Normal-state Hall-effect measurements on $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ single crystals

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The temperature dependence of the Hall effect was studied on single crystals of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with the magnetic field perpendicular to the *ab* plane and the current flowing in the *ab* plane. The anomaly in the Hall coefficient at around 120 K found in some of the 1:2:3 compounds is not observed in Pr-doped Y-Ba-Cu-O crystals. We observed that an increase in Pr concentration reduces the mobile carrier density and its strong temperature dependence. The reduction of the total conduction carriers can be attributed to hole filling or hole localization. Our results suggest that it is more likely that hole filling is responsible for the suppression of T_c in the system.

I. INTRODUCTION

Although intensive studies have been performed on the system of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ during the last five years,[1-3] the answers to a number of questions regarding the system remain unclear and open for discussion. Even the basic issue of the fundamental mechanisms causing the depression of T_c as the Pr concentration increases remains a subject for debate. The other questions include: (1) What is the formal valence of Pr in the system?, (2) Why does the mobile hole density reduce as the Pr doping increases?, (3) How could hole localization be distinguished from hole filling?, and (4) If hole localization causes the reduction of T_c what is the physical mechanism behind the localization? Since a proper understanding of the transport properties of the high-T_c superconductors is essential toward the understanding of the superconductivity of these oxides,[4] Hall-effect measurements are of central importance in providing additional experimental evidence toward resolving some of these questions. To date, the only Hall-effect measurement performed on $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ was done on polycrystalline samples by Matusuda *et al.*[5] Hall-effect measurements on single crystals of the system remain untouched in spite of the importance of these experiments. Single-crystal experiments lead more readily to the intrinsic transport properties of the system, particularly those influenced by the pronounced anisotropy of these oxides systems.

In this paper, we report a systematic study of the longitudinal resistivity ρ_{xx}, the Hall coefficient R_H, and the charge-carrier density n_H in the single crystals of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

II. EXPERIMENTAL DETAILS

The single crystals of $Y_{1-x}Pr_xBa_2Cu_3O_7$ investigated in the study were produced in gold crucibles by a self-flux method. For pure Y-Ba-Cu-O crystals grown by other researchers using a similar method, chemical analysis revealed that approximately 10% of the copper atoms in the Cu-O chains are replaced by gold.[6] Similar results could occur for our Pr-doped Y-Ba-Cu-O samples. The crystals were cleaved into bar shapes suitable for Hall-effect measurements. Typical dimensions of the single crystals are $1\times 0.8\times h$ mm^3, where the sample thickness h changes from 0.04 to 0.8 mm depending on the Pr concentration. All single crystals were annealed in flowing oxygen at about 400 °C for a week just prior to any measurements. Zero-field-cooled dc magnetization experiments as a function of temperature have been performed on these crystals before the transport measurements to confirm the quality of the crystals. A five-probe contact arrangement was used for the longitudinal-resistivity and Hall-effect measurements. Electrical leads were attached to the crystal face with silver epoxy, and then oxygen annealed to 400 °C for 1 h to reduce contact resistance. The typical contact resistance after this procedure was on the order of 1 Ω. More experimental details can be found in our previous paper.[7]

All of the measurements were carried out in a commercial superconducting quantum interference device magnetometer[8] in magnetic fields up to 5.5 T. Voltage was measured using a Keithley nanovoltmeter (model 181). A current of 5 mA, which corresponds to a current density of about 10 A/cm^2 was used throughout the experiment. It was observed that current-voltage relations showed an ohmic behavior at the current value for all of the samples in the temperature region reported here. As shown in the inset of Fig. 1, a potentiometer, which has much larger resistance than the specimen resistance plus contact resistances was used to yield zero or close to zero potential difference between the probes 1 and 2 in the absence of a magnetic field. At a fixed temperature, four measurements of voltage V_{12}, with reversals of **I** and **H**, are needed to cancel out thermoelectric voltages that do not reverse sign with the current reversal and a small component of contact misalignment voltage that was not precisely nulled by the potentiometer. All data were acquired using magnetic-field sweeps at fixed temperature. The temperature dependence of the longitudinal resistivity was measured in a separate run.

