Influence of doping level on the Hall coefficient and on the thermoelectric power in $Nd_{2-x}Ce_xCuO_{4+\delta}$

C. H. Wang, G. Y. Wang, T. Wu, Z. Feng, X. G. Luo, and X. H. Chen*
Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China
(Received 12 June 2005; revised manuscript received 26 August 2005; published 28 October 2005)

The Hall coefficient R_H and thermoelectric power (TEP) are studied systematically in the single crystals of $Nd_{2-x}Ce_xCuO_4$ from the underdoped to overdoped regimes. Both R_H and TEP decrease and change signs with the increasing doping level x. A striking feature of our study is that the temperature dependence of the Hall angle follows the T^4 behavior in the underdoped regime, while the quadratic law is followed in the overdoped regime. This feature is closely related to the evolution of the Fermi surface, which is observed by ARPES.

DOI: 10.1103/PhysRevB.72.132506 PACS number(s): 74.25.Fy

$Nd_{2-x}Ce_xCuO_{4+\delta}$ (NCCO) belongs to an interesting class of materials called electron-doped cuprates. With the substitution of Nd by Ce, the electrons are believed to be injected to the CuO_2 plane since the Hall coefficient (R_H) and the thermoelectric power (TEP) remains negative.[1] However, R_H and TEP increase and eventually change sign to positive with further doping of Ce.[2–7] A similar feature has been observed by changing the oxygen content.[4,8] In another n-type cuprate $Pr_{2-x}Ce_xCuO_{4+\delta}$ (PCCO), the change of R_H sign with temperature[9–11] and doping[12] was also observed. These behaviors strongly indicate that at moderate doping, NCCO and PCCO have two bands with different types of charge carriers: a hole carrier and an electron carrier. The Fermi surface (FS) obtained by angle-resolved photoemission spectroscopy (ARPES) indirectly supports this conclusion. Armitage *et al.*[13] suggested that the existence of an FS patch in the slightly doped samples is marked by an electron pocket at $(\pi,0)$ and the FS patch gradually changes to a large holelike FS with the appearance of a section near the zone diagonal $(\pi/2,\pi/2)$ of the Brillouin zone with increasing doping. The presence of the two separate FS pockets may result from the band-folding effect induced by the antiferromagnetic correlations.[14] Theoretical calculations indicate that the two FS pockets can be effectively described as a two-band system.[14,15] Recently, Luo and Xiang proposed a weakly coupled two-band model with $d_{x^2-y^2}$ pairing symmetry. This model accounts for the anomalous temperature dependence of superfluid density (ρ_s) in an n-type cuprate superconductor very well.[16]

The Hall angle has another interesting feature. It is well known that the Hall angle follows a T^2 law in a hole-doped system. Anderson[17] emphasized that the transport is governed by two different scattering times for the high T_c cuprates, $\tau_{tr}(T^{-1})$ for in-plane resistivity and $\tau_H(T^{-2})$ for the Hall angle. A different point of view is that the cotangent of the Hall angle ($\cot\theta_H$) is proportional to the square of the scattering rate, which can be independently measured by the zero-field resistivity.[18] Recently, a striking study by Ando *et al.*[19] was that the temperature dependence of resistivity follows approximately T^2 in lightly doped $YBa_2Cu_3O_{7-y}$ (YBCO) and $La_{2-x}Sr_xCuO_4$ (LSCO). Their study states that in lightly hole-doped cuprates, the transport behavior is Fermi-liquid-like, and results from the quasiparticles on the Fermi arcs. As we know, the resistivity is also not T-linear in electron-doped cuprates. In comparison with hole-doped cuprates, it is quite interesting to study the Hall angle and its relation to the resistivity in the NCCO system. Although the nearly T^4 behavior of Hall angle has been mentioned by Fournier *et al.*[8] in optimum doped $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ thin film, Hall angle behavior still was not clear in n-type cuprates. Therefore, it is quite meaningful to study variation of Hall angle behavior with temperature and doping in this kind of system.

