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Strongly anisotropic electrical properties of single-crystal $YBa_2Cu_3O_{7-x}$

T. Penney, S. von Molnár, D. Kaiser, F. Holtzberg, and A. W. Kleinsasser
IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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Crystals of orthorhombic, superconducting $YBa_2Cu_3O_{7-x}$ have been prepared. They are twinned in the nearly tetragonal *ab* plane. The resistivity and Hall effect have been measured in the normal state in the *ab* plane, the highly conducting plane of the Cu-O layers. We find that the resistivity in the *ab* plane, measured with currents exclusively in the plane, is strictly linear in temperature from room temperature down to the fluctuation regime near the superconducting transition. This result confirms previous less direct measurements in which the currents flowed in the much more resistive *c* direction as well. We find the Hall constant for the magnetic field parallel to *c* and the currents in the *ab* plane, to be *p* type and inversely proportional to temperature. This latter behavior is extremely unusual and unexplained, but similar to that found in polycrystalline $YBa_2Cu_3O_{7-x}$ material. It is in contrast to our previous result for the magnetic field in the *ab* plane. In that case, the Hall constant is *n* type and nearly temperature independent. Both the Hall effect and the resistivity demonstrate the extremely anisotropic nature of this system.

The electrical resistivity of the orthorhombic high-temperature superconductor $YBa_2Cu_3O_{7-x}$ in the normal state has been shown to be extremely anisotropic.[1-3] Our previous results[1] are shown in Fig. 1. The resistivity in the *c* direction, perpendicular to the Cu-O planes, was found to increase with decreasing temperature above the superconducting transition, indicating incipient localization in that direction. The derived *ab*-plane resistivity was found to be linear in T, and about two orders of magnitude smaller than in the *c* direction.

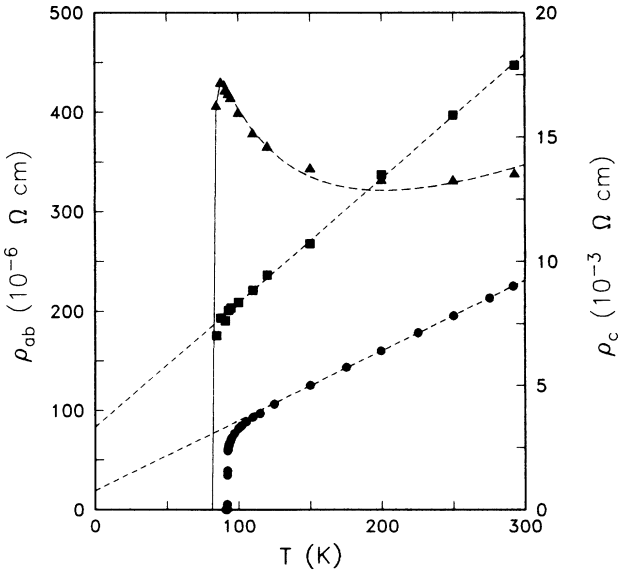

FIG. 1. Resistivity in the *c* direction (▲, scale right) showing incipient localization and in a twinned *ab* direction (■, scale left) both from Ref. 1. The contacts were in the plane containing *c* and *ab*. The dot-dashed curve through the ρ_c data is a fit to $A/T+BT$. Also shown is the new resistivity for a twinned *ab* direction (●, scale left). The contacts were in the *ab* plane. The straight dashed lines are fits showing the linear temperature dependence.

The Hall constant was measured previously for conduction in a plane containing *c* and the twinned *ab* direction, with the magnetic field perpendicular to the *c* direction.[1] The Hall constant was found to be *n* type and nearly temperature independent, as in a metal. This behavior was in sharp contrast to that found in polycrystalline materials, in which the Hall constant was *p* type and proportional to $1/T$, a very unusual temperature dependence.[4-7]

The purpose of this work is to determine directly the resistivity in the *ab* plane and measure the Hall effect in the *ab* plane with the magnetic field parallel to *c*. We find the Hall constant is *p* type and proportional to $1/T$, as found for the polycrystalline samples. The occurrence of this unusual result in a crystal shows that it is an intrinsic result. The resistivity and Hall effect show qualitatively different behavior for currents in the Cu-O planes or perpendicular to them. These strong anisotropies and unusual temperature dependences are fundamental to understanding these high-temperature superconductors.

In a related work,[8] it was found that the specific heat of crystals exhibits a linear term γ even below T_c. This term, which has also been seen in polycrystalline materials, is completely unexpected, if there is a superconducting energy gap. It has been argued,[8] that this γ is electronic in origin and may be related to states at the Fermi energy either localized or extended.