III. RESULTS AND DISCUSSION

The Hall resistance, which is equal to the Hall voltage divided by the current passing through the sample, is a

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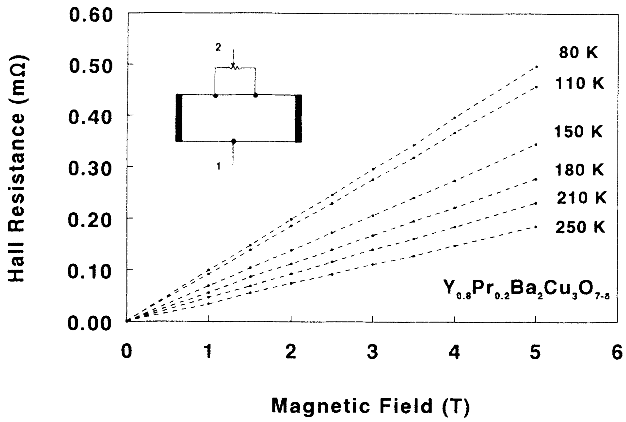

FIG. 1. Magnetic-field dependence of the Hall resistance at various representative temperatures for $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-\delta}$. The inset shows the configuration for the measurements.

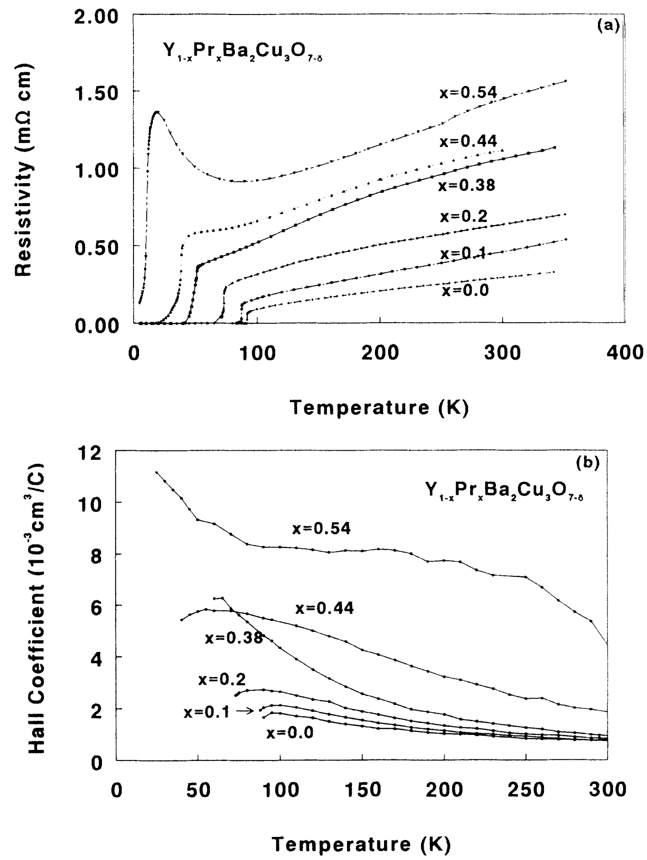

FIG. 2. Temperature dependence of (a) the resistivity and (b) the Hall coefficient in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ crystals with $x=0.00$, 0.10, 0.20, 0.38, 0.44, and 0.54.

