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Thermodynamic properties of $Pr_{1.85}Ce_{0.15}CuO_{4-\delta}$

Hamza Balci and R. L. Greene
Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742, USA
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We present specific heat measurements on optimally doped $Pr_{1.85}Ce_{0.15}CuO_{4-\delta}$ (PCCO) single crystals from which we determine the condensation energy, entropy, and the thermodynamic critical field. Our analysis of the specific heat jump at T_c suggests that the coupling in electron-doped cuprates is weaker than in the hole-doped cuprates. In addition, the entropy balance in the superconducting state suggests that any depression in density of states (DOS) at $T>T_c$, i.e., a pseudogap, would have to be very small (less than 10% of average DOS). Finally, a study of the residual electronic specific heat of an optimally doped PCCO before and after oxygen reduction suggests that this anomalous contribution is due to normal regions in the sample.

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There has been a significant increase of interest in the superconducting and the normal state properties of electron-doped high-T_c superconductors in the past few years. However, some important fundamental parameters of these materials have not been accurately measured yet. In this paper we report the results on thermodynamic properties, such as the specific heat jump at the transition temperature (T_c), the condensation energy, and the thermodynamic critical field taken on single crystals of $Pr_{1.85}Ce_{0.15}CuO_{4-\delta}$ (PCCO). We discuss these results in the context of the pseudogap and strong coupling effects in the electron-doped cuprates. In addition, we present comparative data for optimally doped PCCO before and after annealing to study the origin of the well-known residual electronic specific heat in the superconducting state.

Previous measurements on electron-doped cuprates have studied the thermodynamic properties of these materials.[1–3] However, polycrystalline samples of varying quality have made it very difficult to establish consistent results regarding these properties. The recent improvements in samples, particularly in single crystal samples, have not been accompanied by remeasurements of the thermodynamic properties. Hence, the motivation of this work is to fill this gap in terms of reliable experimental data on high quality single crystals.

When discussing the coupling effects we assumed a BCS-type electron-boson coupling, even though it is not clear at this moment if such effects are significant or relevant for high-T_c superconductors. However, the hole-doped data in the literature have usually been analyzed in this manner, and in order to make a comparison with that data we also used the same formalism.

The PCCO single crystals are grown by the directional solidification technique. The nonsuperconducting as-grown crystals are annealed at 900 °C in an inert atmosphere of flowing argon gas in order to attain superconductivity. The cerium concentration of the crystals was determined using wavelength dispersive x-ray analysis (WDX) to an accuracy of ±0.005. The experiments were performed in a Quantum Design physical property measurement system (PPMS) with a modified sample holder in order to eliminate the field dependence of the addenda. The data were taken using thermal relaxation calorimetry.[4] Au-7%Cu wires (1–3 mil in diameter) are used as a weak link to connect the holder to the thermal bath, and the thermometers were calibrated in different magnetic fields. Our setup was tested by measuring a 3 ± 0.1 mg high purity copper sample, and a 3.2 ± 0.1 mg Nb sample. Our measurements were within 5% of the standard values (uncertainties in determining the mass of the sample or differences in the purity of the standard sample and our sample are included in this error).

The specific heat jump at T_c is due to the free energy difference between the superconducting and normal states. The sharp transitions of conventional superconductors have made it possible to determine the size of this jump very accurately.[5] However, in electron-doped cuprates, issues such as broad superconducting transitions and small samples have made it very difficult to measure this jump.[3] By using a sensitive thermal relaxation calorimetry technique and small PCCO single crystal samples, we measured the specific heat of the normal and the superconducting states. The normal state was reached by applying a magnetic field ($H>H_{c2}$) parallel to the *c* axis of the crystal. Figure 1(a) shows the raw data at $H=0$ T and $H=5$ T for a PCCO $x=0.15$ single crystal ($H_{c2}\approx5$ T for this crystal). As is clear from Fig. 1(a), the zero field data are very smooth due to the broad superconducting transition ($T_c=23\pm3$ K). Hence, it is very difficult to extract the specific heat jump by just analyzing the zero field data. On the other hand, the difference between the 5 and 0 T data [Fig. 1(b)] shows a clear peaklike structure at $T=18.2$ K, which is close to the temperature where superconductivity is established throughout the sample. The size of this jump is $(C_{sc}-C_n)/T_c=\Delta C/T_c=6.1$ mJ/mole K^2, where "mole" means per mole of Cu. This jump is approximately three times higher than some of the previous results on polycrystalline samples of PCCO (Refs. 1 and 3) and is in good agreement with high quality $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ (NCCO) polycrystalline samples.[2] A lower limit for the size of the specific heat jump at T_c has been estimated from magnetization measurements on NCCO single crystals to be $\Delta C/T_c=3$ mJ/mole K^2 (Ref. 6), which is consistent with our data.

