

## Evidence for a quantum phase transition in electron-doped $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ from thermopower measurements

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The evidence for a quantum phase transition under the superconducting dome in the high- $T_c$  cuprates has been controversial. We report low-temperature normal state thermopower ( $S$ ) measurements in electron-doped  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$  as a function of doping ( $x$  from 0.11 to 0.19). We find that at 2 K both  $S$  and  $S/T$  increase dramatically from  $x=0.11$  to 0.16 and then saturate in the overdoped region. This behavior has a remarkable similarity to previous Hall effect results in  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ . Our results are further evidence for an antiferromagnetic to paramagnetic quantum phase transition in electron-doped cuprates near  $x=0.16$ .

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The existence of a quantum phase transition at a doping under the superconducting dome in high- $T_c$  superconductors is still controversial. Evidence for a quantum critical point has been given for hole-doped cuprates<sup>1-3</sup> but the  $T=0$  normal state is difficult to access because of the large critical field ( $H_{c2}$ ). Electron-doped cuprates have a relatively low  $H_{c2}$  and several studies have suggested that a quantum phase transition exists in those cuprates. Electrical transport<sup>4</sup> on electron-doped  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$  (PCCO) shows a dramatic change of Hall coefficient around doping  $x_c=0.16$ , which indicates a Fermi surface rearrangement at this critical doping. Optical conductivity experiments<sup>5</sup> revealed that a density-wave-like gap exists at finite temperatures below the critical doping  $x_c$  and vanishes when  $x \geq x_c$ . Neutron scattering experiments<sup>6</sup> on  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$  (NCCO) found antiferromagnetism as the ground state below the critical doping while no long-range magnetic order was observed above  $x_c$ . Other suggestive evidence<sup>7</sup> comes from the observation of a low-temperature normal state insulator to metal crossover as a function of doping, and the disappearance of negative spin magnetoresistance at a critical doping.<sup>8</sup> All these experiments strongly suggest that an antiferromagnetic (AFM) to paramagnetic quantum phase transition occurs under the superconducting dome in the electron-doped cuprates.

The quantum phase transition in electron-doped cuprates is believed to be associated with a spin density wave (SDW) induced Fermi surface reconstruction.<sup>5,9</sup> Angle-resolved photoemission spectroscopy experiments<sup>10</sup> on NCCO reveal a small electronlike pocket at  $(\pi, 0)$  in the underdoped region and both electron- and holelike Fermi pockets near optimal doping. This interesting feature is thought to arise as a result of the SDW instability that fractures the conduction band into two different parts.<sup>9</sup> If one continues to increase the doping (above  $x_c$ ), the weakening of the spin density wave leads to a large holelike Fermi pocket centered at  $(\pi, \pi)$  in the overdoped region.<sup>9,11</sup>

Nevertheless, the presence of a quantum critical point (QCP) under the superconducting dome in electron-doped cuprates is still quite controversial.<sup>12</sup> Other experimental probes of the critical region are needed. In this paper, we present a systematic study of the magnetic-field-driven

normal state thermopower on PCCO films. We find a doping dependence similar to that seen in the low-temperature normal state Hall effect measurements.<sup>4</sup> From a simple free electron model comparison of these two quantities, we find a strikingly similar behavior of the effective number of carriers. This strongly suggests that a quantum phase transition takes place near  $x=0.16$  in PCCO.

High-quality PCCO films with thickness about 3000 Å were fabricated by pulsed laser deposition on  $\text{SrTiO}_3$  substrates ( $10 \times 5 \text{ mm}^2$ ). Detailed information can be found in our previous papers.<sup>13,14</sup> The films were characterized by ac susceptibility, resistivity measurements, and Rutherford backscattering.

