Field and Hall effects in semiconducting $YBa_2Cu_3O_{6+\delta}$

A. Levy, J. P. Falck, M. A. Kastner, and R. J. Birgeneau
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

A. T. Fiory and A. F. Hebard
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

W. J. Gallagher and A. W. Kleinsasser
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

A. C. Anderson
Lincoln Laboratories, Lexington, Massachusetts 02173
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The field-effect mobility, Hall coefficient, and conductivity as functions of the oxygen concentration and temperature are reported for $YBa_2Cu_3O_{6+\delta}$ films on the insulating side of the insulator-to-metal transition. The temperature dependence of the conductivity and Hall coefficient indicate that for small δ the excess oxygen introduces acceptor states at about 30 meV above the valence-band edge. The field effect reveals a space-charge layer in which carriers are depleted at the air-$YBa_2Cu_3O_{6+\delta}$ interface. The size of the field effect is limited by localized states at the interface.

One of the common characteristics of the high-T_c copper oxide superconductors is the existence of an antiferromagnetic semiconducting phase near the superconducting one.[1] In contrast to other copper oxides, $YBa_2Cu_3O_{6+\delta}$ can be easily doped in oxygen, converting it chemically from one phase to the other.[2] Since the primary role of doping is to increase the charge concentration, it has been suggested[3] that charge carriers might be induced by an external electric field rather than by doping to drive the material across the phase boundary. The feasibility of this approach is determined by the density of states in the band gap of the semiconductor. If the density of states is too high, the external electric field required to shift the Fermi level will be inaccessible.

In order to characterize the bulk and surface localized states in semiconducting $YBa_2Cu_3O_6$ and those introduced by adding oxygen, we have measured the conductivity, Hall coefficient, and field-effect mobility as functions of temperature and oxygen content in thin films of $YBa_2Cu_3O_{6+\delta}$. We find that for small δ the material behaves like a somewhat compensated p-type semiconductor with a depletion region near the air-$YBa_2Cu_3O_{6+\delta}$ interface. Although we find evidence for a high density of localized interface states on some films, this density varies greatly with the structure of the interface. Thus, interfaces may exist for which the electric-field-driven transformation to the superconducting phase is possible.

Two $YBa_2Cu_3O_{6+\delta}$ films were grown on $LaAlO_3$ substrates using the *in situ* off-axis rf magnetron sputtering method. A detailed description of the growth method was reported elsewhere.[4] As grown, the films displayed a sharp superconducting transition at 88 K. Samples 1–3 were cut from one film, and samples 4 and 5 originated from the other. To vary the oxygen concentration the films were then annealed in Ar containing a low partial pressure of oxygen.

Field-effect experiments were made using the method of Fiory *et al.*[5] at temperatures from 4 to 300 K with applied gate voltages between -1 and $+1$ kV. Repetitive Br etching[5,6] consistently produced the same field effect on these air-$YBa_2Cu_3O_{6+\delta}$ interfaces. Hall bars were subsequently lithographically patterned, and the Hall effect was measured at fields from -0.65 to $+0.65$ T, over which range the Hall voltage was found to be linear with applied magnetic field.

In the top half if Fig. 1 we present the conductance as a function of temperature for all of the films studied. The conductance of samples 2–5 can be fitted by the sum of two contributions: The component that is dominant at high T is thermally activated, that is, $g = g_0 \exp(-E_a/kT)$ where E_a is the activation energy and k is the Boltzmann constant. The best fit to the experimental results yields $E_a = 20\pm3$, 40 ± 6, 40 ± 6, and 140 ± 15 meV for samples 2–5, respectively. The second component behaves like that which arises from variable range hopping between localized states near the Fermi energy and is given by $g = g_1 \exp(-(T_0/T)^n)$. The best fit gives $n = \frac{1}{2}$ although lower-temperature data are required to rule out other exponents. Sample 1 has a very weak temperature dependence, indicating that it is close to the crossover from strong localization to nearly metallic conductance. The gradual decrease of E_a as the carrier density is decreased from sample 2 to 4 is typical of doped semiconductors near the insulator-to-metal transition.[1] The abrupt increase of E_a (for sample 5) signals the elimination of the shallow impurities.

