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 $La_{1.78}Sr_{0.22}Cu_{1-x}Ni_xO_4$. 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 $\gamma(H)=\gamma(0)[1+D(H/H_{c2})\ln(H_{c2}/H)]$ 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.[1,2] In addition, the low-temperature specific heat (C) 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 γ have been interpreted as strong evidence for linear nodes of the order parameter.[3–12] Very recently, the scaling behavior of the electronic specific heat contribution $C_e(T,H)$ has been predicted theoretically[13,14] and confirmed by experiments.[5,9–11] However, several papers have reported that nonlinear H dependence of γ was also observed in conventional superconductors,[15,16] and raised the question whether the $H^{1/2}$ dependence of γ 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 γ, 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.[5] Nevertheless, in other work, either evidence of the T^2 term was ambiguous or it had to be identified through sophisticated fits.[6–10] These difficulties make $C(T,H)$ studies of impurity-doped cuprate superconductors of particular interest. If the recently developed theory[17–19] 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, $La_{1.78}Sr_{0.22}Cu_{1-x}Ni_xO_4$ 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[5] and is ideal to compare with the Ni-doped samples. Polycrystalline samples of $La_{1.78}Sr_{0.22}Cu_{1-x}Ni_xO_4$ 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.[5] 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 to 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

$$C(T,H)=\gamma(H)T+\beta T^3+nC_{S=2}(T,H), \tag{1}$$

where βT^3 is the phonon contribution and $nC_{S=2}$ is the magnetic contribution of spin-2 paramagnetic centers (PC's)

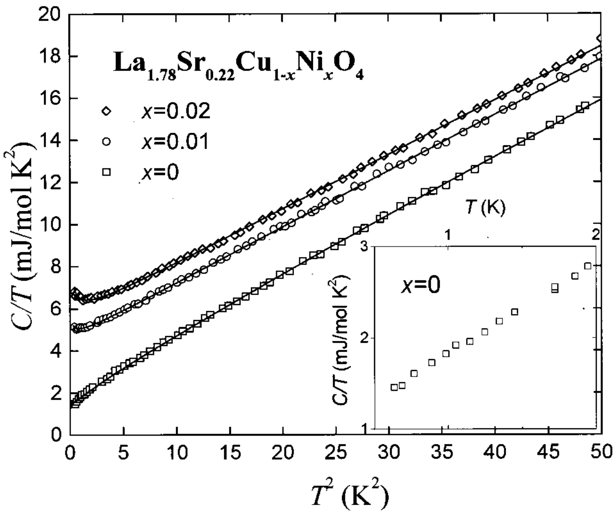

FIG. 1. C/T vs T^2 of $La_{1.78}Sr_{0.22}Cu_{1-x}Ni_xO_4$ with $x=0$, 0.01, and 0.02 at $H=0$. The solid lines are the results of the fit to Eq. (1). Inset: C/T vs T for $T<2$ K, where the contribution from the T^2 term is apparent.

associated with CuO_2 planes.[20–22] Since $La_{1.78}Sr_{0.22}Cu_{1-x}Ni_xO_4$ has only CuO_2 planes and lacks CuO chains, $nC_{S=2}$ was used rather than the conventional Schottky anomaly, which is thought to be related to CuO chains.[7,22] Phenomenologically, inclusion of $nC_{S=2}$ also yields a better fit than that of the Schottky anomaly.

$C(T,0)$ of samples with $x=0$, 0.01, and 0.02 is shown in Fig. 1. For $x=0$, at zero field C/T vs T^2 shows an obvious downward curve at low temperatures due to the T^2 term in C. For $x=0.01$, this downward curve becomes a straight line except below 1 K where the magnetic contribution becomes important. An increase in γ 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 γ 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 $nC_{S=2}$ 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 $La_{1.78}Sr_{0.22}Cu_{1-x}Ni_xO_4$ can be satisfactorily described by Eq. (1). The contribution of $nC_{S=2}$ 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 $H\geqslant 4$ 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 $C_{S=2}$ in Ref. 20 results from experimental data with $H<4$ T,[21] and is best suited for low magnetic fields. From the low-field fitting results, n for $x=0$, 0.01, and 0.02 is about 0.3, 0.9, and 1.8 $\times 10^{-4}$, 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 $nC_{S=2}$.