For weak-coupling BCS theory: $\Delta C/T_c\gamma_n=1.43$, which is in very good agreement with data on conventional superconductors,[5] with a few exceptions like mercury. Theoretical work showed that the ratio $\Delta C/T_c\gamma_n$ can be larger in the strong-coupling limit[7] (which explains lead and mercury data). Specific heat data on hole-doped cuprates showed much larger values for $\Delta C/T_c\gamma_n$ than the BCS weak-coupling limit (see Ref. 8 for an extensive

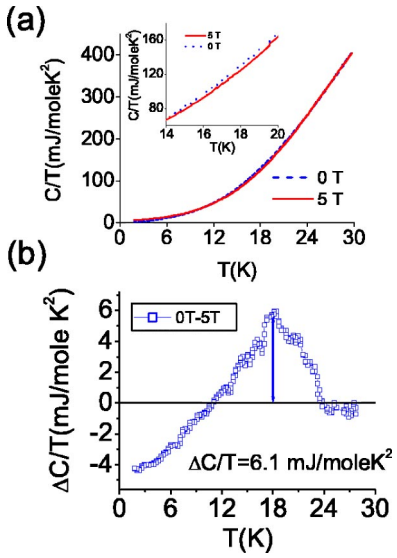

FIG. 1. (Color online) (a) Temperature dependence of specific heat for an optimally doped crystal, $Pr_{1.85}Ce_{0.15}CuO_4$ ($T_c=23\pm3$ K), at $H=0$ T and $H=5$ T ($H\|c$ axis). The inset shows $H=0$ T and $H=5$ T data around T_c. (b) The difference between the superconducting state ($H=0$ T) and the normal state ($H=5$ T) as a function of temperature.

list for measurements up to 1990 and Ref. 9 for recent data on a high quality crystal). The experimental data on YBaCuO (YBCO) show $\Delta C/T_c\gamma_n\approx2.5-3.5$ for samples having
different superconducting volume ratios and different levels of disorder.[9–12] Reference 10 extrapolates to $\Delta C/T_c\gamma_n=4.8$ for a fully superconducting YBCO sample. Reference 7 calculates an upper limit of $\Delta C/T_c\gamma_n\approx10$ for strong-coupling *d*-wave superconductors. Our data on PCCO show that $\Delta C/T_c\gamma_n=1.6\pm0.1$. In this calculation $\gamma_n=3.8\pm0.2$ mJ/mole K^2 (from specific heat data shown in Fig. 3) and $\Delta C/T_c=6.1\pm0.3$ mJ/mole K^2 have been used. However, the fact that the superconducting transition is broad and that our magnetization measurements give 70% superconducting volume fraction suggests that the magnitude of the jump is definitely larger than the BCS weak-coupling limit. As will be discussed later, the experimental condensation energy of our sample is approximately 65% of the ideal *d*-wave case, which is similar to the superconducting volume fraction we estimate from our magnetization data. Considering a similar superconducting ratio for the jump in the specific heat implies that $\Delta C/T_c\gamma_n\approx2.3\pm0.2$ for a 100% superconducting PCCO sample.

The experimental γ_n is also larger than the band structure calculations, which is evidence for electron-boson coupling effects. Such calculations determine the density of states at the Fermi level to be $N(E_f)\approx1.3$ states/eV cell (Ref. 13). The expression

$$\gamma_n=\frac{\pi^2}{3}N(E_f)k_B^2(1+\lambda), \tag{1}$$

where λ is the electron-boson coupling constant, can be used to estimate γ_n using band structure density of states (DOS). Substituting $\lambda=0$ and $N(E_f)=1.3$ states/eV cell yields $\gamma_n=3.1$ mJ/mole K^2. The experimental values on our PCCO $x=0.15$ crystals vary between $\gamma_n=3.8-5.3$ mJ/mole K^2. Substituting the experimental γ_n values into Eq. (1) yields $\lambda\approx0.2-0.7$. A similar analysis on hole-doped superconductors[14] shows much larger coupling constants, which suggests that coupling effects are weaker in electron-doped cuprates compared to the hole-doped cuprates. This result is also consistent with angle-resolved photoemission spectroscopy (ARPES) measurements[15] which were interpreted in terms of smaller electron-boson coupling in electron-doped cuprates compared to the hole-doped cuprates. The larger $\Delta C/T_c\gamma_n$ ratios in hole-doped cuprates[16] also support this idea.