High-resolution thermopower is measured using a steady state method by switching the temperature gradient to cancel the Nernst effect and other possible background contributions. The sample is mounted between two thermally insulated copper blocks. The temperature gradient is built up by applying power to heaters on each block and the gradient direction is switched by turning on or off the heaters. The temperature gradient is monitored by two Lakeshore Cernox bare chip thermometers. Thermopower data are taken when the gradient is stable and averaged for many times to reduce the systematic error. The voltage leads are phosphor bronze, which has a small thermopower even at high field.<sup>15</sup> The thermopower contribution from the wire is calibrated against  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c=92 \text{ K}$ ) for  $T < 90 \text{ K}$  and Pb film for  $T > 90 \text{ K}$ , and is subtracted out to get the absolute thermopower of the PCCO sample.

We measured the zero-field and in-field resistivity of all the doped PCCO films. The results are similar to our previous report.<sup>4</sup> A 9 T magnetic field ( $H \parallel c$ ) is enough to suppress the superconductivity for all the dopings. This enables us to investigate the low-temperature normal state properties in PCCO. A low-temperature resistivity upturn is seen for doping below  $x=0.16$ , which suggests a possible insulator to metal crossover as a function of doping.<sup>7</sup>

Thermopower is measured on the PCCO films doped from  $x=0.11$  to 0.19. In zero field, a sharp superconducting transition is clearly seen in the thermopower. In the inset of Fig. 1, we show the thermopower  $S$  of  $x=0.16$  ( $T_c=16.5 \text{ K}$ ) as a

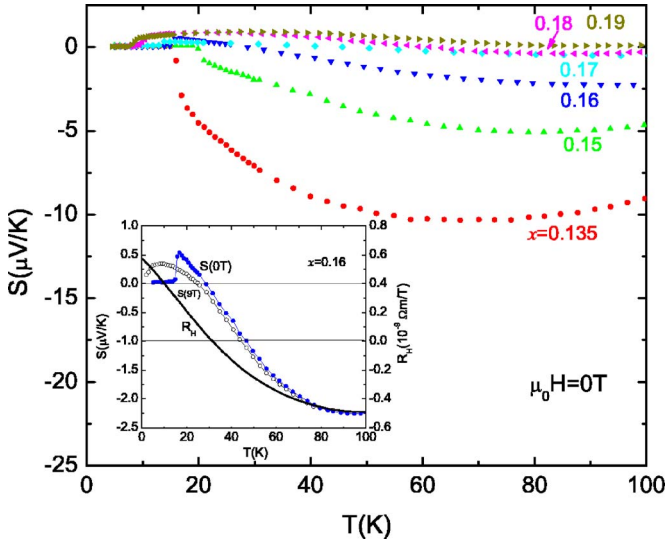


FIG. 1. (Color online) Thermopower  $S$  versus temperature ( $T < 100$  K) at zero field for all the superconducting PCCO films. Inset is the thermopower  $S$  of  $x=0.16$  film at zero field (solid blue circle) and  $\mu_0 H = 9$  T (open circle) as a function of temperature. Solid line is the temperature dependence of the Hall coefficient for the same film.

function of temperature. Our high-resolution thermopower setup enables us to observe small changes of signal. When the sample goes to the superconducting state,  $S=0$ , a small change  $\Delta S = 0.5 \mu\text{V/K}$  is easily detectable, which indicates a better sensitivity than our previous one-heater-two-thermometer setup.<sup>16</sup> We also show the Hall coefficient  $R_H$  as a function of temperature for the same film in the graph. A sign change of both  $S$  and  $R_H$  is observed at the same temperature.

In the main panel of Fig. 1, we show the zero-field thermopower for all the superconducting films. A clear superconducting transition is seen in these films. The normal state  $S$  ( $T > T_c$ ) is negative in the underdoped region. It becomes positive in the overdoped region at low temperature (to be shown later). The magnitude of  $S$  in the underdoped region is large as expected for a system with less charge carrier density while it is much smaller in the overdoped region. Previous zero-field thermopower measurements on NCCO crystals<sup>17</sup> are qualitatively similar to our data.