In this report the Hall effect and the thermoelectric power were systematically studied. The Hall contact configuration is the standard ac six-probe geometry with a magnetic field up to 10 T. The Hall signal was extracted from the antisymmetric part of the transverse signal measured with the opposite field direction to remove the longitudinal contribution due to the misalignment of the Hall voltage contact point. The TEP measurements were performed using small and reversible temperature differences of 0.2 to 0.5 K. Two ends of the single crystals were attached to two separated copper heat sinks to generate the temperature gradient along the crystal *ab* plane. Two Rh-Fe thermometers were glued to the heat sink (next to the single crystals). Copper leads were adhered to the single crystals and all the data were corrected for the contribution of the Cu leads.

As shown in Fig. 1(a), the resistivity shows an upturn at the low temperature for the underdoped samples. Especially for $x=0.025$, such low temperature insulating behavior becomes obvious around 240 K, similar to the report by Onose *et al.*[1] However, the metallic behavior can be observed in the high temperature range. For the overdoped samples, metallic behavior exists in the whole temperature range and superconductivity was observed for the crystal with $x=0.17$. The temperature-dependent Hall coefficient and Hall mobility ($\mu_H=R_H/\rho_{ab}$) are plotted in Figs. 1(b) and 1(c), respectively.

The Hall coefficient and Hall mobility show a continuous variation with temperature. R_H and μ_H are negative in the whole temperature range for nonsuperconducting, underdoped samples with $x=0.025$ and 0.06, while positive for nonsuperconducting, overdoped samples with $x=0.20$. For $x\sim0.17$, R_H and μ_H change their signs with decreasing temperature. Such doping-dependent behavior is similar to that observed in $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ films[4,8] and $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ single crystals[9,11] by varying oxygen content. Furthermore, in optimum doped ($x\sim0.15$) and slightly

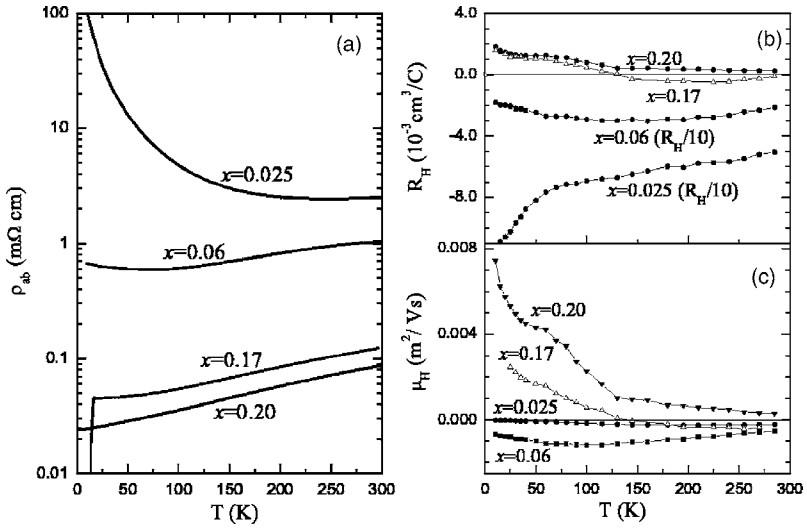

FIG. 1. Temperature dependence of (a) in-plane resistivity (ρ_{ab}), (b) Hall coefficient R_H, and (c) Hall mobility ($\mu_H = R_H/\rho_{ab}$).

overdoped superconducting ($x \sim 0.17$) compositions, the change of the Hall coefficient sign with temperature has been reported.[4,6,8,10] The conventional single-carrier transport cannot explain such strange behavior and two types of the carriers have to be introduced to explain these behaviors. R_H shows a downturn for $x=0.025$, but for $x=0.06$ the absolute value of R_H slightly decreases. This case is similar to the behavior in a lightly doped LSCO system, in which R_H increases in low temperatures for low doping level, while slightly decreases when doping level up to 0.07.[19]

Figure 2(a) shows the temperature dependence of thermoelectric power (TEP) for underdoped and overdoped samples. TEP monotonically decreases with increasing doping level. For the overdoped sample, the TEP is positive. The TEP has a similar behavior to the doping-dependent tendency of R_H. This further indicates that two types of the carriers exist in the system. For the $x=0.025$ sample, the TEP monotonically increases with increasing temperature and no saturation is observed. When doping up to 0.06, a broad peak of TEP is observed. Similar behavior also occurs in the crystals with $x=0.12$ and 0.14, as shown in Fig. 2(b). The temperature corresponding to the peak decreases with increasing the doping level. Similar behavior has been reported in $Sm_{2-x}Ce_xCuO_{4+\delta}$ (SCCO) polycrystalline samples,[7] NCCO single crystals,[20] and $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ thin films with changing the oxygen content.[8] Figure 2(c) shows temperature-dependent TEP for the crystals with $x=0.17$ and 0.20. The magnitude of TEP is very small. Typically, only the TEP of metal can have such a small magnitude.

