Temperature dependent change in the symmetry of the order parameter in an electron-doped high-temperature superconductor

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(March 22, 2022)

We present specific heat measurements which show an unexpected phase transition from d-wave symmetry to s-wave symmetry as the temperature is reduced in electron-doped Pr$_{2-x}$Ce$_x$CuO$_{4-\delta}$ (PCCO), in both optimal and over-doped single crystals. The field dependence of electronic specific heat ($C_{el}$) is linear at $T=2K$, consistent with s-wave symmetry, and non-linear, consistent with d-wave symmetry, at $T\geq3K$. This behavior is most consistent with a phase transition in the symmetry of the order parameter as the temperature is changed. Such a phase transition could be an explanation for the previous controversial results of different experiments, performed at different temperatures in the electron-doped cuprates.

Particle-hole symmetry is an important ingredient of any theory attempting to explain the mechanism of high temperature superconductivity. Despite its fundamental importance, this issue has not been resolved yet, i.e. there is no consensus as to whether the electron-doped (n-type) and hole-doped (p-type) cuprates are essentially the same or very different. The symmetry of the order parameter is one of the important parameters to compare the n-type cuprates to the p-type family. Unlike the p-type cuprates, which are now generally considered to have d-wave symmetry [1,2], the pairing (gap) symmetry of the n-type cuprates continues to remain controversial, despite the enormous improvement in the sample quality and experimental techniques since their discovery over 10 years ago. In addition to experiments that support an s-wave symmetry [3] or a d-wave symmetry [4–8], there are a few experiments that suggest a transition from d-wave symmetry to s-wave symmetry as the doping is increased [9,10].

Specific heat has traditionally been used to study the superconducting (SC) gap since it is a direct measurement of the density of states (DOS). The difficulty of detecting the small T\textsuperscript{2} temperature dependence (5\% of the phonon specific heat at 4 K in YBCO [12]) expected at zero field from a d-wave superconductor [11] makes field dependence studies the preferred method of studying the gap symmetry. In a simple isotropic s-wave superconductor, the specific heat is linear in magnetic field for fields larger than $H_{c1}$ ($H$>$H_{c1}$) [13]. For a d-wave superconductor, $C_{el}$ has a $\sqrt{H}$-type field dependence in the low temperature ($T<<T_c$) and intermediate field regime ($H_{c1}<<H<<H_{c2}$) [14].

In our case measuring the field dependence of $C_{el}$ is particularly advantageous since our PCCO crystals do not have electronic or nuclear Schottky contributions (see Fig. 1) in the temperature ($T>2K$) and field ($H<10T$) range of our measurements. The field independent adenda leaves $C_{el}$ the only field dependent part of our specific heat measurements. Therefore, our field dependent data was acquired at a constant temperature while the magnetic field is ramped up (zero field cooled) or down. No hysteresis has been observed in our specific heat between increasing and decreasing field.

We measured the heat capacity of Pr$_{2-x}$Ce$_x$CuO$_{4-\delta}$ (PCCO) single crystals grown by the directional solidification technique with cerium dopings of $x=0.150\pm0.005$ and 0.165$\pm0.005$. The non-superconducting 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 WDX to an accuracy of $\pm0.005$. The experiments were performed in a Quantum Design PPMS with a modified sample holder using thermal relaxation calorimetry [15]. Au-7%Cu wires (1-3 mil diameter) are used as a weak link to connect the holder to the thermal bath. The thermometers were calibrated at different magnetic fields in order to take into account their small magnetoresistance. Our setup was tested by measuring a 3 mg high purity copper sample, and a 3.2 mg Nb sample, and our measurements were within 5 \% of the standard values.

Fig. 1 shows temperature dependence data on an optimally-doped PCCO crystal with $T_c=22\pm2$ K and mass of 3.2 mg in several magnetic fields ($H$/c-axis). The absence of any Schottky upturn at low temperatures shows that the sample is free of any measurable magnetic impurities. The specific heat in this case can be represented as $C = \gamma(0) + \gamma(H) T + \beta T^3$, where $\gamma(0)$ is the coefficient of the zero field residual heat capacity, $\gamma(H)$ is the coefficient of the field dependent $C_{el}$, and $\beta$ is the coefficient of the phonon specific heat. The gap symmetry is investigated by studying $\gamma(H)$. For $H \geq H_{c2}$, $\gamma(H) = \gamma_n$, where $\gamma_n$ is the Sommerfeld constant. The $\gamma(0)$ term is also found in hole-doped cuprates, and there are several proposals to explain its origin [16–18]. By making a linear fit to the $C/T$ vs $T^2$ data shown in the inset of Fig. 1 ($\beta$ is kept constant for the two fields), we find $\gamma(0)=2.1\pm0.2$ mJ/moleK\textsuperscript{2}, $\gamma_n=5.3\pm0.2$ mJ/moleK\textsuperscript{2}, and $\beta=0.23\pm0.02$ mJ/moleK, which results in a Debye temperature $\theta_D=390\pm15$ K.