When a 9 T magnetic field is applied along the  $c$  axis, the superconducting films are driven to the normal state for  $T < T_c$ . As seen from the inset of Fig. 1, when the superconductivity is destroyed, the normal state thermopower is obtained. In Fig. 2, we show the normal state thermopower for all the films. The low-temperature ( $T < 15$  K) normal state thermopower is shown in the inset. We showed in Fig. 1 that for  $x=0.16$  the thermopower changes from negative to positive for  $T < 30$  K, in good agreement with the Hall effect measurements.<sup>4</sup> For the overdoped films  $x=0.17$  and  $0.18$ , we observe similar behavior with a sign change occurring below 45 and 60 K, respectively. However, the thermopower is always positive for  $x=0.19$ . Similar to the the Hall effect, the thermopower for  $x \geq 0.16$  is nearly the same for  $T < 10$  K, as shown in the inset of Fig. 2. The dramatic

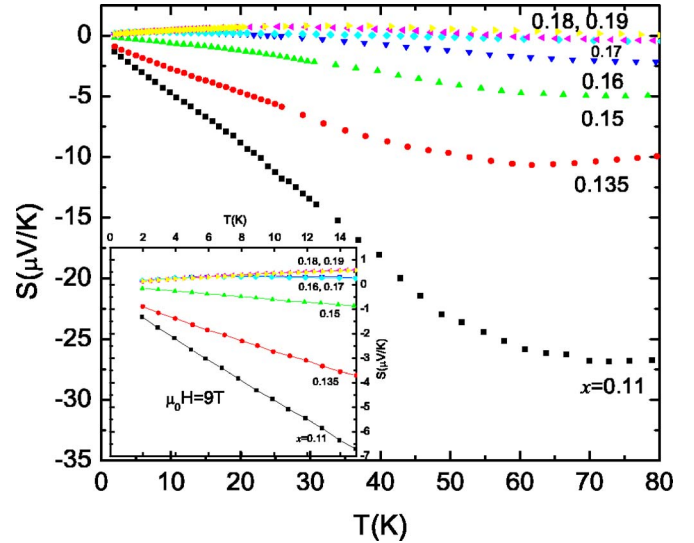


FIG. 2. (Color online) The normal state thermopower  $S$  ( $\mu_0 H = 9\text{ T} > \mu_0 H_{c2}$ ) of all the doped films versus temperature. Inset shows the low-temperature ( $T < 15$  K) data.

change of the thermopower at low temperature from  $x=0.15$  to the overdoped region suggests a sudden Fermi surface rearrangement around the critical doping  $x=0.16$ .

In the Boltzmann picture, thermopower and electrical conductivity are related through the expression<sup>18</sup>

$$S = \frac{-\pi^2 k_B^2 T}{3e} \left. \frac{\partial \ln \sigma(\epsilon)}{\partial \epsilon} \right|_{\epsilon=E_F} \quad (1)$$

In the simple case of a free electron gas, this yields  $S/T = -(\pi^2 k_B^2 / 3e) N(\epsilon_F) / n$  [ $N(\epsilon_F)$  is the density of states at the Fermi energy and  $n$  is the total number of charge carriers]. However, in real metals, the energy dependence of the scattering time at the Fermi level,  $[\partial \ln \tau(\epsilon) / \partial \epsilon]_{\epsilon=E_F}$ , also affects the thermopower. In the zero-temperature limit, it has been shown that this term also becomes proportional to  $N(\epsilon_F) / n$  when the impurity scattering dominates.<sup>19</sup> In electron-doped cuprates, there is strong evidence<sup>4</sup> for impurity scattering at low temperatures. The residual resistivity is about  $50 \mu\Omega\text{ cm}$  for an optimally doped film, which is quite large compared to clean metals, and the temperature dependence of the resistivity becomes almost constant below 20 K. This is all suggestive of strong impurity scattering. The scattering most likely comes from Ce and oxygen disorder and one would expect a similar disorder at all dopings, although this is hidden by the anomalous (and unexplained) resistivity upturn for the lower dopings. Therefore, we expect that the thermopower is proportional to  $N(E_F) / n$  will be a valid approximation for our electron-doped PCCO films. This theory thus provides a solid theoretical basis for an experimental observation: in a wide variety of correlated metals, there is an experimental correlation between the magnitude of thermopower and specific heat in the zero-temperature limit.<sup>20</sup>

