Temperature Dependence of the Hall Angle in Single-Crystal $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$

A. Carrington, A. P. Mackenzie, C. T. Lin, and J. R. Cooper
Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge, England CB3 0HE
(Received 18 February 1992; revised manuscript received 9 September 1992)

We report the measurements of the Hall coefficient (R_H) and a-b-plane resistivity $\rho(T)$ of cobalt-doped $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$ single crystals ($0 \leq x \leq 0.096$) from 20 to 400 K. Co doping gives rise to an unusual downward curvature in $\rho(T)$ while the inverse Hall coefficient $[1/R_H(T)]$ also becomes nonlinear. Despite this, Anderson's formula for the Hall angle θ_H, namely, $\cot\theta_H = AT^2 + B$ continues to remain valid. In contrast to Zn, doping with Co decreases A while B remains constant. A simple model involving a square Fermi surface with rounded corners that could also account for the $AT^2 + B$ law is proposed.

PACS numbers: 74.70.Vy, 72.10.Di, 72.15.Gd

The normal-state properties of the high-temperature cuprate superconductors are thought to be anomalous. In pure $YBa_2Cu_3O_7$, for example, both the resistivity (ρ) and the inverse Hall coefficient ($1/R_H$) vary linearly with temperature. Similar temperature dependences are also observed in many other cuprate superconductors [1]. Anderson has recently proposed [2] that these effects can be understood if the transport properties are governed by two separate scattering times. In his picture one transport lifetime τ_{tr} determines the resistivity, whereas R_H depends on both τ_{tr} and a separate transverse scattering lifetime τ_H. The relaxation rate τ_H^{-1} is governed mainly by spinon-spinon interactions and has the characteristic T^2 dependence expected for fermion-fermion scattering. The Hall angle ($\tan\theta_H = R_H B/\rho$, where B is the magnetic field) is only a function of τ_H and should therefore have a simpler temperature dependence than R_H. In the Anderson picture it is given by

$$\cot\theta_H = AT^2 + B . \quad (1)$$

The parameter A sets the energy scale for the spinon-spinon scattering, and B is a measure of the in-plane impurity scattering rate. For the case of in-plane zinc dopants in crystals of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$, the above law was found to fit the data well [3]. In these samples, however, ρ and $1/R_H$ both vary approximately linearly with T, and so it is conceivable that the agreement with Eq. (1) is merely a reflection of these two well-documented temperature dependences. In this Letter we consider the effects of out-of-plane cobalt substitution in crystals of $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$. Although this substitution causes both $\rho(T)$ and $1/R_H(T)$ to become nonlinear, $\cot\theta_H$ still obeys a T^2 law over a wide temperature range. Within the above picture this is strong evidence for the existence of a separate scattering lifetime τ_H with the temperature dependence given by Eq. (1).

However, we show here that a band model involving a square Fermi surface with rounded corners, for example, that calculated by Pickett *et al.* [4] for the CuO_2 planes of $YBa_2Cu_3O_{7-\delta}$, could also account for the above law in a rather straightforward way. So the applicability of Eq. (1) to high-T_c oxides is not decisive evidence in favor of Anderson's picture.

The preparation of the single crystals of $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$ is described elsewhere [5]. Two series of crystals were used in the present work. Batches I and II were grown in different crucibles (Al_2O_3 or SnO_2) and given different annealing treatments in flowing O_2 (1 week at 535 °C or 1 week at 420 °C, respectively). All the crystals were subjected to electron probe microanalysis (EPMA) in order to determine the cation stoichiometry and oxygen content [6]. Batch-II crystals were essentially fully oxygenated, whereas, on average, crystals from batch I had a relative oxygen deficiency of 0.1 per formula unit. For both batches, the oxygen content increases with increasing cobalt, in agreement with findings for sintered samples [7]. Batch-I crystals contained approximately 0.5 at% of Al, but no Sn was detected in the batch-II crystals down to detection limits estimated at 200 ppm. Detailed EPMA measurements made at many points on the surface indicated Co inhomogeneity in some samples. Working at 30 kV, the average depth of production of Co $K\alpha$ x rays is approximately 1–2 μm, so it is not possible to check the entire volume of a crystal. However, care was also taken to check for inhomogeneity by means of magnetic and electrical measurements. The superconducting transition was checked for width and structure using ac susceptibility (ACS) with a 1-G field applied along the crystalline c axis. Crystals showing no signs of double transitions (10%–90% transition widths typically less than 5 K) were then cut into rectangular bar samples (typical dimensions 0.6 mm $\times$0.15 mm$\times$8 μm). The resistivity was measured using a standard four-terminal method with current flow in the a-b plane. Two current contacts covering the ends of the crystal and four voltage contacts to the sides were made using Dupont 6838 silver epoxy. After a heat treatment of less than 30 min at 470 °C in an oxygen atmosphere the contact resistance was typically around 1 Ω. The measurements were repeated for several different combinations of the voltage leads to check for any signs of inhomogeneity affecting the normal-state resistivity.

