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# Properties of epitaxial films of $YBa_2Cu_3O_{7-\delta}$

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We present measurements of the properties of epitaxial thin films of superconducting $YBa_2Cu_3O_{7-\delta}$, with $T_c$ about 90 K, transition widths of ~2.5 K, and critical currents in excess of $10^5 A/cm^2$ at 77 K. The temperature dependence of the upper critical field exceeds 4 T/K for fields parallel to the film (i.e., $H\perp$ to the $c$ axis) and the anisotropy of the upper critical field ranged between two and three. Our tunneling gaps ($\Delta \sim 15-21$ meV) are similar to previous results on ceramic and single-crystal samples of $YBa_2Cu_3O_{7-\delta}$. Infrared measurements of the gap energy suggest a larger value than previous measurements on polycrystalline material. The temperature dependence of the Hall coefficient is similar to that for the bulk.

In a recent publication[1] we presented data on large critical currents in epitaxially grown thin films of $YBa_2Cu_3O_{7-\delta}$. Typically the critical currents were two orders of magnitude larger than those reported earlier on ceramic samples. We have now made a number of different measurements on epitaxial films and we summarize our findings here. Since these measurements were made, single-crystal data[2,3] have also become available and some comparison between single-crystal, epitaxial, and ceramic samples is presented here.

Thin films of the superconductor were grown by electron beam evaporation of Y, Ba, and Cu in an oxygen environment.[4] The as-deposited films were first flash-annealed for 1 sec to near the melting point of the compound in an oxygen atmosphere and subsequently annealed for a longer period, as described in our earlier paper, to produce epitaxial films. The structure of these films has been characterized both by x-ray diffraction and electron microscopy and we summarize the essential components of these findings. Further details will be published elsewhere.[5] The superconducting film is epitaxial and single crystal at and near the substrate film interface where the $c$ axis of the orthorhombic structure is perpendicular to the plane of the film. Closer to the top surface of the film there are crystals with $c$ axis in the plane of the film. However, the $c$ axis is aligned either with the $a$ or the $b$ axis of the underlying film. Instead of a grain boundary there are domain walls separating these crystals. In addition to these domain walls there is evidence of extensive twinning and the presence of yttrium and copper-oxide precipitates. In summary, the films can be viewed roughly as a bilayer with one layer being predominately a single crystal with the $c$ axis perpendicular to the plane of the film. The second layer contains crystals whose $c$ axis is aligned either along the $a$ or the $b$ axis of the first layer.

Magnetic measurements in low fields at 4.5 K shown in Fig. 1 and critical fields, as determined by magnetoresistance measurements near $T_c$, shown in Fig. 2, allow the lower $H_{c1}$ and upper $H_{c2}$ critical fields to be evaluated. The lower field $H_{c1}$ is defined as the point where the slope of $M$ vs $H$ departs from linearity. It is estimated to be 30 Oe. This is corrected for demagnetization by first calculating the initial susceptibility in the linear region which is about $\chi \approx 58$ and then finding the demagnetization coefficient $n$ from $\chi = 1/4\pi(1-n)$, yielding a value of a lower critical field $= H/(1-n) < 22000$ G. This value is considerably larger than that found[6] for a small bulk crystal where it was about 7000 G. We believe that there is considerable uncertainty in our estimate of $H_{c1}$ because of the large demagnetization corrections and the difficulty in detecting the deviation from the linear susceptibility regime.

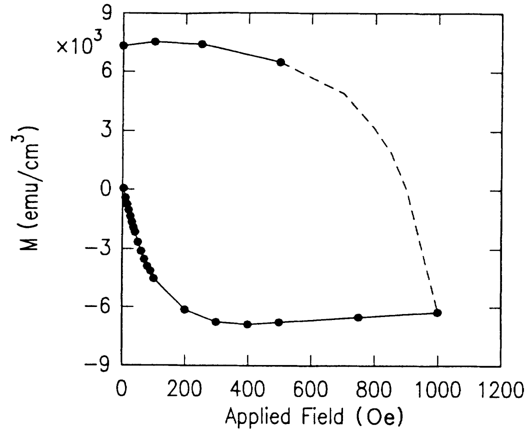

FIG. 1. Magnetization in gauss vs applied field in kOe at 4.4 K with the applied field perpendicular to the plane of the film. This measurement is on sample A.