Let us examine our data with this picture in mind. Figure 3(a) presents  $S/T$  as a function of temperature below 40 K for all the doped films. As seen in the figure, there is a dra-

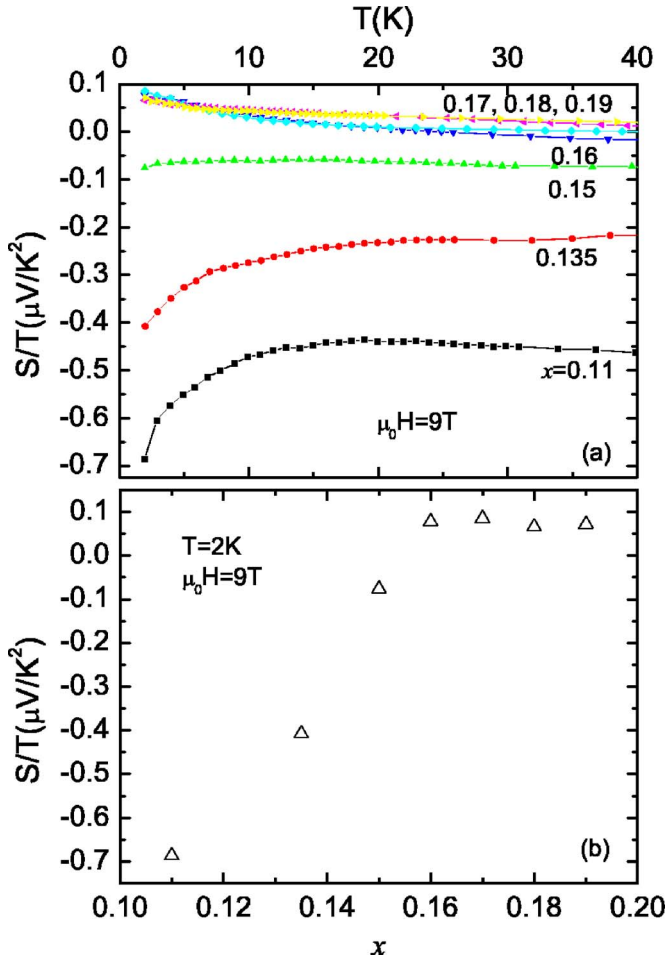


FIG. 3. (Color online) (a)  $S/T$  versus temperature ( $T < 40\text{ K}$  and  $\mu_0 H = 9\text{ T}$ ) for all the films. (b)  $S/T$  ( $T = 2\text{ K}$  and  $\mu_0 H = 9\text{ T}$ ) as a function of doping  $x$ .

matic difference between the underdoped and the overdoped films. For underdoped samples,  $S/T$  displays a strong temperature dependence below 20 K, which is reminiscent of the low-temperature upturn in resistivity and Hall effect.<sup>4,7</sup> One possible explanation for this feature would be charge localization.<sup>21</sup> If all, or some of, the itinerant carriers localize at very low temperatures, then the decrease in conductivity is expected to be concomitant with an increase in the entropy per itinerant carrier (which is the quantity roughly measured by  $S/T$ ). We find this to be qualitatively true as shown in Fig. 4, which displays  $S/T$  and conductivity for  $x = 0.11$  in a semi-log plot. Below 10 K, both quantities are linear functions of  $\log_{10} T$ . Note that for the resistivity, it has been shown<sup>7</sup> that the logarithmic divergence saturates below 1 K. Therefore, further thermopower measurements below 2 K would be very useful.