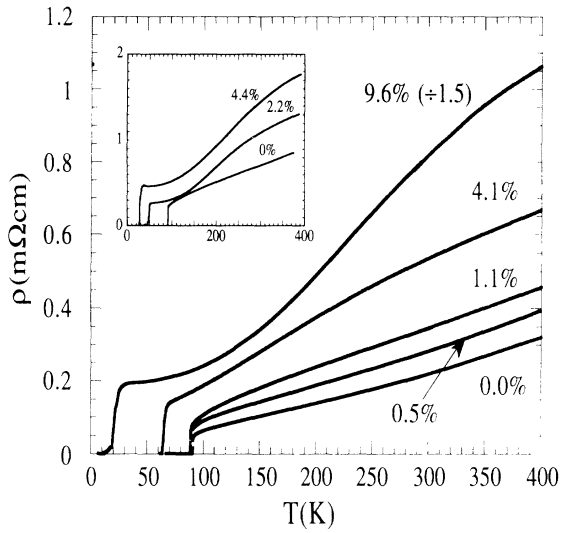

FIG. 1. In-plane resistivity vs temperature for the second batch of $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$ crystals with $0 \leq x \leq 0.096$. Inset: In-plane resistivity for the higher-resistivity batch-I Co-doped crystals, with $x = 0.0$, 0.022, and 0.044.

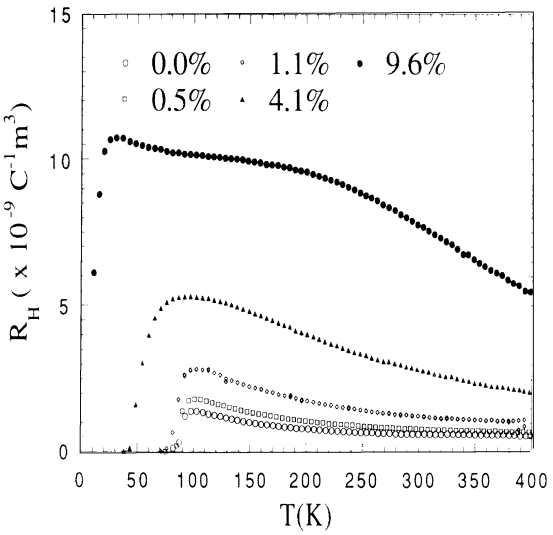

FIG. 2. In-plane Hall coefficient (R_H) vs temperature for the crystals whose resistivities are shown in the main part of Fig. 1. R_H for the Co-doped crystals does not follow the $1/T$ dependence shown by the undoped sample.

Several crystals from each growth batch were studied in this way, and only those which showed no signs of inhomogeneity in either the EPMA, ACS, or resistivity were used for Hall effect measurements. R_H was measured in a 7-T field applied perpendicular to the a-b plane.

Figure 1 shows that for both batches of crystals, $\rho(T)$ develops pronounced curvature which extends to 400 K. For crystals with $T_c < 60$ K, $\rho(T)$ apparently tends to a constant value before dropping to zero at T_c. There is an indication that this may be due to localization effects in that a slight upturn in ρ is observed above T_c for the largest values of x. The form of $\rho(T)$ for our single-crystal samples is similar to that found for sintered samples of the same Co concentration that have been annealed in the same way. The major difference is that the latter have a large temperature-independent component to the resistivity. This is an important point and may well mean that Hall and magnetoconductivity measurements on sintered samples are influenced by the c-axis resistivity or grain boundary effects. The relatively low residual resistivities that we observe in our Co-doped crystals are consistent with cobalt being an out-of-plane dopant rather than an in-plane one. There is other evidence for this from neutron diffraction studies [7,8], thermogravimetric analysis [7], and x-ray absorption measurements [9].