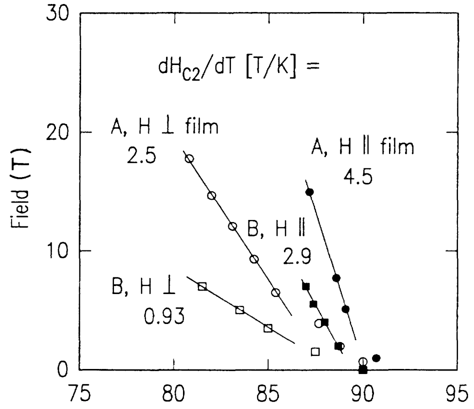

FIG. 2. Values of the upper critical field $H_{c2}$ vs temperature. Each data point is determined from the midpoint of the resistance temperature curve. Two samples are shown as A measured to high fields at MIT and a sample B measured at lower fields at IBM. The difference in the two samples is probably caused by inhomogeneities.

The upper critical fields $H_{c2}$ were measured resistively with the standard four-probe method in dc magnetic fields up to 20 T in water-cooled Bitter magnets at the Francis Bitter National Magnet Laboratory facility. Most of the data were taken at fixed values of $T$ and swept field. Measurements of $H_{c2}$ were made with the applied field either parallel to the plane of the film, $H_{c2\parallel}$, or perpendicular to the plane of the film $H_{c2\perp}$. In both orientations the current is in the plane of the sample. The resistance at the midpoint of the resistive transitions for each of the orientations was obtained using the extrapolation of the high-temperature resistance above about 110 K as described in the work of Orlando *et al.*[7] Because we are approaching the transition from the normal state, there is only a small amount of excluded flux and therefore negligible demagnetizing or geometric effects. These results are shown in Fig. 2. For sample A, the midpoint $(dH_{c2\parallel}/dT)_{T=T_c} \simeq 4.5$ T/K observed for the parallel orientation is very high compared to that in the polycrystalline Y-Ba-Cu-O materials and corresponds to that estimated earlier[7] for the onset critical field slope. The $(dH_{c2\perp}/dT)_{T=T_c} \simeq 2.5$ T/K is observed for the perpendicular orientation of the applied field. The data all show curvature at very low field becoming linear as the temperature decreases and the field increases. The corresponding slopes using zero resistance as the criteria and at high fields are 2.3 and 0.7 T/K. For sample B, measured at IBM, and using the midpoint criteria to determine $H_{c2}$, we obtain $(dH_{c2\parallel}/dT)_{T=T_c} = 2.94$ T/K and $(dH_{c2\perp}/dT)_{T=T_L} = 0.93$ T/K, again giving a ratio of the midpoint slopes $\simeq 3$.

Measurements of the anisotropy in a conventional single crystal grown by the flux method have been made by Iye, Tamegai, Takeya, and Takei.[2] These authors reported measurements up to 9 T as a function of crystallographic orientation on two crystallites and obtain a ratio of $\approx 2$ at 90 K and $\approx 5$ at 86 K. The general features of the zero resistance for these single crystals are similar to those which we observed in this epitaxially grown film. Magnetic measurements by Worthington, Gallagher, and Dinger[8] in bulk single crystals show an anisotropy ratio of $\approx 5$ in fields up to 15 T at 90 K.

From the anisotropy measurements a reasonable value of the ratio $H_{c\parallel 2}/H_{c\perp 2}$ is approximately 3. We use the expression $H_{c\perp 2} = \Phi/2\pi\xi_\parallel^2$, where $\xi_\parallel$ is the coherence length in the plane of the film (the basal or *ab* plane) and $\Phi$ is the flux quantum ($2\times 10^{-7}$ gcm$^2$). The value of $H_{c\perp 2}$ at 0 K is obtained from the relation $H_{c\perp 2}(T) = H_{c\perp 2} \times [1-(T/T_c)^2]$. The above values give $\xi_\parallel \approx 25$ Å for the coherence length in the plane and a factor of 3 less perpendicular to the plane based on the ratio[9] $H_{c\parallel 2}/H_{c2\perp} = \xi_\parallel/\xi_\perp$. The value of $\xi_\perp \approx 8$ Å is among the smallest ever reported and is comparable to the lattice parameter of the material. Because these coherence lengths are very much smaller than the film thickness ($\approx 1$ $\mu$m) thin-film geometric anisotropy effects are probably negligible. In polycrystalline samples the width of the grain boundaries is usually comparable to atomic dimension. This, combined with the sensitivity of superconductivity to composition and structure in these materials, may make them particularly sensitive to preparation conditions and its correlation with critical currents. It also provides credence to the glassy behavior proposed by Müller, Takashige, and Bednorz[10] for these materials.

