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Superconducting effective-mass anisotropy in $Tl_2Ba_2CaCu_2O_x$

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Using torque magnetometry, we have obtained a lower bound of $\sim 10^5$ for the anisotropy of the superconducting effective mass in a single crystal of $Tl_2Ba_2CaCu_2O_x$. This is the largest such anisotropy yet reported for a high-T_c material.

Our first evidence that thallium-based materials may be the most anisotropic of all the high-T_c superconductors was provided by the work of Kang, Kampwirth, and Gray.[1] Their resistive H_{c2} measurements on an oriented thin-film sample of $Tl_2Ba_2CaCu_2O_x$ suggested a superconducting effective-mass anisotropy of about 10^4. A subsequent torque-magnetometry investigation of a thin-film sample of the same material indicated an anisotropy of the same order of magnitude.[2] However, a more recent penetration-depth estimate,[3] using aligned grains of the closely related material $Tl_2Ba_2Ca_2Cu_3O_x$, reported a value about a thousand times smaller. An early torque estimate[4] of the anisotropy of another grain-aligned sample of the same material gave a similarly low result. These are very puzzling discrepancies. The structure of the 2:2:1:2 compound is very similar to that of the 2:2:2:3, and one would anticipate comparable anisotropies. The fact that large values have only been reported for thin films suggests the possibility of some geometrical artifact. We have therefore made torque measurements on a bulk single-crystal sample of $Tl_2Ba_2CaCu_2O_x$ and report an anisotropy value even larger than that obtained in the thin-film work. This establishes that the large mass anisotropies obtained on thin films are not artifactual. As will be discussed, we believe that the low values obtained with grain-aligned samples arise from problems with the starting material.

The self-flux method used for growing a crystal for this investigation has been described previously.[5] In this method, thallium oxide is added after the other elements are prereacted, and large platelike crystals can be obtained with edge dimensions of the order of 1 mm. However, since small crystals are more likely to be homogeneous than large ones, we used a small section cut from such a parent crystal. It had a shape approximating that of a rectangular parallelepiped, with dimensions $\sim 50 \times 50 \times 250\ \mu m^3$. The c axis lay along one of the short dimensions, and the crystal was mounted in the magnetometer so that the magnetic field always lay in the plane defined by the two short dimensions. Torque measurements were made over the temperature range $62 < T < 115$ K with a null-deflection torque magnetometer[6] having a temperature stability of ± 0.01 K and an angular resolution of $\pm 0.03°$. The maximum torque was observed when the field made an extremely small angle ($\sim 0.4°$) with the Cu-O planes. Figure 1 shows the temperature dependence of the maximum torque. There is substantial rounding above 90 K, with the transition to the normal state not being completed until ~ 108 K. The behavior in the rounded region is likely to be influenced by fluctuations and also perhaps by sample inhomogeneities. A theoretical description of the torque incorporating such effects is not yet available, so we shall first discuss our observations for temperatures below 90 K. We note that extrapolation of the linear region below 90 K to zero torque gives an estimate for the transition temperature of 100 K, within a degree of that obtained by the same procedure in earlier thin-film torque work on the same material.[2]

If θ is the angle between the magnetic field and the c axis, the standard London model[7] gives for the torque, $\tau(\theta)$:

$$\tau(\theta) = \frac{\phi_0 H V}{64\pi^2\lambda^2}\,\frac{\gamma^2-1}{\gamma^{1/3}}\,\frac{\sin(2\theta)}{\epsilon(\theta)}\ln\frac{\gamma\eta H_{C2\parallel}}{H\epsilon(\theta)}\,,\qquad \epsilon(\theta) = (\sin^2\theta + \gamma^2\cos^2\theta)^{1/2}. \tag{1}$$

In this equation, $\gamma = (m_c/m_a)^{1/2}$, where m_a and m_c are

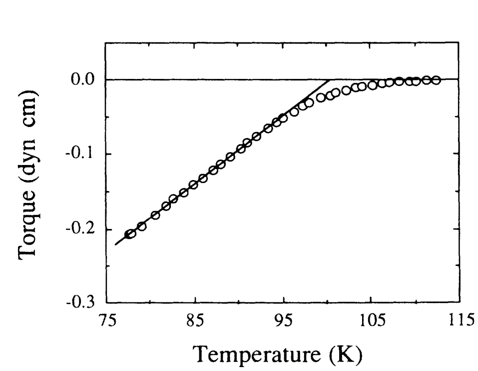

FIG. 1. Temperature dependence of the torque observed at fixed field ($H = 1$ T) and angle ($\theta = 89.6°$) for the single crystal of $Tl_2Ba_2CaCu_2O_x$ described in the text. A straight line is drawn through the data below 90 K and extrapolated to zero torque, giving an estimate of ~ 100 K for the transition temperature. The data for all the other figures in this paper were obtained on the same crystal.

the Ginzburg-Landau superconducting effective masses for electron-pair motion in the planes and along the c axis, respectively. $H_{C2\parallel}$ is the upper critical field measured along the c axis, and η is a constant of order unity.[7] Figure 2 shows the angular variation of the torque, measured at a fixed field and temperature, and normalized to its maximum value. We were able to obtain such data down to $T=75$ K. Below this temperature, irreversibility prevented measurement of the complete angular characteristic. Still, this is a wider reversible region than was available in the thin-film work,[2] where a strong irreversibility set in below $T\sim 90$ K. The theoretical line is the mean-square fit of all the data to Eq. (1), with the parameters $\eta H_{C2\parallel}=11$ T and $\gamma=210$.

