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Ion-size effect on transport properties in $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems (R=Tm, Ho, Gd, and Nd)

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We report detailed studies of the normal-state resistivity and Hall effect in bulk $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems (R=Tm, Ho, Gd, and Nd). We find a linear temperature dependence of the normal-state resistivity ρ_n ($\rho_n \propto T$) and the Hall number n_H ($n_H \propto T$) above T_c. For a fixed temperature both ρ_n and n_H are dependent on the ionic radius of the rare earth $r_{R^{3+}}$; viz., the larger the R^{3+} ionic radius, the larger ρ_n ($\rho_n \propto r_{R^{3+}}$), but the lower n_H ($n_H \propto 1/r_{R^{3+}}$). At a constant temperature the $\rho_n \propto 1/n_H$ relation is well confirmed for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ compounds with different R ions. The cotangent of the Hall angle follows a universal T^2 dependence i.e., cot $\theta_H = \alpha T^2 + C$. The slope α decreases with increasing ion size of the rare earth, but the quantity C remains almost constant for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ compounds with different R. The reduction of T_c and the R^{3+} ion-size dependence of ρ_n and n_H is interpreted in terms of hole generation and hole localization by Ca doping. [S0163-1829(96)04129-X]

I. INTRODUCTION

One of the most puzzling problems in the study of high-T_c superconductors has been the anomalous linear temperature dependence of their normal-state resistivity ρ_n and the Hall number n_H above T_c over a wide temperature range,[1] which is inconsistent with an isotropic single-band Fermi-liquid description. A complete understanding of these properties is still lacking.

In an isotropic parabolic single-band Fermi-liquid system, the Hall number $n_H = V/eR_H$ would be the number of carriers per unit cell. For the high-T_c cuprate superconductors, due to its T dependence and the complex band structure, n_H may not represent the actual carrier concentration. However, the value of n_H at a particular T correlates rather consistently with the carrier concentration determined by other methods. n_H scales with the actual carrier concentration.

In any transport model, one expects that the carrier concentration scales with the conductivity, namely, $\rho \propto 1/n$. However, for most of the high-T_c cuprate superconductors, both ρ and $n_H \propto T$, and, then, $\rho \propto n_H$ instead of $\rho \propto 1/n$ in the simple Drude model. This fact seems to be the most puzzling in the normal-state transport properties of the high-T_c cuprates: *The higher the carrier density, the smaller the conductivity*.

Extensive studies of the Hall effect have been carried out on following 123 systems: (1) $YBa_2Cu_3O_{7-\delta}$ with changing the oxygen content δ,[2–8] (2) $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with changing the Pr content x,[9,10] (3) $YBa_2Cu_{3-x}M_xO_{7-\delta}$ (M =Zn, Co, Fe) with changing the transition-metal content x[11–14] and (4) $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with changing the Ca content x and the oxygen content δ.[15–19]

In order to explain the unusual temperature dependence of the Hall coefficient in the normal state of high-T_c superconductors, several approaches have been suggested, including conventional band-structure calculations[20] and strongly correlated models.[21,22] A non-Fermi-liquid-based approach has been suggested by Anderson[23] and a band model involving a square Fermi surface with rounded corners has been suggested by Pickett *et al.*[24] to understand the Hall-effect ''puzzle'' in high-T_c superconductors. Alexandrov *et al.*[25] showed that a quantitative explanation is possible for the temperature dependence of the R_H and resistivity using a variation of the bipolaron theory which takes into account Anderson localization of the bosons by disorder.

Among all cation dopings, Ca substitution for Y in $YBa_2Cu_3O_{7-\delta}$ has received much attention.[15–19,26–33] The valence state of Ca^{2+} is lower than that of Y^{3+}; such a substitution will generate excess holes and T_c is suppressed by the overdoping effect. On the other hand, it has been known that Ca doping is likely to cointroduce oxygen vacancies and this effect reduces the number of generated holes. This indicates that doping with Ca has a counterbalance effect on the suppression of the T_c. Ca doping is able to increase the T_c of the oxygen-deficient and tetragonal Y-Bu-Cu-O samples.[18,33] Recently, Yakabe *et al.*[19] showed that there is a maximum T_c of about 90 K with variation of the carrier density in single-phase $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films up to 50% Ca concentration. The value of the maximum T_c is independent of Ca concentration.

Ca doping is able to revive the superconductivity (to $T_c \sim 40$ K) of $PrBa_2Cu_3O_{7-\delta}$, which is a semiconductor.[34,35] Also, the introduction of Ca will increase T_c from 0 to about 82 K in $YBa_2Cu_{2.64}Co_{0.36}O_{7-\delta}$.[36] Gnansekar *et al.*[37] reported that they prepared thin films of $M_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ (M =Lu, Tb, Th) in single phase. The superconducting transition temperature of the films varies from ≈12 to ≈45 K. The significance is that the composition $MBa_2Cu_3O_{7-\delta}$ (M=Lu, Tb, Th) does not form in single phase in bulk form and, in the case of Tb and Th, not even in thin film form.

All of the Hall experiments above[2–19] have focused on the change of the concentration x of the dopants or the oxygen reduction δ. As a modification of our previous observation that the R^{3+} ion size has a very strong effect on supercon-

TABLE I. Lattice constants a, b, and c, unit cell volume V, and orthorhombic lattice strain $e=2(b-a)/(b+a)$ for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$.