A somewhat surprising feature observed in these samples is that the width of the resistive transition increases with decreasing temperature for both $H$ parallel or perpendicular to the plane. If the width remains broad for single-crystal materials in general (this is presently borne out by the epitaxial data as well as the single-crystal data in Ref. 2) it will be an important consideration in applications of these materials at high fields at liquid-nitrogen temperatures because zero resistance disappears in the range of 5 to 10 T at 77 K.

The superconducting energy gaps of these films were measured using infrared and tunneling techniques. The infrared measurements were made for frequencies from 6–400 meV using a scanning interferometer, as described previously.[11,12] Figure 3(a) shows the ratio of the reflectivity in the superconducting state (13, 68, and 80 K) to the reflectivity for the film in the normal state (98 K). In an ideal BCS superconductor this ratio should increase to a maximum at $2\Delta$, and then approach unity at higher frequencies. For this sample, the enhanced reflectivity due to the gap extends to nearly 50 meV. The relatively broad decrease in the reflectivity ratio towards unity, as well as the phonon-related structure in the reflectivity ratio[11] at 19 meV, between 25 and 43 meV, and at 71 meV, make it difficult to assign a precise value to the gap energy. An estimate for the gap in this sample from our infrared data is $2\Delta \sim 37 \pm 9$ meV, which corresponds to $2\Delta/k_BT_c \sim 4.5$. Surprisingly, no evidence for a reduction of the gap with increasing temperature is observed even quite close to $T_c$.

The tunneling measurements were made with a Pt-Rh tunneling tip as described previously.[13,14] As for other high-$T_c$ superconducting oxides, it was necessary to press the tip deeply into the sample in order to get finite tunneling currents at low tip-sample voltages, and we were sel-

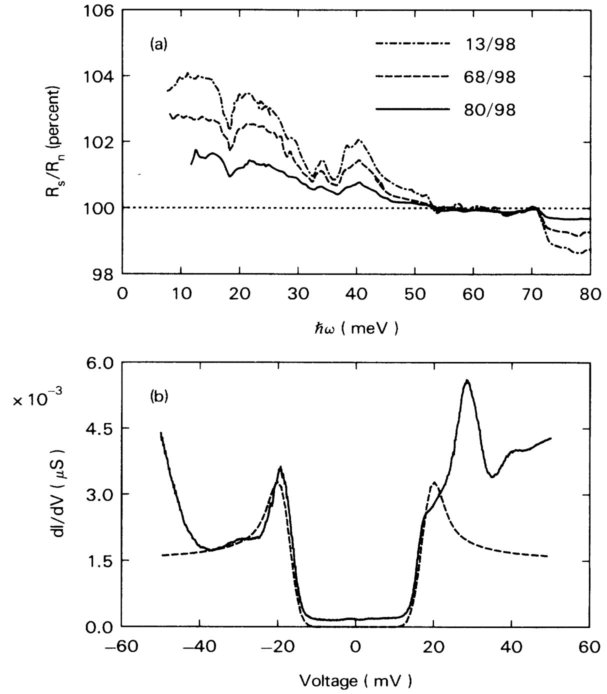

FIG. 3. Infrared (a) and tunneling (b) measurements of the superconducting energy gap in epitaxial thin films of $YBa_2Cu_3O_{7-y}$. In Fig. 3(a) the three curves correspond to the ratio of the reflectivity in the superconducting state at 13, 68, and 80 K, to the reflectivity in the normal state at 98 K. In Fig. 3(b) the solid curve is the experimental dynamic conductance ($dI/dV$) characteristic for tunneling from a Pt-Rh tip into the thin film at a temperature of 5 K. The dashed curve is a theoretical fit to this data as described in the text.

dom able to obtain tunneling characteristics approaching the ideal expected for tunneling from a normal metal into a superconductor. Nevertheless, we were able to obtain the data shown as the solid curve in Fig. 3(b). These data show the low conductance below the gap voltage, and the "overshoot" in the conductance above the gap voltage, characteristic of tunneling into superconductors, but the conductance-voltage characteristic is asymmetric, and has additional structure above the gap voltage. Nevertheless, an estimate of the gap energy can be made by comparing these data with theory. The dashed curve is the prediction of standard tunneling theory using the BCS density of states with a Gaussian distribution of energy gaps centered around $\Delta = 18$ meV, with a full width at half maximum of this distribution of 5 meV. The reasonable fit of this curve to the data for the initial onset of conductivity allows us to estimate the energy gap as $18 \pm 2.5$ meV, corresponding to $2\Delta/k_B T_c \sim 4.5 \pm 0.6$, if we take the half maximum points in the gap distribution for the upper and lower limits on $\Delta$, with $T_c = 92$ K.