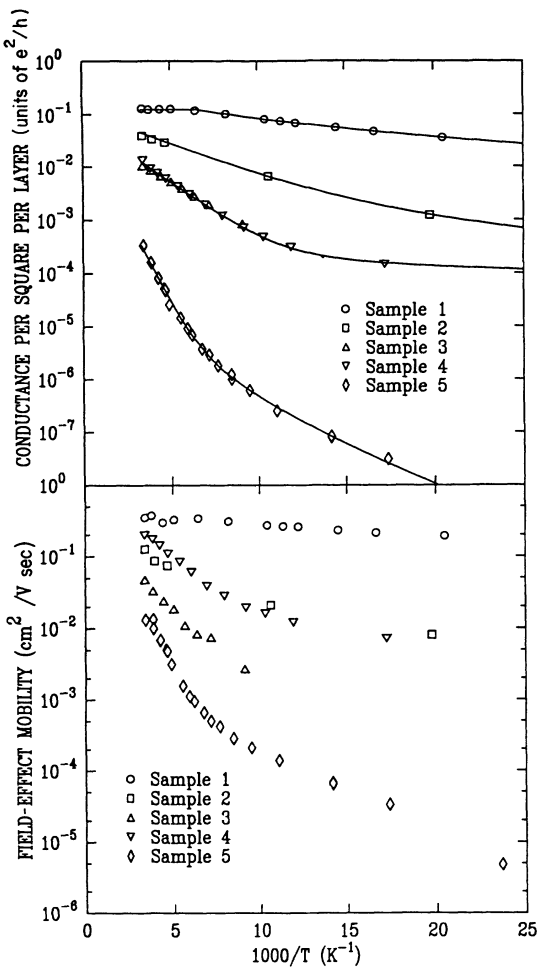

FIG. 1. Conductance per square per layer, and field-effect mobility as functions of the temperature for $YBa_2Cu_3O_{6+\delta}$. Solid lines are least-squares fits to the sum of a simply activated component and a variable-range-hopping component.

The Hall coefficient also displays a behavior typical of doped semiconductors. Hall charge-carrier densities are plotted as a function of temperature in Fig. 2. The Hall coefficient is always positive, indicating that the charge carriers are holes. The most conducting sample (1) displays an almost constant charge density, indicating once again that this film is nearly metallic. For samples 3 and 4 the mobile hole density, like the conductivity, is thermally activated. The activation energy is $E_a = 30 \pm 5$ meV, which is close to the activation energy (40 meV) of the conductance for these two samples, showing that the primary temperature dependence of the conductivity comes from the T dependence of the hole density.

The defects or impurity states that determine the position of the Fermi energy once the shallow acceptors are removed partially compensate the acceptors. Whereas the activation energy in an uncompensated doped semiconductor is half the binding energy of the hole to the impurity, it is equal to the binding energy in the compensated case.[7] Thus, the 30-meV activation energy provides

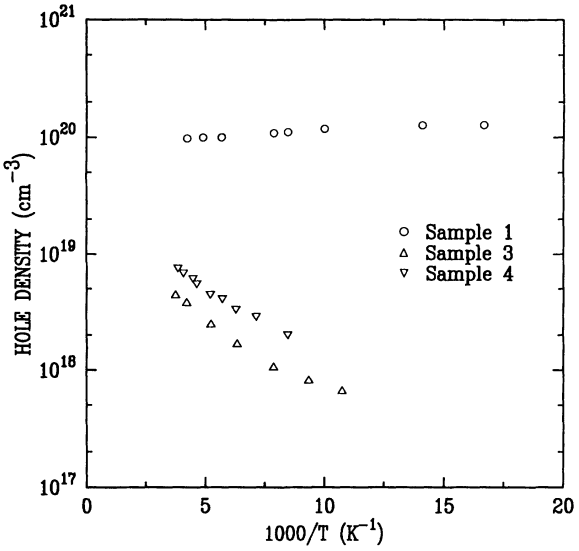

FIG. 2. Charge-carrier (hole) density extracted from Hall-effect experiments on $YBa_2Cu_3O_{6+\delta}$ vs temperature.

a measurement of the binding energy of the hole to the oxygen acceptor in $YBa_2Cu_3O_{6+\delta}$. This agrees within the reported errors with the value 34 meV found[1] for the binding energy of the oxygen acceptor in La_2CuO_{4+y}.

For samples 3 and 4 there is no evidence in Fig. 2 for saturation of the carrier density up to room temperature. Thus we can only place a lower bound of $\sim 10^{19}$ cm^{-3} on the carrier densities. It is clear, however, by comparing the behavior of sample 1 with that of samples 3 and 4 that the transition from strong localization to nearly metallic behavior occurs near 10^{20} cm^{-3}, approximately 1% of the copper atom concentration. Superconductivity is seen[8] only above $\sim 2\%$ of holes within the CuO_2 planes.

