Absence of nodes in the energy gap of the high-temperature electron-doped Pr$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$ superconductor using thermal conductivity and specific heat measurements

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We present data analyses of the thermal conductivity and specific heat of electron-doped Pr$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$. The zero-field thermal conductivity and specific heat of this optimally electron-doped system can be only explained by a nodeless gap symmetry. The magnetic-field dependence of the electronic specific heat in the vortex state is in quantitative agreement with an $s$-wave theory. Our quantitative data analyses provide bulk evidence for a nodeless gap symmetry in optimally electron-doped cuprates.

An unambiguous determination of the gap symmetry in the bulk of cuprates is crucial to the understanding of the pairing mechanism of high-temperature superconductivity. Three major gap symmetry contenders have been $s$-wave, $d$-wave, and extended $s$-wave ($s+g$ wave). Both $d$-wave and extended $s$-wave have line nodes and change signs when a node is crossed. The majority of measurements probing low-energy excitations in the superconducting state (e.g., magnetic penetration depth, thermal conductivity, and specific heat) have pointed towards the existence of line nodes in the gap function of hole-doped cuprates [1–4]. Qualitatively, these experiments are consistent with both $d$ and extended $s$-wave gap symmetries. In contrast to hole-doped cuprates, the earlier Raman scattering [7, 8] provide evidence for pure $d$-wave symmetry in optimally overdoped and overdoped ($n$-type) cuprates. Surface-sensitive angle-resolved photoemission spectroscopy (ARPES) [9, 10] also supports $d$-wave gap symmetry for optimally electron-doped cuprates. The thermal properties of the optimally electron-doped cuprates consistently provide bulk evidence for a nodeless $s$-wave gap symmetry.

The low-temperature electronic thermal conductivity $\kappa_{el}$ and specific heat $C_{el}$ can be used to distinguish between a nodeless gap function and a gap function with line nodes. Specific heat experiments are insensitive to the phase of the gap, but can provide bulk information on the behavior of the density of states $N(E)$ near the Fermi level $E_F$. The quantity $C_{el}/T$ is proportional to $N(E)$ averaged over an interval $k_BT$ around $E_F$. For a $d$-wave or extended $s$-wave symmetry, the gap vanishes on lines of nodes on the Fermi surface, therefore $N(E)$ averaged over all directions in the reciprocal space behaves as $N(E) \propto |E|$. This implies $C_{el}/T \propto T$ for $T << T_c$ in zero magnetic field. In contrast, for a fully gapped superconductor, $C_{el}/T \simeq 0$ under the same conditions. Similarly, the quantity $\kappa_{el} \propto T$ at $T << T_c$ in zero magnetic field for $d$-wave or extended $s$-wave gap symmetry while for a fully gapped superconductor, $\kappa_{el}/T \simeq 0$ under the same conditions.

More specifically, the quantity $\kappa_{el}/T$ in zero magnetic-field is directly related to the Fermi velocity $v_F$ and momentum $h k_F$ in the nodal directions, and to the slope $S = d\Delta(\theta)/d\theta$ at nodes, where $\Delta(\theta)$ is a gap function and $\theta$ is the angle measured from the Cu-O bonding direction. The former two quantities can be obtained from angle-resolved photoemission spectroscopic data while the latter one can be readily calculated from the gap function.
The residual thermal conduction is due to a fluid of zero-energy quasiparticles induced by the pair-breaking effect of impurity scattering near the nodes in the gap. Calculations for the heat transport by nodal quasiparticles in two dimensions give a general expression \[ \kappa_{el} / T = \frac{k_B^2}{\hbar} \frac{n \nu_F}{d} \left( \frac{v_F}{v_2} + \frac{v_2}{v_F} \right), \] (1)

where \( n/d \) is the stacking density of CuO$_2$ planes, \( v_2 = S/(\hbar K_F) \). One can readily show that \( S = 2\Delta M \) for a simple d-wave gap function: \( \Delta(\theta) = \Delta_M \cos 2\theta \) (where \( \Delta_M \) is the gap along the Cu-O bonding directions). Similarly, the low-temperature electronic specific heat in zero magnetic-field is proportional to \( T^2 \), i.e., \( C_{el} = \alpha T^2 \), where \( \alpha \) is a constant.

