

Field-effect conductance of La_2CuO_4

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Field-effect mobility and conductance of La_2CuO_4 single crystals as functions of temperature are presented. An analysis of the observed high field-effect mobility of La_2CuO_4 ($\sim 2 \text{ cm}^2/\text{V s}$) indicates that the density of localized states near the surface is much smaller than in films of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ studied previously.

Although the charge carrier density required for high-temperature superconductivity in the copper oxides is usually achieved by doping, it has been suggested¹ that this density might be induced instead with an electric field, as is done in a semiconductor field-effect transistor. Whereas several groups have attempted to drive $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ from the superconducting state to the insulating state,² our efforts have been directed to achieving the opposite.^{3,4}

In a previous paper⁴ we reported results of field-effect and transport measurements as functions of temperature on $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ thin films. We showed that the conductivity and Hall coefficient of insulating $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$, like those⁵ of $\text{La}_2\text{CuO}_{4+y}$, were typical of a compensated *p*-type doped semiconductor. Although this suggested that both materials could be used as the semiconductor in a field-effect transistor, we found the field-effect mobility in $\text{YBa}_2\text{CuO}_{6+\delta}$ films to be very low, substantially lower than the valence band mobility. This indicated that the induced charge resided in localized states rather than in extended states. It therefore appeared impractical to induce superconductivity in these films. Furthermore, we showed that in semiconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ the field-effect mobility and conductivity had the same temperature dependence. This was interpreted as indicating that the Fermi level was pinned by surface states.

In this paper we report the results of field-effect experiments on insulating La_2CuO_4 single crystals. We show that, in contrast to $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ films, the Fermi level is only weakly pinned near the surface of La_2CuO_4 crystals. The much higher field-effect mobility of the latter ($\sim 2 \text{ cm}^2/\text{V s}$) indicates that it might be a better candidate for use in a field-effect transistor. We also derive a formula for the temperature dependence of the field-effect mobility. We show that, irrespective of the specific density of states of the semiconductor, if the surface is depleted the conductance and the field-effect mobility have the same temperature dependence.

We next describe the fabrication and measurement techniques. Two $\text{La}_2\text{CuO}_{4+y}$ single crystals were grown in air from a melt of La_2O_3 and CuO_3 contained in a Pt crucible. A detailed description of the growth method

was reported elsewhere.⁶ The two crystals were cut into rectangular parallelepipeds, approximately $0.8 \times 0.85 \times 0.2 \text{ cm}^3$ in size and annealed at 900°C to eliminate the excess oxygen always present in as-grown crystals. The magnetic susceptibility was then measured as a function of temperature. The peak in the susceptibility gave Néel temperature $T_N = 323 \text{ K}$, indicating that, indeed, the crystals contained no excess holes.⁵

The large crystal surfaces were polished to produce optically smooth samples and the crystals were then etched in a solution of 1% Br in ethanol.⁷ Composite Ag/Au contacts were sputtered at the corners of the samples through a shadow mask and then annealed at 500°C in vacuum in order to minimize contact resistance.

For a field-effect experiment one must create a parallel plate capacitor, one plate of which is the semiconductor, in this case La_2CuO_4 . One then measures the change in the conductance of the semiconductor as a function of the charge added to the capacitor; the charge is proportional to the voltage applied to the metal counterelectrode or gate. To this end, an insulating $7\text{-}\mu\text{m}$ -thick Kapton sheet was mounted on top of the sample to form the insulator, and a second Kapton sheet coated with gold was placed, with the gold side down, on top of the first to be used as the gate. The two Kapton layers were then pressed against the La_2CuO_4 crystal. A schematic drawing of the fabricated device is presented in Fig. 1(a).

The sheet conductance was measured using the van der Pauw method⁸ at frequencies from dc to 100 Hz. The accumulated charge was measured as a function of gate voltage using an electrometer; no gate leakage was detected at gate voltages from -1 to 1 kV . Measurements were made from 4 to 300 K in a continuous flow cryostat, where the samples were held in vacuum. Repetitive Br etching consistently produced the same field effect at these La_2CuO_4 surfaces. For all measurements reported, the conductance change was linear in the gate voltage.