R	a	b	c	V	e
Nd	3.854	3.911	11.723	176.7	0.0147
Gd	3.830	3.889	11.683	174.0	0.0152
Ho	3.815	3.878	11.661	172.5	0.0163
Tm	3.798	3.862	11.615	170.4	0.0167

ducting and magnetic properties in $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$,[38–50] we have carried out transport measurements in $R_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-\delta}$ systems,[51] in which instead of a change of concentration, we change the R^{3+} ion while leaving the concentration of Pr and oxygen unchanged. We found that at a constant temperature both ρ_n and n_H are linearly dependent on the ion size of the rare earth, viz., the larger the R^{3+} ionic radius, the larger ρ_n, but the lower n_H. The cotangent of the Hall angle follows a universal T^2 dependence, i.e., $\cot\theta_H=\alpha T^2+C$. Both the slope α and the quantity C are insensitive to the R ion and remain almost constant. On the basis of our data we proposed a T_c-n_H diagram which manifests an ‘‘underdoping’’ behavior of $R_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-y}$ systems.[51]

In this paper we report detailed studies of the normal-state resistivity and the Hall effect of bulk $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems (R=Tm, Ho, Gd, and Nd) in which instead of a change of concentration, we change the R^{3+} ion while leaving the concentration of Ca ($x=0.1$) unchanged. We found that at a constant temperature both ρ_n and n_H are dependent on the ionic radius of the rare earth, $r_{R^{3+}}$, viz., the larger the R^{3+} ionic radius, the larger ρ_n ($\rho_n \alpha r_{R^{3+}}$), but the lower n_H ($n_H \alpha 1/r_{R^{3+}}$). For a fixed temperature the relation of $\rho \propto 1/n_H$ is well confirmed for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems with different R ions. *The higher the carrier density, the higher the conductivity*. The cotangent of the Hall angle follows a universal T^2 dependence, namely, $\cot\theta=\alpha T^2+C$. The slope α decreases with increasing ion size of the rare earth, but the quantity C remains almost constant for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ compounds with different R ions.

II. EXPERIMENTAL TECHNIQUES

The ceramic $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) samples were synthesized using a conventional solid-state reaction method. Stoichiometric amounts of high-purity R_2O_3 (R=Tm, Ho, Gd, and Nd), $BaCO_3$, $CaCO_3$, and CuO powders were mixed, ground, and calcined at 915 °C for about 24 h in air in Al_2O_3 crucibles, followed by a slow cooling in the furnace. The resultant powder was then reground again and pressed with about 4 tons/cm^2 into pellets, which was then heated at 925–935 °C for 3 days in flowing oxygen, followed by annealing at 680 °C for 10 h, and then slow cooled to 420 °C, where they remained for 20 h before a final slow cool to room temperature. All specimens were annealed in an atmosphere of flowing oxygen to ensure a sufficient oxygen content in the final product. This sinter procedure was repeated at least three times. All samples were prepared at the same time in the same furnace, respectively, to ensure the same sample qualities.

The structures of the samples were investigated using a Rigaku Rotaflex rotating anode powder x-ray diffractometer (Cu $K\alpha$ radiation).

The dc magnetization was measured by a Quantum Design magnetometer. The resistivity was measured by the standard four-probe technique. To measure the Hall effect and the longitudinal resistivity a five-probe arrangement was used on rectangular-shaped samples. The rectangular samples were cut from sintered pellets with typical dimensions $2\times5\times0.5$ mm^3. In order to perform precise Hall measurements, it was essential to minimize the misalignment of the Hall arms and also to achieve low contact resistance. The contacts were made using gold wires and silver epoxy. After a heat treatment of 2 h at 450 °C in flowing oxygen, the contact resistance was typically less than 0.5 Ω for contact surfaces smaller than 0.1 mm^2. Samples were mounted on small sapphire substrates.

The experiments were performed in a commercial Oxford Dewar with a superconducting magnet. To extract the Hall voltage, a signal was measured at two reversal directions of the measuring current (100 mA) and two reversal directions of the magnetic field (±7 T). The temperature was measured by a carbon glass thermometer.

III. RESULTS AND DISCUSSION

The x-ray diffraction patterns at room temperature (Fig. 1) show that all $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) samples have orthorhombic perovskitelike structure and contain no extra peaks due to impurity phases within the experimental error. It was indicated in the literature that only at Ca concentration does x at higher than about 0.2–0.3 impurity phases appear in bulk materials of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$.[31] Recently, Sun *et al.*[15] showed that for c-axis-oriented $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films deposited by laser ablation there is no impurity phase found even for $x=0.5$ and 0.7. Yakabe *et al.*[19] obtained single-phase $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films prepared by rf thermal plasma deposition method up to 50% Ca.

The lattice parameters a, b, and c, the unit cell volume V, and the orthorhombic lattice strain e, defined as $e=2(b-a)/(b+a)$, of all samples are listed in Table I. We observed that the structure of all studied systems remains orthorhombicity $(e>0)$. However, the e parameter, i.e., the orthorhombicity, decreases with increasing R^{3+} radius (Table I). The main peak split is not obviously for sample $Nd_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (Fig. 1). The lattice parameters a, b, and c and the unit cell volume V of all samples are increasing linearly with radius of the R ion (Fig. 2). We believe that Ca^{2+} occupies the Y^{3+} site. If Ca^{2+} ($r_{Ca^{2+}}=0.99$ Å) occupies Ba^{2+} ($r_{Ba^{2+}}=1.34$ Å) sites, a shorter c axis would be expected.[15] It is noticeable that the increase of the c axis from 11.615 Å for

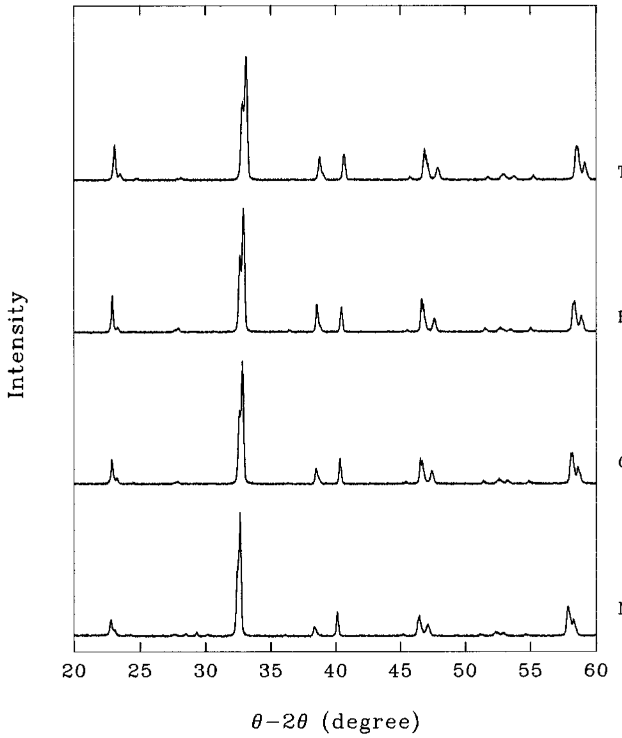

FIG. 1. X-ray powder diffraction patterns with Cu $K\alpha$ radiation for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems.

