Impurity scattering effects on the low-temperature specific heat of $d$-wave superconductors

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Recently, impurity scattering effects on quasiparticles in $d$-wave superconductors have attracted much attention. In particular, the thermodynamic properties in magnetic fields are of interest. We have measured the low-temperature specific heat $C(T,H)$ of La$_{1.78}$Sr$_{0.22}$CuO$_4$. The impurity scattering effects on $C(T,H)$ of cuprate superconductors were clearly observed and are compared with the theory of $d$-wave superconductivity. It is found that impurity scattering leads to the relation $\gamma(H) = \gamma(0) [1 + D(H/H_c^2) \ln(H_c^2/H)]$ in small magnetic fields. Surprisingly, the scaling of $C(T,H)$ is broken down by impurity scattering.

Tunneling and angle-resolved photoemission spectroscopy experiments, which are sensitive to either the interface of the junction or the surface of the sample, have suggested dominant $d$-wave pairing symmetry in hole-doped cuprate superconductors. In addition, the low-temperature specific heat $C(T)$ is thought to be one of the best indicators of $d$-wave pairing among the bulk properties. The $T^2$ temperature dependence of the electronic term in $C$ at zero magnetic field $H=0$ and the $H^{1/2}$ dependence of the linear-term coefficient $\gamma$ have been interpreted as strong evidence for linear nodes of the order parameter. Very recently, the scaling behavior of the electronic specific heat contribution $C_g(T,H)$ has been predicted theoretically and confirmed by experiments. However, several papers have reported that nonlinear $H$ dependence of $\gamma$ was also observed in conventional superconductors, and raised the question whether the $H^{1/2}$ dependence of $\gamma$ is indeed due to $d$-wave pairing. In addition, although most studies of $C(T,H)$ in cuprates agree on the $H^{1/2}$ dependence of $\gamma$, controversy remains about the existence of the $T^2$ term at $H=0$. Chen et al. have presented data showing clear evidence of the $T^2$ term in La$_{1.78}$Sr$_{0.22}$CuO$_4$ and the disappearance of this $T^2$ term in a magnetic field, both consistent with the predictions for $d$-wave superconductivity. Nevertheless, in other work, either evidence of the $T^2$ term was ambiguous or it had to be identified through sophisticated fits. These difficulties make $C(T,H)$ studies of impurity-doped cuprate superconductors of particular interest. If the recently developed theory of the impurity scattering effects on quasiparticle excitation in cuprates could be verified by $C(T,H)$ measurements, it would strongly indicate that the observed properties of $C(T,H)$ are characteristic of $d$-wave pairing. These studies may also help to improve the theories of quasiparticles in cuprates. 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 impurity-doped cuprates. Comparisons between $C(T,H)$ of the nominally clean samples and of the impurity-doped ones may have fruitful implications for the existing puzzles.

To serve these purposes, La$_{1.78}$Sr$_{0.22}$Cu$_{1-x}$Ni$_x$O$_4$ samples were chosen for two main reasons. The $C$ of Ni-doped samples has a much smaller magnetic contribution than that of Zn-doped samples, and the data analysis can be simplified. Moreover, La$_{1.78}$Sr$_{0.22}$CuO$_4$ has been shown to be a clean $d$-wave superconductor and is ideal to compare with the Ni-doped samples. Polycrystalline samples of La$_{1.78}$Sr$_{0.22}$Cu$_{1-x}$Ni$_x$O$_4$ with nominal $x=0, 0.01, and 0.02$ were carefully prepared from $La_2O_3$, SrCO$_3$, and CuO powders of 99.999% purity. Details of the preparation have been described elsewhere. The powder x-ray-diffraction patterns of all samples used in the experiments show a single $T$ phase with no detection of impurity phases. The transition temperature $T_c$ from the midpoint of the resistivity drop is 28.7, 21.2, and 17.4 K for $x=0, 0.01$, and 0.02, respectively. The transition width (90–10% from the resistivity drop) of $T_c$ is 3 K or less for all samples, suggesting a decent homogeneity. $C(T)$ was measured from 0.6 to 9 K with a $^3$He thermal relaxation calorimeter using the heat-pulse technique. The precision of the measurements in this temperature range is about 1%. To test the calibration of the thermometer and the measurements in $H$, a copper sample was measured, and the scatter of data in different magnetic fields was about 3% or better. Details of the calorimeter calibration with the copper sample can be found in Ref. 5.

