Hall coefficient for oxygen-reduced $Nd_{2-x}Ce_xCuO_{4-\delta}$

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The Hall coefficient $R_H(T)$ has been measured for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ c-axis-oriented thin films at various oxygen deficiency levels produced by successive reduction treatments. The results definitely reflect the change in $R_H(T)$ brought about by a decrease in the oxygen content with the Ce concentration precisely fixed. It is found that with decreasing oxygen content R_H increases monotonically and changes sign from negative to positive. Regardless of the sign, R_H shows significant temperature dependence at low temperatures. Superconductivity is observed in the oxygen compositional range in which R_H changes sign. The sign reversal is interpreted in terms of the band-structure effect rather than the two-band model.

I. INTRODUCTION

The significantly temperature- and doping-dependent Hall coefficient $R_H(T)$ is one of the most interesting normal-state properties of high-T_c superconductors.[1] Among them, R_H of $Nd_{2-x}Ce_xCuO_{4-\delta}$ is particularly interesting in that it is negative[2] in contrast to the positive sign for the other high-T_c cuprates. On the one hand, this fact provides a support for electron doping[3] in the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system, which places crucial constraints on the theory of high-T_c superconductivity. On the other hand, no general consensus has yet been reached on a negative sign for R_H in $Nd_{2-x}Ce_xCuO_{4-\delta}$. Experimentally, each sign has been observed in different specimens, resulting in a controversy.

For example, earlier experiments on ceramic specimens,[2] single crystals,[4] and c-axis-oriented thin films[5-7] with $x \sim 0.15$ indicated a negative sign for R_H at temperatures below 300 K. On the other hand, on the basis of elaborate experiments on single crystals, Wang *et al.*[8] reported that R_H for $Nd_{2-x}Ce_xCuO_{4-\delta}$ crystals ($x=0.15$) is positive for most of the specimens they measured. Even in a crystal that showed a negative R_H, a positive R_H was definitely observed at temperatures below 80 K. While their measurements on single crystals provide reliable data, subsequent Hall measurements on crystals by Hagen *et al.*[9] have confirmed the opposite, that is, a negative R_H for nearly identical composition. This makes the interpretation of the transport properties of $Nd_{2-x}Ce_xCuO_{4-\delta}$ quite complicated. Indeed, although their R_H behavior differed, the crystals used for the measurements by the two groups showed quite similar $\rho(T)$ and T_c characteristics.

Theoretical estimates for R_H made by Hamada *et al.*,[10] based on local-density-functional band-calculation results,[11] indicate a positive sign over quite a wide compositional range around the optimum x, and this clearly disagrees with the experimental results by Hagen *et al.*[9] and the earlier experiments. Therefore it is essential to clarify the origin of the R_H sign change and the significant discrepancies among experimental results.

It is generally accepted[9] that there are two factors which cause a scatter of the R_H data in the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system: the Ce concentration x and the oxygen deficiency δ. The Ce concentration is relatively easily determined, whereas both the precise control and the determination of the oxygen content are difficult, since the compositions for superconductivity are in a finite oxygen content region which is slightly less than the stoichiometry.[12] The oxygen deficiency δ for superconductivity in the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system is estimated to be 0.01–0.02, that is, approximately 0.5% of the total oxygen. Thus the variation in oxygen deficiency associated with individual specimens is much less than 0.5%, and such a slight variation is usually quite difficult to characterize accurately in small crystals or thin films. (By contrast, the oxygen variation of the $YBa_2Cu_3O_{7-\delta}$ system is more than one order of magnitude larger.) Therefore it is difficult to characterize x and δ adequately, and they change from sample to sample, resulting in a large scattering in the R_H data.

In order to clarify definitely the effect of oxygen deficiency on the behavior of R_H, we have adopted a successive reduction treatment (SRT) method, where a single specimen is employed and reduced successively to ensure that the oxygen content is reduced monotonically while x is fixed precisely during the experiments. This method has provided clear evidence that $R_H(T)$ is very sensitive to the variations in the oxygen content and changes sign from negative to positive as $Nd_{2-x}Ce_xCuO_{4-\delta}$ is reduced. The sign reversal occurs in the oxygen content range in which the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system exhibits superconductivity. This result also provides a reasonable explanation for the discrepancies among the experimental results for various $Nd_{2-x}Ce_xCuO_{4-\delta}$ specimens.