The Debye temperature is the same (within the accuracy of our measurements) in all the crystals we studied,
and the value of $\gamma(0)$ changes between 1.4-2.2 mJ/moleK$^2$ in the different optimally-doped crystals we studied. The $\gamma_n$ for different optimally-doped crystals depends on the annealing time (oxygen content) and we have observed a variation between 4.0-5.3 mJ/moleK$^2$. The upper critical field $H_{c2}$ determined from specific heat measurements also depends on the annealing time. Fig. 1 shows that the upper critical field for this sample is $H_{c2} < 8T$ since there is no difference in the specific heat data between 8T and 10T. The $H_{c2}$ of the different optimally-doped samples changed between 5.0-7.0 ($\pm 0.5T$) depending on the annealing time of the crystals.

Fig. 2 shows the field dependence of an optimally-doped crystal ($T_c=23\pm3K$, mass=3.4 mg). Only the field dependent part of $C_{el}$ is shown in Fig. 2 since the zero-field specific heat, which includes the phonon contribution ($\beta T^3$) and the zero field residual heat capacity ($\gamma(0)T$), is subtracted out. The field dependence is clearly non-linear at $T \geq 3K$. However, a dramatic change in the field dependence is observed when the temperature is reduced to 2K, where a linear field dependence dominates up to about 3T. Fig. 2-B shows that the change in the field dependence of $C_{el}$ between 4.5K and 2K is accompanied by a suppression of the electronic specific heat. This suggests that the density of electronic states is suppressed, or possibly a gap is opened at the Fermi level, since the electronic specific heat is a measure of DOS.

This change in the field dependence of $C_{el}$ from linear at $T=2K$ to non-linear at higher temperatures has been observed on four optimally-cerium doped crystals with different oxygen concentrations. In addition to the optimally-cerium doped crystals, crystals of higher cerium doping also show a similar field dependence. Fig. 3-A shows the field dependence of specific heat for an over-doped crystal ($x=0.165\pm0.005$, $T_c=15\pm1.5K$, mass=2.2 mg). The trend from linear to non-linear field dependence as the temperature is increased is also evident in this crystal. In addition, Fig. 3-B shows that there is a small suppression of $C_{el}$, and hence electronic DOS, as the temperature is reduced from 3K to 2K.

There are several possible scenarios to explain such an unusual change in the field dependence of $C_{el}$: a phase transition in the symmetry of the order parameter from d-wave at high temperatures ($T \geq 3K$) to s-wave at lower temperatures ($T \leq 2K$); an anisotropic s-wave gap which has a minimum around 3K; or a vortex-vortex interaction effect which results in a non-linear field dependence in an s-wave superconductor at $T \geq 3K$. Now we will discuss each of these scenarios in more detail.

Vortices can interact with each other via quasiparticle (QP) transfer between their cores. At high magnetic fields (large number of vortices) or high temperatures (larger vortex-core size) the quasiparticle wavefunctions in the core of one vortex overlap with the quasiparticle wavefunctions in neighboring vortices, and hence inter-vortex quasiparticle transfer becomes possible. These inter-vortex QP transfers result in a shrink-
dependence is non-linear even at fields as low as 0.1 T. Yet at T=2K the field dependence remains linear up to 3T. Due to the similar effects of magnetic field and temperature on the QP excitation spectrum in an anisotropic s-wave gap, for T=2K we would expect the field dependence to become non-linear at much lower fields than 3T (H<1T). Since this is not what we observe in our data, we believe that the change from linear field dependence to non-linear field dependence in C_eff of PCCO is not due to an anisotropic s-wave gap.

Finally we consider a phase transition in the symmetry of the order parameter from s-wave (T≤2K) to d-wave (T≥3K). This interpretation is particularly attractive since it has the potential of reconciling the results of many conflicting experiments. The SQUID, ARPES, and Raman [5-7] measurements that suggested d-wave symmetry in electron-doped cuprates are almost exclusively performed above 4.2K. On the other hand penetration depth (0.4K-Ref. [3]) and point contact tunnelling spectroscopy (1.8K-Ref. [9]), are performed at T<2K and they are consistent with s-wave symmetry. The only inconsistent experiment with this picture is a penetration depth experiment which suggested d-wave symmetry down to T=0.4K(Ref. [4]).