In the polycrystaline $Sm_{2-x}Ce_xCuO_{4+\delta}$ (SCCO),[7] the TEP sign changes with decreasing temperature for the overdoped SCCO samples, while TEP remains positive in our overdoped crystal and no sign change is observed. This case is similar to the optimum sample that no sign change is observed in NCCO thin films,[8] while sign change is observed in PCCO polycystalline samples.[21] The sign change for polycystalline samples may result from the inhomogeneity of the oxygen content in grains.

In Fig. 3, the cotangent of the Hall angle as a function of temperature is plotted for the crystals with $x=0.025$, 0.06, and 0.20. In Figs. 3(a) and 3(b), a T^4 power law behavior is clearly observed above 240 K and 90 K for the samples with $x=0.025$ and 0.06, respectively. The downturn around 240 K and 90 K coincides with the low-temperature upturn in the

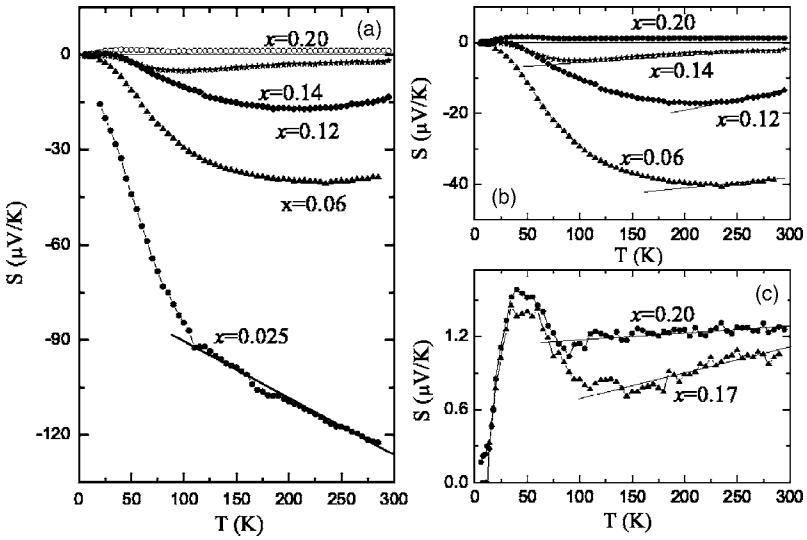

FIG. 2. (a) Temperature dependence of thermoelectric power (TEP) for the $Nd_{2-x}Ce_xCuO_4$ crystals with different doping levels. (b) TEP vs T for $x=0.06$, 0.12, 0.14, 0.20. (c) TEP vs T for the overdoped samples.