$Tm_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ to 11.723 Å for $Nd_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ is less than that of the ionic radii from 0.87 Å for Tm^{3+} to 0.995 Å for Nd^{3+}. The lattice undergoes a monotonic compression when the Y site in the 123 series is substituted by R^{3+} with a larger radius.

In fully oxygenated $YBa_2Cu_3O_{7-\delta}$, Ca doping is accompanied by a reduction in oxygen content. However, Ca doping below 6% has little effect on the oxygen content.[16] Fisher *et al.*[31] suggested that in Ca-doped compounds $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$, $\delta=\delta_0+x/2$. In our case $x=0.1$; therefore, we could reasonably assume that the oxygen content does not vary much.

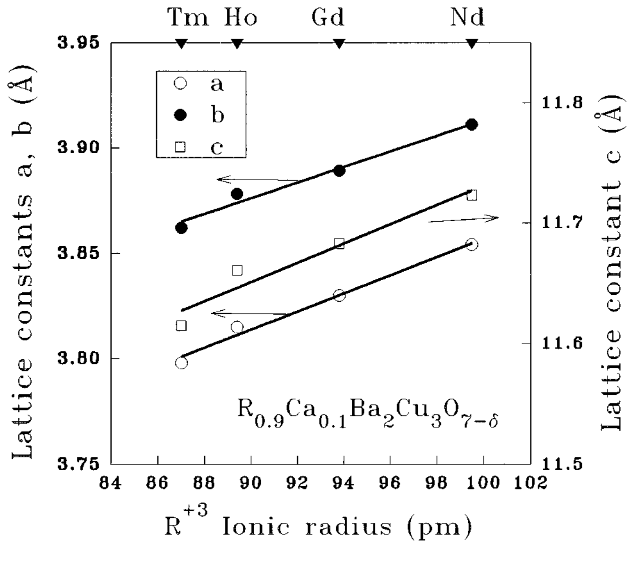

FIG. 2. Lattice constants a, b, and c vs ionic radius of R^{3+} for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems.

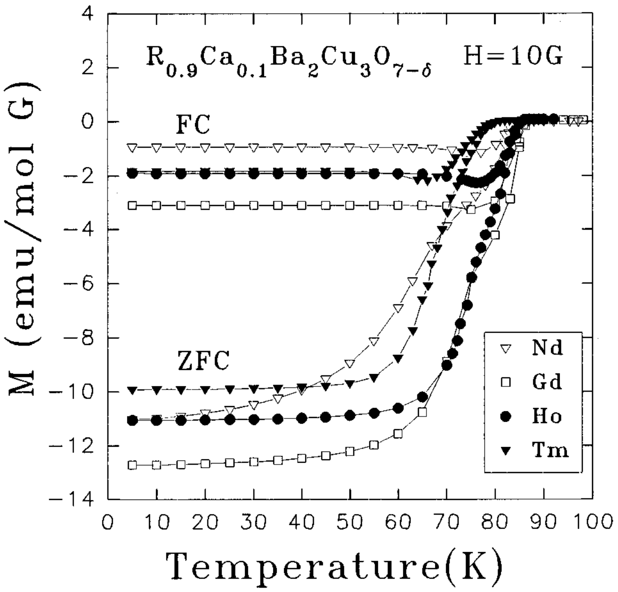

FIG. 3. Temperature dependence of dc molar magnetization for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems in a field of 10 G.

The temperature dependences of the dc molar magnetization, $M(T)$, of $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems over the temperature region 5–90 K were measured both in zero-field cooling (ZFC) and field cooling (FC). The results are shown in Fig. 3. The $M(T)$ curves demonstrate a superconducting transition.

The normal-state resistivity ρ was measured in the temperature range between T_c and 280 K for all samples. The results are shown in Fig. 4. The results indicate that all

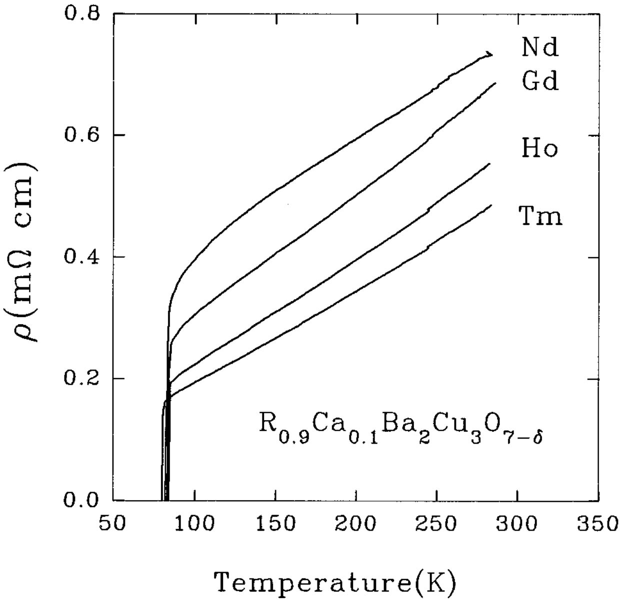

FIG. 4. Temperature dependence of resistivity ρ for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems.

samples are ''metallic'' with a linear temperature dependence in the measured temperature range.