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II. SAMPLES AND SUCCESSIVE REDUCTION TREATMENT

Specimens used were c-axis-oriented $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ films epitaxially grown on $SrTiO_3$ (100) substrates by magnetron sputtering.[13] The typical film thickness was about 350 nm. After sufficient oxygenation at 1055 °C for 1 h, the films were patterned into Hall bars measuring 0.3×1.8 mm^2 with leads to electrode pads. Hall measurements were performed under a 0.77-T reversing field at temperatures up to 300 K. After R_H and ρ had been measured, each specimen was subjected to reduction in a vacuum ($<1\times10^{-6}$ Torr) at temperatures ranging from 450 to 550 °C typically for 0.5 h. This single treatment reduced the specimen slightly. (The decrease in δ, however, is not specified for the reason mentioned in the previous section.) Then R_H and ρ were measured again. This procedure was repeated until the film was reduced too far or the electrodes were unexpectedly damaged. This SRT method has provided definite information concerning the effect of variations in the oxygen content on the transport properties of the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system with an x of 0.15.

Although the SRT method was tried on more than ten specimens, few survived the planned number of cycles. In most cases, the electrodes were damaged during the heat treatments, although great care was taken to clean the specimen surface of any grease or silver paste during the SRT. Nonetheless, by combining the data obtained for several of the specimens, it is possible to extract definitely the essential features of the relationship between oxygen content and R_H behavior as described below.

III. RESULTS

Figure 1 shows the plots of R_H-T and ρ-T (inset) for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ films before reduction (as oxygenated), after reduction at 860 °C for 1.5 h in an Ar flow (a typical method[13] for obtaining optimum T_c and ρ), and after excessive reduction at 600 °C for 0.5 h in a vacuum. First, these data show that the films used in the experiment exhibit a T_c of $\sim$20 K when they are reduced properly, indicating that the cation ratio and the crystal quality were optimized sufficiently. Second, the data imply that reduction can lead to a positive R_H with metallic $\rho(T)$ behavior and no superconducting transition above 4 K.

Figures 2–4 show the systematic changes in the R_H-T and ρ-T (insets) curves for three samples that survived SRT for a relatively longer time than the others. In Figs. 2–4, it is commonly seen that, as the oxygen content is decreased, the semiconductive T dependence of ρ becomes less pronounced at low temperatures and the metallic region starts to extend to lower temperatures. Corresponding to this behavior, $|R_H|$ decreases and the T dependence is suppressed at low temperatures. It is also interesting to note that, for oxygenated samples or those after the first few treatments, both $|R_H|$ and ρ increase semiconductively with decreasing T. This semiconductive T dependence of ρ does not obey the variable-range

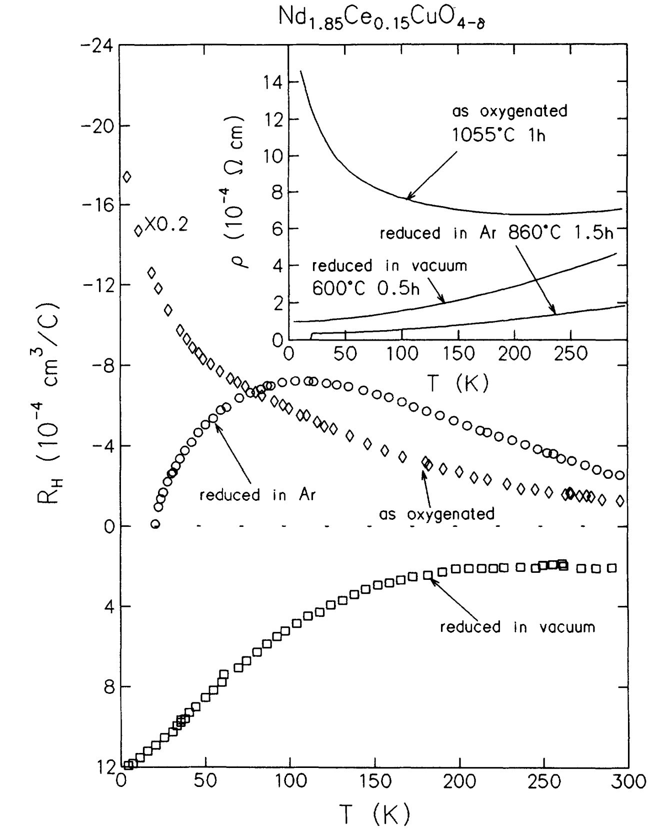

FIG. 1. R_H-T plots for a $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ film before reduction, after reduction in Ar at 860 °C for 1.5 h, and after excessive reduction in a vacuum at 600 °C for 0.5 h. The inset shows the corresponding ρ-T plots.

