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Normal-state Hall effect in $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ single crystals

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We have measured the normal-state Hall effect on single crystals of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ with the magnetic field perpendicular to the *ab* plane and the current in the *ab* plane. The Hall coefficient is positive for all crystals ($0 \leq x \leq 0.20$) over the entire temperature range of our measurement ($T_c \leq T \leq 300$ K). A strong temperature dependence of the Hall coefficient was also observed. We show that the Hall angle in the normal-state follows the relation $\cot \Theta_H = AT^2 + B$, which is in agreement with Anderson's prediction for the two-dimensional Luttinger liquid.

INTRODUCTION

It has been known that the Hall-effect measurement is a useful tool in determining the polarity and the density of the carriers which are responsible for the transport behavior in conventional metals and semimetals. However, in all classes of high-T_c oxide superconductors, the normal-state Hall coefficient shows an anomalous temperature dependence. The studies of the normal-state Hall effect in Co- and Ni-doped $YBa_2Cu_3O_{7-\delta}$ (YBCO) systems,[1] Zn-doped YBCO,[2] Pr-doped YBCO,[3,4] $La_{1.85}Sr_{0.15}Cu_{1-x}T_xO_{4-\delta}$ (T=Fe, Co, Ni, Zn, Ga) systems,[5] Tl-based oxides,[6] and the T'-phase $Nd_{2-x}Ce_xCuO_{4-\delta}$ system[7] all display a strong temperature dependence of the Hall coefficient, therefore leading to a strong temperature dependence of the carrier concentration. Among these experiments, various kinds of sample forms including ceramic materials, films, and single crystals were used, yet the observed behavior of the Hall coefficients was very similar. Because of this universal behavior, the anisotropy and the weak links between the grains were not considered to be the origin of the anomalous Hall coefficients. In addition, the temperature dependence of the carrier concentration is suppressed with increasing impurity composition for most of the doped oxide superconductors. The conventional Fermi-liquid single-band model seems inappropriate in describing these anomalies in the Hall-effect measurements. A possible multiple-band model[8] that assumes the temperature dependence of the scattering rates of holes and electrons are different was suggested to interpret the data. However, many parameters are needed in order to obtain a satisfactory fitting. Because of this, the result is not very convincing. In addition to the conventional way of interpreting these transport anomalies, a completely different approach was tried to describe the ground state of the high-T_c superconductors. Anderson has proposed a general scheme within a Luttinger-liquid theory of these two-dimensional quantum fluids[9] to correlate the longitudinal resistivity and Hall measurement. The fundamental postulate of his theory is that the intrinsic electronic degrees of freedom of spin and charge are separated. Two kinds of quasiparticlelike elementary excitations were then named. Spinons with spin and no charge actually form the Fermi surface, while holons carry the charge, but possess no spin. In the Anderson quasiparticle picture, the longitudinal conductivity $\sigma_{xx} \propto \tau_{\mathrm{tr}} \propto 1/T$, whereas the transverse (Hall) conductivity $\sigma_{xy} \propto \tau_{\mathrm{tr}}\tau_{\mathrm{sp}} \propto 1/T^3$. Here, $1/\tau_{\mathrm{tr}}$ and $1/\tau_{sp}$ are the transport and transverse relaxation rates, respectively. These results predict a τ^2 dependence of the expression for the Hall cotangent ($\cot \Theta_H \equiv \sigma_{xx}/\sigma_{xy}$) and an additional temperature-independent term that reflects the magnetic dopant scattering. The Anderson model had proven a great success in describing normal-state transport properties in various classes of high-T_c superconductors.

In this paper, the temperature dependence of normal-state longitudinal resistivity ρ_{xx} and Hall coefficient R_H will be presented in Fe-doped YBCO single crystals. We will investigate the effect of the replacement of Cu by magnetic ions of Fe on the normal-state transport properties of YBCO single crystals in detail, and test the applicability of the Anderson theory in describing the ground state of this system. The correlation of ρ_{xx} and R_H and the dependence on the impurity will also be discussed.