The T_c values of $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ determined from both resistivity and magnetization measurements by the onset of the superconducting transition were 86, 89, 88, and 86 K for $R=$Tm, Ho, Gd, and Nd, respectively, and exhibit an almost R-independent T_c ranging from 86 to 89 K (±1.5 K). It should be emphasized that for Ca-doped systems in this doping level ($x=0.1$) no correlation of T_c with R^{3+} ion size was found. This is unlike that in Pr-doped $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ systems[38,39] in which we demonstrated an R^{3+} ion size effect on T_c. The undoped $RBa_2Cu_3O_{7-\delta}$ systems have a nearly optimal value of the carrier concentration. Then the T_c reduction after Ca doping could be described as an overdoping effect in the fully oxygenated samples of $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$. However, Awana *et al.*[32,33] suggested an alternate explanation which involves the creation of disorder in CuO_2 planes by Ca doping. They argued that in Ca-doped compounds the coordination number of Ca is dependent on the oxygen content and the concentration of doped Ca in the material.[33] The effect of disorder in reduction T_c should not be ignored.

It is traditional to express the total electrical resistivity as the sum of two terms. One is the temperature-dependent term arising from the dynamic deviations from crystal perfection. Another is the temperature-independent residual resistivity arising from the static imperfections, such as impurities and lattice defects. The normal-state resistivity ρ of $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ ($R=$Tm, Ho, Gd, and Nd) systems could be fitted by the relation $\rho(T)=\rho_0+aT$, where $a=d\rho/dT$ is the slope in $\rho(T)$ curves and ρ_0 is the extrapolated value of ρ at $T=0$ and close to zero for undoped samples.

With increasing R^{3+} ion size, the resistivity curves $\rho(T)$ are shifted progressively upwards (Fig. 4), so that the primary effect of the R ion size is to add a nominally temperature-independent contribution ρ_0 to the transport scattering rate. This may be due to a progressive decrease in carrier concentration (our Hall measurements support this point of view) or/and a progressive increase of an unsuspected temperature-independent scattering (impurity scattering) contribution by increasing R^{3+} ion size in samples.

It is the most striking aspect of the normal-state resistivity data that at a constant temperature the normal-state resistivity increases linearly with increasing R^{3+} ion size. The experimental results for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ ($R=$Tm, Ho, Gd, and Nd) systems at temperatures of 100, 150, 200, and 250 K are shown in Fig. 5. It should be also noted that in Pr-doped $R_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-\delta}$ systems we have obtained a similar R^{3+}-ion-size effect on ρ_n.[43,50,51]

Hall measurements were made with the same samples which we discussed above. Our results demonstrated that the Hall voltage V_{xy} at a constant temperature was linear in H and no saturation up to the maximum field of 7 T.

The Hall coefficient R_H above T_c is holelike for all samples. The temperature dependence of R_H is shown in Fig. 6. The experimental values of R_H are in the range 0.3×10^{-9}–2.0×10^{-9} m^3/C. R_H increases as the temperature decreases.

It is convenient to normalize the Hall constant to the unit cell volume V (see Table I) so that, in the case of a parabolic single band, the Hall number n_H (derived from $n_H=V/eR_H$) is the number of carriers per unit cell where e is the electron charge. The temperature dependence of the Hall number n_H is presented in Fig. 7.

As shown in Figs. 6 and 7, we find for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ ($R=$Tm, Ho, Gd, and Nd) systems a nearly $1/T$ dependence of R_H and therefore a nearly linear temperature dependence of n_H, widely seen in many high-T_c cuprate superconductors.[1–19] Figure 7 also indicates that the

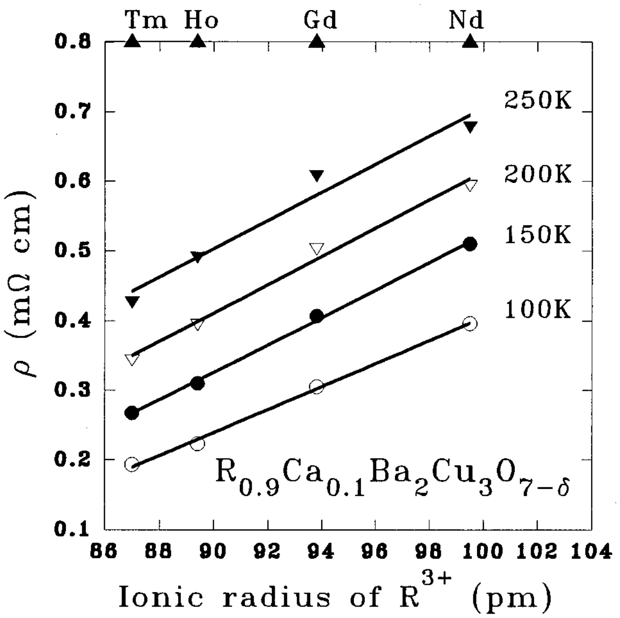

FIG. 5. Normal-state resistivity ρ at temperatures of 100, 150, 200, and 250 K vs ionic radius of R^{3+} for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ ($R=$Tm, Ho, Gd, and Nd) systems.

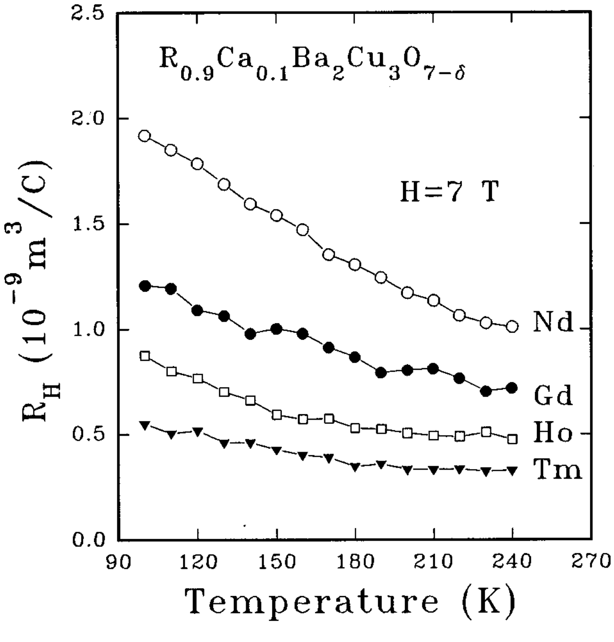

FIG. 6. Temperature dependence of the Hall coefficient, R_H, in a field of 7 T for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ ($R=$Tm, Ho, Gd, and Nd) systems.