In contrast to the underdoped films, the temperature dependence of  $S/T$  in the overdoped region is weaker and there is clearly a finite  $S/T$  even at zero temperature. Taking the magnitude of  $S/T$  at 2 K as our reference, we can examine the doping dependence of the ratio  $N(\epsilon_F)/n$  for itinerant carriers at this temperature. Figure 3(b) presents the doping dependence of  $S/T$  at 2 K. A strong doping dependence for  $x \leq 0.16$ , a sharp kink around  $x = 0.16$ , and a saturation in the

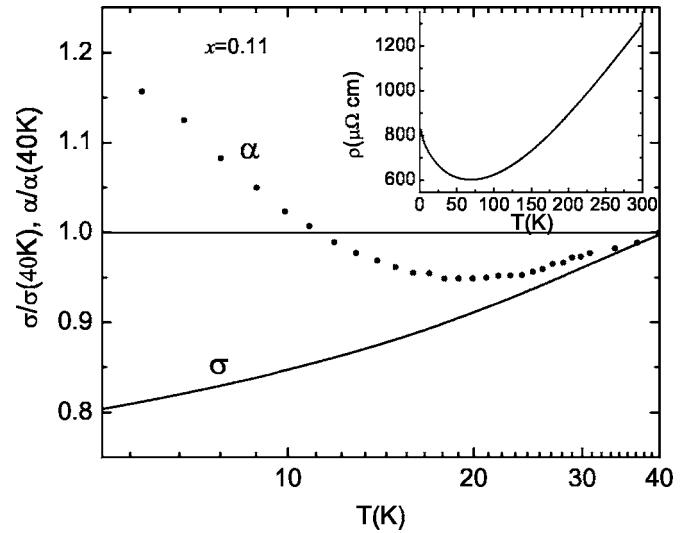


FIG. 4. Normalized  $\alpha = S/T$  and  $\sigma(T)$  for  $x = 0.11$  versus temperature for  $T \leq 40\text{ K}$ . Inset shows the temperature dependence of in-plane resistivity  $\rho(T)$  for the same film.

overdoped region are visible. The dramatic change of  $S/T$  at low temperatures from the underdoped to overdoped regions is similar to the Hall effect<sup>4</sup> at 0.35 K, in which a sharp kink was observed around  $x = 0.16$ . Both  $S/T$  and  $R_H$  change from negative in the underdoped region to a saturated positive value above  $x = 0.16$ .

The similarity of the doping dependence of  $S/T$  and  $R_H$  implies a common physical origin. To explore the relation between  $S/T$  and  $R_H$ , let us assume a simple free electron model, where thermopower displays a very simple correlation with the electronic specific heat  $C_{el} = (\pi^2 k_B^2 T/3)N(\epsilon_F)$ . Following the analysis of Ref. 20, a dimensionless quantity

$$\hat{q} = \frac{S N_{Av} e}{T \gamma} \quad (2)$$

can be defined ( $N_{Av}$  is Avogadro's number and  $\gamma = C_{el}/T$ ), which is equal to  $N_{Av}/n$ . For a simple metal,  $R_H = V/ne$  ( $V$  is the total volume). If we define

$$q' = R_H e / V_m \quad (3)$$

where  $V_m$  is the unit cell volume, then  $q'$  is also equal to  $N_{Av}/n$ . By this simple argument, we can compare  $S$  and  $R_H$  directly. Because we do not have data for  $\gamma$  except at optimal doping, we assume it does not change much with doping. With the  $\gamma$  value<sup>22</sup> (4 mJ/K<sup>2</sup> mol) for  $x = 0.15$  and  $S/T$  and  $R_H$  at 2 K, we can plot both  $q$  and  $q'$  together, as shown in Fig. 5. We find a remarkable similarity in the doping dependence of these two dimensionless quantities, both in trend and in magnitude. Note that no dramatic changes in either  $q$  or  $q'$  are observed near  $x = 0.13$ , where it is claimed that AFM long-range order vanishes<sup>12</sup> from recent neutron scattering measurements. We should mention that assuming a constant  $\gamma$  as a function of doping in our range of investigation ( $x = 0.11 - 0.19$ ) is, of course, subject to caution due to a lack of experimental data. However, it has been found<sup>22</sup> that the specific heat coefficient  $\gamma$  is the same for an as-grown