The details of crystal growth were given elsewhere.[9-11] Crystals were grown either as flat plates or as rectangular parallelepipeds. The crystals were grown in a restricted air flow in order to maintain low solution temperatures and then post-annealed in flowing oxygen at 420°C for 30 h. The transition temperature was 92.0 K with a width of 0.3 K. Polarized light reveals {110} twin planes with ⟨110⟩ directions. The crystal used for this study was of uniform 40-μm thickness but somewhat irregular in shape in the *ab* plane, about 700×900 μm^2. Low-temperature-

processed contacts for these measurements were made by bonding gold wires to annealed gold pads.[12] The large area evaporated pads were about 200×300 μm each. For the purposes of the Montgomery[13] anisotropic resistivity calculation, we have assumed an effective sample size of 560×430 μm. The corners of this effective sample with zero contact size are taken as the centers of the finite pads on the actual sample. The Hall voltage was measured at 1 T and was linear in magnetic field.

In our previous work, four electrical contacts were placed on the corners of an *ab*-*c* face of the crystal where *ab* indicates one of the twinned directions. The four-probe resistances, R_1 and R_2, were measured with the current passing through adjacent contacts aligned either perpendicular or parallel to *c*. If the components of the resistivity tensor ρ_a and ρ_b are the same, and denoted ρ_{ab}, the components ρ_c and ρ_{ab} may be calculated[13] from R_1 and R_2 (which are mixtures of ρ_{ab} and ρ_c). Previously, we found that R_1 was not linear in T, but the calculated ρ_{ab} was linear in T. In the present work, we measure the resistivity in the *ab* plane directly without the interference from the *c* direction.

The new measurement of the *ab*-plane resistivity is shown in Fig. 1 together with the previous results from Ref. 1. The new results directly show a linear T dependence for the resistivity in the *ab* plane. The new results show a smaller *ab* plane resistivity and higher transition temperature due to improved annealing[11] and contact processing.[12] The previous results showed that the resistivity in the *c* direction ρ_c had an upturn above T_c, indicative of incipient localization.

The unusual behavior shown by the transport and specific heat, as well as the large value for T_c have spawned a number of exotic theories. An idea of the vastly different points of view can be obtained from the review by Rice.[14] Below, we briefly describe the resonating valence bond (RVB) models of Anderson and co-workers[15,16] and Kivelson and co-workers[17,18] and their possible application to our results. In the RVB at half filling, there is one electron per site which, with a neighbor, forms a spin-zero valence bond (boson). At less than half filling, the charge carriers are holes, i.e., positive spinless bosons. In addition, there are neutral spin-$\frac{1}{2}$ fermions which are left when an electron is unbonded. In the long-range RVB model,[15] these fermions are gapless and will produce a linear term γ in the specific heat, even below T_c, as observed. In short-range RVB models,[17] the fermions have a gap, but bosonic excitations[18] may produce the γ term.

In the RVB, the bosons and fermions are confined to the Cu-O planes. Conduction in the plane is limited by the scattering of the bosons from the fermions. For gapless RVB,[16] only the fermions within T/T_F will scatter, thus the resistivity is linear in T/T_F even to high temperature, since T_F is an electronic scale. Conduction between planes is only by the tunneling of electrons. Electrons are produced by the scattering of bosons and fermions, so the conduction is linear in T/T_F and ρ_c follows $1/T$.

Our *c*-axis resistivity data can be fit to $\rho_c=1.3/T+(3.2\times10^{-5})T$ which is the dotted line in Fig. 1. The data could also be fit to other forms, such as a linear term plus an exponential. It has been proposed[16] that the true behavior is $1/T$ and that the T term is unavoidable contamination from the one-hundred-times lower *ab* plane resistance and is seen due to sample defects. The recent work of Hagen *et al.*[2] is in general agreement with ours. Their *c*-axis resistivities for several samples are fit to $1/T$ and T terms with slightly different parameters. Their calculated *ab* plane resistivities are linear in T and similar in magnitude to our new results. The work of Buravov *et al.*[3] raises an interesting point. Their sample with the lowest resistivity is similar to ours and that in Ref. 2. However, samples with larger *ab* plane resistivities show larger upturns above T_c. They conclude that this is an extrinsic effect, probably due to some inhomogeneity.

The Hall data are shown in Fig. 2. For the magnetic field H in the *ab* plane, the Hall constant, R_H, is electronlike and nearly temperature independent as reported in Ref. 1. In sharp contrast, our new results for H perpendicular to the *ab* plane, reveal a holelike Hall constant with a $1/T$ temperature dependence. The inverse of the Hall constant, normalized to the formula volume is given in Fig. 2. The strange temperature dependence is not understood, but was previously found[4-7] in polycrystalline samples of $YBa_2Cu_3O_{7-x}$. The signs of the Hall effect are consistent with all RVB models since conduction in the plane is by positive holes in the boson band and conduction between planes is by electron tunneling. Also in agreement with the observation of holes, Emery[19] has proposed a Hubbard model, in which the carriers are holes in