Another way to test the gap symmetry is to study the electronic specific heat in the vortex state. According to a simplified argument \[21\], the energy of carriers circulating around a vortex is shifted by the Doppler effect. This shift has a dramatic effect on the density of states when the gap is small, so that the essential contribution comes from the vicinity of the nodes. In the low-temperature limit, the density of states at \( E_F \) becomes proportional to \( \sqrt{H} \) for one vortex so that \( C_{el} / T \propto \sqrt{H} \). In an isotropic s-wave superconductor, no significant contribution should be expected at low temperatures from such a mechanism, but localized states in vortex cores contribute a term which is proportional to \( H/H_c2 \), that is, \( C_{el} / T \propto H \). However, the above simple picture should be valid only near the lower critical field \( H_{c1} \) (Ref. \[22\]). By taking account of the core excitations from the bound states in a vortex core and the quasiparticle transfer between vortices, Ichikawa et al. \[22\] showed \( C_{el}(T, H)/T \) for an insulating s-wave superconductor is proportional to \( H^{0.67} \) for \( H \leq H_{c2} \) and \( T = 0 \) while \( C_{el}(T, H)/T \) for a d-wave superconductor is approximately proportional to \( \sqrt{H} \) only for \( H < 0.1H_{c2} \) and \( T = 0 \).

Figure 1a shows \( \kappa/T \) as a function of \( T^{1.7} \) for an insulating parent compound Nd$_2$CuO$_4$. The data are from Ref. \[23\]. Low-temperature thermal conductivity data of several superconductors have been fitted by an empirical formula: \( \kappa/T = A + BT^p \), where \( A \) and \( B \) are constants, and the exponent \( p \leq 2 \) (Ref. \[24\]). The constant \( A \) is equal to \( \kappa_{el}/T \) in a d-wave superconductor and \( A = 0 \) for a gapped s-wave superconductor. For the insulating material Nd$_2$CuO$_4$ where \( \kappa_{el} = 0 \), so the phonon contribution up to 0.5 K can be fitted by the empirical formula with \( A = 0 \) and \( p = 1.49 \) (solid line). Fitting the limited data above 0.38 K (dashed linear line) gives \( A = 0.45 \) mW/K.cm and \( p = 1.7 \). The inferred large value of \( A = 0.45 \) mW/K.cm for this insulating compound is unphysical, indicating that the fit to the limited data points leads to a wrong conclusion.

Figure 1b shows \( \kappa/T \) as a function of \( T^{1.7} \) for electron-doped Pr$_{1.85}$Ce$_{0.15}$CuO$_{4-y} \) \( (T_c = 21 \text{ K}) \) in zero magnetic field. The data are from Ref. \[23\]. Since the phonon contribution \( \kappa_{ph}/T \) of the related compound Nd$_2$CuO$_4$ follows a single power law with the exponent of 1.49 in the whole temperature range from 0.07 K to 0.5 K, one should fit the data by the equation: \( \kappa/T = A + BT^{1.49} \). The best fit (solid line) leads to \( A = \kappa_{el}/T = -0.036 \pm 0.015 \) mW/K.cm. The negligibly small value of \( \kappa_{el}/T \) should provide compelling evidence for a nodeless gap symmetry, in agreement with other independent bulk-sensitive experiments mentioned above. On the other hand, the fit to the data above 0.33 K (dashed linear line) yields \( A = 0.50 \) mW/K.cm and \( p = 1.7 \), which appears to be consistent with d-wave gap symmetry. Since the fit to the limited data points of the insulating Nd$_2$CuO$_4$ leads to an unphysical conclusion,
the similar fit to the limited data points of the superconducting Pr$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$ may also give rise to a wrong conclusion.

\[ \kappa/T = \kappa_{el}/T + \kappa_{ph}/T \]