The gap measurements of our epitaxial thin films are significant for two reasons. First, the absolute values obtained from the tunneling measurements are roughly comparable to those obtained previously for bulk polycrystalline and single-crystal samples of $YBa_2Cu_3O_{7-\delta}$.[13–15] Second, the infrared and tunneling measurements give results that are roughly comparable to each other for the epitaxial films, whereas previous infrared studies of polycrystalline samples of $La_{2-x}Sr_xCuO_4$ (Refs. 11 and 16) and $YBa_2Cu_3O_{7-\delta}$ (Refs. 14 and 17) samples had indicated that the infrared-derived gaps were approximately a factor of 2 smaller than from tunneling measurements. Although we do not completely understand the differences between the infrared measurements on the thin film and polycrystalline samples, the oriented nature of the film suggests anisotropy in the gap as a possible explanation. The gaps we obtain from the tunneling and infrared measurements are larger than the BCS prediction of $2\Delta/kT_c = 3.53$, but are only slightly larger than those observed for such strongly coupled superconductors as Pb and Hg.

The midpoint of the resistive superconducting transition (Fig. 4) is at 90.0 K while the 10% and 90% points are at 89.4 K and 92.0 K, respectively. The transition is sharp and shows signs of superconducting fluctuations which will be discussed in detail in another paper.[18] The Hall constant $R_H$ was measured in a field of 1 T perpendicular to the film. It is convenient to plot (Fig. 4) the Hall number $V_0/R_He$ where $V_0 = 174$ Å$^3$ is the formula volume. In a simple system where one set of carriers in a parabolic band dominates the conductivity, the Hall number is the number of carriers per formula unit and the Hall mobility $\mu_H = R_H/\rho$ is the true mobility. Such is the case for the $La_{2-x}Sr_xCuO_{4-\delta}$ system for Sr concentrations less than a critical value.[19,20] In that case the Hall number is positive, nearly temperature independent and is approximately equal to the Sr concentration and the number of holes determined by wet chemical analysis. In the present case the Hall number is strongly temperature dependent. In fact it is linear in $T$ with an intercept of $-50$ K. Previous measurements on ceramic $YBa_2Cu_3O_{9-\delta}$ show similar behavior both in the values and the temperature dependences of resistivity and Hall number.[3] Specifically, the linear $T$ dependence for Hall number was observed but the $T$ intercept was 0 and $-10$ K for two samples

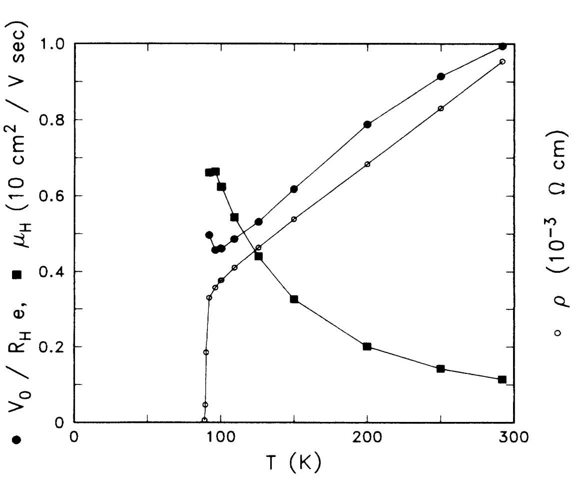

FIG. 4. Resistivity ($\rho$), Hall number ($V_0/R_He$), and Hall mobility ($\mu_H = R_H/\rho$) vs temperature.

prepared by different methods. The similarity of the results for ceramic materials and the epitaxial film indicates that the results are characteristic of the bulk material and not intergranular material, since only thin 90° domain boundaries occur. The simplest explanation of the temperature-dependent Hall number is that both holes and electrons contribute. Their compensation is temperature dependent due to different temperature-dependent mobilities. We cannot determine unique values for the hole and electron concentrations and their mobilities, since only two parameters are measured. However, since $R_H$ is reduced from either the hole or electron value, the Hall number is an upper limit on both concentrations. There can be no more than 0.5 holes or electrons just above $T_c$ in this model. Another possibility is that in these metals some sort of unusual transport is taking place and the hole concentration is linear in $T$.

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