Magnetic-field dependence of electronic specific heat in $Pr_{1.85}Ce_{0.15}CuO_4$

Hamza Balci,[1] V. N. Smolyaninova,[1] P. Fournier,[2] Amlan Biswas,[1] and R. L. Greene[1]
[1]*Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742*
[2]*Centre de Recherche sur les Propriétés Électroniques de Matériaux Avancés, Département de Physique, Université de Sherbrooke, Québec, Canada J1K 2R1*

(Received 6 June 2002; published 13 November 2002)

The specific heat of electron-doped $Pr_{1.85}Ce_{0.15}CuO_4$ single crystals is reported for the temperature range 2–7 K and magnetic field range 0–10 T. A nonlinear magnetic-field dependence is observed for the field range 0–2 T. Our data support a model with lines of nodes in the gap function of these superconductors. Theoretical calculations of the electronic specific heat for dirty *d*-wave, clean *d*-wave, and *s*-wave symmetries are compared to our data.

DOI: 10.1103/PhysRevB.66.174510 PACS number(s): 74.25.Bt, 74.20.Rp, 74.25.Jb

The order parameter (gap) symmetry of high-T_c cuprate superconductors is an important parameter in attempting to understand the pairing mechanism in these materials. For hole-doped cuprates experimental evidence strongly favors *d*-wave symmetry.[1,2] Surprisingly, early experiments on electron-doped (*n*-type) $Nd_{1.85}Ce_{0.15}CuO_4$ (NCCO) suggested an *s*-wave symmetry. Recent penetration depth,[3] tricrystal,[4] photoemission,[5] Raman scattering,[6] and point contact tunneling experiments[7] on NCCO and $Pr_{2-x}Ce_xCuO_4$ (PCCO) favored a *d*-wave symmetry. In addition to these measurements, which showed *s*- or *d*-wave symmetry, there are penetration depth[8] and point contact tunneling[7] experiments that showed evidence of a change in the order parameter as the doping changes from underdoped (*d* wave) to overdoped (*s* wave). However, since these prior measurements on the *n*-type cuprates are surface sensitive there is a need for bulk measurements (e.g. specific heat) to convincingly determine the pairing symmetry, as was the case for the *p*-type cuprates.[9–12]

The specific heat is sensitive to low temperature electronic excitations. Different gap symmetries have different densities of electronic states close to the Fermi level. Conventional low-T_c superconductors show an *s*-wave gap symmetry in which the electronic specific heat has an exponential temperature dependence, $C_{el} \propto T^{1.5} e^{-\Delta/kT}$, where Δ is the energy gap.[13] For a clean *d*-wave superconductor electronic excitations exist even at the lowest temperatures. The electronic density of states is predicted to have a linear energy dependence close to the Fermi level, and this shows up in the electronic specific heat as $C_{el} \propto T^2$.[14]

In the mixed state, there are two types of quasiparticle excitations in the bulk of the superconductor: bound states inside the vortex cores, and extended states outside the vortex cores. In conventional *s*-wave superconductors, the in-core bound states dominate the quasiparticle excitations; therefore, the electronic specific heat is proportional to the number of vortices. The number of vortices is linear in field, therefore the electronic specific heat is also linear in field.[15] In a superconductor 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 specific heat has a $\sqrt{H}$ dependence in the clean limit[16] at $T=0$. For non-zero temperatures there is a minimum field that depends on temperature after which the $\sqrt{H}$ dependence should be observed. In the dirty limit the energy scale related to impurity bandwidth (or impurity scattering rate) is much larger than the energy scale related to Doppler shift due to magnetic field (the dominant mechanism for the clean *d*-wave case), and much less than the superconducting gap maximum. In this limit, i.e., $k_B T \ll (H/H_{c2})\Delta_0 \ll \gamma_0 \ll \Delta_0$ ($\hbar$ is set to 1), where Δ_0 is the gap maximum and γ_0 is the impurity bandwidth [or (1/2) the quasiparticle scattering rate at zero energy], the magnetic field dependence deviates from $\sqrt{H}$, and an $H\log(H)$ like dependence is predicted below a certain field H^*, which depends on temperature and impurity concentration in the sample.[18]