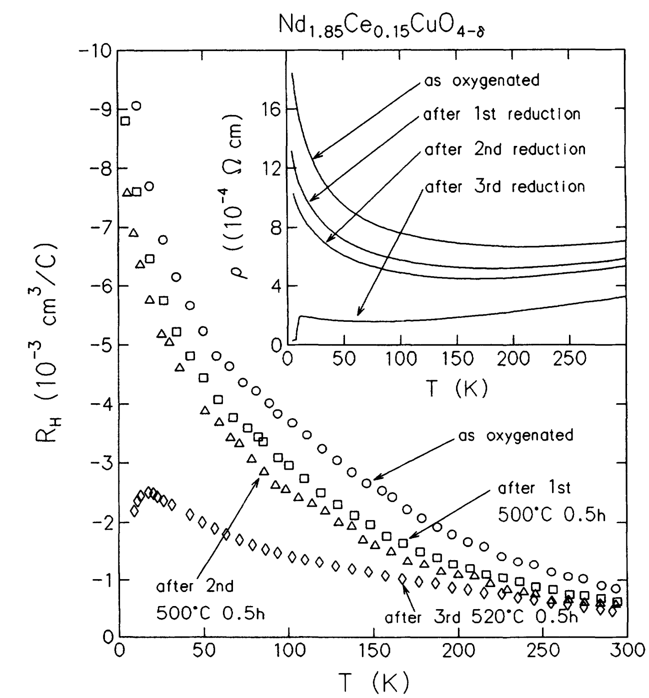

FIG. 2. Variations in the R_H-T and ρ-T (inset) curves of a $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ film caused by a SRT.

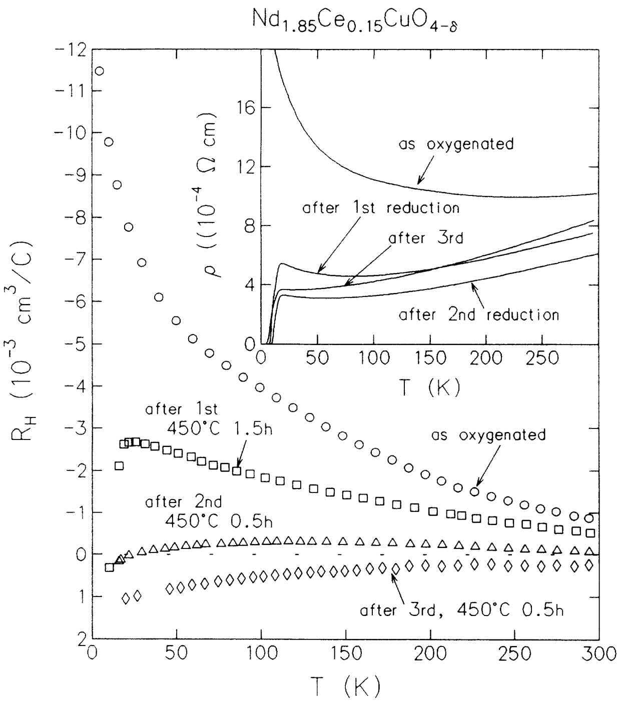

FIG. 3. Variations in the R_H-T and ρ-T (inset) curves of a $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ film caused by a SRT. This film was initially reduced excessively and then oxygenated again at 550 °C for 8 h before the SRT.