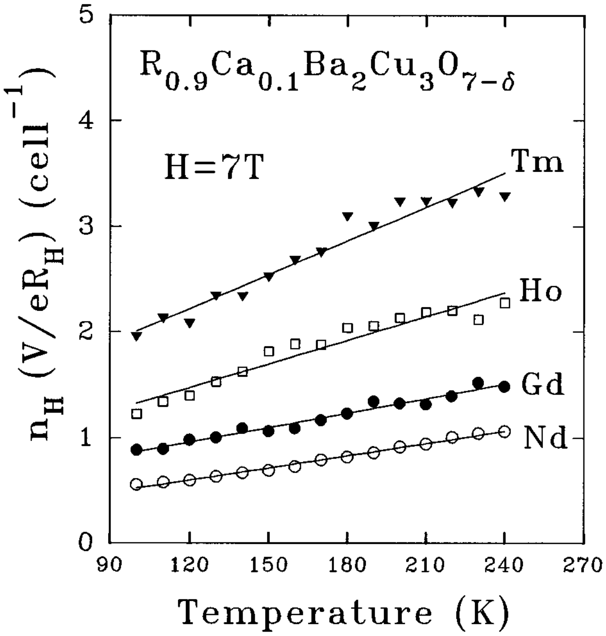

FIG. 7. Temperature dependence of the Hall number per unit cell volume, n_H ($n_H \equiv V/eR_H$), in a field of 7 T for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems.

slope dn_H/dT is found to be suppressed as the R^{3+} ionic radius increases.

The transport measurements performed in sintered bulk samples are usually complicated by the character of the granularity in these samples (weak links between grains) and confused by anisotropic effect inside the grains. In spite of this, the data of the Hall effect measurements for $YBa_2Cu_3O_{7-\delta}$ single crystals when the magnetic field is along the c axis[52,53] are, in general, in good agreement with results on polycrystals.[54]

We have estimated that the signal error of our experimental system is about $10^{-7} \sim 10^{-8}$ V. However, the Hall voltage V_{xy} at low temperatures is on the order of 10^{-6} V and $V_{xy} \sim 1/T$. Above 240 K the Hall signals are small and sensitive to thermal shift during the measurements. Therefore, our Hall measurements were performed limited in the temperature range of 100–240 K.

Our experimental data show that at a constant temperature the Hall number n_H monotonicly decrease with increasing R^{3+} ionic radius in $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems (R=Tm, Ho, Gd, and Nd). In Fig. 8 we present the correlation between $1/n_H$ and R^{3+} ion radius at constant temperatures (100, 150, 200, and 240 K). In every case the

$$1/n_H \propto r_{R^{3+}} \tag{1}$$

is satisfied, where $r_{R^{3+}}$ is the R^{3+} ion radius.

On the other hand, at a constant temperature an approximate description of the R^{3+} ionic radius dependence of the Hall carrier density n_H is also can be given by the relation (Fig. 9)

$$n_H = A + B(r_{R^{3+}} - r_{Ca^{2+}})^2, \tag{2}$$

where $r_{R^{3+}}$ and $r_{Ca^{2+}}$ are the radii of the R^{3+} ion and Ca^{2+} ion, respectively, and A and B are two fitting parameters. The parameter A corresponds the Hall carrier density n_H of the compound $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ with $r_{R^{3+}} = r_{Ca^{2+}}$. Due to the difference between $r_{Nd^{3+}}$ and $r_{Ca^{2+}}$ ($r_{Nd^{3+}} - r_{Ca^{2+}} = 0.5$ pm) and parameter B being small ($B \ll A$), the fitting values of the parameter A are very close to experimental values of the Hall number n_H of $Nd_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ at these temperatures.

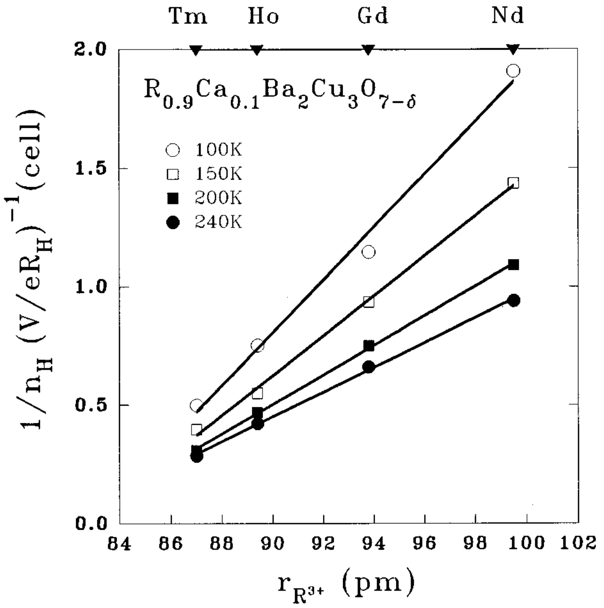

FIG. 8. $1/n_H$ ($n_H \equiv V/eR_H$) vs ionic radius of R^{3+}, $r_{R^{3+}}$, at temperatures of 100, 150, 200, and 240 K for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-y}$ (R=Tm, Ho, Gd, and Nd) systems.