For a clean d-wave superconductor in a finite field H, an increase in γ is predicted to be proportional to $H^{1/2}$ at low temperatures, due to the Doppler shift on the quasiparticle energy.[3,4] In the unitary limit, impurity scattering leads to a modification of the density of states, and the H dependence of γ becomes[17–19]

$$\gamma(H)=\gamma(0)[1+D(H/H_{c2})\ln(H_{c2}/H)], \qquad (2)$$

where $D\approx\Delta_0/32\Gamma$. Δ_0 is the superconducting gap, Γ 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

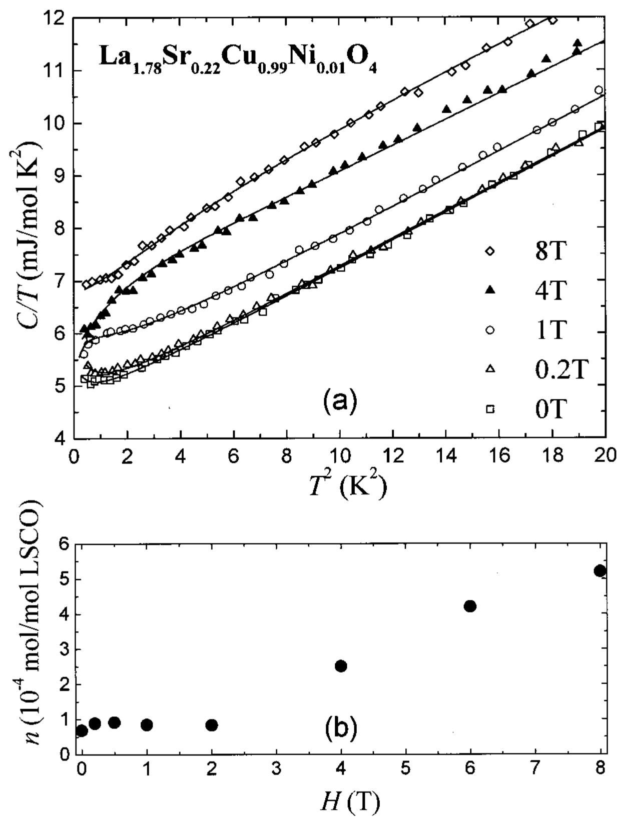

FIG. 2. (a) C/T vs T^2 of $La_{1.78}Sr_{0.22}Cu_{0.99}Ni_{0.01}O_4$ in magnetic fields. The solid lines are the results of the fit to Eq. (1). For clarity, only data in $H=0$, 0.2, 1, 4, and 8 T are shown. (b) The concentration n of the spin-2 PC's from the fit.

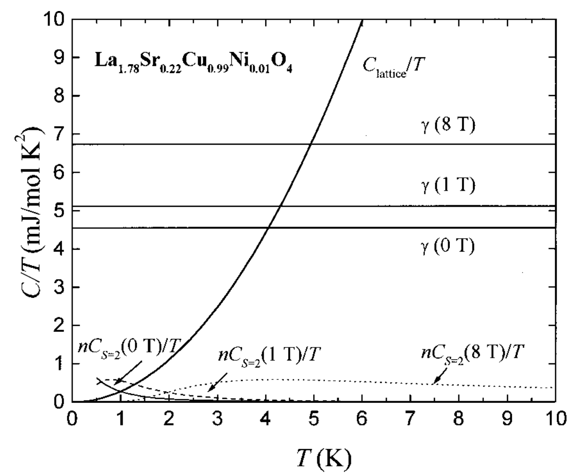

FIG. 3. The components of $C(T,H)$ of $La_{1.78}Sr_{0.22}Cu_{0.99}Ni_{0.01}O_4$.