In this paper we present magnetic field dependent specific heat measurements on *n*-type cuprates which probe the symmetry of the superconducting state. The electronic specific heat has been observed to have a nonlinear magnetic field dependence. The theoretical model for a clean *d*-wave symmetry fits reasonably well to our data; however, there are deviations from this type of field dependence below $H^* = 0.6$ T (Fig. 3). We find that an $H\log(H)$ type dependence gives a better fit to our data over the whole range, which means our data can better be described by a dirty *d*-wave symmetry. It is important to emphasize that the main point of this work is to address the question of an *s* wave vs a *d* wave, rather than a clean *d* wave vs a dirty *d* wave.

The specific heat data was obtained in the temperature range 2–7 K and the magnetic field range 0–10 T using the relaxation method.[19] The measurements were repeated in two systems, a home-made setup and a Quantum Design PPMS with some modifications on the sample holder to remove the field dependence of the original chip. The addenda consist of a sapphire substrate with a thermometer and heater, and Wakefield thermal compound to hold the PCCO crystal. The addenda were measured separately, and found to have no magnetic field dependence within the resolution of our experiment($\pm 2.5\%$). The experiment was done on several optimally doped $Pr_{1.85}Ce_{0.15}CuO_4$ single crystals (the mass of the crystals was 3–5 mg). The sample heat capacity is approximately equal to two times that of the addenda at $T = 2$ K, and equal to that of the addenda at $T = 10$ K. The crystals were grown by the directional solidification

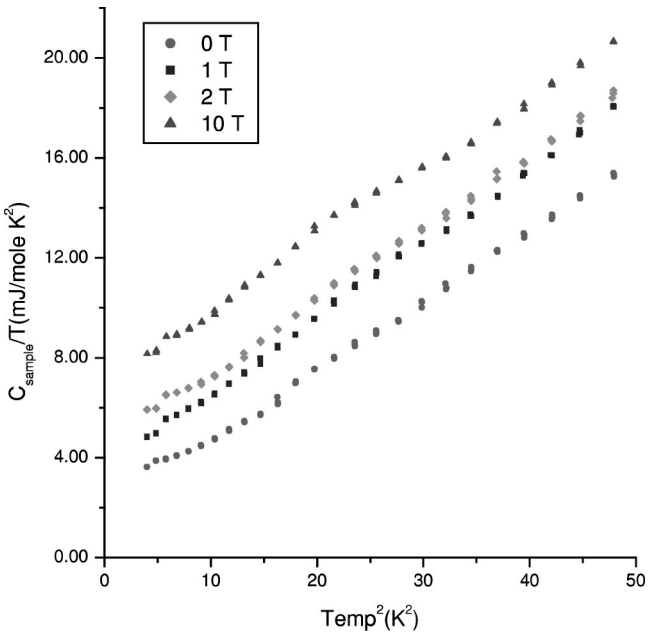

FIG. 1. C/T vs T^2, where C is the sample total specific heat, at four different fields (0, 1, 2, and 10 T) in the temperature range 2–7 K. The magnetic field is perpendicular to the ab-plane.

technique.[20] The samples were characterized with a superconducting quantum interface device magnetometer and found to be fully superconducting, with similar transition temperatures $T_c = 22\ \mathrm{K} \pm 2\ \mathrm{K}$.