Values of $\rho(300)$ for batch-II crystals with $x = 0$ are 220 ± 20 $\mu\Omega$ cm, in good agreement with data in the literature for twinned crystals. Batch-I crystals have larger resistivities and Hall coefficients than batch-II crystals. Curiously, for the undoped crystals, the Hall angle is very similar for both batches. The reason for this is not clear but a possible explanation is that (in addition to the slight oxygen deficiency of batch I) the Al impurities in batch-I crystals are not uniformly distributed and thus block conduction in certain regions. In this case the geometric thickness of the crystal will be greater to the electrical one.

The temperature dependences of R_H for batch-II crystals are shown in Fig. 2. While the undoped samples show a $1/T$ dependence, in agreement with the literature, the doped crystals show deviations from this behavior. The data are replotted as $\cot\theta_H$ [which is equivalent to the ratio of the resistivity (ρ_{xx}) to the Hall resistivity (ρ_{xy}) or the corresponding conductivity ratio σ_{xx}/σ_{xy}] versus T^2 in Fig. 3. For the undoped crystals from batch II [as well as an $YBa_2(Cu_{0.98}Zn_{0.02})_3O_{6.9}$ crystal with $\rho(300)$ of 400 $\mu\Omega$ cm and T_c of 60 K] there are small deviations from T^2 above 260 K which are similar to those in the data of Chien, Wang, and Ong [3]. With increased Co content (and also for the undoped crystals from batch I) good T^2 behavior is obtained up to the highest temperatures measured (400 K). One possible reason for these deviations is small changes in carrier concentration caused by the onset of oxygen disorder in the chains. We note that the small effect of (1-2)% Co doping (with up to 6% of the chain Cu sites substituted by Co) on $\cot\theta_H$ suggests that, *in our crystals*, there are only minor conductivity contributions from the Cu(1) chains. Below 120 K upward deviations from the T^2 law for the higher Co contents in Fig. 3 may be due to weak localization effects. For Zn-doped samples, B in Eq. (1) increases linearly with x but the parameter A is essentially unchanged [3], consistent with the interpretation that Zn is an in-plane scatterer and pair breaker [10] which has little effect on the carrier concentration. Co is known to occupy the Cu chain sites of the structure [8,9], and is

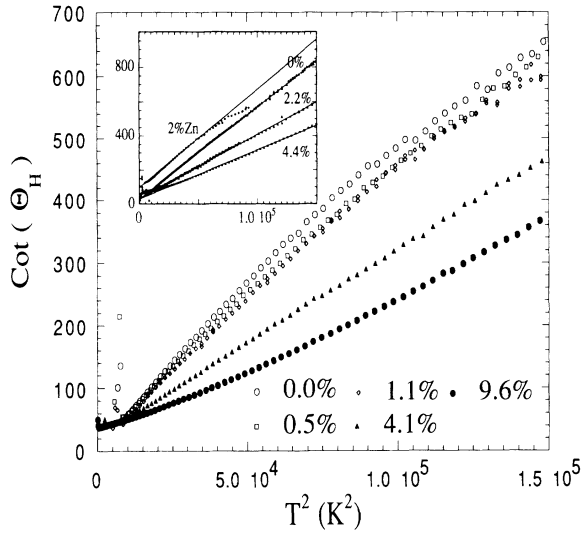

FIG. 3. $\cot\theta_H(\equiv\rho/R_HB$, where the magnetic field B is 7 T) plotted against T^2 for the batch-II crystals. Inset: $\cot\theta_H$ for the batch-I crystals. Data for a 2%-Zn-doped crystal are also shown. Note the similarity of the $\cot\theta_H$ data for the undoped sample in both batches of crystals.

thought to change the critical temperature by changing the hole concentration [11]. The difference between the effect of Co and Zn doping is perhaps shown most clearly by thermoelectric power measurements [12]. The results here show that doping with Co decreases A (Fig. 3) while leaving the residual scattering parameter B unchanged.

Within Anderson's approach the results in Fig. 3 imply that cobalt doping up to relatively high levels substantially modifies the T dependence of τ_{tr} but does not alter that of τ_H. We have no definite interpretation for the unusual T dependence of τ_{tr} in the Co-doped crystals. A similar downward curvature in $\rho(T)$ of oxygen-depleted $YBa_2Cu_3O_{7-\delta}$ has been ascribed to superconducting fluctuations [13]. At high temperatures the anomalous Maki-Thompson (MT) fluctuation term should be dominant and in a normal metal would alter τ_{tr} because the fluctuations alter the scattering rate of the normal carriers. Using the 2D MT formula [14] with reasonable parameter values [15] we find that fluctuations can increase τ_{tr} by a factor of 2 in the region 100–150 K. However, the overall temperature dependence of ρ cannot be fitted by this formula. Another very promising possibility is that τ_{tr} is affected by the development of a gap in the spin excitation spectrum at low energies, such as that detected by neutron scattering studies of oxygen-depleted $YBa_2Cu_3O_{7-\delta}$ [16].