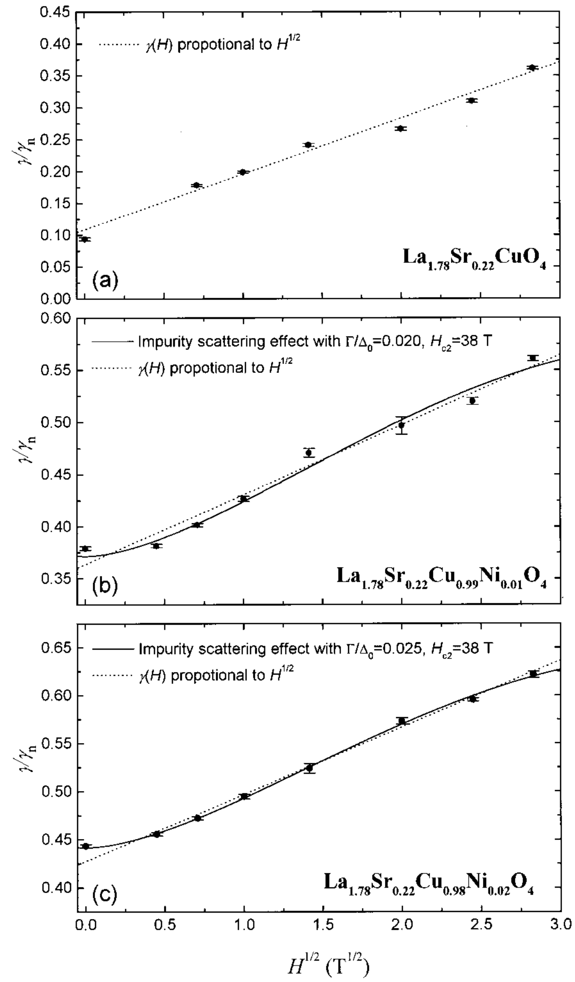

FIG. 4. Normalized $\gamma(H)$ vs $H^{1/2}$ for three $La_{1.78}Sr_{0.22}Cu_{1-x}Ni_xO_4$ samples. The solid lines are the results of the fit to Eq. (2), which includes the impurity effects on $C(T,H)$. Dashed lines represent $\gamma(H)\propto H^{1/2}$, expected in clean *d*-wave superconductors. In (a) no solid line is presented since the fit to Eq. (2) gives an unrealistic value of $H_{c2}>1000\,\mathrm{T}$. $\gamma_n = 12\,\mathrm{mJ/mol\,K^2}$ is the normal-state γ of the samples (Ref. 5).