An independent way of estimating the Sommerfeld constant, γ_n, is to use the relation

$$-\frac{\partial H_{c2}}{\partial T}=A\rho\gamma_n\eta, \tag{2}$$

where ρ is the resistivity at T_c, η is a coupling constant, and $A=1.25(\mathrm{T/K})(\mathrm{m\Omega\ cm})^{-1}(\mathrm{mJ/mole\ Cu\ K^2})^{-1}$ (Ref. 17). Equation (2) is valid only in the dirty limit, and it is not clear at this moment if our samples are in this limit. However, the aim of this analysis is to get an estimate for γ_n using the results of independent measurements and compare this estimate with the results of our specific heat measurements. Transport measurements have shown that $\partial H_{c2}/\partial T\approx-0.4$ T/K (Ref. 18), and $\rho\approx0.05$ mΩ cm (Ref. 19). Assuming a weak-coupling limit ($\eta=1$), we obtain $\gamma_n=6.4$ mJ/mole K^2. This value of γ_n is an upper bound for the experimental γ_n since any $\eta>1$ would reduce γ_n. Therefore, our experimental results of $\gamma_n=3.8-5.3$ mJ/mole K^2 are in agreement with the estimate of γ_n from Eq. (2).

The superconducting state has a lower entropy than the normal state. This entropy difference is obviously zero at two points: $T=T_c$ and $T=0$. At some temperature between these two, the entropy difference shows a maximum. The entropy difference between the two states can be calculated from

$$S_n(T)-S_{sc}(T)=\int_0^T\left(\frac{C_{sc}-C_n}{T'}\right)dT', \tag{3}$$

where C_n and C_{sc} refer to the normal and superconducting specific heats, respectively. An important thermodynamic quantity that can be calculated from our specific heat data is the condensation energy of the superconducting state, which is the free energy difference between the superconducting and the normal states. The condensation energy can be calculated from

$$E_c(T)=\int_T^{T_c}[S_n(T')-S_{sc}(T')]dT'. \tag{4}$$

Figure 2(a) shows the condensation energy and the entropy difference as a function of temperature for an optimally doped PCCO crystal. The condensation energy for a flat density of states is given by

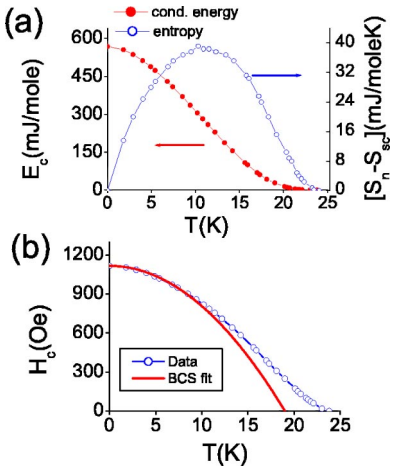

FIG. 2. (Color online) (a) The entropy difference between the superconducting and normal states and the condensation energy of the superconducting state as a function of temperature. (b) The temperature dependence of the thermodynamic critical field for $Pr_{1.85}Ce_{0.15}CuO_4$ and a BCS fit of the form $H_c(T)=H_c(0)[1-(T/T_c)^2]$.

