Influence of doping level on the Hall coefficient and on the thermoelectric power in $Nd_{2−x}Ce_xCuO_4$

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Hall coefficient $R_H$ and thermoelectric power TEP are studied systematically in the single crystals $Nd_{2−x}Ce_xCuO_4$ (NCCO) with different $x$ from underdoped to overdoped regime. $R_H$ and TEP decrease and change their sign from negative to positive with increasing doping level $x$. A striking feature is that the temperature dependence of the Hall angle follows a $T^4$ behavior in the underdoped regime, while a $T^2$ law in the overdoped regime. This behavior is closely related to the evolution of Fermi surface with doping level observed by the angle-resolved photoemission spectroscopy (ARPES).

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$Nd_{2−x}Ce_xCuO_{4+δ}$ (NCCO) belongs to a quite interesting class of materials which is called as electron doped cuprates. With the substitution of Nd by Ce, the electrons were injected to the $CuO_2$ plane since the Hall coefficient ($R_H$) and the thermoelectric power (TEP) remains negative. However, $R_H$ and thermoelectric power gradually increase and eventually change sign to positive with further doping $Ce^{2+}$. Similar feature has been observed with changing the oxygen content. In another n-type cuprate $Pr_{2−x}Ce_xCuO_4$ (PCCO), the change of $R_H$ sign with temperature and doping were also observed. Those strange behaviors strongly indicate that at moderate doping, NCCO and PCCO have two bands with different types of charge carriers, one is hole carrier and the other is electron carrier. The Fermi surface (FS) obtained by ARPES indirectly supports this conclusion. Armitage et al. suggested that the existence of 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 hole-like FS with the appearance of 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. The theoretical calculations indicate that the two FS pockets can be effectively described as a two-band system. Recently, Luo and Xiang proposed a weakly coupled two-band model with $d_{x^2−y^2}$ pairing symmetry to account for the anomalous temperature dependence of superfluid density ($\rho_s$) in n-type cuprate superconductor very well.

Hall angle is another interesting feature. It is well known that Hall angle follows a $T^2$ law in hole doped system. Anderson emphasized that the transport is governed by two different scattering time for the high $T_c$ cuprates, $\tau_{el}(T^{-1})$ for in-plane resistivity and $\tau_H(T^{-2})$ for Hall angle. Another point of view is that the cotangent of Hall angle ($\cot(\theta_H)$) is proportional to the square of the scattering rate which can be independently measured by the zero-field resistivity. Recently, a striking finding by Ando et al. is that the temperature dependence of resistivity nearly follows $T^2$ in lightly doped YBCO and LSCO. Their finding gives another picture 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. in optimum doped $Nd_{1.85}Ce_{0.15}CuO_{4−δ}$ thin film, Hall angle behavior was still not clear in n-type cuprates yet. 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 thermoelectric power were systematically studied. The Hall contact configuration is standard ac six-probe geometry with magnetic field up to 10 Tesla. 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 difference of 0.2-0.5 K. Two ends of the single crystals were attached to two separated copper heat sink to generate the temperature gradient along the crystal ab-plane. Two Rh-Fe thermometers were glued to the heat sink (just 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 figure 1(a), the resistivity shows an upturn at the low temperatures 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. 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 fig.1(b) and (c), respectively.

Hall coefficient and Hall mobility show a continuous variation with temperature. $R_H$ and $\mu_H$ are negative in the whole temperature range for nonsuperconducting, underdoped samples with x=0.025 and 0.06, while positive for nonsuperconducting, overdoped sample with x=0.20. For x~0.17, $R_H$ and $\mu_H$ change their sign at a certain temperature with decreasing temperature. Such doping dependent behavior is similar to that observed in $Nd_{1.85}Ce_{0.15}CuO_4$ films and $Pr_{1.85}Ce_{0.15}CuO_4$ single crystals by varying oxygen content. Furthermore, in optimum doped (x~0.15) and slightly overdoped superconducting (x~0.17) compositions, the change of Hall coefficient sign with temperature has been reported. The conventional single-carrier transport can not explain such behavior adequately, and two types of the carriers have to be used 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 lightly doped LSCO system, in which $R_H$ increases in low temperatures for low doping level, while slightly decreases when doping level up to 0.025.

Figure 2(a) shows the temperature dependent thermoelectric power (TEP) for underdoped and overdoped samples. TEP monotonously 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 $R_H$. It further indicates that two types of the carriers exist in the system. For x=0.025 sample, the TEP monotonically increases with increasing temperature and no saturation is observed. When the 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. The similar behavior has been reported in $Sm_{2-x}Ce_xCuO_4$ (SCCO) polycrystalline samples and NCCO single crystals and $Nd_{1.85}Ce_{0.15}CuO_4$ thin films with changing the oxygen content. Fig.2(c) shows temperature dependent TEP for the crystals with x=0.17 and 0.20. The small magnitude of TEP is typical metal.

In the polycrystalline $Sm_{2-x}Ce_xCuO_4$ (SCCO), the TEP sign changes with decreasing temperature for the overdoped SCCO samples, while TEP remains positive in our overdoped crystal, and no sign change was observed. This case is similar to the optimum sample that no sign change is observed in NCCO thin films, while sign change is observed in PCCO polycrystalline sample. The sign change for polycrystalline samples may result from the inhomogeneity of the oxygen content in the grains.