Finally we point out that the unusual T dependence of R_H and the T^2 dependence of $\cot\theta_H$ might also be understood in terms of a 2D Fermi surface (FS) with relatively large flat regions and smaller rounded corners. Within standard Boltzmann transport theory Ong [17] has given a simple expression for σ_{xy} for a 2D Fermi surface of arbitrary shape, namely, $\sigma_{xy}=(1/d)(2e^2/h)\phi/\phi_0$, where e is

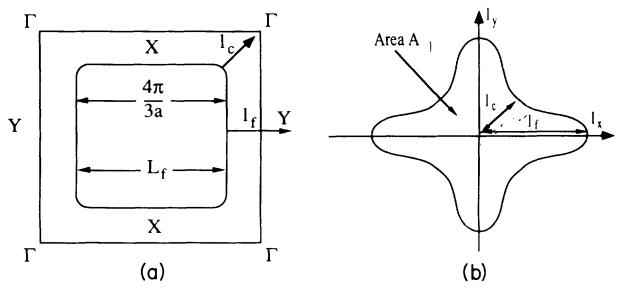

FIG. 4. (a) Idealized sketch of CuO_2-plane Fermi surface of $YBa_2Cu_3O_{7-\delta}$ as calculated by Pickett *et al.* [4]. The mean free paths are denoted by l_c and l_f on the curved and flat parts, respectively. (b) Corresponding area in the mean free path plane for using Ong's method to calculate σ_{xy}.

the electronic charge, h is Planck's constant, d is the interplanar spacing (in this case $c/2=5.85$ Å), ϕ_0 is the flux quantum, and $\phi=BA_l$ with B the magnetic field. A_l is the area in the mean free plane (l_x,l_y) generated as a carrier traces out the 2D Fermi surface in $\mathbf{k}$ space. With the usual approximation that $\boldsymbol{l}\|\mathbf{v}_k$ the Fermi velocity, and assuming that the flat parts of the FS in Fig. 4(a) have $|\boldsymbol{l}|=l_f$ and the curved parts $|\boldsymbol{l}|=l_c$, it follows that A_l is approximately proportional to l_fl_c [Fig. 4(b)]. Provided the large flat parts (of length L_f) dominate the conductivity then $\sigma_{xx}=(2e^2/d\pi h)l_fL_f$, and so $\cot\theta_H\propto L_f/l_c$. Thus the AT^2+B behavior arises from particle-particle scattering plus a residual T-independent term (B) on the curved parts of the FS. The unusual T dependence of R_H arises because l_c and l_f have different dependences.

Estimates of the values l_c and l_f can be made from our data as follows. A_l is not exactly proportional to l_fl_c, because the proportionality factor depends on the ratio l_c/l_f and on how $\boldsymbol{l}$ changes between the flat and curved regions of Fig. 4(a), which in turn depend on details of the scattering mechanism and band structure. Given the different T dependences of l_c and l_f, one would expect there to be a temperature at which $l_c=l_f$ and thus $A_l=\pi l_fl_c$. Taking $L_f\approx 4\pi/3a$ [4], where $a=3.8$ Å, it follows that (in a measurement field of 7 T)

$$l_c(\text{Å})=6600/\cot\theta_H \qquad (2)$$

at this temperature. Extrapolating our ρ and $\cot\theta_H$ data for the undoped crystal from batch II leads to $l_c=l_f\approx 6$ Å at approximately 450 K, giving the physically reasonable estimates of $l_c\approx 120$ Å and $l_f\approx 30$ Å at 100 K. We note that since A_l/l_cl_f has a weak dependence on the l_c/l_f ratio (in the extreme cases $l_c\gg l_f$ or $l_f\gg l_c$, $A_l\approx\sqrt{2}\pi\times l_fl_c$), this model predicts deviations of $\cot\theta_H$ from a perfect T^2 law, in addition to the two sources mentioned above.

