Superconductivity and calorimetric studies of Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ + $\delta$
under different annealing conditions

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Abstract

Polycrystalline samples of electron-doped Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ + $\delta$ have been prepared under different annealing conditions and investigated by means of X-ray-diffraction, oxygen content analysis, electrical resistivity, magnetic susceptibility and low temperature specific heat measurements. X-ray-diffraction patterns show that samples contain a single T$'_{0}$ phase. The superconducting transition temperatures $T_{cm}$ taken with the onset of diamagnetism in magnetic-susceptibility measurements are 20 and 19.5 K for sample annealed in flowing Ar gas and in vacuum ($\approx 10^{-3}$ torr), respectively. The data of the samples, which are annealed in flowing Ar gas, show clear evidence for an $\alpha T^2$ term at zero magnetic field in superconducting electronic specific heat, and are consistent with d-wave superconductivity. However, this behavior is not observed in the other sample, which is annealed in vacuum. These results indicate that different heat treatments affect the oxygen content, homogeneity, superconducting transition temperature $T_{c}$, superconducting volume fraction, and the superconducting pairing symmetry of Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ + $\delta$.

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1. Introduction

Rare-earth cuprates of composition R$_2$CuO$_4$ (R = Pr, Nd, Sm and Eu) with the tetragonal T$'_{0}$ structure play a unique role among cuprates, becoming the so-called electron-doped superconductors when Ce or Th is doped and the oxygen content of sample is reduced by proper heat treatment [1–4]. In order to improve the quality of sample, the correlation between the preparation of sample and superconducting properties in Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ + $\delta$ has been extensively investigated by different annealing conditions [5]. In the past years, the great discussion over pairing symmetry in the hole-doped cuprates has been resolved, and is in favor of predominantly d-wave orbital order parameter symmetry for hole-doped (p-type) high-$T_{c}$ superconductors [6–11]. However, the symmetry of

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magnetic-susceptibility and LTSH measurements. These results enable us to clarify the heat treatment effect on the superconductivity and the observation of pairing symmetry using LTSH experiments in the electron-doped Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$. Furthermore, we compare the results of $T_c$ (superconducting transition temperature) for electron-doped Pr$_{1.85}$Ce$_{0.15}$Cu$_{1-y}$M$_x$O$_{4.065}$ and hole-doped La$_{1.6}$Sr$_{0.4}$Cu$_{1-y}$M$_x$O$_4$ (M = Ni and Zn) to provide possible explanations for these behaviors observed in LTSH of Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$.