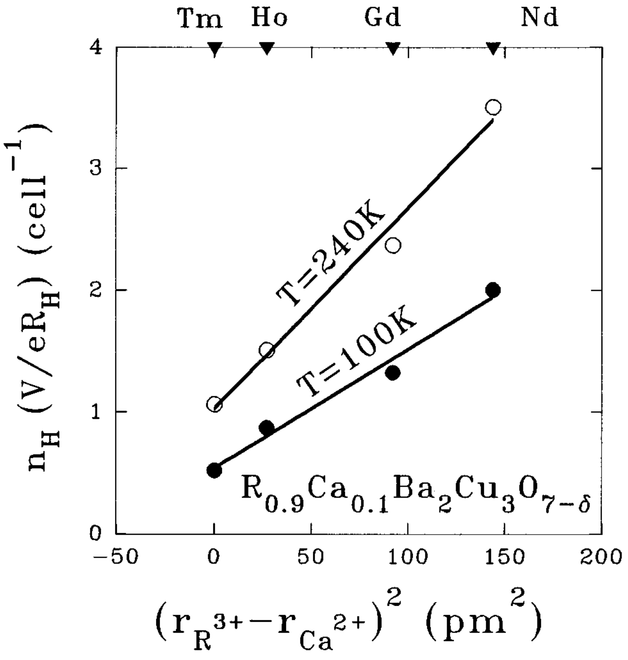

FIG. 9. n_H ($n_H \equiv V/eR_H$) vs $(r_{R^{3+}} - r_{Ca^{2+}})^2$ for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems [solid lines are fitting curves fitted by the formula $n_H = A + B(r_{R^{3+}} - r_{Ca^{2+}})^2$].

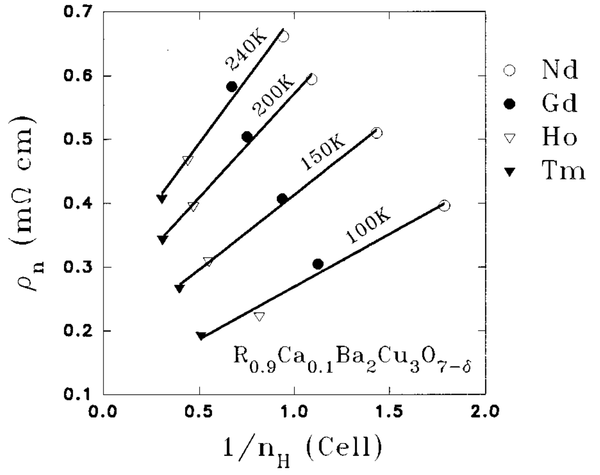

FIG. 10. Normal-state resistivity ρ_n vs $1/n_H$ at temperatures of 100, 150, 200, and 240 K for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems.

If Ca plays a role just as a carrier provider, thus, Ca doping with the same concentration ($x=0.1$) should generate the same number of carriers in different $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ compounds. It is not consistent with the observed R^{3+} ion size dependence of n_H.

It is generally believed that the holes in the 123 compounds can be divided into two types: mobile and nonmobile. The mobile holes, which are matched with a Hall number n_H, are located in the CuO_2 sheets, others are believed to form electron-hole pairs which cannot move and are localized on the CuO chains.

In our recent paper[51] we reported detailed Hall measurements on Pr-doped $R_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-\delta}$ systems (R=Yb, Er, Dy, Gd, Eu, and Nd), in which n_H decreases roughly linearly with increasing R^{3+} ionic radius. The quite different inclination may suggest the completely different mechanisms of T_c suppression in Ca- and Pr-doped systems.

The variation of the carrier concentration is also expected to affect the resistivity ρ. In any transport model, one expects $\rho \propto 1/n$. However, from Figs. 4 and 7 we can see that for a given compound both ρ and $n_H \propto T$, and then, $\rho \propto n_H$, instead of $\rho \propto 1/n$. This fact seems to be the most puzzling in the normal-state transport properties of the high-T_c cuprates: *The higher the carrier density, the smaller the conductivity.*

In Fig. 10, we present the correlation between measured ρ and $1/n_H$ at constant temperatures (100, 150, 200, and 240 K) for different $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ compounds. In every case, the $\rho \propto 1/n_H$ relation is well confirmed. This behavior is normal: *the higher the carrier density, the higher the conductivity.* Similar results were obtained in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ systems with variable oxygen content.[16,17] Although the parameter n_H interpretation in the studied systems is debatable, however, the measured n_H and ρ at fixed temperature correlates rather consistently with the $\rho \propto 1/n_H$ relation. This is evidence that n_H scales with actual mobile carrier concentration.

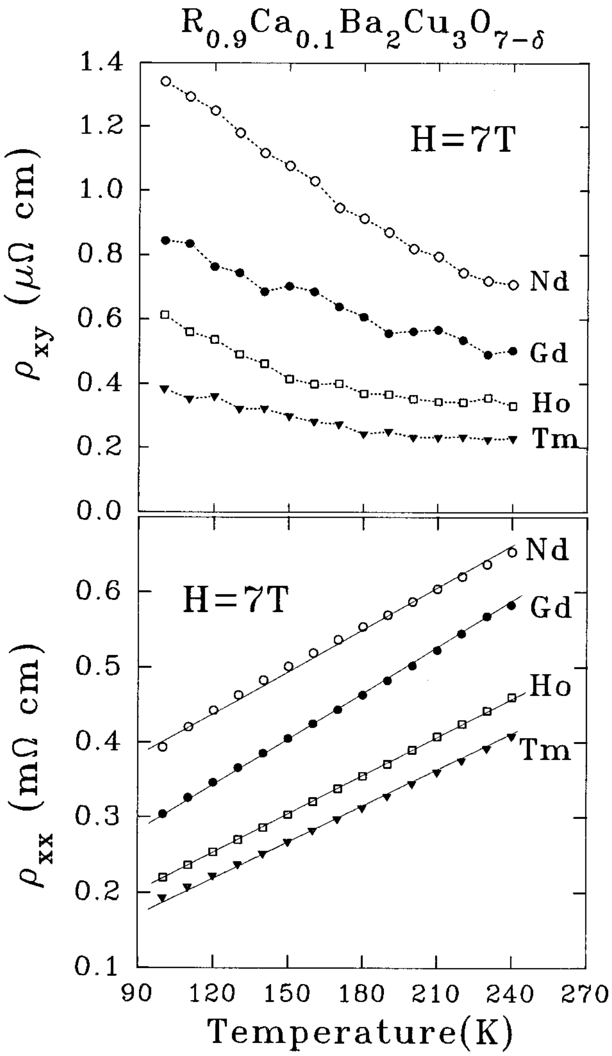

FIG. 11. Temperature dependence of the Hall resistivity ρ_{xy} and magnetic resistivity ρ_{xx} in a field of 7 T for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems.