In fig.3, the cotangent of Hall angle as a function of temperature is plotted for the crystals with x=0.025, 0.06 and 0.20. In fig.3(a) and (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 resistivity $\rho_{ab}$ shown in fig.1(a). The $T^4$ law behavior in the crystals with x=0.025 and x=0.06 can not be explained by Anderson’s two dimensional Luttinger liquid theory as it predicts. the $T^2$ dependent cotangent of Hall angle based on spinon-spinon scattering. The resistivity in NCCO system has closely a $T^2$ dependence except for the upturn of the low temperature $\rho$ until the pseudogap opening temperature for the sample x=0.06. Varma and Abra-
hams’s theory seems to be reasonable for $T^4$ law since they predicted that the $\cot \theta_H$ should follow the square of the resistivity dependence. Wood et al. have suggested this kind of possibility because they found that $\cot \theta_H$ followed $T^{3.4}$ behavior with $\rho_{ab} \propto T^{1.7}$ in their ion-irradiated NCCO thin films. Following the argument of Ando et al. in LSCO system, we can come to another picture that the $T^4$ law might result from 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 governs the transport behavior in lightly doped NCCO, which is the same way as that the Fermi arc dominates the transport behavior in lightly doped LSCO. Therefore, the electron pocket must play an important role to explain this strange $T^4$ law. The difference between $T^4$ law in NCCO and $T^2$ law in hole-doped cuprates suggests that the property of the electron pocket is quite different from Fermi arc, and confirms the particle-hole asymmetry in some sense. However, the data deviate from the $T^4$ law for $x=0.20$ sample as shown in Fig.3(c), a T-square dependent the Hall angle is observed in whole temperature range shown in fig.3(d). This observation agrees to the above picture, that is: the electron pocket has already deformed and a large hole-like FS begins to emerge for the overdoped sample. Therefore, the large hole-like pocket at $(\pi/2, \pi/2)$ dominates the charge transport, so that a $T^2$ 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 band, one can consider the possibility to extract scattering rates for the two bands from the data of 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. However, one difficulty is that the sign of Hall coefficient changes, and it is very hard to get the temperature dependent Hall angle around $x = 0.15 \sim 0.18$.

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 groups. Here, let us look at it from a different point of view. Fig. 4 shows the variation of $eR_H x/V$ with $T$, where $e$ is electron 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 $eR_H x/V$ is very close to -1 around 300 K for the crystals with $x=0.025$ and 0.06. The absolute value of $eR_H x/V$ decreases significantly with increasing $x$ to the overdoping regime. The sign of $eR_H x/V$ changes around 130 K for the sample with $x=0.17$, while remains positive in the whole temperature range for the sample of $x=0.20$. 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 $eR_H x/V$ should not be smaller than $\frac{x}{1+x}$ in single-band model, so that the theoretical lower limit is around 0.15 for $x=0.17$ and 0.17 for $x=0.20$. But the actual value of $eR_H x/V$ 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-bands model, $eR_H x/V$ is proportional to $\frac{n_p \mu_p^2}{(\mu_p + \mu_c)}$. $n_p$, $n_c$ are the carrier density of different bands. $\mu_p$, $\mu_c$ 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 $n_c \mu_c^2$ at room temperature for our sample $x=0.17$, and increases with increasing the doping.

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

![FIG. 4: $eR_H x/V$ as a function of temperature for the $Nd_{2-x}Ce_xCuO_4$ crystals with $x=0.025$, 0.06, 0.17 and 0.20.](image-url)
It is not clear why the two bands exist in the NCCO system. However, ARPES results by Armitage et al.\textsuperscript{13} help us to understand this behavior. The FS patch at $(\pi/2, 0)$ was observed in lightly doped NCCO and makes the $R_H$ negative. It gradually deforms and the positive curvature part of the FS around $(\pi, \pi)$ begins to increase with increasing $C_e$ and eventually a large hole-like FS eventually appears. This part may give a positive contribution to $R_H$. Therefore, the two bands model can be phenomenally understood as a competition between electron-like FS and hole-like FS. Moreover, in slightly doped NCCO the volume of 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 worthy to note that the similar situation exists in $La_{2−x}Sr_xCuO_4$ system. In this case, the value of $eR_Hx/V$ is also close to 1 for lightly doping samples, and $eR_Hx/V$ sign changes in heavily overdoped samples.\textsuperscript{28} In ordinary single band model, the lower limit of $eR_Hx/V$ in hole-doped sample is approximately $0.30, 0.15$ and $0.06$ for $x=0.17, 0.21$ 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.\textsuperscript{28} According to above explanation, the large difference between experimental data and theoretical prediction for the samples with $x=0.21$ and 0.25 suggests the invalidity of “single-band model”. One must consider the competition between electron-like and hole-like FS as the FS eventually becomes electron-like for overdoped hole-type cuprates in heavily doped LSCO.\textsuperscript{19,29}

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

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28. As discovered by Ando et al, the value of $eR_Hx/V$ will still
decrease and eventually saturate when the temperature increases further above the room temperature. Fortunately, it will 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.

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