In a metal-insulator-semiconductor field-effect transistor (MISFET) the accumulated charge in the semiconductor (δQ) is given by the product $\epsilon \mathcal{E}$, where ϵ is the dielectric constant of the insulator, and \mathcal{E} is the applied field. The field-effect conductance is the increase in con-

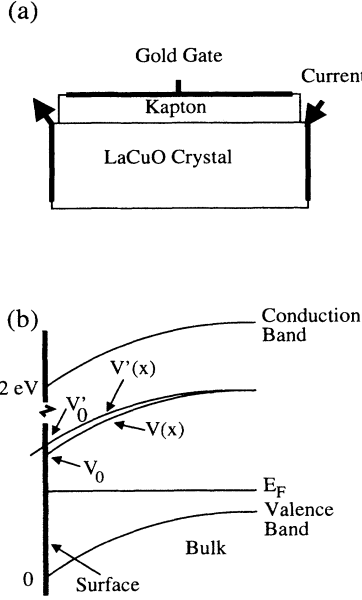


FIG. 1. (a) Schematic diagram of a La_2CuO_4 field-effect device using a Kapton insulator. (b) Schematic energy band diagram near a (p -type) semiconductor surface.

ductance of the semiconductor when an electric field is applied. This is given by $\delta G = \delta Q \mu_{\text{FE}} = (\epsilon \mathcal{E}) \mu_{\text{FE}}$, where the field-effect mobility (μ_{FE}) is the average mobility of the accumulated charges.

It was shown in Ref. 4 that for $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$, μ_{FE} had roughly the same temperature dependence as the conductance. However, the magnitude of μ_{FE} was found to be significantly lower than the Hall mobility of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ ($\sim 3 \text{ cm}^2/\text{V s}$). The low value of μ_{FE} suggested that most of the added charge carriers resided in localized states. We show next that the similarity of the temperature dependence of μ_{FE} and the conductance is a result of the pinning of the Fermi level in depletion by a high density of localized states.

In general, the conductance of a sample parallel to its surface is given by

$$G = \int \sigma(x) dx, \quad (1)$$

where $\sigma(x)$ is the conductivity at a depth x into the sample. We assume that the contribution to the change of the conductivity because of modulation of the Fermi level comes mainly from the modulated charge carrier density in the valence band (for a p -type semiconductor). In this case,

$$\sigma(x) = \sigma_0 \exp[V(x)/kT], \quad (2)$$

where σ_0 is the bulk conductivity, k is the Boltzmann constant, and T is the temperature. $V(x)$ is the difference in energy between an electron state at the valence band edge at a depth x and a state at the valence band edge in the bulk of the sample. A sketch of the energy bands is given in Fig. 1(b).

To specify the potential as function of depth into the film, one must solve the Poisson equation

$$d^2V(x)/dx^2 = 4\pi e \rho(x) \quad (3)$$

with boundary conditions

$$V(x=0) = V_0, \quad dV/dx(x=\infty) = 0,$$

where V_0 is the potential energy of an electron at the surface of the sample and ρ is the charge density. This latter quantity is given as an integral of the Fermi function, $F(E)$ over the local density of states $D(E - V(x))$:

$$\rho(x) = \int dE F(E) D(E - V(x)). \quad (4)$$

Here we make the conventional assumption that the density of states does not depend explicitly on x . Thus the charge concentration becomes only a function of the local potential $V(x)$

In the field-effect experiment the applied gate voltage induces a change in the surface potential V_0 . The new surface potential V'_0 results in a new solution $V'(x)$ of the Poisson equation [Eq. (3)]. However, since only the boundary condition has changed $V'(x)$ is given by a translation in x of $V(x)$; the translation δx_t is chosen such that the boundary conditions are satisfied. The new solution of the Poisson equation is given, to first order, by

$$V'(x) = V(x - \delta x_t) = V \left[x - \frac{V'_0 - V_0}{(dV/dx)_{x=0}} \right]. \quad (5)$$