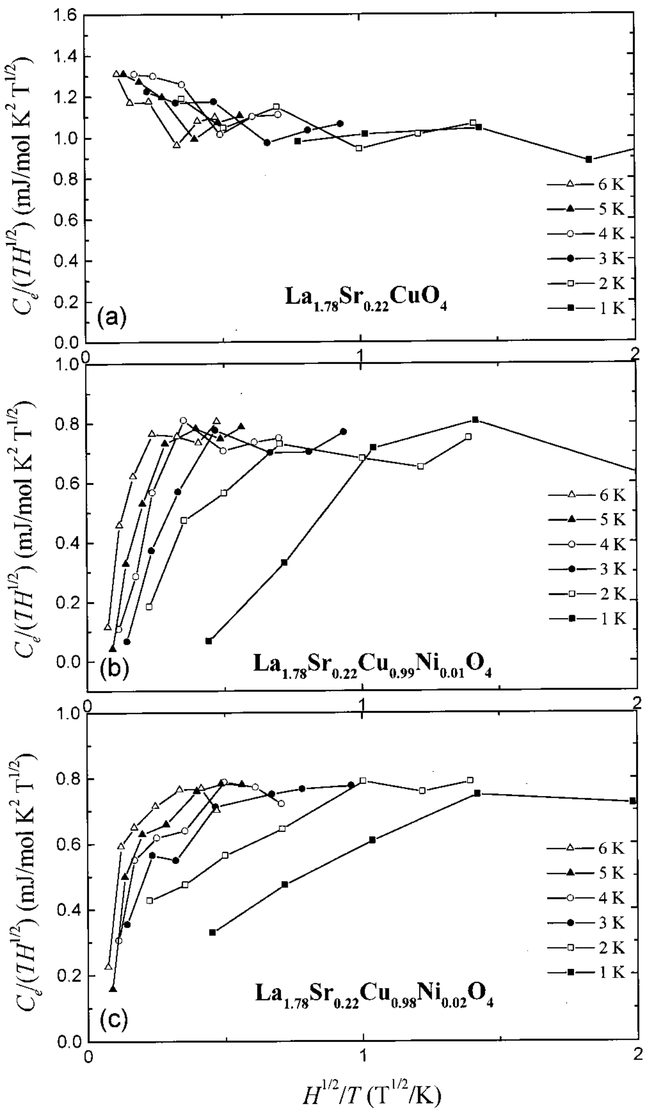

FIG. 5. Plots of $C_e/(TH^{1/2})$ vs $H^{1/2}/T$ for (a) $x=0$, (b) $x=0.01$, and (c) $x=0.02$. Note that the scaling which holds in (a) breaks down in (b) and (c) due to impurity scattering.

is supported by experimental evidence. To compare $\gamma(H)$ of the clean sample with that of the Ni-doped ones, γ vs $H^{1/2}$ of all samples is plotted in Fig. 4. If γ 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 γ [Fig. 4(a)]. In Ni-doped samples, the H dependence of γ 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 $H_{c2}\approx 38\,\mathrm{T}$. An increase in Γ/Δ_0 by a factor of 2 is expected for $x=0.02$ from the nominal doping concentration; nevertheless, this small increase in Γ/Δ_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 γ/γ_n corresponding to those of Γ/Δ_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 $H_{c2}>1000\,\mathrm{T}$.