$$E_c = \alpha N(0)\Delta_0^2/2 = \alpha\frac{3}{\pi^2}\frac{1}{k_B^2}\gamma_n(0)\Delta_0^2/2, \tag{5}$$

where Δ_0 is the superconducting gap maximum. For a BCS *s* wave superconductor $\alpha=1$, and for a BCS *d*-wave superconductor $\alpha\approx 0.4$. The upper critical field of this crystal was found from specific heat measurements to be approximately 5 T. The smaller H_{c2} of this crystal compared to other optimally doped crystals we measured ($H_{c2}\approx 7$ T) could be due to a smaller superconducting gap [tunneling spectroscopy measurements typically show $\Delta\approx 4$ meV (Ref. 20)]. It is also possible that this crystal is cleaner than the other crystals we studied, and hence has a lower H_{c2}. Using $\Delta_0\approx 3$ meV $\approx 34\times k_B$, $\alpha=0.4$, and $\gamma_n=3.8$ mJ/mole K^2 for $Pr_{1.85}Ce_{0.15}CuO_{4-\delta}$ results in $E_c=782\pm 100$ mJ/mole. Our experimental value of 568 mJ/mole is approximately 70% of the BCS *d*-wave prediction, and less than 30% of the *s*-wave prediction. Considering the similar superconducting volume fraction of the sample, ≈70%, we conclude that our data are more consistent with *d*-wave symmetry. This conclusion is also in agreement with our previous heat capacity experiment where a nonlinear field dependence of electronic specific heat was found.[21] Data on hole-doped cuprates have a similar deficiency in E_c from BCS *d*-wave theory.[16] Such a discrepancy could have various sources, including a less than 100% superconducting sample.

The entropy $S(T)$ is a measure of the total number of electronic excitations at temperature T, while $S(T)/T$ is a measure of the density of states averaged over an energy $\approx k_B T$. In a simple metal $S(T)/T$ is a constant, i.e., independent of temperature. Similarly in a conventional superconductor, this quantity is constant in temperature for $T>T_c$. In other words, the area under $(C_{sc}-C_n)/T$ from $T=0$ to $T=T_c$ adds up to zero and hence the entropy is balanced. In hole-doped cuprates around optimal doping, the area under $(C_{sc}-C_n)/T$ from $T=0$ to $T=T_c$ does not add up to zero, and

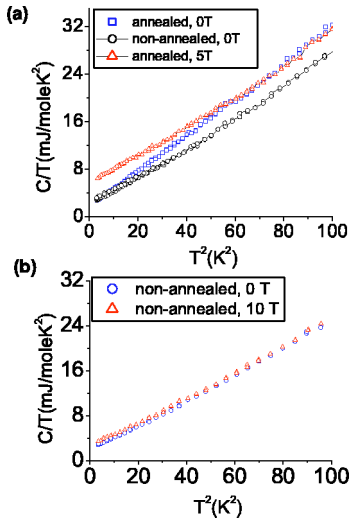

FIG. 3. (Color online) (a) The temperature dependence of an optimally doped PCCO crystal before and after annealing. The $\gamma(0)$ is the same for both the annealed and the nonannealed samples. (b) Another nonannealed sample in 0 T and 10 T magnetic fields.

hence a depression in DOS, or $S(T)/T$, at $T>T_c$ is necessary in order to attain entropy balance.[12] This depression in $S(T)/T$, or average DOS, has been taken as an evidence for a pseudogap.

Our data show that in optimally doped *n* type cuprates the entropy is almost balanced between the normal and the superconducting states for $0<T<T_c$. Linearly extrapolating the $(C_{sc}-C_n)/T$ to $T=0$ results in 35 mJ/mole K for the negative area in Fig. 1 (between $T=0$ K and $T=10.8$ K), whereas the positive area is 38 mJ/mole K (between $T=10.8$ K and $T=24.0$ K). The ≈8–9% difference between the two entropies is the error margin of our analysis. This result suggests that even if there is a pseudogap above T_c for electron-doped cuprates at optimal doping, the depression in the density of states would be less than 10% of the available states. ARPES (Ref. 22) and optical conductivity[23,24] measurements performed on electron-doped cuprates are in agreement with this conclusion: Ref. 23 does not observe any pseudogap in NCCO, and Ref. 24 observes a very small gap, which vanishes at a slightly higher doping than optimally doped. However, this does not rule out the existence of a pseudogap for $T<T_c$, i.e., a pseudogap coexisting with the superconducting gap, as has been suggested from tunneling experiments.[25,26]