The analysis of $C(T,H)$ was carried out for data from 0.6 to 7 K. Varying the temperature range to 8 or 6 K does not lead to any significant change of the results. Both individual-field and global fits have been executed and give similar results and conclusion. In this paper, the results from the individual-field fit are reported. Data from all samples are described by

$$C(T,H) = \gamma(H)T + \beta T^3 + n C_{S-2}(T,H),$$

where $\beta T^3$ is the phonon contribution and $n C_{S-2}$ is the magnetic contribution of spin-2 paramagnetic centers (PC’s)
yields a better fit than that of the Schottky anomaly. Results, suited for low magnetic fields. From the low-field fitting re-

H but there is variation when $H$ resulting from the fit does not change significantly with $n$ compared with other terms is shown in Fig. 3. As expected, the temperature upturn in $C/T$ with increasing $x$ can also be recognized directly from data shown in Fig. 1. Both the disappearance of the $T^2$ term and the increase in $\gamma$ are considered to be manifestations of impurity scattering. The low-temperature upturn in $C/T$ at both $x = 0.01$ and $0.02$ can be attributed to $nC_{5-2}$ as shown by the solid lines resulting from a fit to Eq. (1). To further show the quality of the fit in a magnetic field, $C(T,H)$ of $x = 0.01$ at low temperatures is shown in Fig. 2(a) as an example, together with the solid lines representing the fit of data to Eq. (1). The results illustrate that $C(T,H)$ of La$_{1.78}$Sr$_{0.22}$Cu$_{0.99}$Ni$_{0.01}$O$_4$ can be satisfactorily described by Eq. (1). The contribution of $nC_{5-2}$ compared with other terms is shown in Fig. 3. As expected, $n$ resulting from the fit does not change significantly with $H$, but there is variation when $H \geq 4$ T as shown in Fig. 2(c). Similar results for $n$ vs $H$ were found in all three samples. It is likely that the effective Hamiltonian for $C_{5-2}$ in Ref. 20 results from experimental data with $H < 4$ T, and is best suited for low magnetic fields. From the low-field fitting results, $n$ for $x = 0.01$, and 0.02 is about 0.3, 0.9, and 1.8 $\times 10^{-3}$, respectively. The value of $n$ for $x = 0$ is taken from a fit of the data in $H$ and used in the fit at $H = 0$. The solid line for $x = 0$ in Fig. 1 shows that the data can accommodate a small $nC_{5-2}$.

For a clean $d$-wave superconductor in a finite field $H$, an increase in $\gamma$ is predicted to be proportional to $H^{1/2}$ at low temperatures, due to the Doppler shift on the quasiparticle energy. In the unitary limit, impurity scattering leads to a modification of the density of states, and the $H$ dependence of $\gamma$ becomes

$$\gamma(H) = \gamma(0)[1 + D(H/H_{c2})\ln(H_{c2}/H)],$$

where $D \approx \Delta_0/32\Gamma$. $\Delta_0$ is the superconducting gap, $\Gamma$ is the impurity scattering rate, and $H_{c2}$ is the upper critical field. The unitary limit is widely considered as a good approximation to the nature of the impurity scattering in cuprates, and

FIG. 1. $C/T$ vs $T^2$ of La$_{1.78}$Sr$_{0.22}$Cu$_{0.99}$Ni$_{0.01}$O$_4$ with $x = 0$, 0.01, and 0.02 at $H = 0$. The solid lines are the results of the fit to Eq. (1). Inset: $C/T$ vs $T$ for $T < 2$ K, where the contribution from the $T^2$ term is apparent.

FIG. 3. The components of $C(T,H)$ of La$_{1.78}$Sr$_{0.22}$Cu$_{0.99}$Ni$_{0.01}$O$_4$.