The Hall resistivity ρ_{xy} and magnetic resistivity ρ_{xx} measured in a field of 7 T are displayed in Fig. 11. The computed values of $\cot\theta_H=\rho_{xx}/\rho_{xy}$ in the field of 7 T as a function of T^2 are shown in Fig. 12. According to Anderson's suggestion[23] based on the two-dimensional Luttinger-liquid model, the Hall angle θ_H can be expressed by a universal quadratic temperature dependence of $\cot\theta_H$:

$$\cot\theta_H=\rho_{xx}/\rho_{xy}=\alpha T^2+C. \tag{3}$$

It should also be noted that a band model involving a square Fermi surface with rounded corners could also lead to the above T^2 law.[24] Therefore, one cannot conclude the validity of Anderson's picture[23] simply based on the applicability of Eq. (3) to the observed results.

In Fig. 13, an approximate description of the R^{3+} ionic radius dependence of the parameter α is given by the relation

$$\alpha=0.014+10^{-4}(r_{R^{3+}}-r_{Ca^{2+}})^2. \tag{4}$$

The value of 0.014 corresponds to a value of α for the compound $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ with $r_{R^{3+}}=r_{Ca^{2+}}$. The fitting value of 0.014 is very close to experimental values of α for $Nd_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$.

Figure 14 demonstrates that both α and dn_H/dT are linearly dependent on Hall carrier density n_H. This means that

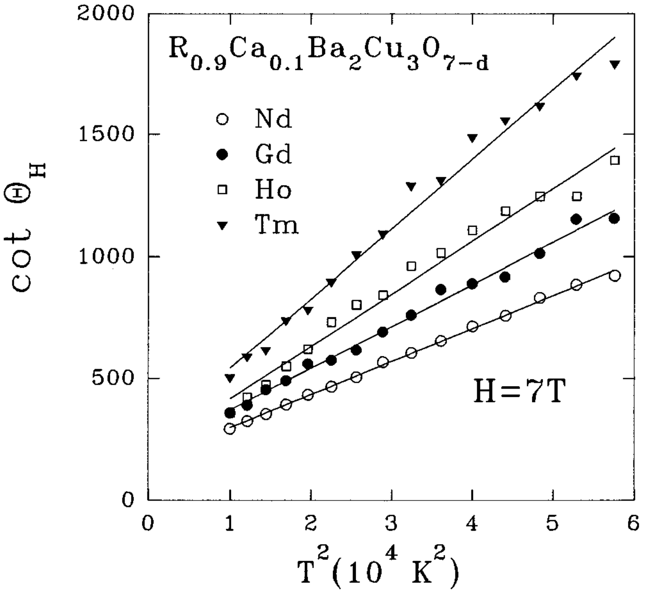

FIG. 12. Variation of the cotangent Hall angle cot θ_H with T^2 at 7 T for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems.

the temperature dependences of n_H and cot θ_H are suppressed for a compound with a smaller Hall carrier density (Figs. 7 and 14) or with a larger R^{3+} ionic radius (Figs. 7, 12, and 13) in $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems. We present evidence for the existence of a linear relationship between α and n_H, which is consistent with results obtained in oxygen-depleted $YBa_2Cu_3O_{7-\delta}$ films.[4] The origin of this feature is not completely clear at present.

In the literature an universal behavior for all investigated films was found: The larger dn_H/dT, the higher T_c.[17] Contrary to the $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films, in our case no correlation between dn_H/dT and T_c was found in $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems.

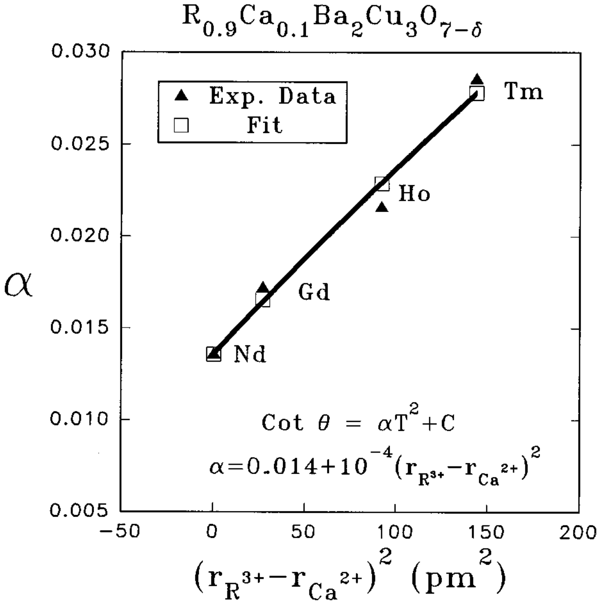

FIG. 13. Slope α of the curve cot $\theta_H(T^2)$ in a field of 7 T vs $(r_{R^{3+}}-r_{Ca^{2+}})^2$ for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems [solid line is a fitting curve fitted by the formula $\alpha=0.014+10^{-4}(r_{R^{3+}}-r_{Ca^{2+}})^2$].