The specific heat of a *d*-wave superconductor usually has the following main contributions: the electronic contribution, which could have the form γT or γT^2 depending on the field and temperature range the measurement is done, the phonon contribution, which at the temperature range of our experiment can be written as βT^3, and a Schottky contribution, which is caused by spin-1/2 paramagnetic impurities.[21] Furthermore $\gamma = \gamma(0) + \gamma(H)$, where $\gamma(H)$ gives the field dependent part of the electronic specific heat coefficient, and $\gamma(0)T$ is the residual linear temperature dependent part of the electronic specific heat. $\gamma(0)$ is sample dependent, and it is origin is not completely understood. Nonelectronic two-level systems away from the copper-oxide planes are one of the possible candidates for the origin of this term.[18] It has been observed for all hole-doped samples studied. Figure 1 shows the temperature dependence of the specific heat at four different fields 0, 1, 2, and 10 T applied perpendicular to the ab plane of the crystal. The field range 0–2 T is the relevant field range to extract the gap symmetry information,[16] and at $H = 10$ T the sample is completely in the normal state ($H_{c2} = 8$ T at $T = 2$ K). Driving the sample to the normal state enables us to extract an important parameter, $\gamma_n = 6.7 \pm 0.5\ \mathrm{mJ/mole\,K^2}$, which is needed to compare our data to theoretical predictions quantitatively. A global fit which assumes the phonon coefficient β constant for all fields and γ variable gives a $\gamma(0) = 1.4 \pm 0.2\ \mathrm{mJ/mole\,K^2}$. This value of $\gamma(0)$ is consistent with the values found for $\gamma(0)$ in the hole-doped superconductors [$\gamma(0) \approx 1\ \mathrm{mJ/mole\,K^2}$ for YBCO (Refs. 9–11)].

The fact that we do not have any Schottky upturn at low temperatures for any field shows that our sample is free of magnetic impurities. From the slope of the lines, obtained through a global fit, $\beta = 0.29 \pm 0.01\ \mathrm{mJ/mole\ K^4}$, and a Debye temperature $\Theta_D = 362 \pm 4$ K has been extracted. These values are in reasonable agreement with the other published data in the literature [$\beta = 0.244$ mJ/mole K (Ref. 4) and $\Theta_D = 382$ K (Ref. 17)].

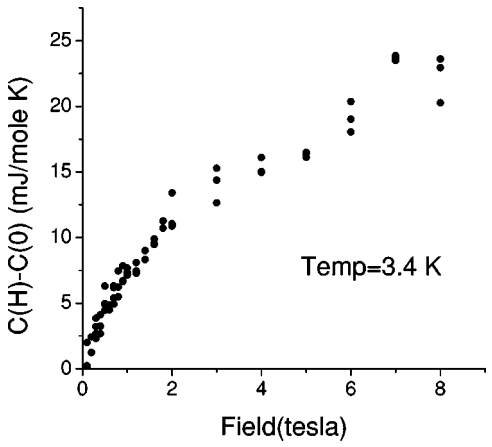

FIG. 2. $C(H)$-$C(0)$ vs magnetic field, or the field dependent electronic specific heat vs magnetic field. A nonlinear behavior is observed below 2 T. The electronic specific heat has saturated to the normal state value at 8 T.

Since the phonon specific heat is field independent and there is no Schottky contribution to the specific heat, subtracting the zero field specific heat from the specific heat at other fields gives the field dependent part of the electronic specific heat. Figure 2 shows the field dependent part of the electronic specific heat, $\gamma(H)T$, vs magnetic field at 3.4 K in the field range 0–8 T. Figure 3 shows theoretical fits to the 3.4-K data in the field range 0–2 T. These data are the same as the data in Fig. 2 but only the low field part is shown, and the three points taken for each field in Fig. 2 are averaged and shown as one point in Fig. 3. The low field part is im-