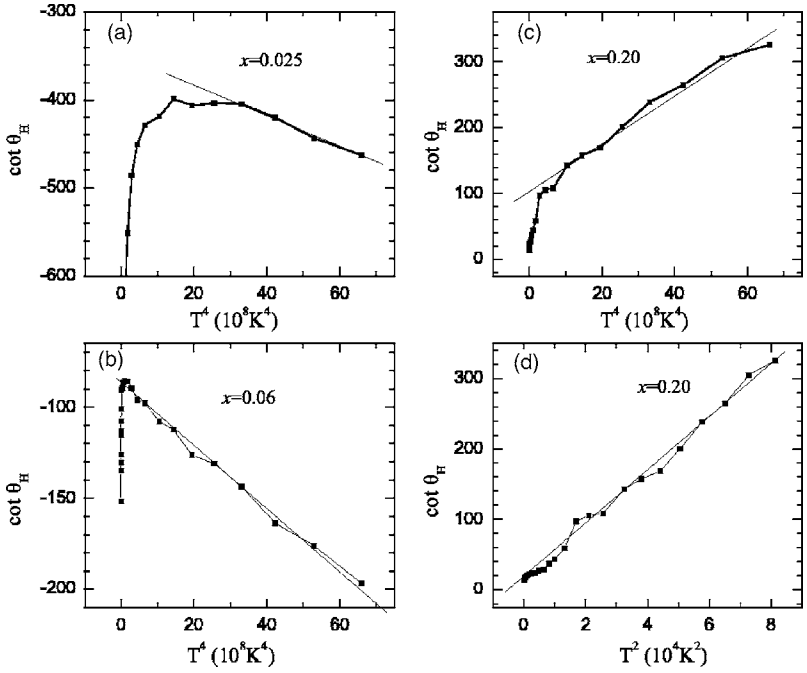

FIG. 3. Temperature dependence of cot $\theta_H(\sim\rho_{ab}/R_H)$ at 10 T in T^4 scale for the crystals $Nd_{2-x}Ce_xCuO_4$. (a) $x=0.025$, (b) $x=0.06$, (c) $x=0.20$, and (d) $x=0.20$ in T^2 scale.

resistivity ρ_{ab} shown in Fig. 1(a). The T^4 law behavior in the crystals with $x=0.025$ and $x=0.06$ cannot be explained by Anderson's two-dimensional Luttinger liquid theory, as it predicts that the cotangent of Hall angle is T^2 dependent based on spinon-spinon scattering.[17] The resistivity in the NCCO system is close to the T^2 dependence, except for the upturn of the low temperature ρ at the pseudogap opening temperature[1,22] for the sample $x=0.06$. Varma and Abrahams's theory seems to be reasonable for T^4 law since they predicted that the cot θ_H should follow the square of the resistivity dependence.[18] Wood *et al.* suggested this possibility because they found that cot θ_H followed $T^{3.4}$ behavior with $\rho_{ab}\propto T^{1.7}$ in their ion-irradiated NCCO thin films.[23] Following the argument of Ando *et al.* in an LSCO system, we come to the idea that the T^4 law might result from an electron pocket [a small FS around $(\pi,0)$] as the doped electrons concentrate to this electron pocket in lightly doped NCCO. As we will see below, the electron pocket in fact governs the transport behavior in lightly doped NCCO, which is the same situation as that of the Fermi arc dominating the transport behavior in lightly doped LSCO.[19,24] Therefore, the electron pocket should play an important role in explaining this strange T^4 law. The difference between the T^4 law in NCCO and the T^2 law in hole-doped cuprates suggests that the property of the electron pocket is quite different from the Fermi arc and confirms the particle-hole asymmetry in some sense. However, the data deviate from the T^4 law for the $x=0.20$ sample as shown in Fig. 3(c); the T-square dependence of the Hall angle is observed in the whole temperature range shown in Fig. 3(d). This observation agrees with the above theory, that is, the electron pocket has already deformed and a large holelike FS begins to emerge for the overdoped sample. Therefore, the large holelike pocket at $(\pi/2,\pi/2)$ dominates the charge transport so that the T^2 law observed in hole-doped cuprates appears in the heavily doped n-type cuprates. If the quartic law is a universal law for electron-type bands, one can consider the possibility of to extracting scattering rates for the two bands from the data of the Hall angle. Another interesting idea is that one may link this change of Hall angle with the possible quantum critical point on the analogy of their hole-doped partners.[19,25,26] However, one difficulty is that the sign of Hall coefficient changes and it is very hard to get the temperature-dependent Hall angle around $x=0.15$–0.18.

It is believed that for the electron-doped cuprates two different types of bands take effect in the transport behavior of those samples as emphasized by many researchers.[3,4,6] Here, let us look at it from a different point of view. Figure 4 shows the variation of eR_Hx/V with T, where e is electron