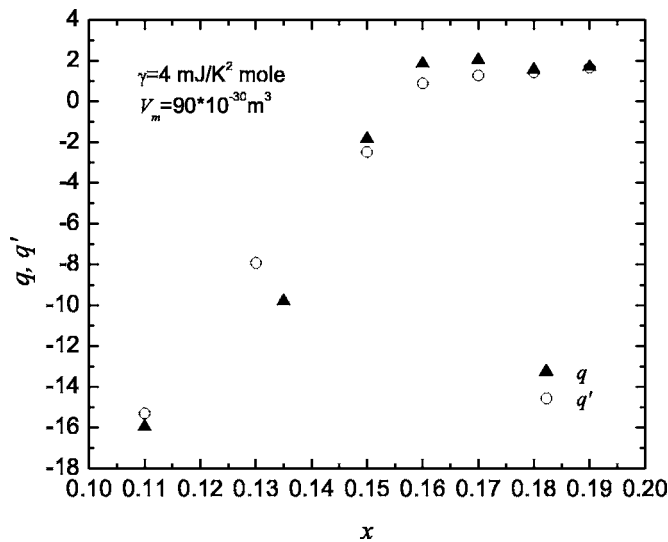


FIG. 5. Doping dependence of  $q(2\text{ K})$  and  $q'(2\text{ K})$  of PCCO films [ $q$  and  $q'$  are defined by Eqs. (2) and (3) in the text].

crystal and a superconducting  $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$  crystal. Neutron scattering studies have shown that an as-grown  $x=0.15$  crystal is equivalent to an annealed  $\text{Pr}_{1.88}\text{Ce}_{0.12}\text{CuO}_4$  crystal.<sup>23</sup> This strongly suggests that  $\gamma$  will not change much with Ce doping at least in the critical range around optimal doping. Therefore, no significant change in the doping dependence of  $q$  due to this correction is expected.

We believe that the saturation of  $S/T$  in the overdoped region is a result of the Fermi surface rearrangement due to the vanishing of antiferromagnetism above a critical doping. To our knowledge, there is no theoretical prediction for the doping dependence of the thermopower in an antiferromagnetic quantum critical system. Although the temperature

dependence of thermopower near zero temperature is given by Paul *et al.*<sup>24</sup> for such a system near critical doping, we are not yet able to access the very low temperature region ( $T < 2\text{ K}$ ) to test these predictions in PCCO. Nevertheless, an amazing agreement between thermopower and Hall effect measurements is shown in our simple free electron model. This model is certainly oversimplified since there is strong evidence for two types of carriers near optimal doping.<sup>25–27</sup> But many of these transport data<sup>25–27</sup> imply that one type of carrier dominates at low temperature. Thus a simple model may be reasonable. However, to better understand this striking result a more detailed theoretical analysis will be needed.

Interestingly, the number  $q$  in overdoped PCCO is close to 1. It was shown that when  $q$  is close to unity, a Fermi liquid behavior is found in many strongly correlated materials.<sup>20</sup> This suggests that overdoped PCCO is more like a Fermi liquid metal than underdoped PCCO. When  $x$  is above the critical doping  $x=0.16$ ,  $q$  and  $q'$  are close to  $1/(1-x)$ , which suggests that the holelike Fermi surface is recovered in accordance with local density approximation band calculations and the Luttinger theorem.

In summary, we performed high-resolution measurements to investigate the low-temperature normal state thermopower ( $S$ ) of electron-doped cuprates  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ . We find a strong correlation between  $S/T$  and the Hall coefficient ( $R_H$ ) at 2 K as a function of doping. Using a simple free electron model, which relates thermopower to the electronic specific heat, we conclude that our observations support the view that a quantum phase transition occurs near  $x=0.16$  in the PCCO system.

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