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 $C_e(T,H)\equiv C(T,H)-\gamma(H=0)T-\beta T^3-nC_{S=2}$. For a clean *d*-wave superconductor, if $C_e/(TH^{1/2})$ vs $H^{1/2}/T$ is plotted, all data at various 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 $YBa_2Cu_3O_{7-\delta}$ and $La_{1-x}Sr_xCuO_4$.[5,9–11] 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.[17,23] 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 $H^*/H_{c2}\approx\Gamma/\Delta_0$.[17,18] However, $\gamma(H)$ should not deviate from Eq. (2) too much if H is only slightly larger than H^*.[24] In the case of $H\gg H^*$, $\gamma(H)$ would mimic the $H^{1/2}$ behavior.[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.[25] In both C and susceptibility (χ) measurements, no paramagnetic contribution from Ni was observed. The C reported in this paper and related preliminary studies on χ are consistent with these results.[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 χ). The large magnetic contribution usually makes studies of impurity scattering effects on $C(T,H)$ inconclusive.[27,28] More detailed studies are desirable on these properties of C and χ 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 $C_e(T,H)$ 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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[1] J. F. Annett, N. D. Goldenfeld, and A. J. Leggett, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1996), Vol. 5.
[2] H. Ding, M. R. Norman, T. Yokoya, T. Takeuchi, M. Randeria, J. C. Campuzano, T. Takahashi, T. Mochiku, and Kadowaki, Phys. Rev. Lett. **78**, 2628 (1997), and references therein.
[3] G. E. Volovik, Pis'ma Zh. Eksp. Teor. Fiz. **58**, 457 (1993) [JETP Lett. **58**, 469 (1993)].
[4] H. Won and K. Maki, Europhys. Lett. **73**, 2744 (1995).
[5] S. J. Chen, C. F. Chang, H. L. Tsay, H. D. Yang, and J.-Y. Lin, Phys. Rev. B **58**, R14 753 (1998).
[6] K. A. Moler, D. J. Baar, J. S. Urbach, Ruixing Liang, W. N. Hardy, and A. Kapitulnik, Phys. Rev. Lett. **73**, 2744 (1994).
[7] K. A. Moler, D. L. Sisson, J. S. Urbach, M. R. Beasley, and A. Kapitulnik, Phys. Rev. B **55**, 3954 (1997).
[8] R. A. Fisher, J. E. Gordon, S. F. Reklis, D. A. Wright, J. P. Emerson, B. F. Woodfield, E. M. McCarron III, and N. E. Phillips, Physica C **252**, 237 (1995).
[9] D. A. Wright, J. P. Emerson, B. F. Woodfield, J. E. Golden, R. A. Fisher, and N. E. Phillips, Phys. Rev. Lett. **82**, 1550 (1999).
[10] R. A. Fisher, B. Buffeteau, R. Calemezuk, K. W. Dennis, T. E. Hargreaves, C. Marcenat, R. W. McCallum, A. S. O'Connor, N. E. Phillips, and A. Schilling, Phys. Rev. B **61**, 1473 (2000).
[11] B. Revaz, J.-Y. Genoud, A. Junod, A. Erb, and E. Walker, Phys. Rev. Lett. **80**, 3364 (1998).
[12] N. Momono and M. Ido, Physica C **264**, 311 (1996).
[13] S. A. Simon and P. A. Lee, Phys. Rev. Lett. **78**, 1548 (1997).
[14] G. E. Volovik, Pis'ma Zh. Eksp. Teor. Fiz. **65**, 465 (1997) [JETP Lett. **65**, 491 (1997)].
[15] A. P. Ramirez, Phys. Lett. A **211**, 59 (1996).
[16] J. E. Sonier, M. F. Hundley, and J. W. Brill, Phys. Rev. Lett. **82**, 4914 (1999).
[17] C. Kübert and P. J. Hirschfeld, Solid State Commun. **105**, 459 (1998); Phys. Rev. Lett. **80**, 4963 (1998).
[18] Y. S. Barash, A. A. Svidzinskii, and V. P. Mineev, Pis'ma Zh. Eksp. Teor. Fiz. **65**, 606 (1997) [JETP Lett. **65**, 638 (1997)].
[19] E. Janod, R. Calemczuk, J.-Y. Henry, and J. Flouquet, Physica C **281**, 176 (1997); the theory including the effects of impurity scattering was written by G. E. Volovik in Appendix A of this paper.
[20] O. N. Bakharev, M. V. Eremin, and M. A. Teplov, Pis'ma Zh. Eksp. Teor. Fiz. **61**, 499 (1995) [JETP Lett. **61**, 515 (1995)].
[21] P. G. Baranov and A. G. Badalyan, Solid State Commun. **85**, 987 (1993).
[22] J. P. Emerson, D. A. Wright, B. F. Woodfield, J. E. Golden, R. A. Fisher, and N. E. Phillips, Phys. Rev. Lett. **82**, 1546 (1999).
[23] G. E. Volovik (private communication).
[24] P. J. Hirschfeld (private communication).
[25] T. Nakano, N. Momono, T. Nagata, M. Oda, and M. Ido, Phys. Rev. B **58**, 5831 (1998).
[26] J.-Y. Lin, H. D. Yang, T. I. Hsu, and H. C. Ku (unpublished).
[27] J.-Y. Lin, C. F. Chang, and H. D. Yang, Physica B (to be published).
[28] D. L. Sisson, S. G. Doettinger, A. Kapitulnik, R. Liang, D. A. Bonn, and W. N. Hardy, Phys. Rev. B **61**, 3604 (2000).