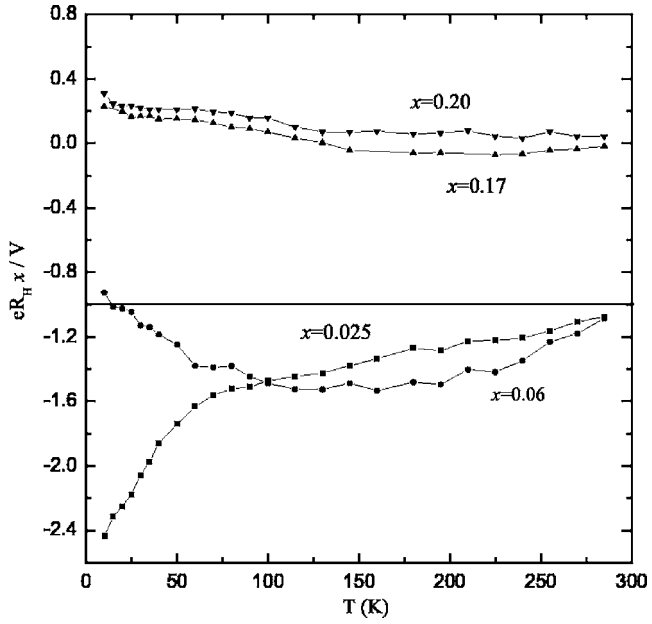

FIG. 4. eR_Hx/V as a function of temperature for the $Nd_{2-x}Ce_xCuO_4$ cystals with $x=0.025$, 0.06, 0.17, and 0.20.

charge and V is unit volume per Cu. The value should be -1 if the nominal electron density x approximately accounts for the carrier density. From the plot, it is easy to find that eR_Hx/V is very close to -1 around 300 K for the crystals with $x=0.025$ and 0.06. The absolute value of eR_Hx/V decreases significantly with increasing x to the overdoping regime. The sign of eR_Hx/V changes at around 130 K for the sample with $x=0.17$, while it remains positive in the whole temperature range for the sample with $x=0.20$. Since the largest volume of FS is proportional to $1+x$ for the electron-doped samples, the effective carrier density should be bounded by $1+x$ and the theoretical value of eR_Hx/V should not be smaller than $x/(1+x)$ in the single-band model, so that the theoretical lower limit is around 0.15 for $x=0.17$ and 0.17 for $x=0.20$. However, the actual value of eR_Hx/V is approximately -0.01 for the sample with $x=0.17$ at room temperature and 0.04 for the sample with $x=0.20$. Therefore, one can conclude that the single-band model is not valid in these cases. In the frame of two-band models,[3,4,6] eR_Hx/V is proportion to $(n_p\mu_p^2-n_e\mu_e^2)/(n_p\mu_p+n_e\mu_e)^2$ (n_p, n_e are the carrier density of different bands and μ_p, μ_e are the mobility of each band, respectively). According to the above formula, our results can be well understood if we suppose that the value of $n_p\mu_p^2$ is very close to $n_e\mu_e^2$ at room temperature for our sample $x=0.17$, and increases with increasing the doping level.

It is not clear why the two bands exist in the NCCO system. However, the results of ARPES by Armitage *et al.*[13] help us to understand this behavior. The FS patch at $(\pi,0)$ was observed in lightly doped NCCO and makes the R_H negative. It gradually deforms and the positive curvature part of the FS around (π,π) begins to increase with increasing Ce, and eventually a large holelike FS eventually appears. This part may give a positive contribution to R_H. Therefore, the two-band model can be phenomenally understood as a competition between electronlike FS and holelike FS. Moreover, in slightly doped NCCO, the volume of the electron pocket (FS patch) is approximately equal to the doping density x. Our data suggest that the FS patch dominates the transport in the lightly doped samples around 300 K. It is worthnoting that a similar situation exists in the $La_{2-x}Sr_xCuO_4$ system. In this case, the value of eR_Hx/V is also close to 1 for lightly doping samples,[19] and the eR_Hx/V sign changes in heavily overdoped samples.[27] In the ordinary single-band model, the lower limit of eR_Hx/V in a hole-doped sample is $x/(1-|x|)$. It should be 0.20, 0.27, and 0.33 for the samples with $x=0.17$, 0.21, and 0.25, respectively. Based on the results by Ando *et al.*, it is found that the experimental lower limit is approximately 0.30, 0.15, and 0.06 for those cases.[28] According to the above explanation, the large difference between the experimental data and the theoretical prediction for the samples with $x=0.21$ and 0.25 suggests the invalidity of the single-band model. One must consider the competition between electronlike and holelike FS as the FS eventually becomes electronlike for overdoped hole-type cuprates in heavily doped LSCO.[19,29]