The Hall mobility, shown in Fig. 3, is nearly independent of doping and has magnitude $\mu_H \sim 2$ cm^2/V sec. This is quite close to the value ~ 3 cm^2/V sec found for

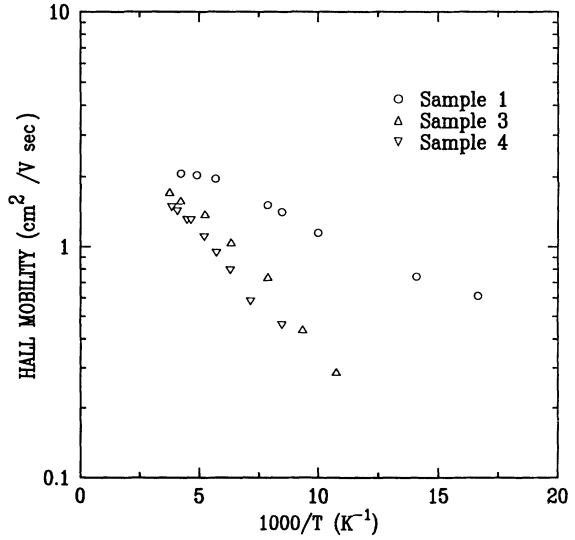

FIG. 3. Hall mobility vs temperature for $YBa_2Cu_3O_{6+\delta}$.

$La_{2-x}Sr_xCuO_{4+y}$. Using the free-electron mass one finds from these mobilities that the scattering time at room temperature is comparable to that in the highest-T_c superconductors. The decrease of the mobility as T decreases is probably caused by the transition from simply activated conductance to variable range hopping.[1]

In the field-effect experiment the applied voltage induces a charge per unit area δQ near the surface of the sample. As a result, the conductance per square of the film changes to δG. The field-effect mobility is given by $\mu_{FE}=dG/dQ$. For all our measurements δG is found to be proportional to δQ. The field-effect mobility is plotted versus $1/T$ in the lower half of Fig. 1. It is seen that μ_{FE} has roughly the same temperature dependence as the conductance.

Comparing samples 3 and 4 we find that, whereas their conductances and Hall coefficients are nearly the same, their field-effect mobilities differ appreciably. Using scanning electron microscopy we detected inclusions of the a-axis $YBa_2Cu_3O_{6+\delta}$ phase on the surface of the film from which samples 1–3 were taken. Inclusions of the a-axis oriented phase have been observed in the past,[9] and are known to increase with the thickness of the film; the samples that show the a-axis phase are from the thicker of the two films. The nearly identical conductivities and Hall coefficients of samples 3 and 4 show that grain boundaries do not have a significant influence on the transport properties. The lower values of μ_{FE} for sample 3 therefore suggest that, for samples 1–3 most of the added charge is localized in surface states and that the a axis has a higher density of surface states than the c axis.

The high density of surface states fixes the position of the Fermi energy E_F in the band gap at the surface. We show next that the similarity of the temperature dependences of μ_{FE} and the conductance is consistent with the assumption that the charge carriers are depleted near the semiconductor surface.

In general, the conductance of the film is given by

$$G=\int \sigma(x)dx=\int_0^W \sigma(x)dx+\sigma(d-W)\ , \qquad (1)$$

where W is the width of the space-charge region, in which the conductivity depends on the charge density and thereby on position x, d is the film thickness, and σ is the conductivity in the interior of the film. In depletion G is dominated by the second term, and the change in G results from the change in W. In addition, W is simply related to the charge added per unit area to the bulk of the semiconductor Q_B by $dW/dQ_B=[e(N_A-N_D)]^{-1}$, where N_A and N_D are the densities of acceptors and compensating donors, respectively. Consequently, the field effect mobility is given by

$$\mu_{FE}=dG/dQ=-\sigma(dQ_B/dQ)[e(N_A-N_D)]^{-1}\ , \qquad (2)$$

where dQ_B/dQ is the fraction of added charge that ionizes shallow impurities; the balance is trapped in surface states and localized states in the depletion region. From Eq. (2) one predicts that the ratio σ/μ_{FE} is independent of temperature. As seen in Fig. 4, σ/μ_{FE} is, indeed, constant between ~ 100 and 300 K for all but the most resistive sample.