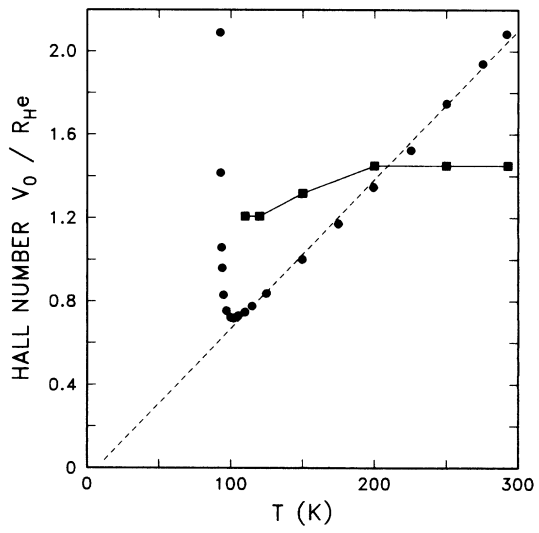

FIG. 2. Hall number, that is, the inverse Hall constant $1/R_{He}$ normalized to the formula unit volume, $V_0=175$ Å^3. The squares show the nearly temperature independent *n*-type Hall number for the magnetic field H in the *ab* plane, from Ref. 1. The solid line is a guide to the eye. The dots show the *p*-type Hall number for the new sample with H perpendicular to the *ab* plane. The solid line is a linear fit to the data above T_c showing a very small intercept, that is R_H is almost purely $1/T$. Near T_c, the Hall voltage tends to zero so the Hall number diverges. In simple metals, the Hall number gives the approximate carrier concentration per formula unit if only holes or electrons conduct.

the O(2*p*) states. The superconducting pairing is mediated by exchange coupling to the Cu spins. The signs, and rough order of magnitude, of the Hall data are also consistent with the calculation, by Allen, Pickett, and Krakauer,[20] of an anisotropic local density functional band structure. However, there is no apparent origin for the temperature dependence in any of these models.

The $1/T$ dependence of the Hall constant, observed for H perpendicular to the *ab* plane (and in polycrystalline material) is very unusual. For a simple metal, the Hall constant is temperature independent and approximately $R_H = 1/ne$. A temperature-dependent Hall constant may indicate the presence of electron and hole bands, with the temperature dependence coming from different hole and electron mobilities. For two bands, the system is underdetermined, and a unique solution is not possible. An interesting solution has been suggested by Davidson, Palevski, Brady, and Santhanam.[21] A $1/T$ Hall constant will result for two bands under very special conditions. First, $n = p$ for all temperatures. Second, the hole and electron mobilities have the $1/T$ dependence expected for a metal, and exactly the same value to order $1/T$. The mobilities must, however, differ slightly in value in the next order, i.e., $\mu_{p,n} = C(1 \pm D/T)T$. These assumptions lead to $R_H e = 2D/pT$. Such extremely strict conditions, if true, indicate an amazing symmetry between the holes and electrons.

Cheong *et al.*[5] and Forro, Petravic, and Leontic[7] have noted that the $1/T$ dependence was observed in the pseudo-one-dimensional organic conductor tetrathiafulvalene-tetracyanoquinodimethane.[22] This behavior was studied for tetrathiafulvalene-tetracyanoquinodimethane and hexamethylenetetraselenafulvalene-tetracyanoquinodimethane by Cooper and co-workers[22,23] and Weger.[24] Their explanation was based on the existence of two different chains (donor and acceptor). An electron hops between chains in time $\tau_\perp$ and scatters along a chain in time, τ_v. At low temperature, $\tau_\perp$ is the shorter and a coherent state of the two chains results. This state is a semimetal with a very small number of holes and electrons which results in a very large Hall constant. At room temperature, τ_v is the shorter. Scattering on the chain occurs before the coherent state can be formed. The result is a single metallic band with the Hall number of order unity. This change in behavior from a coherent semimetal with a small number of carriers to a diffusive metal with a large number occurs smoothly and qualitatively explains the observed $1/T$ temperature dependence of the Hall constant. This mechanism might apply in our case with the chains and planes playing the role of the two chains in the original case. It does seem unlikely, however, that a model based on a change from one type of behavior to another would give such an accurate $1/T$ dependence as we observe.