Using Eqs. (1) and (2), the change in the conductance δG caused by application of the gate voltage is given by

$$\delta G = \int \sigma_0 \exp[V(x)/kT] [\delta V(x)/kT] dx, \quad (6)$$

where $\delta V(x)$ is defined as the change in the potential: $V' - V$. However, since the new potential is given by a translation of the zero gate voltage solution the change in the potential at a depth x is

$$\delta V(x) = \frac{dV}{dx} \delta x_t = \frac{dV/dx(V'_0 - V_0)}{dV/dx|_{x=0}}. \quad (7)$$

Substituting this in Eq. (6) gives

$$\delta G = \sigma_0 \delta x_t [\exp(V_0/kT) - 1] \quad (8)$$

and consequently the field-effect mobility is given by

$$\mu_{\text{FE}} = \delta G / \delta Q = \sigma_0 [\exp(V_0/kT) - 1] \delta x_t / \delta Q. \quad (9)$$

Since V_0 is negative when the sample is in depletion the exponential term can be neglected. Furthermore, since δx_t is dominated by localized charges it is temperature independent. We therefore conclude that the field-effect mobility and the conductance have the same temperature dependence in this situation. This result is quite general since it comes from a simple linearization of Eqs. (3) and (4) and, therefore, requires only that the shift of E_F at all points x is small. When the density of localized states is high δx_t is small; the field is screened by the localized states. This makes μ_{FE} small.

The above analysis confirms the interpretation of the field-effect and conductivity measurements of Ref. 4. We had concluded there that the depletion region at the air/ $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ interface resulted from a relatively

high density of surface states. However, the density of these states depends in detail on the structure of the interface. We next describe the results of the measurement of the field-effect conductance on another copper oxide external surface, that of La_2CuO_4 .

The conductance per square and the field-effect mobility of the La_2CuO_4 crystals are displayed in Fig. 2. We discuss first the results of the measurements on the first crystal. It is clear that, like $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$, the conductance and the field-effect mobility of this crystal have the same temperature dependence. We observe that the conductance is thermally activated. That is, $G = G_0 \exp(-E_a/kT)$ where E_a is the activation energy. The best fit to the experimental data yields $E_a = 95 \pm 10$ meV. Since the binding energy of holes to oxygen acceptors in La_2CuO_4 is 35 meV,⁵ the high activation energy is a confirmation that shallow impurities have been eliminated. The best fit to the field-effect mobility yields an activation energy of $E_a = 90 \pm 10$ meV, the same, within error, as that of the conductance. Since the conductance has the same temperature dependence as the field effect, we conclude that the surface is in depletion.

However, the field-effect mobility of La_2CuO_4 is found to be large ($\sim 1 \text{ cm}^2/\text{V s}$ at 300 K), comparable to the Hall mobility⁵ ($\sim 3 \text{ cm}^2/\text{V s}$). By comparison, the field-effect mobility of $\text{YBa}_2\text{Cu}_3\text{O}_6$ at room temperature is only $\sim 2 \times 10^{-2} \text{ cm}^2/\text{V s}$. Since the activation energies of G and μ_{FE} for $\text{YBa}_2\text{Cu}_3\text{O}_6$ are no larger than those of La_2CuO_4 , we conclude that the density of localized states in La_2CuO_4 is relatively small.

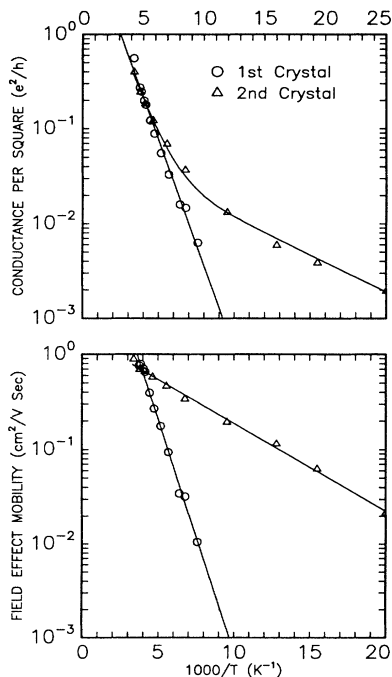


FIG. 2. Conductance per square and field-effect mobility of two La_2CuO_4 crystals as a function of temperature. Solid lines are a least-squares fit to a sum of thermally activated components.