In conclusion, the Hall angle for the underdoped crystals with $x=0.025$ and $x=0.06$ follows the T^4 law, while it obeys the quadratic law for the overdoped sample with $x=0.2$, although the resistivity remains nearly T^2 law in all the samples. This feature is quite different from the hole-doped systems. It is closely related to the different evolution of Fermi surface with doping level. By the study of eR_Hx/V, we also try to understand the behavior of change of the R_H sign in a unified viewpoint for both hole-doped LSCO and electron-doped cuprates. Our finding confirms that one must use a two-band model to explain the sign change of R_H and thermoelectric power with doping. The two-band model is associated with the mysterious change of Fermi surface observed by ARPES.

This work is supported by the Nature Science Foundation of China, and by the Knowledge Innovation Project of the Chinese Academy of Sciences and the Ministry of Science and Technology of China.

*Corresponding author. Electronic address: chenxh@ustc.edu.cn

[1] Y. Onose *et al.*, Phys. Rev. Lett. **87**, 217001 (2001).
[2] S. J. Hagen *et al.*, Phys. Rev. B **43**, 13606 (1991).
[3] P. Seng, Phys. Rev. B **52**, 3071 (1995).
[4] Wu Jiang *et al.*, Phys. Rev. Lett. **73**, 1291 (1994).
[5] Wu Jiang *et al.*, Phys. Rev. B **48**, 657 (1993).
[6] Z. Z. Wang *et al.*, Phys. Rev. B **43**, 3020 (1991).
[7] H. S. Yang *et al.*, Physica E (Amsterdam) **403**, 203 (2004).
[8] P. Fournier *et al.*, Phys. Rev. B **56**, 14149 (1997).
[9] Matthias Brinkmann, Heinrich Bach, and Kurt Westerholt, Phys. Rev. B **54**, 6680 (1996).
[10] P. Fournier *et al.*, Phys. Rev. Lett. **81**, 4720 (1998).
[11] M. Brinkmann *et al.*, Physica C **269**, 76 (1996).
[12] Y. Dagan *et al.*, Phys. Rev. Lett. **92**, 167001 (2004).
[13] N. P. Armitage *et al.*, Phys. Rev. Lett. **88**, 257001 (2002).
[14] Q. S. Yuan *et al.*, Phys. Rev. B **69**, 214523 (2004).
[15] C. Kusko, R. S. Markiewicz, M. Lindroos, and A. Bansil, Phys. Rev. B **66**, 140512(R) (2002).
[16] H. G. Luo and T. Xiang, Phys. Rev. Lett. **94**, 027001 (2005).
[17] P. W. Anderson, Phys. Rev. Lett. **67**, 2092 (1991).
[18] C. M. Varma and Elihu Abrahams, Phys. Rev. Lett. **86**, 4652 (2001).
[19] Y. Ando *et al.*, Phys. Rev. Lett. **92**, 197001 (2004).
[20] X. Q. Xu *et al.*, Phys. Rev. B **45**, 7356 (1992).
[21] Sung Ik Lee *et al.*, Phys. Rev. B **41**, 2623 (1990).
[22] C. H. Wang *et al.*, Supercond. Sci. Technol. **18**, 763 (2005).
[23] S. I. Woods *et al.*, Phys. Rev. B **66**, 014538 (2002).
[24] T. Yoshida *et al.*, Phys. Rev. Lett. **91**, 027001 (2003).
[25] J. Orenstein and A. J. Millis, Science **288**, 468 (2000).
[26] Y. Ando and T. Murayama, Phys. Rev. B **60**, R6991 (1999).
[27] H. Y. Hwang *et al.*, Phys. Rev. Lett. **72**, 2636 (1994).
[28] As reported by Ando *et al.*, the value of eR_Hx/V will decrease and eventually saturate when the temperature increases further above room temperature. Fortunately, it does not affect our conclusion. It is interesting that one can conclude that the saturated value is equal to $x/(1-|x|)$ for slightly hole-doped cuprates, which is valid for the case of $x=0.02$ and $x=0.14$ in LSCO.
[29] A. Ino *et al.*, Phys. Rev. B **65**, 094504 (2002).