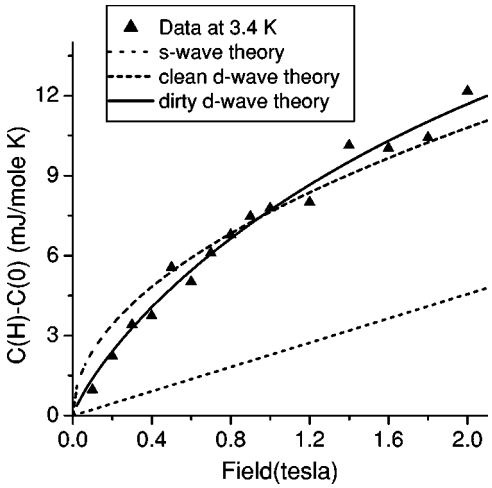

FIG. 3. The field dependent electronic specific heat vs magnetic field data at 3.4 K, and the theoretical fits to the data. The solid curve is the dirty *d*-wave fit, the dashed straight line is the *s*-wave fit, and the dashed curve is the clean *d*-wave fit.

portant because the theoretical work on *d*-wave symmetry (clean or dirty) has focused on the dilute vortex limit ($H_{c1} \ll H \ll H_{c2}$) to be able to ignore vortex-vortex interaction, so both Eqs. (1) and (2) are valid in this limit. The clean *d*-wave fit is calculated using the equation[11]

$$C_{el} = \gamma_n T \left(\frac{8}{\pi}\right)\left(\frac{H}{H_{c2}/a^2}\right)^{1/2} \quad \text{for} \quad \left(\frac{TH_{c2}^{1/2}}{T_c H^{1/2}}\right) \ll 1 \qquad (1)$$

where $\gamma_n = 6.7$ mJ/mole K^2 (from the intercept of our 10-T data in Fig. 1), $H_{c2} = 10$ T and $a = 0.7$ are used [a is a geometrical factor that depends on the vortex lattice geometry, and the value 0.7 was found experimentally for YBCO (Ref. 9)]. The clean *d*-wave fit is clearly better than the linear *s*-wave fit. The possible nonlinear behavior in an *s*-wave superconductor will be discussed below. However, as we shall now show, the dirty *d*-wave model is the best model to describe our data.

Even though the clean *d*-wave fit has a much better consistency than the linear *s*-wave fit, there seem to be deviations between our data and the clean *d*-wave theory below $H^* = 0.6$ T, which would be expected from a dirty *d*-wave superconductor. In fact, being in the dirty limit is not unexpected, since the penetration depth measurements performed on similar crystals, grown by this group, were also consistent with dirty *d*-wave symmetry.[3] For clean *d*-wave symmetry the change in the penetration depth as a function of temperature is linear in temperature [$\Delta\lambda(T) \propto T$], whereas a quadratic temperature dependence [$\Delta\lambda(T) \propto T^2$] is expected if the nodes are filled by impurity states, i.e., dirty *d* waves. A quadratic temperature dependence was observed consistently by two different groups on many crystals they studied.[3] If a dirty *d*-wave function of the type $C_{el}(H) = AH \log(B/H)$ is fitted to our data, a slightly better fit is obtained for the fitting parameters $A = 6.2 \pm 0.6$ mJ/mole K T and $B = 17.6 \pm 4.7$ T. The scatter in the data makes it very difficult to choose between clean *d*-wave and dirty *d*-wave symmetries. However, since there is evidence for dirty *d*-wave symmetry from previous penetration depth measurements done on similar crystals, the data analysis was focused on comparing our data with the theory of dirty *d*-wave symmetry.