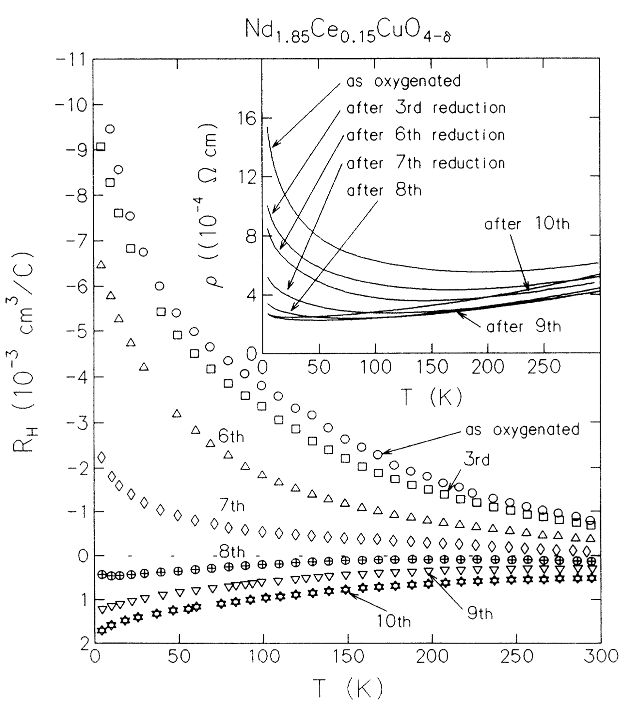

FIG. 4. Variations in the R_H-T and ρ-T (inset) curves of a $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ film caused by a SRT.

hopping law in either two or three dimensions (2D or 3D). This presents a sharp contrast to the lightly doped $La_{2-x}Sr_xCuO_4$ system[14] ($x=0.04$ for example), where ρ increases with decreasing T as $\rho(T)=\rho_0\exp(-\alpha T^{1/3})$ for the 2D variable-range hopping conduction, and $R_H(T)$ is almost T independent, whereas in the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system both ρ and R_h diverge at $T\to 0$ with the Hall mobility $\mu_H=R_H/\rho$ at a finite value when the system is lightly doped (before reduction). Therefore the localization behavior in the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system is distinctively different from that in the $La_{2-x}Sr_xCuO_4$ system in that in the latter the localization results from a decrease in the mobility, while in the former it is associated with a decrease in the carrier density.

For the first few SRT cycles, ρ decreases nearly proportionally to R_H and μ_H is nearly constant for $T>150$ K, as seen in Fig. 5. This behavior probably means that R_H reflects the change in carrier density in this semiconductive region. This is reminiscent of the behavior seen in the lightly doped region of the high-T_c superconductors characterized by the strong electron correlation.[1] However, this relationship between R_H and ρ collapses as the specimen is further reduced, as seen in Fig. 5, where μ_H decreases almost monotonically with the oxygen reduction.

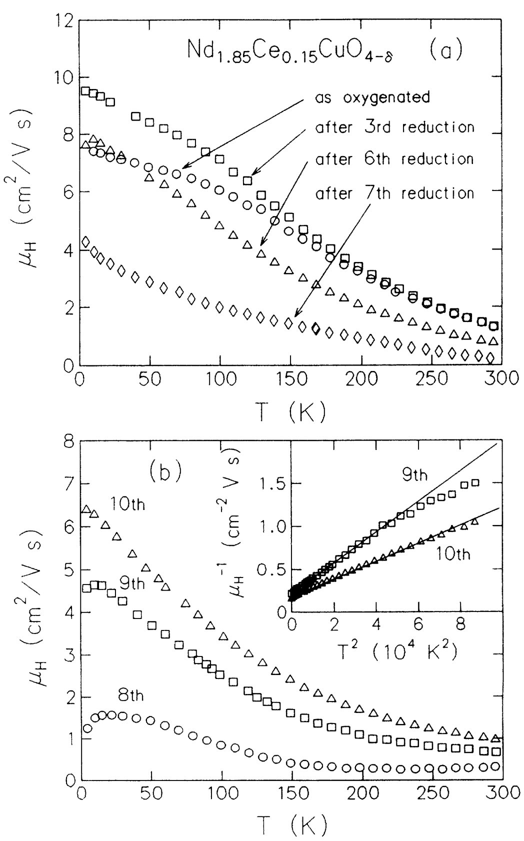

FIG. 5. Variations in the μ_H-T (inset) curves of a $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ film caused by a SRT when (a) $R_H<0$ and (b) $R_H>0$. The inset of (b) shows the plots of μ_H^{-1}-T^2. The solid lines are guides for the eye.