At high temperature, the conductance of the second crystal is also thermally activated. The best fit to the experimental results yields $E_a = 100 \pm 20$ meV. Fitting the lower-temperature conductance, assuming thermal activation, results in an activation energy of 15 ± 5 meV. This is close to the value of the single activation energy 18 ± 3 meV found for the field-effect mobility.

The field-effect mobility extrapolates to a value of $2 \text{ cm}^2/\text{V s}$ at high temperature. As mentioned above, this value is comparable to that found by Hall-effect measurements in La_2CuO_4 .⁵ The similarity of the values of μ_{FE} for both crystals indicates that the density of localized states is small for both crystals.

We propose the following model to explain the difference in the temperature dependence of the field-effect mobility and the conductance of the second crystal: As demonstrated by the high (100 meV) activation energy and high (323 K) Néel temperature the oxygen impurity band is eliminated in the bulk of the crystal after annealing. Recent photoemission measurements in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ show that the Fermi energy is near the middle of the ~ 2 eV charge transfer gap.⁹ Although the gap in La_2CuO_4 is similar, we have found that the conductivity activation energy in crystals with $T_N = 325$ K is usually ~ 0.1 eV. This suggests that there is a small density of defect states which pins the Fermi energy about 0.1 eV above the valence band edge. However, we propose that because of localized surface states, E_F lies only 18 meV above the mobility edge near the surface. In this case there is an accumulation layer near the La_2CuO_4 surface. At high temperature the conductance is dominated by the bulk with its large activation energy but large volume. However, at low temperatures the conductance is dominated by the surface, which has a lower activation energy. This also explains why the activation energy of the conductance at low T (15 meV) is very close to that of the field-effect mobility: The field-effect experiment probes the outermost few layers and therefore has a constant activation energy at all temperatures. The observation that the surface of the first crystal is in depletion whereas the surface of the second one is in accumulation is further evidence that the density of localized states is small. If it were large, all samples would be similar.

An alternative explanation for the low activation energy near the surface of the sample might be the existence of an oxidized surface layer which would contain a high density of acceptors. To explore this possibility we left the sample in a pumped cryostat at room temperature for several days. The low pressure in the cryostat is expected to cause oxygen to diffuse out of the crystal, leaving a more stoichiometric surface (less oxidized). After a week we measured the field-effect mobility and found it to be identical to the one measured previously, suggesting that there was no excess oxygen present. As a second test we etched the crystal in a solution of 1% Br in ethanol for 6 s. This removed about 1000 \AA from the sample surface.⁷ We found that after etching the room-temperature field-effect mobility had not changed.

Studies of high-temperature superconductors as a function of thickness have shown¹⁰ that the insulator-to-superconductor transition takes place at a conductance of

$4e^2/h$. Using this criterion, one finds that field-induced superconductivity requires $\varepsilon\mathcal{E}\mu_{\text{FE}} > 1.8 \times 10^9$ cm/s. Using a ferroelectric insulator one can approach¹¹ $\varepsilon\mathcal{E} \sim 5 \times 10^8$ V/cm. Thus, electric-field-induced superconductivity should be possible if the surface mobility is as high as the valence-band mobility measured by the Hall effect (~ 3 cm²/V s) at low temperature. This might be feasible using La₂CuO₄ as the semiconductor. Experiments are underway to explore this possibility.

In summary, we have found a much higher value of the field-effect mobility in La₂CuO₄ single crystals than in YBa₂Cu₃O₆ films. This indicates that for La₂CuO₄, a large fraction of the field-induced charge is accumulated

in extended (nonlocalized) valence band states. However, a higher electric field than we have applied is required to induce superconductivity.

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