linear function of magnetic field at least down to the superconducting transition temperature for all of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ crystals. Figure 1 shows a typical magnetic-field dependence of the Hall resistance at various temperatures for a crystal of $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-\delta}$. Hall coefficients, and the carrier numbers are derived from the slopes of these linear curves. The temperature dependence of the longitudinal resistivity and the Hall coefficient are displayed in Figs. 2(a) and 2(b), respectively. The behavior of $\rho_{xx}(T)$ is the same as reported previously.[9] For $x<0.4$, all of the crystals have a metalliclike behavior from room temperature down to about 100 K and $\rho_{xx}(T)$ depends linearly on temperature in this temperature regime. The samples with composition $0.40<x<0.56$ show a broad maxima in $\rho_{xx}(T)$ near T_c. When $x>0.56$, the samples show a semiconductinglike behavior. As shown in Fig. 2(b), with increasing Pr concentration, the Hall coefficient R_H (measured with the magnetic field parallel to the c axis, and the current in the ab plane) remains positive and its magnitude increases monotonically with increasing Pr concentration at a fixed temperature. For all the crystals with $x<0.4$, the Hall coefficients show $1/T$ dependence down to T_{max}, where T_{max} is not too far above T_c. For the samples with $x>0.4$, the Hall coefficient decreases continuously as the temperature increases, but its temperature dependence becomes much weaker than $1/T$. The upturns of R_H have been attributed to fluctuation effects.[10] The fact that the maxima of the Hall coefficients are located only a few degrees above T_c is very different from what has been found in $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ and $YBa_2(Cu_{1-x}Co_x)_3O_{7+\delta}$ samples,[11] where samples with moderate T_c (38 and 50 K, for example) show maxima in the Hall coefficient around 120 K where the carrier number per copper atom is 0.10 to 0.15. Notice that 120 K is well above the T_c of these samples. If the anomaly is indeed accompanied by a structural change as the authors suggested, it seems that no such structure change would occur in our corresponding $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples. It is expected that the lattice parameters will change monotonically as the temperature is lowered down to T_c in Pr-doped Y-Ba-Cu-O samples.

The $1/T$ dependence of the Hall coefficient contradicts the prediction of the conventional one-band model for a metal. The linear temperature dependence of the charge-carrier density derived from $R_H=1/n_H e \propto 1/T$ is difficult to reconcile with the value of n derived from $\sigma=ne^2\tau_{tr}/m^* \propto 1/T$. Experimentally, superconducting-penetration-depth measurements by muons did not observe any temperature dependence of the charge-carrier density.[12] Several scenarios have been proposed to explain the anomalous temperature dependence. The $1/T$ dependence of R_H could arise from the two-band model at low-field limit

$$eR_H=(n_h\mu_h^2-n_e\mu_e^2)/(n_h\mu_h+n_e\mu_e)^2 \tag{1}$$

and

$$\sigma=n_h e\mu_h+n_e e\mu_e , \tag{2}$$

where $n_h(n_e)$, $\mu_h(\mu_e)$ are charge-carrier density and mobility of hole (electron), respectively. Obviously, there are more unknown parameters than the number of equations. The relations $R_H \propto 1/T$, and $\sigma \propto 1/T$ can be produced mathematically by assuming a rather unusual relation among the parameters. For example, Davidson *et al.*[13] assumed n_h and n_e are temperature independent and equal, and the scattering rates differ only in the second-order term of the Taylor expansion