Another important quantity that can be calculated from our data is the thermodynamic critical field, $H_c(T)$. The free energy difference between the superconducting and the normal states can be expressed as $E_c=\mu_0 H_c^2/8\pi$. Figure 3 shows the temperature dependence of H_c, and the BCS fit to the data using $H_c(T)=H_c(0)[1-(T/T_c)^2]$ (Ref. 27). In calculating the BCS fit we used $H_c(0)=1100\pm 100$ Oe, and $T_c=19$ K (a value between the peak temperature $T=18.2$ K of Fig. 1 and the onset temperature of superconductivity from magnetization, $T=20$ K). Figure 3 shows that there is a good agreement between our data and the BCS fit between $T=0$ K and $T=T_c/2$, beyond which the theory underestimates the experimental data. For a conventional *s*-wave superconductor such

an underestimation would suggest strong electron-phonon coupling. However, the difference between the fit and the data for conventional superconductors is usually less than ≈5% (Ref. 5), which is much smaller than what we observe in our data. Such significant differences between BCS theory and data on cuprates in the vicinity of T_c have been attributed to superconducting fluctuations and strong-coupling effects.[16,28] Our estimate of $H_c = 1100 \pm 100$ Oe is in reasonable agreement with previous specific heat measurements on NCCO that found $H_c = 1400$ Oe (Ref. 2).

Specific heat measurements on cuprates have shown a residual electronic specific heat at zero magnetic field, $C_{res} = \gamma(0)T$. Improvements in the sample quality have made the magnitude of this term smaller; however, this residual specific heat has still been observed in all cuprate samples studied to date. Despite many studies and speculations in the literature, the origin of this term has not been conclusively identified yet.[10] We studied the magnitude of this term by measuring the specific heat of a crystal before and after annealing. To our surprise, we did not observe any change in the magnitude of the $\gamma(0)$ term between the semiconducting nonannealed crystals and the superconducting annealed crystals. Figure 3 shows an example of such data on an optimally doped crystal ($T_c = 23 \pm 3$ K, and mass = 5 mg). The fact that a residual specific heat is observed in the nonannealed (nonsuperconducting) sample rules out the possibility of $\gamma(0)$ being due to nodal excitations of the *d*-wave gap. This result is consistent with a thermal conductivity experiment on PCCO which showed $\kappa/T \approx 0$ at $T = 0$ K (Ref. 29).

In order to study any possible two-level spin system cause of this linear term, we studied the field dependence of the specific heat of a nonannealed optimally doped crystal. As shown in Fig. 3(b), there is a very small field dependence, if any, up to 10 T magnetic field between 2 and 10 K, and the residual heat capacity was essentially the same in all fields (only 0 and 10 T data are shown for clarity but 2, 4, 6, and 8 T data also look similar). The two-level spin systems that are observed in cuprates (as Schottky anomalies at $T < 5$ K) usually have a strong field dependence between 0 and 10 T. The absence of any field dependence in the specific heat of nonannealed crystals suggests that the linear term does not have this origin. It is possible that larger fields or lower temperatures are necessary to observe the two-level spin contribution, but this would be very unusual.

The absence of any difference in the magnitude of $\gamma(0)$ before and after annealing, and the absence of any field dependence in the nonannealed crystals, are most consistent with the existence of metallic regions in the sample which are not affected by the annealing procedure. This is also consistent with the reduction in $\gamma(0)$ with improvements in the sample quality. Supporting evidence for this possibility comes from the ratio $\gamma_n/[\gamma_n + \gamma(0)]$. Attributing the $\gamma(0)$ term to the metallic phase, i.e., nonsuperconducting, and γ_n to the superconducting phase (it is assumed that the volume ratio is similar to the density of states ratio) then the ratio $\gamma_n/[\gamma_n + \gamma(0)]$ should be similar to the superconducting volume fraction from magnetization measurements (≈0.70), which is close to what we observe in our data: $\gamma_n/[\gamma_n + \gamma(0)] = 3.8/(3.8 + 1.9) = 0.67$.

In summary, the measurements reported in this paper on the thermodynamic quantities of an optimally doped *n*-type cuprate have several important implications. In this doping the *n*-type cuprates show electron-boson coupling effects however, the strength of this coupling is weaker than in the hole-doped cuprates. The condensation energy of these materials is more consistent with *d*-wave superconductivity compared to *s*-wave superconductivity. The approximate entropy balance suggests that even if there is a pseudogap at $T > T_c$ for the optimally doped PCCO, the size of this gap is very small (less than 10% of average DOS). And finally, the residual linear contribution to the specific heat can best be described as the electronic specific heat of metallic (nonsuperconducting) regions in the sample.

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