We compared the experimental values of coefficients *A* and *B* with the theoretical predictions[18] calculated from the equation,

$$C_{el}(H) = \gamma_n T \left(\frac{\Delta_0}{8\gamma_0}\right)\left(\frac{H}{H_{c2}/a^2}\right)\log\left(\frac{\pi H_{c2}}{2a^2 H}\right), \qquad (2)$$

where $2\gamma_0$ is the zero energy quasiparticle scattering rate (also called the impurity bandwidth), Δ_0 is the superconducting gap maximum, and a is a geometrical factor related to the vortex lattice geometry. Substituting $H_{c2} = 10$ T and $a = 1$, the fitting parameter

$$B = \left(\frac{\pi H_{c2}}{2a^2}\right)$$

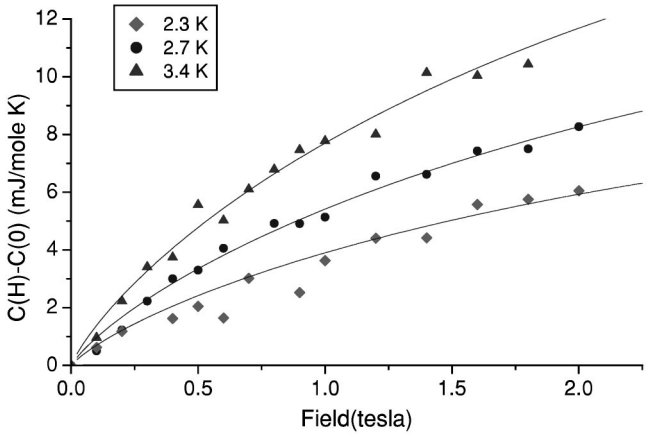

FIG. 4. The field dependent electronic specific heat vs magnetic field data for 2.4, 2.7, and 3.4 K. The lines are the dirty *d*-wave theory fits to the data.

can be calculated to be 15.7 T, in reasonably good agreement with the value generated by our data $B = 17.6 \pm 4.7$ T. The other fitting coefficient *A* can be calculated from

$$A = \gamma_n T \left(\frac{\Delta_0}{8\gamma_0}\right)\left(\frac{1}{H_{c2}/a^2}\right).$$

However, the parameter γ_0, which is related to the density of impurities in the sample and is sample dependent, is not known. Therefore by using the experimental $A = 6.2 \pm 0.7$ mJ/mole K T value, γ_0 can be estimated to be 2.1 K. A more widely cited scattering rate is the normal state electron scattering rate Γ. Γ is due to only impurity scattering, and it is also called the bare scattering rate. By using the estimated value of γ_0 in the equation for strong scattering limit(unitarity limit), $\gamma_0 \simeq 0.61\sqrt{\Gamma\Delta_0}$,[18] a bare scattering rate of $\Gamma = 0.26$ K can be calculated ($\hbar$ and k_B are set to 1).

Our analysis at the other temperatures (Fig. 4) also produced results similar to the $T = 3.4$ K data. For $T = 2.3$ K, $A = 3.1 \pm 0.2$ mJ/mole K T and $B = 18.0 \pm 4.7$ T are found and for $T = 2.7$ K $A = 4.3 \pm 0.5$ mJ/mole K T and $B = 18.7 \pm 4.9$ T are found. Theoretically the coefficient *B* should be the same for all temperatures, and the coefficient *A* should be linearly proportional to the temperature. The best fits to the data generated the same values for *B* within the error range, and the values for *A* scale with temperature, even though not in perfect agreement with the theory.[22]

We should mention that the *s*-wave theory we used to fit our data neglects nonlinear effects that might arise in the vicinity of H_{c1} due to vortex-vortex interaction or due to a possible change in the size of the vortex cores. Some experiments performed on *s*-wave superconductors have shown a nonlinear, even $\sqrt{H}$, magnetic field dependence for C_{el}. However the field dependence is not consistent for different temperatures, which means depending on what temperature the field dependence is probed, the electronic specific heat has a different field dependence. Different groups have observed $C_{el} \propto H^n$ for almost any value of *n* between 0.5 and 1 depending on what material they studied and at what temperature range they performed their experiment.[23,24] While

we cannot definitively rule out *s*-wave symmetry as an explanation for our data we believe that a dirty *d*-wave symmetry gives the most consistent and plausible fit to our data.[25–28]

In conclusion, our specific heat data strongly suggest that the *d*-wave symmetry in electron doped PCCO at optimal doping is a bulk property of the material. However, due to nonmagnetic impurities in our sample, the electronic specific heat follows a magnetic field dependence of type $H\log(H)$ below $H=0.6$ T, consistent with dirty *d*-wave symmetry. In addition, the normal state Sommerfeld constant of PCCO, $\gamma_n=6.7\pm0.4$ mJ/mole K^2, has been measured.