The above qualitative picture of a phase transition is also consistent with quantitative analysis both at 4.5K and 2K. The C_eff of a d-wave superconductor has a \( \sqrt{H} \) type field dependence given by [29]:

\[
C_{el} = A\sqrt{H} = \gamma_n T \left( \frac{8}{\pi} \right)^{1/2} \left( \frac{H}{(H_{c2}/a^2)} \right)^{1/2} .
\]  

This equation is valid at T \( \ll T_c \) and H \( \ll H_{c2} \). Fig. 2-B shows a d-wave fit given by Eq.(1) to the 4.5 K data and a linear fit to 2K data. In calculating A, the coefficient of the \( H^{1/2} \) term, \( \gamma_n=4.2 \) mJ/mole K^2, \( H_{c2}=7T \), and \( a=0.7 \) were used. The \( \gamma_n \) and \( H_{c2} \) are determined from our specific heat measurements. Using these parameters a reasonably good fit of our data to \( \gamma(H)=AH^{1/2} \) is obtained at T=4.5K (Fig. 2-B). An s-wave superconductor on the other hand has a linear field dependence: \( C_{el} = kT \gamma H/H_{c2}(T) \), where \( k \) is a geometrical constant of order 1. Using \( \gamma_n=4.2 \) mJ/mole K^2 and \( H_{c2}=7T \) at T=2K we find the theoretical \( C_{el} = 1.2kH \). A linear fit to our data yields \( C_{el} = 2.0H \). A comparison with data results in \( k=1.7 \), which is a reasonable value for \( k \).

Such a phase transition should also be observed in the temperature dependence of the specific heat. We estimate the magnitude of this feature to be approximately 5% of the total heat capacity around 3K (the suppression in Fig.2-b is approximately 5% of the total heat capacity), and expect it to be spread over a temperature range of 1-2K. We were not able to resolve this transition in the temperature dependence of the specific heat because of our limited resolution (5%), however more sensitive measurements using ac heat capacity are in progress.

The data on the over-doped crystal (shown in Fig. 3) is also consistent with s-wave theory at T=2K. Using \( H_{c2}=3.6 \) T, \( \gamma_n=2.8 \) mJ/mole K^2 (determined as for the optimally-doped crystal), an s-wave estimate of 1.6\( \kappa \) is obtained for the slope at T=2K. A linear fit to the data yields 2.2 mJ/mole K T. This results in \( \kappa=1.4 \) for the over-doped crystal, which is again a reasonable value for \( \kappa \). The low \( H_{c2} \) (\( H_{c2}=2.90 \)2T at T=3K) makes a comparison with d-wave theory difficult since the condition \( H_{c1} \ll H \ll H_{c2} \) is only satisfied in a very narrow field range. However, the trend from linear to non-linear field dependence as the temperature is increased suggests that the x=0.165 crystal behaves similarly to the x=0.150 crystals.

The phase transition suggested by our data is compatible with a theoretical model proposed by Khodel et al. [30] which suggests a phase transition in the gap symmetry (from nodal to fully-gapped) in n-type cuprates based on the location of the Fermi surface "hot-spots". The consistent picture formed by this model and our data implies that the hot spots and hence the antiferromagnetic spin fluctuations are an important ingredient of superconductivity in the n-type cuprates.

In conclusion, the results of our specific heat measurements can be summarized as:

- a dramatic change is observed in the magnetic field dependence of the electronic specific heat in a very narrow temperature range; non-linear at T≥3K and linear at T=2K.
- there is a suppression of DOS, consistent with opening of a gap at the Fermi surface, as the field dependence changes from non-linear to linear.

In light of these observations we conclude that the symmetry of the order parameter in the n-type cuprates is not a simple d-wave symmetry as in the p-type compounds. In particular the s-wave symmetry observed at T=2K is a definite evidence for this difference. The change in the field dependence of C_eff is most consistent with a phase transition in the symmetry of the order parameter from d-wave to s-wave. Such a phase transition in the symmetry of the order parameter can explain most of the prior conflicting symmetry experiments, since almost all experiments that suggest d-wave symmetry are performed at T≥4K, and those that suggest s-wave symmetry are performed at T≤2K.

Acknowledgements

We would like to thank Victor Yakovenko, Jeff Sonier, Chris J. Lobb, and Yoram Dagan for helpful discussions. This work was supported by the NSF DMR 01-02350.
FIG. 1. Temperature dependence of specific heat for an optimally-doped crystal, Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ ($T_c=22\pm2$K), at different magnetic fields (H//c-axis). The saturation of the specific heat, i.e. field-independent, at 8T suggests that $H_d\leq8T$. The inset shows $C/T$ vs $T^2$ for 0T and 10T magnetic fields from which $\gamma(0)$, $\gamma_\alpha$, and $\beta$ are extracted.

FIG. 2. A-Field dependent part of the electronic specific heat ($C(H)-C(0)$) for an optimally-doped PCCO crystal ($T_c=23\pm3$K) between 2-4.5K. At 2K the field dependence is linear consistent with a fully-gapped order parameter. At slightly higher temperatures the field dependence changes from linear to non-linear. B-The field dependent specific heat is divided by temperature to show the suppression in the specific heat, and hence DOS. The curved line is a d-wave fit to 4.5K, and the dashed line is an s-wave fit to 2K data.

FIG. 3. A- Field dependence of specific heat for an over-doped PCCO crystal ($T_c=15\pm1.5$K). The field dependence of the specific heat is similar to the optimally-doped crystals, i.e. linear at 2K and non-linear at higher temperatures. B-The field dependent specific heat is divided by temperature to show the suppression in the specific heat, and hence DOS, similar to the optimally-doped crystal.