2. Experimental

The polycrystalline samples of Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ were prepared by the conventional solid-state reaction method. High-purity (99.99%) Pr$_6$O$_{11}$, CeO$_2$ and CuO powders were mixed and fired in air at 900 °C for 24 h, then furnace cooled down to room temperature. The resultant powders were pressed into pellets and heated at 1000 °C in air for 48 h, and then air quenched to room temperature. This process was repeated at least three times with intermediate grinding to ensure the homogeneity of samples. To study heat treatment effect on the superconducting properties of Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$, samples were prepared under different annealing conditions. For oxygen reduction, samples were annealed under Ar atmosphere or vacuum ($\sim$10$^{-3}$ torr). The annealing temperature is from 800 to 950 °C in intervals of 10 °C. For clarity and brief description, we only present typical data of four annealed samples in this paper: sample A was annealed at 850 °C for 12 h under Ar atmosphere and then furnace cooled down to room temperature. Sample B was annealed at 850 °C for 12 h under Ar atmosphere and then quenched to room temperature. Sample C was annealed in vacuum ($\sim$10$^{-3}$ torr) at 850 °C for 9 h and then quenched to room temperature. Sample D was annealed at 900 °C for 12 h under Ar atmosphere and then quenched to room temperature. Structural analysis was carried out by powder X-ray diffraction. The oxygen content parameter $\delta$ in Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ was determined from standard iodo-metric titration method. The principle of this method is to determine the valence of Cu ions in the compound and thus we can calculate the oxygen content from electrical neutrality. Electrical resistivity measurement was made by means of a standard four-probe method with the data taken from 10 to 300 K. The DC magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 5–10 K with a field of 10 Oe. Specific heat $C(T)$ was measured from 0.6 to 10 K with a $^3$He relaxation calorimeter using the heat-pulse technique in zero magnetic field. The precision of the measurement in the temperature range is about 1%. To calibrate the calorimeter, $C(T)$ of a copper sample with mass 21.69 mg was measured. A fit of data below 7 K results in a linear term coefficient $\gamma = 0.698 \pm 0.002$ mJ/mol K$^2$ and the Debye temperature $\theta_D = 340$ K, both of which are consistent with the literature values [19] ($\gamma = 0.695$ mJ/mol K$^2$ and $\theta_D = 343$ K), and confirms the good calibration of the calorimeter.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$. It is found that samples A–C contain nearly a single T’ phase, and sample D has an impurity peak around $2\theta = 28.5^\circ$. Conceicao et al. [5] prepared Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ through three different precursors, and reported that the impurity Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ peaks of samples made using conventional solid-state method occur at $2\theta = 28.6^\circ$, 33.2$^\circ$, and 47.6$^\circ$. However, these Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ peaks are not observed in Fig. 1 except for sample D at $2\theta \sim 28.5^\circ$. Indeed, the impurity Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ peaks appear
in X-ray diffraction patterns of Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ while the annealing temperature of sample is above 900 °C in our study. Since sample D does not contain a single T' phase, we only discuss the other three data of samples in the following. The oxygen content parameters δ for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ determined from iodometric titration method are shown in Table 1. The values of δ are 0.175, 0.161 and 0.065 for samples A–C, respectively. This result indicates that the oxygen content of sample annealed in Ar atmosphere is more than that of sample annealed in vacuum. Temperature dependence of the electrical resistivity ρ(T) for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ are shown in Fig. 2. The inset shows ρ(T) in the temperature range of 10–30 K. In these curves, we define five different temperatures $T_{\text{co}}$, $T_{\text{c}(10\%)}, T_{\text{c}(90\%)}, T_{\text{w}(10\%)}, \text{and } T_{\text{w}(90\%)}, \text{ corresponding to where the electrical resistivity begins to drop with decreasing temperature, drops to 10% of its magnitude, drops to 10% of its magnitude, and drops to zero, and difference between $T_{\text{c}(90\%)}$ and $T_{\text{c}(10\%)}$, respectively. These temperatures for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ are also listed in Table 1. All the three samples show semiconducting-like behavior for temperatures above $T_{\text{co}}$, and the normal state electrical resistivity $\rho_{300\,\text{K}}$ are 6.78, 5.65, and 1.96 mΩcm for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.175}$, Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.161}$, and Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.065}$, respectively. It is noted that the superconducting transition widths for all the three samples are broader than that of \(\text{La}_2-x\text{Sr}_x\text{CuO}_4\). This result is also observed in the results reported by Conceicao et al. [5], and may be attributed to a large degree of both cationic and anionic inhomogeneous distribution or less homogeneity in electron-doped superconductors. Indeed, the preparation of n-type Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ is more difficult than p-type \(\text{La}_2-x\text{Sr}_x\text{CuO}_4\) since the process of oxygen reduction for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ will make samples inhomogeneous resulting in the broader superconducting transitions. The resistivity of Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.065}$ is the lowest than that of others at room temperature, but becomes the highest below 80 K, and its superconducting transition width $\Delta T$ ($T_{\text{c}(90\%)}-T_{\text{c}(10\%)}$) is larger than that of others. These features indicate that the sample annealed in vacuum may have a larger degree of both cationic and anionic inhomogeneous 20) or less homogeneity 5) of Ce than those in Ar atmosphere. It is also possible that, in the grain boundary, reduction effect is more significant in the vacuum-annealed sample although cations, including Ce, distribute as uniform as in the Ar-annealed sample. Fig. 3 shows the temperature dependence of magnetic susceptibility, field cooled (FC) and zero-field cooled (ZFC), for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$. The superconducting transition temperatures $T_{\text{cm}}$ taken with the onset of diamagnetism in magnetic susceptibility measurements are 20, 20, and 19.5 K for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.175}$, Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.161}$, and Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.065}$, respectively. The diamagnetic $\gamma(T)$ values of ZFC below $T_{\text{cm}}$ for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.065}$ is larger than those of Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.175}$ and Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.161}$. Brinkmann et al. 21,22 reported that the annealing process at high temperature in Ar atmosphere for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ will decrease the oxygen content of sample resulting in an increasing of free carriers in the Cu–O plane of T’ structure. Since Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ is an electron-doped superconductor, less oxygen content of sample may induce more free electrons in the Cu–O plane. This may be the reason for the $\rho_{300\,\text{K}}$ of Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.065}$ being the lowest and the diamagnetic $\gamma(T)$ values of ZFC below $T_{\text{cm}}$ for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.065}$ being larger than those of the others. It is noted that the difference between the diamagnetic $\gamma(T)$ values of ZFC and FC in Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.065}$ is larger than those of the others, indicating the flux pinning of Pr$_{1.85}$Ce$_{0.15}$CuO$_{4.065}$ in the superconducting state is larger than those of the others. This also proves that the sample annealed in