In Fig. 2, the superconducting transition is seen in $\rho(T)$ after the third reduction treatment. Corresponding to this change in ρ, R_H starts to increase rapidly in the positive direction at $T \rightarrow 0$, although the overall T dependence shows semiconductive behavior. This is commonly observed in the superconductive samples in our experiments.

Figure 3 shows that R_H changes sign from negative to positive as oxygen deficiency increases. This specimen, which became superconductive after the first reduction treatment,[15] remains superconductive after the following few SRT cycles, indicating that the R_H sign for superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ can be positive. When the specimen is further reduced, T_c decreases and the superconductivity disappears. At this stage of the SRT, the specimen still exhibits metallic T dependence even at low temperatures, with a slight increase in ρ.

The set of $R_H(T)$ plots in Fig. 4 clearly shows a systematic increase in R_H and the sign reversal in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ caused by a monotonical decrease in the oxygen content. The film employed in this SRT shows no trace of a superconducting transition as shown in the inset of Fig. 4, even when R_H becomes positive. Since a film cut from a neighboring portion of the same wafer exhibits superconductivity with a T_c of approximately 20 K after reduction in Ar at 860 °C, the absence of a superconducting transition in the set of ρ-T curves may indicate that the oxygen compositional region for the superconductivity is very narrow in the phase diagram of the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system. For the sample in Fig. 4, an upturn is seen in every ρ-T curve at low temperatures. This may be associated with some disorder present in the film, which may provide another reason for the absence of superconductivity. Aside from this, the ρ-T behavior is systematically changed by the SRT from semiconductive to metallic, and $R_H(T)$ also changes systematically from negative to positive with a tendency to increase at low temperatures.

After the tenth SRT, the specimen was oxygenated in flowing oxygen at 500 °C for 1 h. By this oxygenation, R_H decreases to a negative value and ρ increases. The plots of R_H-T and ρ-T (not shown) lie very close to those after the sixth SRT in Fig. 4, indicating that the change in the transport properties is reversible against the variation in the oxygen content. (In an extreme case, excessive reduction resulted in a transparent insulating $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ film, which turned black and semiconductive again by subsequent oxygenation.)

In the present experiments, the R_H values for the superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ range from -3×10^{-3} to greater than 1×10^{-3} cm^3/C. This range covers the experimental data of the earlier works on specimens with similar x values. However, the sample in Fig. 4 with R_H data in this range show no indication of superconductivity, implying that the absolute value of R_H is not necessarily the dominant factor in the occurrence of superconductivity.

Figure 5 shows the changes in μ_H caused by the SRT for the same specimen as that in Fig. 4. Chien, Wang, and Ong[16] observed that R_H for $YBa_2Cu_3O_{7-y}$ crystals behaves as $\cot\theta_H = \rho/R_H B = \mu_H^{-1} B^{-1} \propto T^2$ (or $\tau_H = eB \cot\theta_H / m^* \propto T^2$), with θ_H being the Hall angle and τ_H the transverse relaxation time, which is indicative of the spinon-spinon scattering in the 2D Luttinger liquid. This behavior of $\mu_H^{-1} \propto T^2$ has also been observed for other cuprate superconductors, e.g., for Tl cuprates.[18] In the present study, μ_H^{-1} curves show a significant deviation from the T^2 dependence as clearly seen in Fig. 5. However, when R_H becomes positive after repeated SRT's μ_H^{-1} tends to become T^2 dependent, as seen in the inset of Fig. 5.

IV. DISCUSSION

One of the most important issues concerning the Hall effect in the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system is whether R_H is negative or not. The present results reveal that a slight reduction in the oxygen content significantly changes the R_H-T behavior and also results in a change in R_H sign as the oxygen content is reduced beyond a certain point. This sensitiveness of $R_H(T)$ to the oxygen content gives rise to scattering of the R_H data from sample to sample and from experiment to experiment even in single crystals. This is characteristic of the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system, which is rendered superconductive by a slight reduction, resulting in a rather arbitrary oxygen composition in a limited compositional range.