EXPERIMENTAL DETAILS

Although measurements of the normal-state Hall effect on polycrystal samples of some high-T_c oxides yield results which were found to be close to data taken on single crystals with $H \| c$ axis,[10] we limit our work to single crystals to avoid any unnecessary effects caused by the granularity in ceramic samples. In particular, this approach simplifies the longitudinal resistivity measurements which are usually complicated by weak links between grains and are confused by anisotropic effects. The crystals selected in this study were grown by a self-flux method.[11,12] The high quality of the single crystals was carefully identified by dc-magnetization experiments. A detailed characterization of the crystals has been provided previously.[13] The crystals used in this report are plate shaped with typical dimensions $2 \times 1 \times 0.04$ mm^3. All single crystals used in the measurements were annealed at 420 °C under flowing oxygen for a week just prior to the measurement. Based on experience we believe that all crystals are fully oxygenated. A standard five-probe dc technique was used to do the longitudinal resistivity and Hall-effect measurements in the same crystal. A typical contact resistance is less than 1 Ω. All of the transport measurements were

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carried out in the magnetic field of a Quantum Design superconducting quantum interference device (SQUID) magnetometer. A direct current of 5 mA was driven in the *ab* plane and the applied magnetic field up to ±5 T was applied along the *c* axis.

EXPERIMENTAL RESULTS AND DISCUSSION

The temperature dependences of the in-plane longitudinal resistivity ρ_{xx} for various iron compositions are shown in Fig. 1. All single crystals used in this experiment display a sharp resistive transition into the superconducting state. With zero applied field, the transition width δT_c is only 3 K for the high iron composition crystal reported in this paper. Combining the resistivity with the dc-magnetization data indicates that our crystals are of high quality and that the Fe distribution is homogeneous. The actual Fe content in the $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ crystal was determined by comparing the midpoint resistive transition temperature to published work on polycrystalline samples.[14,15] This method was shown to be reliable when compared to concentrations determined via scanning electron microscopy (SEM) energy dispersive x-ray (EDX) studies on other crystals.[13] The noteworthy feature in the resistivity data of Fig. 1 is the metallic behavior obtained in the normal state up to 300 K for all crystals. The resistivity is monotonically increased with increasing temperature. The normal-state resistivity can even extrapolate linearly to zero as T goes to zero for pure YBCO, while for the higher iron doping, there exists a finite but small residual resistivity when extrapolating to zero temperature. This residual resistivity tends to increase as the dopant content increases. In addition, the slope of the normal-state resistivity $d\rho_{xx}/dT$ was found to increase gradually as the iron content increases. This observation is similar to the result found in Zn-doped and in Pr-doped YBCO crystals.[2,4] The absence of a residual resistivity in the pure YBCO is one piece of evidence that suggests the failure of the Fermi liquid in the Anderson theory.[16] Moreover, the linearity of longitudinal resistivity extending to high temperature (300 K) is also an unusual behavior based on the Fermi-liquid picture. Our normal-state longitudinal resistivity measurement, including the linearity of ρ_{xx}, the appearance of residual resistivity, and the change of $d\rho_{xx}/dT$, provides strong support for the Anderson non-Fermi-liquid picture.[17] In this model the magnetic doping binds a spinon, which reduces T_c and is the origin of the residual resistance. It should be noted that not all of the high-T_c oxides display these features in their electrical transport properties. A different observation of a concave downward $\rho_{xx}(T)$ was found in the $YBa_2Cu_4O_{8-\delta}$ system.[18] Based on these data, Pickett and coauthors[19] do not eliminate the possibility of using the Fermi-liquid theory to describe these transport properties in high-T_c oxides. In order to clarify this argument, more experiments are needed on diverse systems of high-quality cuprate crystals.