Table 1
The oxygen content parameter δ and the superconducting critical temperatures of Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ under different annealing conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ</th>
<th>$T_{\text{co}}$ (K)</th>
<th>$T_{\text{c}(10%)}$ (K)</th>
<th>$T_{\text{c}(90%)}$ (K)</th>
<th>$\Delta T = T_{\text{c}(90%)} - T_{\text{c}(10%)}$ (K)</th>
<th>$T_{\text{w}(10%)}$ (K)</th>
<th>$T_{\text{w}(90%)}$ (K)</th>
<th>$\rho_{300,\text{K}}$ (mΩcm)</th>
<th>$\rho_{25,\text{K}}$ (mΩcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.175</td>
<td>18.5</td>
<td>18.1</td>
<td>15.3</td>
<td>2.8</td>
<td>14</td>
<td>5.65</td>
<td>9.62</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.161</td>
<td>20.5</td>
<td>20</td>
<td>18</td>
<td>2</td>
<td>17.2</td>
<td>6.78</td>
<td>12.47</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.065</td>
<td>20</td>
<td>19.4</td>
<td>16.2</td>
<td>3.2</td>
<td>13.5</td>
<td>1.96</td>
<td>15.36</td>
<td></td>
</tr>
</tbody>
</table>

The temperatures are extracted from the $\rho(T)$ data shown in Fig. 2 and defined in the text. The values of the electrical resistivities $\rho_{300\,\text{K}}$ and $\rho_{25\,\text{K}}$ for Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ are also shown.
vacuum ($\text{Pr}_1.85\text{Ce}_{0.15}\text{CuO}_{4.065}$) has less homogeneity and more defects than those in Ar atmosphere. This point is further supported by the results of Fig. 2. $\text{Pr}_1.85\text{Ce}_{0.15}\text{CuO}_{4.065}$ having the largest value of $r_{20 K/r_{300 K}}$ indicates that it has the strongest localization effect than the others.

From the results of X-ray-diffraction and magnetic susceptibility, we can make sure the quality of sample is good enough to carry out the LTSH measurements.

Fig. 4 shows the specific heat $C(T)$ data of $\text{Pr}_1.85\text{Ce}_{0.15}\text{CuO}_{4.175}$ in zero magnetic field. In $d$-wave superconductors, at zero magnetic field, the electronic specific heat $C_e$ is proportional to $T^2$ rather than $\exp(-\Delta/T)$ as in conventional $s$-wave superconductors, where $\Delta$ is the superconducting gap. In order to fit the $C(T)$, $C/T$ versus $T^2$ curve is plotted in Fig. 5. We have attempted to model our LTSH data by assuming that the total specific heat is made of three distinct contributions determined by $C_{\text{tot}} = C_{\text{hyp}} + C_{\text{ele}} + C_{\text{lat}}$ where the $C_{\text{hyp}} = A/T^2$ is the hyperfine contribution caused by the local magnetic field, $C_{\text{ele}} = \gamma T$ is the electronic term due to free charge carriers, $C_{\text{lat}} = \beta T^3$ is the phonon contribution ($T^3$ anharmonic term has negligible effect in our fitting range). Thus the data have been fitted using $C(T) = A/T^2 + \gamma T + \alpha T^2 + \beta T^3$. First, we fit the data using all the four terms. Then we try to fit the data using different assumptions so as to set only one parameter equal to zero. By varying different combinations in the fitting process, the best fit can be found (smallest standard deviation, SD). The fitting results are described by the solid line in Fig. 5, and the important resulting parameters $A$, $\gamma$, $\alpha$, and $\beta$ for $\text{Pr}_1.85\text{Ce}_{0.15}\text{CuO}_{4.065}$ are listed in Table 2. The asterisk * denotes the best fit (smallest SD) parameters. It is found that $\text{Pr}_1.85\text{Ce}_{0.15}\text{CuO}_{4.175}$ and $\text{Pr}_1.85\text{Ce}_{0.15}\text{CuO}_{4.161}$ show an $\alpha T^2$ term existence in the
LTSH at zero magnetic field, which are consistent with \(d\)-wave superconductivity. However, this behavior is not observed in \(Pr_{1.85}Ce_{0.15}CuO_{4.065}\). These different behaviors observed in LTSH for \(Pr_{1.85}Ce_{0.15}CuO_{4+x}\) may be attributed to the different oxygen content of samples (resulting in different amounts of free carriers in the Cu–O plane), or different homogeneity or defects of samples due to different annealing conditions.