The $1/T$ Hall constant has been seen in all of our polycrystalline $YBa_2Cu_3O_{7-x}$ samples, prepared in a variety of ways.[4] Since we now know that the *ab* plane is vastly more conducting than the *c* axis, it is reasonable that the *ab*-plane Hall constant we report here should dominate the polycrystalline behavior, rather than the temperature-independent *n* type one observed in the *ab*-*c* plane. Furthermore, it has been found[25] that the polycrystals have a tendency to crack upon cooling, leaving the *ab* plates connected on their edges but with breaks along *c*. The $1/T$ Hall constant has been seen[5,7] in both polycrystalline $YBa_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$. Cheong *et al.*[5] conclude that it is unlikely to be caused by skew scattering, since they find the same result in both systems. We have seen the same Hall behavior in epitaxial bilayers,[26] where the layer next to the substrate has the *c* axis perpendicular to the substrate and parallel to the magnetic field. The top layer has the *a* or *b* axis perpendicular to the substrate. In addition, a $1/T$ Hall constant has been observed[27] in epitaxial films for which most of the grains are aligned with their *c* axis perpendicular to the film and parallel to the magnetic field. Finally, Davidson *et al.*[21] have observed the $1/T$ dependence between room temperature and 600 K, in polycrystalline films.

The unusual temperature dependence of the Hall effect seems to require either particular circumstances as mentioned above or an exotic model with an intrinsic temperature dependence.

The *ab* plane resistivity shown in Fig. 1 shows rounding, which may be the result of superconducting fluctuations above T_c. One must treat this regime with caution, however, since there is a temperature-dependent term in the Montgomery method.[11] The solid curve in Fig. 3 is the ratio K of the proper Montgomery result to the result obtained from the Van der Pauw[28] analysis using the actual crystal thickness d. The resistivity anisotropy is taken from Tozer *et al.*[1] The reason for the temperature dependence is that even though the crystal is an order or magnitude thinner than its width, the equivalent Montgomery isotropic crystal is roughly cubic, due to the factor of about 100 in the resistivity anisotropy. Furthermore, since the anisotropy changes with temperature, especially near T_c, the effective thickness of the crystal Kd changes also. Both the *ab* plane resistivity and Hall constant

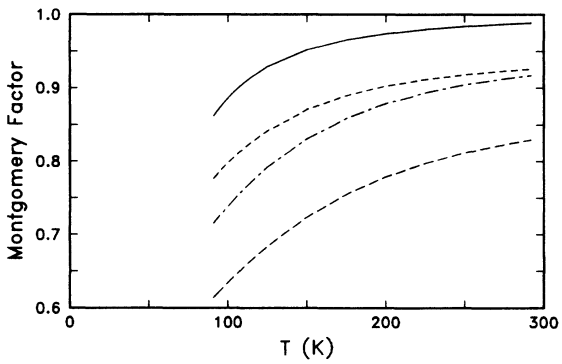

FIG. 3. The ratio of the *ab* plane resistivity calculated properly by the Montgomery method to that by the van der Pauw method using the actual crystal thickness. All curves are for the approximate sample geometry described in the text. The top (solid) curve assumes the resistivity anisotropy of Ref. 1. The lower (dashed) curves take the anisotropy from samples *A*, *F*, and *E* of Ref. 2, but our sample dimensions. The new *ab* plane data shown in Figs. 1 and 2 uses the solid curve. The resistivity is smaller and the Hall number larger than they would be if this factor were ignored.

shown in Figs. 1 and 2 are related to the van der Pauw result by the factor in Fig. 3 (solid curve). Also shown are the same factor calculated for our crystal dimensions but taking the anisotropy from the data of Hagen *et al.*[2] rather than from Ref. 1. In this case, the factor is smaller because their resistivity anisotropy is somewhat larger.

In conclusion, three different groups have seen similar upturns in the *c*-axis resistivity, indicative of incipient localization in that direction. This behavior is of great importance theoretically. Whether it is intrinsic or not is still an open question. The Hall effect, previously reported, for the field in the *ab* plane, is *n* type and nearly temperature independent. In this work, we have measured the *ab* plane resistivity directly in the *ab* plane and find that it is linear in T and about two orders of magnitude smaller than in the *c* direction. The *ab* plane is twinned, so no anisotropy in the plane has been observed. The Hall constant, for the magnetic field perpendicular to the Cu-O planes, is *p* type with a $1/T$ dependence. Since this unusual and unexplained behavior, first seen in polycrystalline materials, has now been observed in a single crystal, it cannot be dismissed as an artifact of the polycrystalline microstructure. The high-temperature superconductor $YBa_2Cu_3O_{7-x}$ has been shown to be strongly anisotropic. In the normal state, the resistivity and Hall effect are qualitatively different for currents flowing in the Cu-O planes or perpendicular to them.

Note added. We have learned that Iye *et al.* (unpublished) have found *ab* plane resistivity and a Hall effect qualitatively similar to those reported here. In contrast to other measurements, they have one sample which shows a *c*-axis resistivity which is linear in T with no upturn and no flattening above T_c. Ossipyan *et al.* (unpublished) in an extension of Ref. 3, have one sample which has a flat temperature-independent *c* axis just above T_c. They conclude, as mentioned above, that the upturn seen by them and others is extrinsic. Of course, the flat behavior still contains some $1/T$ relative to T.

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