We thank Professor Peter J. Hirschfeld, and Professor Chandan Dasgupta for insightful discussions. P.F. acknowledges the support of the Canadian Institute of Advanced Research (CIAR), the Canadian Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council of Canada (NSERC), the Foundation of the Université de Sherbrooke. The work at Maryland was supported by NSF Grant No. DMR 01-02350.

[1] C. C. Tsuei and J. R. Kirtley, Rev. Mod. Phys. **72**, 969 (2000).
[2] D. J. Van Harlingen, Rev. Mod. Phys. **67**, 515 (1995).
[3] J. David Kokales *et al.*, Phys. Rev. Lett. **85**, 3696 (2000); R. W. Prozorov *et al.*, *ibid.* **85**, 3700 (2000).
[4] C. C. Tsuei and J. R. Kirtley, Phys. Rev. Lett. **85**, 182 (2000).
[5] N. P. Armitage *et al.*, Phys. Rev. Lett. **86**, 1126 (2001); T. Sato *et al.*, Science **291**, 1517 (2001).
[6] G. Blumberg *et al.*, Phys. Rev. Lett. **88**, 107002 (2002).
[7] A. Biswas *et al.*, Phys. Rev. Lett. **88**, 207004 (2002).
[8] John A. Skinta *et al.*, Phys. Rev. Lett. **88**, 207005 (2002).
[9] K. A. Moler *et al.*, Phys. Rev. B **55**, 3954 (1999).
[10] D. A. Wright *et al.*, Phys. Rev. Lett. **82**, 1550 (1999).
[11] Y. Wang *et al.*, Phys. Rev. B **63**, 094508 (2001).
[12] M. Chiao *et al.*, Phys. Rev. Lett. **82**, 2943 (1999).
[13] C. Caroli, P. G. de Gennes, and J. Matricon, Phys. Lett. **9**, 307 (1964).
[14] G. E. Volovik, Pis'ma Zh. Éksp. Teor. Fiz. **58**, 457 (1993) [JETP Lett. **58**, 469 (1993)].
[15] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1996).
[16] N. B. Kopnin and G. E. Volovik, Pis'ma Zh. Éksp. Teor. Fiz. **64**, 641 (1996) [JETP Lett. **64**, 690 (1996)].
[17] M. N. Khlopkin *et al.*, Phys. Solid State **41**, 1050 (1999).
[18] C. Kubert and P. J. Hirschfeld, Solid State Commun. **105**, 459 (1998).
[19] R. Bachmann *et al.*, Rev. Sci. Instrum. **43**, 205 (1972).
[20] J. L. Peng, Z. Y. Li, and R. L. Greene, Physica C **177**, 79 (1991).
[21] E. S. R. Gopal, *Specific Heats At Low Temperatures* (Plenum Press, New York, 1966).
[22] J. P. Emerson *et al.*, Phys. Rev. Lett. **82**, 1546 (1999).
[23] A. P. Ramirez *et al.*, Phys. Lett. A **211**, 59 (1996).
[24] J. E. Sonier *et al.*, Phys. Rev. Lett. **82**, 4914 (1999).
[25] Y. Ando *et al.*, Phys. Rev. Lett. **88**, 167005 (2002).
[26] P. Fournier *et al.*, Phys. Rev. Lett. **81**, 4720 (1998).
[27] I. Vekhter *et al.*, Phys. Rev. B **59**, R9023 (1999).
[28] M. Nohara *et al.*, Physica C **341-348**, 2177 (2000).