In Fig. 2, we display a typical magnetic-field dependence of the Hall voltage at various temperatures for a single crystal of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$. As shown in this $x=0.04$ system, the Hall voltage is a linear function of the magnetic field in the normal state for a temperature up to 300 K. Therefore, the Hall coefficients (R_H) are derived from the slopes of these linear curves. The values of R_H are positive over the entire temperature range for all crystals. Generally speaking, R_H increases as the temperature decreases, then it starts to drop as the superconducting transition temperature is approached. The variation of the Hall density with temperature in the normal state which is derived from the Hall coefficient ($n_H=1/eR_H$) is shown in Fig. 3. Our measured Hall coefficient R_H is around 2×10^{-9} m^3/C at 10 K, which corresponds to a value of the Hall number equal to 0.5 holes per unit cell in the pure YBCO sample. This result is in reasonable agreement with previously published work.[20,21] Similar to the reports in other high-T_c oxide superconductors, the Hall density displays a distinctive temperature dependence over the entire temperature range. For low-Fe concentration crystals, we found that the temperature dependence of n_H is linear. The trend in Fig. 3 further indicates that the slope of dn_H/dT decreases as the iron composition increases. For a heavily doped system, the variation of n_H with temperature be-

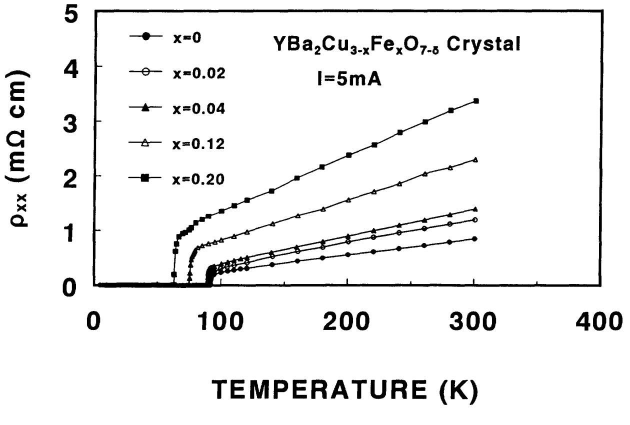

FIG. 1. Temperature dependence of the in-plane longitudinal resistivity in $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ single crystals under zero magnetic field.

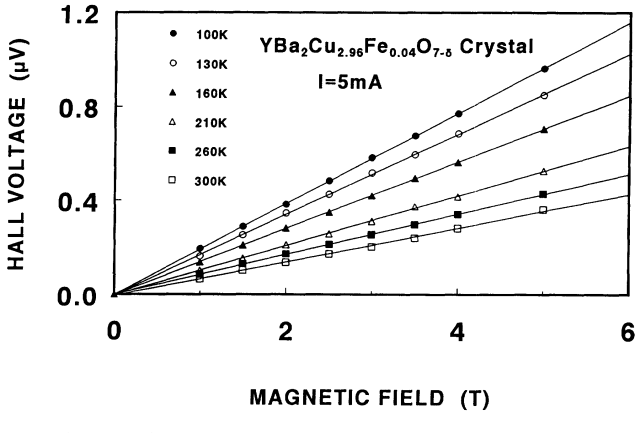

FIG. 2. Typical magnetic-field dependence of the Hall voltage at various representative temperatures for a $YBa_2Cu_{2.96}Fe_{0.04}O_{7-\delta}$ single crystal.

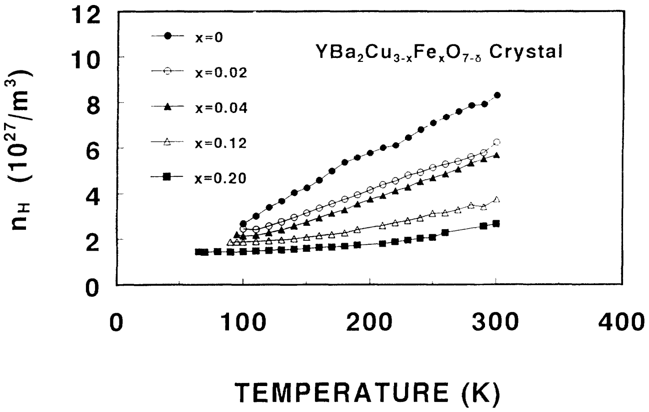

FIG. 3. Temperature dependence of the Hall density in various Fe-doped $YBa_2Cu_3O_{7-\delta}$ crystals.