FIG. 2: a) $\kappa/T$ as a function of $T^{1.5}$ for a heavily overdoped Tl$_2$Ba$_2$CuO$_{6+y}$ ($T_c = 15$ K). The data are from Ref. [28]. Since $\kappa_{ph}/T$ is proportional to $T^{1.5}$ (see Fig. 1a above), we plot $\kappa/T$ as a function of $T^{1.5}$ to clearly see if there is a low-$T$ downturn in electronic thermal conductivity. Following the definition of the parameter $r$ in Ref. [28], we calculate $r = 7.6$ using the reported sample dimensions (the length = 0.3 mm, the cross-sectional area = 0.2 mm x 0.01 mm) [28], and using the electronic contact resistance = 0.2 $\Omega$ (Ref. [28]) and $\kappa_{el}/T = 1.39$ mW/K$^2$cm. b) $\kappa/T$ as a function of $T^{1.5}$ for an overdoped La$_{1.83}$Sr$_{0.17}$CuO$_4$. The data are from Ref. [27]. We calculate $r = 2.3$ using the reported sample dimensions (the length = 0.97 mm, the cross-sectional area = 1.26 mm x 0.212 mm) [28], and using the electronic contact resistance = 0.01 $\Omega$ (Ref. [28]) and $\kappa_{el}/T = 0.5$ mW/K$^2$cm.

There are some other possible explanations for the negligibly small residual linear term within the context of $d$-wave gap symmetry. The first possibility is that $d$-wave nodal quasiparticles become completely localized below 0.5 K. However, the data in the magnetic field of 13 T indicate [29] that the complete localization would occur well below 0.1 K since $\kappa_{el}/T$ is still substantial (0.28 mW/K$^2$cm) at 0.1 K. This apparent contradiction makes this interpretation very unlikely. The second possibility is that the measurement gradually ceases to detect the electronic heat current as electrons fall out of thermal equilibrium with the phonon bath when the temperature is below 0.5 K. Two facts lead us to rule out the electron-phonon decoupling [28] as the main mechanism for the drop. First, identical data are obtained by sending heat directly through the electron system using photons (with no thermal resistance) [29]. Secondly, if this model [28] were relevant, the downturn should be more pronounced in heavily overdoped Tl$_2$Ba$_2$CuO$_{6+y}$ ($T_c = 15$ K) than the overdoped La$_{1.83}$Sr$_{0.17}$CuO$_4$. This is because the parameter $r$ that sensitively controls the extent of the low-$T$ downturn [28] is calculated to be 7.6 for heavily overdoped Tl$_2$Ba$_2$CuO$_{6+y}$, which is a factor of 3.3 larger than that (2.3) for La$_{1.83}$Sr$_{0.17}$CuO$_4$. However, there is no low-$T$ downturn in Tl$_2$Ba$_2$CuO$_{6+y}$ (Fig. 2a) while the significant drop starts below about 0.26 K in La$_{1.83}$Sr$_{0.17}$CuO$_4$ (Fig. 2b). Therefore, it is hard to imagine that this model would be valid only for La$_{1.83}$Sr$_{0.17}$CuO$_4$ and Pr$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$ but not for Tl$_2$Ba$_2$CuO$_{6+y}$.

In Figure 3a, we show the temperature dependence of specific heat for a Pr$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$ crystal ($T_c = 23$ K), at different magnetic fields ($H \parallel c$). The data are taken from Ref. [30]. If the optimally doped cuprate is a gapped $s$-wave superconductor, $C(T, H)/T$ should be expressed as $C(T, H)/T = \gamma_0 (0, H) + \beta T^2$, where the first term is the field-dependent electronic specific heat and the second term is the lattice specific heat due to acoustic phonons. It is clear that the specific heat data at different magnetic fields can be well fitted by the above expression. The average of the fitted $\beta$ values is 0.25 mJ/mol K$^4$, leading to a Debye temperature of 384 K. A finite value of $\gamma_0 (0, 0)$ is also found in hole-doped cuprates, and there are several proposals to explain its origin [31–33].

On the other hand, if electron-doped cuprates are $d$-wave superconductors with line nodes, $C(T, 0)/T$ should be expressed as $C(T, 0)/T = \gamma_0 (0, 0) + \alpha T + \beta T^2$, where the term $\alpha T$ arises from nodal quasiparticle excitation (see discussion above). In Fig. 3b, we fit the zero-field data by $C(T, 0)/T = \gamma_0 (0, 0) + \alpha T + \beta T^2$. Although the three-parameter fit improves the quality of fitting slightly compared with the above two-parameter fit, the fitted parameter $\alpha$ is negative (−0.25±0.05 mJ/mol K$^4$) and unphysical. This suggests that the value of $\alpha$ is negligibly small, in disagreement with pure $d$-wave gap symmetry with line nodes.