FIG. 2. (a) $C/T$ vs $T^2$ of La$_{1.78}$Sr$_{0.22}$Cu$_{0.99}$Ni$_{0.01}$O$_4$ in magnetic fields. The solid lines are the results of the fit to Eq. (1). For clarity, only data in $H = 0$, 0.2, 1, 4, and 8 T are shown. (b) The concentration $n$ of the spin-2 PC’s from the fit.
is supported by experimental evidence. To compare $\gamma(H)$ of the clean sample with that of the Ni-doped ones, $\gamma$ vs $H^{1/2}$ of all samples is plotted in Fig. 4. If $\gamma$ has an $H^{1/2}$ dependence as expected in a clean sample, the data will follow a straight line as represented by the dashed line in Fig. 4. Indeed, data for the sample with $x=0$ indicate a clear $H^{1/2}$ dependence of $\gamma$ [Fig. 4(a)]. In Ni-doped samples, the $H$ dependence of $\gamma$ is weaker than in the clean sample, and the data show a pronounced curvature for small $H$ [Figs. 4(b) and 4(c)]. This behavior makes the $\gamma(H)$ of Ni-doped samples distinct from that of the clean sample. Thus the effect of impurity scattering is evident. Actually, $\gamma(H)$ of both Ni-doped samples can be well described by Eq. (2) with reasonable parameters, as shown by the solid line in Figs. 4(b) and 4(c). The fit gives $\Gamma/\Delta_0 = 0.020$ and 0.025 for $x = 0.01$ and 0.02, respectively, with $H_c \approx 38$ T. An increase in $\Gamma/\Delta_0$ by a factor of 2 is expected for $x = 0.02$ from the nominal doping concentration; nevertheless, this small increase in $\Gamma/\Delta_0$ is in accord with a less rapid $T_c$ suppression in the $x = 0.02$ sample. Furthermore, as a result of the impurity scattering, the values of $\gamma/\gamma_n$ corresponding to those of $\Gamma/\Delta_0$ are in good agreement with the calculated values in Refs. 17 and 18 for both Ni-doped samples. On the other hand, an attempt to fit $\gamma(H)$ of the clean sample with Eq. (2) has proven to be fruitless and resulted in an unrealistic $H_c > 1000$ T.

The most crucial test of the recent theory for a $d$-wave superconductor with impurities probably lies in the breakdown of the scaling behavior of $C_e(T,H) = C(T,H) - \gamma(H) = 0$) $T - BT^3 - nC_5$. For a clean $d$-wave superconductor, $C_e(T,H)$ vs $H^{1/2}$ is plotted, all data at various values of $T$ and $H$ should collapse onto one scaling line according to the recent scaling theory.13,14 This scaling of $C_e(T,H)$ has been observed in YBa$_2$Cu$_{3}$O$_{7-\delta}$ and La$_{1.78}$Sr$_{0.22}$CuO$_{4}$.9-11 As shown in Fig. 5(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 breakdown of the scaling.17,25 This dramatic effect is best illustrated in Figs. 5(b) and 5(c). In contrast to the scaling of $C_e(T,H)$ of the clean sample, the $C_e(T,H)$ data of Ni-doped samples split into individual isothermal lines as predicted by the numerical calculations.17
The very theory also suggests that Eq. (2) is exact only in fields $H< H^*$ where $H^*/H_{c2} \approx \Gamma/\Delta_0$. However, $\gamma(H)$ should not deviate from Eq. (2) too much if $H$ is only slightly larger than $H^*$. In the case of $H>H^*$, $\gamma(H)$ would mimic the $H^{1/2}$ behavior.\textsuperscript{18} With $H^* \approx 1 T$ in the present experiments, $\gamma(H)$ in Figs. 4(b) and 4(c) behaves exactly as is expected. In small $H$, the weak magnetic field dependence is well described by Eq. (2). In large $H$, the data do not obey Eq. (1) as well as in small $H$, and a distinction between Eq. (2) and the $H^{1/2}$ dependence is less easily made. Therefore, the less satisfactory fit in high fields merely reflects the limit of Eq. (2) as expected from the theory.

Experimentally, $n$ of the spin-2 PC’s increases with the doping concentration $x$. However, it is unlikely that the magnetic contribution to $C(T,H)$ comes directly from the Ni ions since $n$ is two orders of magnitude smaller than $x$. Recently, it has been reported that the nominally magnetic Ni ions do not disturb the spin correlation in CuO$_2$ planes even on Ni sites at small $x$ in overdoped cuprates.\textsuperscript{25} In both $C$ and susceptibility ($\chi$) measurements, no paramagnetic contribution from Ni was observed. The $C$ reported in this paper and related preliminary studies on $\chi$ are consistent with these results.\textsuperscript{26} The larger $nC_{S-2}$ in the Ni-doped samples probably comes from defects in the CuO$_2$ planes, which are induced by Ni substitution. On the other hand, Zn substitution has strong effects on $C$ (and $\chi$). The large magnetic contribution usually makes studies of impurity scattering effects on $C(T,H)$ inconclusive.\textsuperscript{27,28} More detailed studies are desirable on these properties of $C$ and $\chi$ in Ni- or Zn-doped cuprates.

In conclusion, impurity scattering effects on $C(T,H)$ of $d$-wave superconductors have been clearly identified. The weak $H$ dependence of $\gamma(H)$ in small magnetic fields and the breakdown of the scaling behavior of $C_s(T,H)$ are both consistent with predictions of recent theory. 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.

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