$$\tau_i(i=h,e)=a/T+b_i/T^2 \ . \tag{3}$$

This model suggests that, as the doping increases, the hole contribution term could become smaller than the electron contribution term, and, therefore, cause a sign change of R_H. This predication is contradicted by the positive R_H for all Pr-doped Y-Ba-Cu-O. The necessity of having equal number of electrons and holes in the system, and nearly complete cancellation between electron and hole contributions to R_H in pure and Pr-doped Y-Ba-Cu-O and other high-T_c superconductors, plus the fact that R_H is pressure independent raises serious doubt about validity of the model. A temperature-dependent Hall coefficient could also arise from an anomalous Hall component that dominates the conventional Lorentz force term. Fiory and Grader[14] explained this anomalous Hall component in the framework of conventional magnetic skew scattering. According to this model, the anomalous Hall coefficient R_s is linearly proportional to the magnetic susceptibility χ. The strong temperature dependence of R_s leads to a strong temperature dependence of χ. The fact that the Hall coefficient R_H has $1/T$ dependence, while χ is almost temperature independent in Y-Ba-Cu-O is inconsistent with this predication. In Pr-doped Y-Ba-Cu-O, the magnetic susceptibility χ follows a Curie-Weiss law, while the temperature dependence of R_H becomes weaker than $1/T$ as the Pr concentration increases, also contradicting the $R_s \propto \chi$ prediction. Although Matsuda *et al.* attribute the anomalous Hall coefficient to magnetic skew scattering in their very recent paper,[15] their arguments that skew scattering plays a dominant role in σ_{xy} are not convincing. Very recently, Anderson[16] proposed a model to account for the $1/T$ dependence of R_H by distinguishing the transport relaxation time τ_{tr} from the cyclotron relaxation time τ_H. Although this model predicates the temperature dependence of $\sigma_{xx} \propto 1/T$, $\sigma_{xy} \propto 1/T^3$, and $\cot\Theta = A + BT^2$ in agreement with experiments, it does not solve the problems associated with a temperature-dependent charge-carrier density or how one could derive the charge-carrier density from the measurements of R_H and ρ_{xx}. Obviously much more work has to be done in order to retrieve a meaningful charge-carrier density from the Hall-effect measurements.

Since the crystal structure does not change with Pr substitution, and at a fixed temperature $1/R_H$ changes monotonically with the Pr concentration, the value of $V/R_H e$ at a fixed temperature can be used as a measure of the charge-carrier density. Shown in Fig. 3 is the temperature dependence of the carrier density derived from $n_H = V/R_H e$. Based on this relationship, we found that the carrier density has a linear dependence on temperature and the slopes of $n_H(T)$ remain essentially constant for samples with $x < 0.4$. When $x > 0.4$, $n_H(T)$ becomes less temperature dependent as the Pr concentration increases. The variability of the locations of the leads in the samples, the finite size of the contacts compared with the size of the samples, and nonuniformity of the sample thickness introduce an uncertainty of less than 50% in

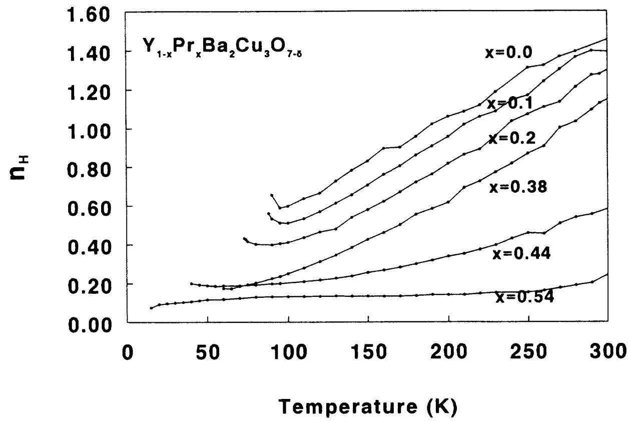

FIG. 3. Temperature dependence of the charge-carrier density in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ crystals with $x = 0.00$, 0.10, 0.20, 0.38, 0.44, and 0.54 at $T = 100$ K.

the calculated values of the carrier density. In Fig. 4, we show the Pr concentration dependence of the carrier number at 100 K. The carrier density for pure Y-Ba-Cu-O is about 0.6 carriers per unit cell at 100 K, which is very close to the published values for single-crystal samples.[10] The values of the carrier density at 100 K for most of the Pr concentrations of the single crystals are very close to the values of the polycrystalline samples.[5] The carrier density has a linear dependence on the Pr concentration. The relation between n_H and x at 100 K can be described by

$$n_H = 0.60 - 0.92x \ . \tag{4}$$

Since coefficient 0.92 is very close to 1, one tempting interpretation of Eq. (4) is that the Pr ion stays in a 4+ or very close to a 4+ valence state, differing from 3+ valence states of most of other rare earth in $RBa_2Cu_3O_{7-\delta}$. The extra electrons from Pr fill holes in the CuO_2 planes, hence reducing the mobile hole concentration and suppressing the superconductivity. Nevertheless this experiment alone cannot exclude hole localization resulting in the same reduction of conduction carrier