In order to discuss the pairing symmetry of electron-doped \(Pr_{1.85}Ce_{0.15}CuO_{4\mp\delta}\) further, we present the results of \(T_c\) (superconducting transition temperature) for electron-doped \(Pr_{1.85}Ce_{0.15}Cu_{1-x}M_{x}O_{4.065}\) and hole-doped \(La_{1.6}Sr_{0.4}Cu_{1-x}M_{x}O_{4}\) (\(M = \text{Ni and Zn}\)). Fig. 6 shows the \(T_c\) versus \(x\) for electron-doped \(Pr_{1.85}Ce_{0.15}Cu_{1-M_{x}}O_{4.065}\) and hole-doped \(La_{1.6}Sr_{0.4}Cu_{1-M_{x}}O_{4}\) (\(M = \text{Ni and Zn}, x = 0-0.02\)). In \(Pr_{1.85}Ce_{0.15}Cu_{1-M_{x}}O_{4.065}\), the depression of \(T_c\) for magnetic Ni doped is greater than that of nonmagnetic Zn doped. This result indicates that the cooper-pair breaking due to magnetic ion in the Cu–O plane plays an important role in the suppression of superconductivity in electron-doped \(Pr_{1.85}Ce_{0.15}Cu_{1-M_{x}}O_{4.065}\). On the contrary, the depression of \(T_c\) for nonmagnetic Zn doped is slightly greater than that of magnetic Ni doped in \(La_{1.6}Sr_{0.4}Cu_{1-x}M_{x}O_{4}\). This indicates the disorder effect due to different atoms in the Cu–O plane plays an important role in the suppression of superconductivity in hole-doped \(La_{1.6}Sr_{0.4}Cu_{1-x}M_{x}O_{4}\). From the results of Fig. 6 and LTSH for \(Pr_{1.85}Ce_{0.15}CuO_{4\mp\delta}\), the pairing symmetry in electron-doped superconductors seems quite different from hole-doped superconductors. The different pairing symmetry observed in LTSH between sample C (\(Pr_{1.85}Ce_{0.15}CuO_{4.065}\)) and samples A and B (\(Pr_{1.85}Ce_{0.15}CuO_{4.045}\) and \(Pr_{1.85}Ce_{0.15}CuO_{4.061}\)) may be attributed to the different amounts of free carriers in the Cu–O plane, or different homogeneity and defects of samples due to different annealing conditions.

In order to study this point further, \(Pr_{2-x}Ce_xCuO_{4\mp\delta}\) (\(x = 0.13-0.17\)) studies are in progress and the results of the LTSH measurements for \(Pr_{2-x}Ce_xCuO_{4\mp\delta}\) will be published elsewhere.

![Fig. 6. \(T_c\) (superconducting transition temperature) versus \(x\) for electron-doped \(Pr_{1.85}Ce_{0.15}Cu_{1-M_{x}}O_{4.065}\) and hole-doped \(La_{1.6}Sr_{0.4}Cu_{1-M_{x}}O_{4}\) (\(M = \text{Ni and Zn}, x = 0-0.02\)).](image)

**4. Conclusions**

We have prepared polycrystalline samples of \(Pr_{1.85}Ce_{0.15}CuO_{4\mp\delta}\) under different annealing conditions. These results were confirmed by X-ray diffraction, oxygen content analysis, electrical resistivity, magnetic-susceptibility and LTSH measurements. Most importantly, the samples which are annealed in flowing Ar gas show a \(d\)-wave superconductivity in LTSH measurements. However, this behavior is not observed in the sample which is annealed in vacuum. These results indicate that different heat treatments may change the oxygen content of samples, or homogeneity and defects of sample, resulting in the different behavior in LTSH of \(Pr_{1.85}Ce_{0.15}CuO_{4\mp\delta}\). In order to study this point further, \(Pr_{2-x}Ce_xCuO_{4\mp\delta}\) (\(x = 0.13-0.17\)) studies are in progress and the results of the LTSH measurements for \(Pr_{2-x}Ce_xCuO_{4\mp\delta}\) will be published elsewhere.
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