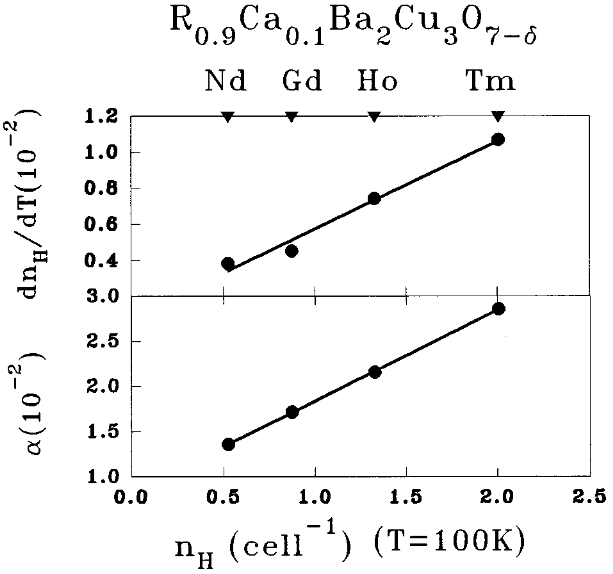

FIG. 14. Slope α of the curve cot $\theta_H(T^2)$ and the slope dn_H/dT of the curve n_H (T) vs the Hall number per unit cell volume, n_H ($n_H \equiv V/eR_H$), at a temperature of 100 K for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (R=Tm, Ho, Gd, and Nd) systems.

Earlier Hall measurements[3,4,8,10–13] on 123-type high-T_c superconductors reveal that Eq. (3) seems to be universal in every system with different dopants and doping levels. However, the behavior of the slope α and intercept C are quite different for different systems.

For the case of in-plane zinc dopants in crystals of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$,[11] C in Eq. (3) linearly increases with increasing zinc concentration, but the parameter α is essentially unchanged. For the case of CuO-chain-site cobalt doping in crystals of $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$,[13] the results showed that doping with Co decreases α while leaving the residual scattering parameter C unchanged. For the case of oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ epitaxial films,[5] the results showed that oxygen reduction increases α, leaving the residual scattering parameter C unchanged. For the case of Y-site doping by Pr in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ epitaxial films,[5] both α and C increase with Pr concentration x.

All of the Hall experiments above[3,4,8,10–13] reveal a unified picture of the Hall effect in various high-T_c cuprate systems. While the increase of C corresponds to a reduction of mobility, the change of α reflects the variation in carrier density.[5]

All of the Hall experiments above[3,4,8,10–13] have focused on the change of the concentration x of the dopants or the oxygen reduction δ. In our previous paper,[51] we presented Hall measurements in $R_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-y}$ systems and, in the present paper, in $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems, in which, instead of a change of concentration, we change the R^{3+} ion while leaving the concentration of Pr or Ca unchanged.

In Pr-doped $R_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-\delta}$ systems, both parameters α and C, in the formula cot $\theta_H=\rho_{xx}/\rho_{xy}=\alpha T^2+C$, remain almost constant and do not change with the changing of R in $R_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-y}$.[51] However, in present Ca-doped $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems, similar to the case of Co-doped $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$ crystals,[13] the results showed that changing the R ion with a larger ion size [as increasing the Co concentration x in $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$ crystals[13]] decreases α, while leaving the residual scattering parameter C unchanged (Fig. 12).

In a unified picture of Hall effect as mentioned above, the parameter C is a measure of the in-plane impurity scattering rate. It is not surprising that C, independent of the R^{3+} ion, substituted into the Y site in $R_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-y}$ and $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems.

The change of α was attributed to the variation in the carrier density.[5] It is not surprising that α and n_H have a similar R^{3+}-ion-size dependence [see Eqs. (2) and (4)], indicating that both effects are closely related.

The observed R^{3+}-ion-size dependence of the Hall number n_H in bulk $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems (R=Tm, Ho, Gd, and Nd) at a fixed Ca concentration ($x=0.1$) presented here reveals that the change of number of the mobile holes in these systems is not only connected to the hole generation by the substitution of Ca^{2+}, but also to the ‘‘moving holes’’ localization caused by disorder and lattice compression. The Ca content controls the carrier density in a nonlinear fashion because carriers are distributed both in the CuO_2 planes and in the CuO chains. The part of the carriers brought about by Ca doping, most probably, is absorbed into the CuO chain charge reservoir. The localization and charge transfer are the major factors affecting the hole concentration in Ca-doped systems.

As mentioned earlier, the lattice of $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems (R=Tm, Ho, Gd, and Nd) compounds undergoes a monotonic compression when the Y site in the 123 series is substituted by R^{3+} with a larger radius. The lattice compression turn leads to the localization of the mobile holes generated by Ca doping. This excess strain due to the lattice compression in these compounds with a larger R^{3+} ion size, though having little effect on T_c, has a strong influence on the resistivity and Hall effect. The effect of the disorder influence on transport properties should not be ignored.

Another possible reason for the R^{3+}-ion-size effect on n_H is that the coordination number of the doped Ca[33,34] which has a strong effect on the hole generation, is R^{3+}-ion-size dependent.

IV. CONCLUSIONS

In conclusion, we find a linear temperature dependence of the normal-state resistivity ρ_n and the Hall number n_H in bulk $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ systems (R=Tm, Ho, Gd, and Nd). At a constant temperature ρ_n and $1/n_H$ are linearly dependent on the ion size of the rare earth. The $\rho \propto 1/n$ relation is well confirmed at a constant temperature for $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ compounds with different R ions. The cotangent of the Hall angle follows a universal T^2 dependence. The slope α decreases with increasing ion size of the rare earth, but the quantity C is insensitive to the R ion and remains almost constant. Our experimental results reveal that Ca doping plays a much more interesting role than just of a carrier provider in $RBa_2Cu_3O_{7-\delta}$ systems. A considerably stronger decreasing of the n_H value in $R_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ compounds as the R^{3+} ion radius rises can be attributed to the strengthening of the localization effect due to the disorder and lattice compression related to Ca doping.

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