting state to explain the absence of the magnetic contribution in C for non-superconducting Zn-doped cuprates.

5. Ongoing subjects

5.1. Observation of $H^{1/2}$ dependence in non-high T_c superconductors

The $\gamma(H) = A\ H^{1/2}$ predicted for *d*-wave superconductors has been clearly observed in hole-doped high-T_c cuprates as described in Section 3. However, the similar curvature was also reported in C/T vs H at low magnetic fields in *s*-wave supeconductors, such as $NbSe_2$ [45,46], V_3Si [24], and $CeRu_2$ [47] and in other unconventional superconductors UPt_3 [48], the organic superconductor (BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [49] and the boroncarbide superconductor $LuNi_2B_2C$ [50]. Ramirez [24] suggested that this behavior at the low fields must be a general feature of all superconductors in the vortex state, independent of the order parameter symmetry, but somehow related to the strength of the vortex–vortex interactions. Sonier et al. [46] suggested that the change of vortex size induced by vortex–vortex interactions will give the downward curvature in C/T vs H. Clearly, the $H^{1/2}$ dependence of C/T in the HTSCs cannot be simply attributed to nodes in the energy gap function without a satisfactory explanation for similar behavior in fully gapped superconductors.

5.2. Pairing state of electron-doped superconductors

There is by now a consensus that the optimally hole-doped high-T_c cuprates exhibit *d*-wave pairing symmetry [1]. However, the issue has been controversial for electron-doped superconductors. It is well known that the electron-doped superconductors are different from their hole-doped counterparts in many ways. For example, the early microwave measurement of the penetration depth $\gamma(T)$ [51,52] and the absence of a zero bias conduction peak [53,54] in $Nd_{1.85}Ce0._{15}CuO_4$ (NCCO) were interpreted within a *s*-wave model. The most recent phase-sensitive experiment [55] and γ (T) measurements [56,57] on NCCO and $Pr_{1.85}Ce0._{15}CuO_4$ (PCCO) concluded a *d*-wave pairing symmetry. Thus the question remains: are the pairing symmetries of electron- and hole-doped high-T_c cuprates exactly the same? As far as we know, there is no LTSH report specifically on this issue by. Our preliminary data on PCCO can be basically described in *d*-wave scenario [58]. More detailed measurements are in progress.

6. Summary

Magnetic field dependent LTSH on high-T_c hole-doped cuprates has provided evidences that the pairing symmetry is *d*-wave consistent with other experiments. The scaling model for clean *d*-wave and the breakdown of its relation in dirty *d*-wave superconductors were demonstrated in Ni-doped LSCO system. Low energy quasiparticles density of states $N(E)$ in dirty *d*-wave superconductors were deduced from the LTSH data. Absence of paramagnetic contribution to LTSH in both Zn-doped superconductor and non-superconductor suggests that a mechanism beyond Kondo screening model is required to explain its magnetic property. Through the persistent specific heat (plus other) experiments and theoretical efforts, the quasiparticles, especially in the vortex state, are now better understood. Although the dawn of knowledge about the quasiparticles of *d*-wave superconductivity is just breaking, the semi-classical approach proves to produce descriptions of the experimental observations to a high degree of accuracy. Probably the only exception is the predicted four-fold oscillations of $C_e(T,H)$ for H parallel the CuO_2 planes [59]. For the present, the experiments either observed no oscillations [35] or reported anisotropy of $C_e(T,H)$ different from the theoretical predictions [60].

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