comes less pronounced. If n_H is proportional to the actual carrier number n, it suggests that the carriers responsible for the transport property dramatically diminish with Fe doping. This result may reflect that the Fe substitution for Cu is primarily on the chain site,[1] which is also consistent with the Mössbauer studies done on $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ single crystals.[22] Nevertheless, the strong temperature dependence of the Hall density cannot be interpreted easily within the conventional Fermi-liquid one-band model. One possible mechanism which is often applied to interpret the strong temperature dependence of the Hall coefficient is magnetic skew scattering. Skew scattering can be characterized simply by the difference of the scattering probabilities in the transverse direction when the scattering potential includes an antisymmetric part. The strong interaction between conduction electrons and local moments provide an extra contribution (R_s) to the Hall coefficient. Because the magnitude of the local moments is strongly dependent on the magnetic field and the temperature, the magnetic Hall coefficient R_s is expected[23] to follow a similar functional dependence on H and T. It is possible to extend this model to the high-T_c oxides if the localized moments exist in the conducting plane. However, in our $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ system, it is very clear that the Hall voltage remains linear in H up to 5 T over the entire temperature range of $T > T_c$ (see Fig. 2). No symptom of saturation on V_T was shown even for the heavily doped system. We believe that within our experimental range of field and temperature, magnetic skew scattering does not make a significant contribution to the Hall coefficient. That is because the thermal energy is dominant over the Zeeman energy of the local spins.[24] That is, $g\mu_B H \ll K_B T$, where g is the g factor, μ_B is the Bohr magneton, and k_B is the Boltzmann constant.

In addition to those descriptions based on the conventional Fermi-liquid concepts, Anderson has demonstrated that the plotting of the Hall cotangent as a function of the temperature is a better way to describe the transport properties of highly correlated electronic systems. By separating the relaxation rates of the carrier between its motion normal to $1/\tau_{\rm tr}$ and parallel to $1/\tau_{\rm sp}$ the Fermi surface, the Anderson theory predicts that the Hall cotangent, $\cot\Theta_H$ can be expressed by

$$\cot\Theta_H = 1/\omega_c\tau_{\rm sp} = AT^2 + B \ . \tag{1}$$

The quantity ω_c is known as the cyclotron frequency. A is a constant, independent of the doping level and B is a constant proportional to the impurity doping. Furthermore, according to Anderson's picture, the constant A is inversely proportional to the bandwidth of the spin excitation (spinon) or the spin-exchange coupling. The Hall cotangent is a measure of the transverse relaxation rate $1/\tau_{\rm sp}$, which is mainly determined by the spinon-spinon scattering at the Fermi surface and should lead to a T^2 dependence. The value of B reflects the contribution from the magnetic doping. In Fig. 4, we display the temperature dependence of the Hall angle shown as $\cot\Theta_H$ vs T^2 for various iron concentrations. The error bars arise mainly from the estimation of the dimensions of the sample and the stability of the temperature. Within our experimental resolution, the slope of the curve is essentially independent for the iron composition. The average value of the slope A for all crystals used is $2.5\times10^{-2}/K^2$ at 5 T. The value is close to the value of $2.1\times10^{-2}/K^2$ at 7 T obtained by Rice *et al.*[25] for the YBCO-based system. In addition, the value of the extrapolation B as T approaches zero increases with impurity concentration. For the pure YBCO crystal, the value of B is close to zero. For the low composition ($x \leq 0.04$), the extrapolation is difficult to separate from the pure crystal due to our experimental resolution. However, for heavy doping ($x \geq 0.12$), the value of B is definitely larger than zero and increases with iron doping (x). Our data yield an estimate for B equal to 1600 x for $H = 5$ T, where "x" is the iron doping. Overall, our analysis is in good agreement with the Anderson theory. From the study of extended x-ray-absorption fine structure (EXAFS) in the Fe-doped system, the iron K near-edge spectra show that the Fe impurities exist mostly as 3+ ions.[26] Most of the trivalent Fe are generally agreed to substitute for Cu(1) in the chain site; therefore, it is not surprising to have a