In order to obtain the zero-temperature $\gamma_0 (0, H)$ more precisely, we fit the data of Fig. 3a using $C(T, H)/T = \gamma_0 (0, H) + \beta T^2$ with a fixed $\beta = 0.25$ mJ/mol K$^4$. Fig. 4 shows $\gamma_0 (0, H) - \gamma_0 (0, 0)$/$\gamma_N$ as a function of $H/H_{c2}$. Here $H_{c2}$ is taken to be 50 kOe (see Fig. 2a of Ref. [30]) and $\gamma_N = \gamma_0 (56 kOe) - \gamma_0 (0) = 4.1$ mJ/mol K$^2$. It is striking that the field dependence of the electronic specific heat for this electron-doped cuprate is in quantitative agree-
tem, Fig. 5 compares less gap symmetry in the optimally electron-doped system with a theory based on isotropic s-wave gap symmetry \[22\]. This excellent agreement clearly indicates that the optimally electron-doped cuprate is a gapped superconductor.

Fitting the zero-temperature data and theoretically calculated values respectively in Fig. 4 by a power law yields an exponent of 0.64±0.04 for the data and 0.663±0.008 for the theory. At finite temperatures, the exponent should increase with increasing temperature, as demonstrated in an s-wave superconductor NbSe\(_2\) (Ref. \[34\]). In order to further verify a nodeless gap symmetry in the optimally electron-doped system, Fig. 5 compares \([C(T, H) − C(T, 0)]/\gamma_N T\) for a Pr\(_{1.85}\)Ce\(_{0.15}\)CuO\(_{4−y}\) crystal (\(T_c = 22\) K) with that for V\(_3\)Si. The data of Pr\(_{1.85}\)Ce\(_{0.15}\)CuO\(_{4−y}\) are reproduced from Ref. \[35\] and the data of V\(_3\)Si are from Ref. \[36\]. The values of \(\gamma_N\) and \(H_{c2}\) for the PCCO compound are taken to be 3.7 mJ/mol K\(^2\) and 43 kOe (see Fig. 2 of Ref. \[35\]), respectively. The value of \(H_{c2}\) for the V\(_3\)Si superconductor is found to be 250 kOe (Ref. \[36\]). Using the specific-heat jump at \(T_c\) (i.e., \(\Delta C/T_c ≃ 90\) mJ/mol K\(^2\) \[37\]) and the relation \(\Delta C/\gamma_N T_c = 2.0\) suitable for V\(_3\)Si \[37\], we calculate \(\gamma_N\) to be 45 mJ/mol K\(^2\). It is evident that the two sets of data almost coincide with each other. Fitting the two sets of data respectively by a power law produces the same exponent of 0.78. Therefore, electron-doped cuprates have a very similar field dependence of the electronic specific heat as the con-
ventional s-wave superconductors.

In summary, independent bulk-sensitive specific heat and thermal conductivity experiments show a nodeless gap symmetry in the bulk of optimally electron-doped cuprates. A $T^2$ dependence of the penetration depth at low temperatures observed in some samples can be well explained in terms of nodeless s-wave gap along with an extrinsic effect due to current-induced nucleation of vortex-antivortex pairs at defects. Although the data of spin-lattice relaxation rate and Knight shift in an underdoped Pr$_{0.9}$LaCe$_{0.09}$CuO$_{4-y}$ are consistent with d-wave gap symmetry, we will show that the data can be better explained by an anisotropic s-wave gap with a minimum gap size being consistent with independent magnetic penetration depth data. Further, the d-wave gap symmetry in Pr$_{0.91}$LaCe$_{0.09}$CuO$_{4-y}$ is incompatible with the observed large residual resistivity ($92 \mu\Omega\text{cm}$), which would suppress $T_c$ to zero. Therefore, these bulk-sensitive experiments consistently point towards a nodeless s-wave gap symmetry, in agreement with predominantly phonon-mediated pairing mechanism.

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