Significant T dependence of R_H or its sign reversal is first usually ascribed to the presence of two types of carriers, i.e., electronlike and holelike carriers (two-band model). In particular, the sign reversal seen in this system produced by a slight change in the oxygen composition may reflect an imbalance in the number of the two types of carriers. In this situation, R_H is expressed as

$$R_H = (n_p \mu_p^2 - n_n \mu_n^2) e / (\sigma_p + \sigma_n)^2 ,$$

where $\sigma_n = e n_n \mu_n$, $\sigma_p = e n_p \mu_p$, and the indices p and n indicate holelike carriers and electronlike carriers, respectively. Generally in metallic oxides, removing one oxygen atom causes a decrease of 8 in the electronic states and of 6 in the number of electrons, resulting in a decrease in the numbers of electron carriers in electron-type oxide conductors. However, in the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system, the oxygen atoms which are removed by the SRT are probably located near the Nd ionic sites[12] and contribute very little to the density of states of the conduction band. Therefore removing one oxygen atom causes an increase of 2 in the number of electrons. Thus the reduction treatments in the present experiments cause an increase in n_p. In this case, the R_H sign change is quite unlikely to occur unless μ_n is decreased by the reduction at least at a faster rate than n_n increases (i.e., in that case $\mu_n n_n = 1/e\rho$ should decrease). However, this condition clearly contradicts the present experimental results which show that the reduction causes a decrease in ρ.

On the other hand, if μ_p is increased significantly by the reduction, the R_H sign can become positive. However, this is also unlikely because it is rarely seen that a small change in a composition causes a drastic change in the mobility or the scattering rate. Therefore it is quite difficult to explain the sign reversal within the framework of the two-band model. This presents a sharp contrast to the model described by Wang *et al.*,[8] where a small hole pocket might play an important role in the occurrence of superconductivity. Interestingly, however, this model correlates with the present finding that the specimens which exhibit superconductivity always lead to an R_H behavior which increases in the positive direction at low temperatures.

Theoretical estimates for R_H based on local-density-approximation band calculations are positive[10] for $\mathbf{H}\|c$ over a wide Ce compositional range covering $x=0.15$. Namely, the band calculation predicts a nearly 2D Fermi surface located at the point X with a rounded square shape leading to a positive R_H. On the other hand, recent angle-resolved photoemission studies[19] have revealed that the experimental results are in good agreement with the theoretical estimations. The present results are also in qualitative agreement with the theory, indicating that the Fermi surface of the $Nd_{2-x}Ce_xCuO_{4-\delta}$ system favors positive R_H values. Thus the sign reversal of R_H for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ at $x=0.15$ is more likely interpreted in terms of the band-structure effect. On the other hand, the negative R_H and its T dependence for oxygenated specimens are probably associated with localization due to disorder which may be present in oxygenated $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. However, the details of the disorder and its relevance to superconductivity are not clear yet.

Takagi, Uchida, and Tokura[2] reported that, as x increases, the sign of R_H changes from negative to positive near $x=0.17$, where the superconductivity disappears. This sign reversal is thought to be due to a crossover from the strongly correlated region to the heavily doped region, where the system is sufficiently described in terms of the weakly correlated Fermi liquid. This R_H behavior is similar to the present results. However, the $R_H(T)$ for a lightly doped $Nd_{2-x}Ce_xCuO_{4-\delta}$ crystal is only slightly T dependent[17] and is clearly different from the strongly T-dependent behavior of the oxygenated specimens exhibited here, indicating that oxygenated $Nd_{2-x}Ce_xCuO_{4-\delta}$ at $x=0.15$ is essentially different from lightly doped $Nd_{2-x}Ce_xCuO_{4-\delta}$. The present results imply that $Nd_{2-x}Ce_xCuO_{4-\delta}$ with $x=0.15$ exists in the region where the band-structure effect is dominant, although the T dependence of R_H still cannot be explained by the same effect for reasons described by Ong.[1]

V. CONCLUSIONS

The effect of oxygen reduction on R_H and ρ has been studied for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ c-axis-oriented films by SRT's. This method has clearly revealed that R_H is very sensitive to oxygen deficiency and that the R_H sign for superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ can be positive. For this composition, the sign reversal of R_H, aside from its T dependence, is interpreted in terms of the band-structure effect rather than the two-band model.

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