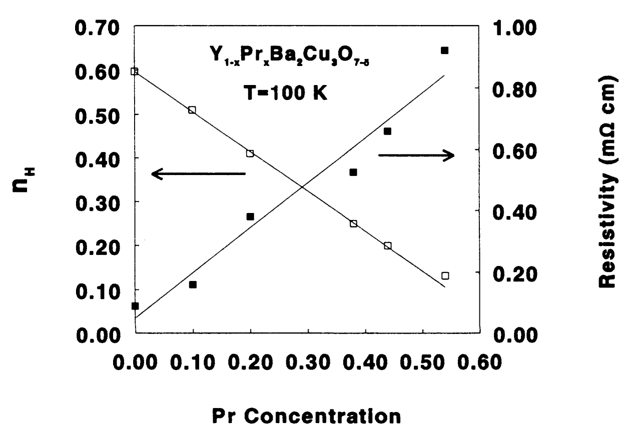

FIG. 4. Pr concentration dependence of the charge-carrier density (open square) and the resistivity (solid square) in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ at $T = 100$ K.

density [Eq. (4)]. Although absolute values of n_H are different from the assumption we made in a previous paper,[7] when our current data are incorporated into the relationship between the normalized upper critical-field slope and the normalized mobile hole density

$$[dH_{c2}/dT]_x[dH_{c2}/dT]_{x=0}=(n_x/n_0)^{\alpha} ,$$

one derives the same Pr concentration dependence of the normalized upper critical field as obtained in Ref. 7. This study shows that the substitution of Pr for Y in the system results in a decrease in the number of mobile charge carriers. The reduction of mobile holes could come either from hole filling or hole localization. If hole localization is the mechanism responsible for the reduction of mobile carrier number, one might expect the following: (1) Semiconducting behavior shows up in superconductive $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ in the low-temperature region (right above T_c); however, for single crystals with $x<0.5$ we observed a metalliclike behavior down to their T_c [Fig. 2(a)]. (2) Since variable-range hopping is a sign of localization, one might expect to observe a stronger temperature dependence of n_H in the variable-range hopping region; however, we observed a weak temperature dependence of n_H in the low-temperature region when $x>0.4$ (Fig. 3). (3) Negative magnetoresistance in the low Pr-doping region is another sign of localization; however, our normal-state magnetoresistance measurements at low temperatures for the $x=0.38$, 0.44, and 0.54 samples show a positive magnetoresistance. Although Fisher and co-workers[17] claimed variable-range hopping might be the dominant conduction mechanism in fully oxygenated $PrBa_2Cu_3O_{7-\delta}$ in the low-temperature region, it does not mean localization plays the dominant role in the suppression of superconductivity of the system. In short, even if localization exists in the system, it may only play a weak role in the reduction of T_c in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. One of the experiments that could possibly resolve the valence of Pr is inelastic neutron scattering. These experiments were carried out by Soderholm on a series of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ polycrystalline samples with $x=0.0$, 0.1, 0.4, and 1.0,[18] but the peaks were broad and weak, and difficult to interpret. It seems necessary to perform this experiment on high-quality large-sized single crystals in order to resolve the valence of the Pr ion in the system.

IV. CONCLUSION

Hall-effect measurements in Pr-doped Y-Ba-Cu-O have revealed that the increase in Pr concentration increases the magnitude of the Hall coefficient at a fixed temperature and reduces its strong temperature dependence, resulting in the reduction of the total number of conduction holes. The transport anomaly found in some of the 123 compounds[11] is not observed in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. Therefore, the anomaly is not a universal behavior in 123 compounds. Further experimental work is required to determine precisely the valence of the Pr ion in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.

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