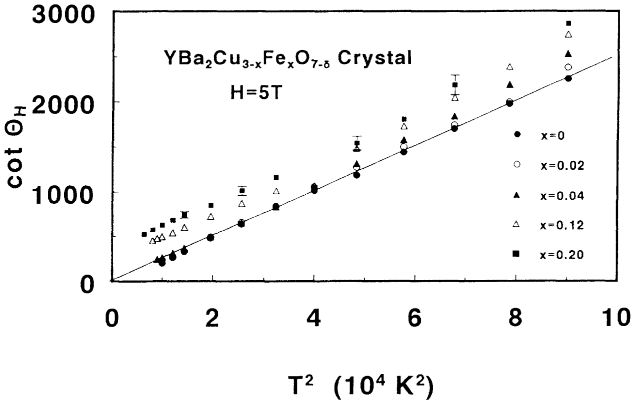

FIG. 4. Temperature dependence of the Hall cotangent at $H = 5$ T shown as $\cot\Theta_H$ vs T^2 for various Fe-doped $YBa_2Cu_3O_{7-\delta}$ crystals. The $\cot\Theta_H$ is calculated from $\rho_{xx}/(R_H \cdot H)$ obtained on the same crystals. The solid line is a linear fit for the $x = 0$ sample.

reduction in the hole number. Unfortunately, with our current experimental accuracy, it is difficult to tell the fraction of the change in the carrier concentration caused by introducing the iron dopant. However, we do not expect the Hall density at 300 K to decrease by a factor of 3 in the $x=0.2$ crystal by only replacing 20% of Cu(1), even assuming all substitutions are on the chain site. In addition, referring to the Mössbauer studies, although the Fe substitution for Cu is primarily on the chain site, there are still about 10% of Fe impurities substituting for Cu that occur in the plane sites.[22,27,28] Based on these arguments, the physical picture in our $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ system is more likely that the magnetic dopant iron forms a localization center in the Cu-O plane and reduces carrier mobility through this mechanism. However, there is discrepancy between our results and the Co-doping YBCO crystal,[29] since both Fe and Co are primarily doped into the chain site. They claim that the Anderson formula for the Hall angle Θ_H remains valid in the Co-doped YBCO crystal except the slope A decreases and the intercept B keeps constant as the Co dopant increases. Since there is no evidence that shows the high Co dopant will migrate into the Cu-O plane, that might cause the intercept B constant for the concentration range $(0<x<0.29)$ used in their report. The constant value of the slope observed in the Fe-doped YBCO crystal indicates that the bandwidths of the spinon does not change significantly as the concentration of the magnetic impurities (Fe) increases in our concentration range. On the contrary, the change of slope in the Co-doped system might indicate that the valence of Co is somewhat different from the values of Fe in the YBCO system. Due to the Fe and Co dopants being mainly in the chain site, in order to have a better understanding of the Anderson model in those systems, it is important to understand the coupling between the impurities and the Cu-O plane, the substitution rates of Fe and Co in the plane site, in particular, for the high-doped situation, and the valence state of Fe and Co ions in the YBCO system. More studies should be performed.

CONCLUSION

Normal-state longitudinal resistivity and Hall-effect measurements were performed on Fe-doped YBCO single crystals. No residual resistivity was observed in the pure YBCO system, while an increasing residual resistivity was obtained by introducing the magnetic dopant. The appearance of magnetic doping also causes a change in the slope of the longitudinal resistivity. These observations are consistent with Anderson's argument of bound spinons. In all crystals of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ $(0\leq x\leq 0.2)$, R_H is found to be positive over the temperature range from T_c to 300 K. The observed Hall coefficient decreases as the temperature increases. The replacement of Cu by magnetic Fe ions reduces the transition temperature and suppresses the variation of Hall density. With increasing iron composition, the Hall coefficient increases at a fixed temperature. No symptom of saturation of the Hall voltage was observed for a magnetic field up to 5 T, which demonstrates that magnetic skew scattering is not the mechanism responsible for the anomalous temperature dependence of the normal-state Hall coefficient. The linearity of $\cot\Theta_H$ vs T^2 in our experiment gives strong support to Anderson's theory. This model provides a more natural method of describing the anomalous normal-state Hall effect and simultaneously accounting for the effect of the impurity moments. Because the value of A in the $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ system is independent of the concentration of the magnetic dopant, we conclude that the impurity moment has only a minor effect on the exchange coupling of the spinons.

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