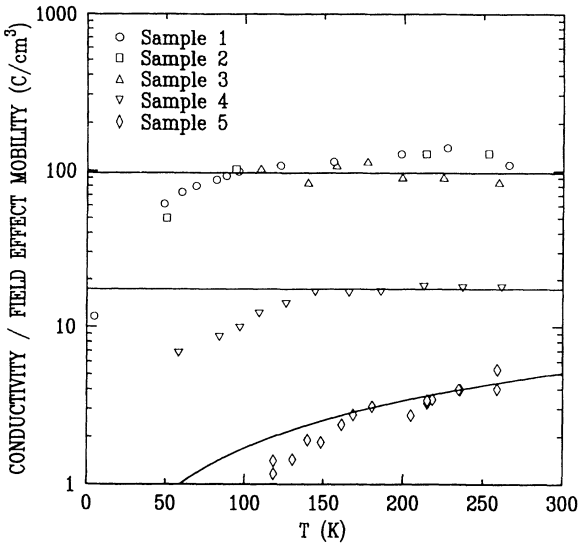

FIG. 4. Ratio of the conductivity to the field-effect mobility as a function of the temperature for $YBa_2Cu_3O_{6+\delta}$. The solid lines for samples 1–4 represent a constant. The curve for sample 5 is the best fit of the data to $\sigma/\mu_{FE}\propto T$. Note that the values for samples 1–3 are high because the high density of interface states make μ_{FE} small.

Note that σ/μ_{FE} is nearly the same for samples 1–3, consistent with the idea that all of these, which come from the same film with a-axis inclusions, have the same high density of surface states, which gives a large value of dQ/dQ_B. For this sample we estimate that the surface density of states is $\sim 10^{14}$–10^{15}/cm^{2}eV, which is very high.

From the data for sample 4 in Fig. 4 one finds $(N_A-N_D)=dQ_B/dQ\times 10^{20}$ cm^{-3}. As discussed above, the density of holes that can be ionized from acceptors N_A-N_D is larger than 10^{19} cm^{-3} for sample 4. Thus the fraction of charge added to the bulk of the semiconductor is larger than $\frac{1}{10}$. The same observation can be made directly by noting that μ_{FE} for sample 4 (Fig. 1) is about ten times smaller than the Hall mobility (Fig. 3) at ~ 300 K. This means that for sample 4 the surface states do not overwhelmingly dominate the field effect as they do for samples 1–3.

The decrease of σ/μ_{FE} at low T for samples 1–4 may result from conduction in the surface states or the space-charge region when the conductivity mechanism changes to hopping. Because the latter mechanism depends exponentially on the density of states at the Fermi energy, and because the density of states may vary nonmonotonically in the space-charge region, the contribution from the latter region is difficult to estimate.

The field effect for sample 5 has a rather stronger temperature dependence than that of the other films. This is consistent with the idea that all shallow acceptors are eliminated in this sample, and that the screening of external fields is, therefore, different. The temperature dependence seen in Fig. 4 may be understood[10] by assuming that the field is screened by a high density of localized states in the band gap in which the band bending is small.

A simple argument leads then to $\sigma/\mu_{FE} \sim T$. The data for sample 5 are in reasonable agreement with this prediction as seen in Fig. 4.

In summary, we have shown that the temperature and doping dependence of the conductance and Hall coefficient are consistent with a model in which $YBa_2Cu_3O_{6+\delta}$ is a doped semiconductor with some compensation. In fact, the properties of this material are remarkably similar to those of $La_{2-x}Sr_xCuO_{4+y}$. In particular, the Hall coefficient provides a good measure of the free carrier density, a property that appears to hold well into the superconducting phase. The activation energy of the hole density shows that the binding energy of the hole to the oxygen acceptor is ~ 30 meV in $YBa_2Cu_3O_{6+\delta}$, close to the value found for La_2CuO_{4+y}. We note that this is a measurement of the binding energy in single crystals of $YBa_2Cu_3O_{6+\delta}$.

Chen *et al.*[11] showed that the small binding energy in La_2CuO_{4+y} comes about because of coupling of the charge carriers to optical phonons. The screening of the Coulomb field by the static dielectric constant, which is $\varepsilon \sim 30$ in La_2CuO_4, reduces the binding energy from the value ~ 0.5 eV it would have if screening were only by the electronic contribution (~ 5) to the dielectric constant. From the small value of the binding energy we find in $YBa_2Cu_3O_{6+\delta}$ we infer that coupling of the holes to the optical phonons is important in this material as well.

From the field-effect measurements we conclude that there is a depletion region at the air-$YBa_2Cu_3O_{6+\delta}$ interface and that the density of states at this interface is relatively high. However, there is now much evidence that the density of states depends on detail on the structure of the interface. In addition to the dependence on surface orientation reported here, it is possible to achieve a lower density of states and a concomitantly higher field-effect mobility at the interface of $YBa_2Cu_3O_6$ and $SrTiO_3$.[12] Thus, there is reason to believe that much higher field effects can be realized. Alternatively, higher field effects can be achieved using thinner and larger-dielectric-constant gate insulators.[13–15]

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