In this picture Zn doping introduces an extra T-independent scattering mechanism which makes B increase linearly with x. Co doping introduces no extra residual scattering but reduces $\cot\theta_H$ via its effect on the hole concentration. From our data it appears that for Co

doping, L_f/l_c (300 K) decreases by approximately a factor of 2.5 as T_c is reduced to 20 K, while $L_f l_f$(300 K) falls by a factor 6. Similar changes in $\cot\theta_H$ with T_c are evident from measurements on oxygen-depleted $YBa_2Cu_3O_{7-\delta}$ films [18]. It is probable that these changes are at least in part caused by a reduction in L_f, and perhaps this implies that flat regions of the FS are favorable for superconductivity. Such a situation occurs for several theoretical models, in particular the nearly nested Fermi liquid [19], the "Van Hove scenario" [20], and some spin fluctuation models [21]. In a full treatment the dependence of the scattering rates on the momentum transfer **q** should also be considered.

In conclusion, the AT^2+B dependence of $\cot\theta_H$ is preserved in a material in which both ρ and $1/R_H$ are nonlinear with T. This can be taken as evidence for the existence of separate Hall and transport scattering rates in $YBa_2Cu_3O_{7-\delta}$ with $1/\tau_H$ obeying a T^2 law as proposed by Anderson. However, it may also be possible to understand this behavior within a more standard Fermi surface picture, and we have given one concrete numerical example of such an interpretation.

We are grateful to L. Forro, S. D. Hughes, W. Y. Liang, J. W. Loram, A. Schofield, and J. M. Wheatley for several useful discussions.

[1] N. P. Ong, in *Physical Properties of High Temperature Superconductors II,* edited by D. M. Ginsberg (World Scientific, Singapore, 1990).
[2] P. W. Anderson, Phys. Rev. Lett. **67**, 2992 (1991).
[3] T. R. Chien, Z. Z. Wang, and N. P. Ong, Phys. Rev. Lett. **67**, 2088 (1991).
[4] W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989); W. E. Pickett, H. Krakauer, R. E. Cohen, and D. J. Singh, Science **255**, 46 (1992).
[5] C. T. Lin, S. X. Li, W. Zhou, A. P. Mackenzie, and W. Y. Liang, Physica (Amsterdam) **176C**, 285 (1991).
[6] A. P. Mackenzie, Physica (Amsterdam) **178C**, 365 (1991).
[7] J. M. Tarascon, P. Barboux, P. F. Micelli, L. H. Greene, G. W. Hull, M. Eibschute, and S. A. Sunshine, Phys. Rev. B **37**, 7458 (1988).
[8] P. Zolliker *et al.*, Phys. Rev. B **38**, 6575 (1988).
[9] C. Y. Yang, A. R. Moodenbaugh, Y. L. Wang, Xu. Youwen, S. M. Heald, D. O. Welch, M. Suenaga, D. A. Fischer, and J. E. Penner-Hahn, Phys. Rev. B **42**, 2231 (1990).
[10] J. W. Loram, K. A. Mirza, and P. F. Freeman, Physica (Amsterdam) **171C**, 243 (1990).
[11] J. Clayhold, S. Hagen, Z. Z. Wang, N. P. Ong, J. M. Tarascon, and P. Barboux, Phys. Rev. B **39**, 777 (1989).
[12] S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B (to be published).
[13] J. R. Cooper, S. D. Obertelli, A. Carrington, and J. W. Loram, Phys. Rev. B **44**, 12086 (1991).
[14] K. Maki and R. S. Thompson, Phys. Rev. B **39**, 2767 (1989).
[15] The parameters used in the Maki-Thompson formula were $\delta=0.05$, $T_c=50$ K, $d=5.85$ Å, where δ is the pair-breaking parameter and d is the interplanar spacing.
[16] J. Rossat-Mignod, L. P. Regnault, C. Vettier, P. Bourges, P. Burlet, J. Bossy, J. Y. Henry, and G. Lapertot, Physica (Amsterdam) **185C**, 86 (1991), and references therein.
[17] N. P. Ong, Phys. Rev. B **43**, 193 (1991).
[18] A. Carrington, D. Walker, A. P. Mackenzie, and J. R. Cooper (unpublished).
[19] A. Virosztek and J. Ruvalds, Phys. Rev. B **43**, 5498 (1991).
[20] P. C. Pattnaik, C. L. Kane, D. M. Newns, and C. C. Tsuei, Phys. Rev. B **45**, 5714 (1992).
[21] D. Pines, Physica (Amsterdam) **185C**, 120 (1991).