As discussed below, it is the behavior in the region where the torque is falling sharply to zero at high angles which controls the anisotropy estimate. The angle at which the torque was half its maximum value was $\sim 89.9°$. Given our limited angular resolution, this meant that the number of data points in the region controlling the estimate of γ was restricted to just two, each with substantial uncertainty. Not surprisingly, it was found that straightforward mean-square fits to all the data gave values of γ with a large scatter from run to run. Taking an average over the four different observation temperatures within the interval $75<T<90$ K gave the result $\gamma=350\pm 100$. We note that a sample curvature of just a few hundredths of a degree would significantly depress the anisotropy estimate. Because of these difficulties, our mass-anisotropy result is best described as an approximate lower bound of 10^5. Note that in the present work the magnetic field always lay parallel to the square cross section of the crystal. By contrast, in the thin-film study the field direction varied from perpendicular to parallel to the film. The general correspondence between the results supports the theoretical expectation[4] that demagnetization effects are negligible.

A disturbing feature of the thin-film torque data[2] was that they gave unphysically large values for the parameter $\eta H_{C2\parallel}$. However, the film exhibited reversible behavior only over a fairly restricted temperature range (90 K $<T<T_c$). In this investigation, the data in the extensive angular region below the peak in the torque remained reversible down to the lowest temperature investigated. These data have therefore allowed us to obtain values of $\eta H_{C2\parallel}$ in an extended temperature range. As is clear from an inspection of Eq. (1), the $\gamma^2\cos^2\theta$ term dominates the angular function $\epsilon(\theta)$ for low angles. In fact, for $\gamma=200$ and for angles less than 88°, the error made in neglecting the $\sin^2\theta$ contribution to $\epsilon(\theta)$ is less than 1%. So, for $0<\theta<88°$, an excellent approximation to Eq. (1) is

$$\tau(\theta)=\left[\frac{\phi_0 H V\gamma^{2/3}}{32\pi^2\lambda^2}\right]\sin\theta\ln\left[\frac{\eta H_{C2\parallel}}{H\cos\theta}\right]. \tag{2}$$

Thus, in the extensive low-angle region, the *angular* variation of the torque is controlled by the parameter $\eta H_{C2\parallel}$ and is independent of the anisotropy. Equation (2) indicates that for fixed temperature and field a plot of $\tau/\sin\theta$ against $\ln(l/\cos\theta)$ should be a straight line. Figure 3 shows a set of such plots for temperatures spanning our measurement range. A value for $\eta H_{C2\parallel}$ was obtained at each temperature by dividing the intercept of each plot by its slope. All the values obtained in this way are plotted in Fig. 4 as a function of temperature. Although there is a sizable scatter, a straight line through all the data provides a reasonable estimate for T_c. Furthermore, the parameter η is expected to be of the order of unity and independent of the material.[7] Using the resistively determined upper-critical-field slope[2] of -1 T/K for $H_{C2\parallel}$, we obtain a value for η of 1.2. A recent torque study[8] of $YBa_2Cu_3O_{7-\delta}$ ($\gamma\sim 7$) reported the value of 1.5 for the same parameter. Considering the markedly different anisotropies of the two materials, these values are in quite good agreement.

The results discussed so far show that the data are in good accord with the accepted theory for temperatures below 90 K, and that the anisotropy is extremely large. As mentioned previously, the broadening of the temperature characteristic shown in Fig. 1 indicates that there are complications for temperatures above 90 K, and it is of in-

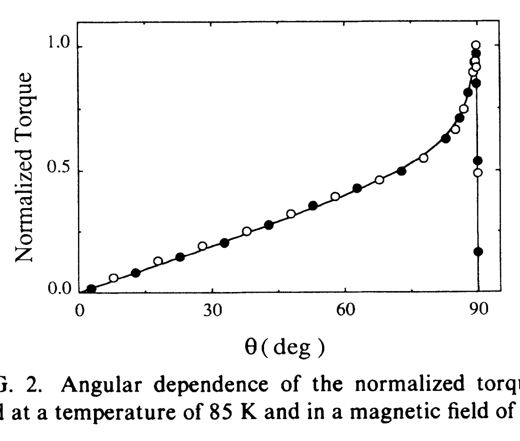

FIG. 2. Angular dependence of the normalized torque observed at a temperature of 85 K and in a magnetic field of 1 T.

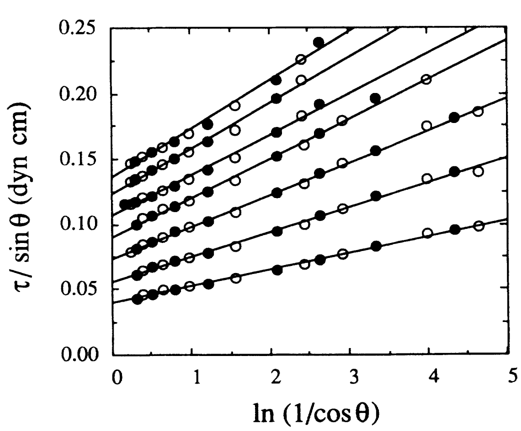

FIG. 3. Logarithmic plots testing the validity of the 3D London model for the variation of torque with angle in a fixed magnetic field of 1 T, as discussed in the text. Solid (open) circles represent data taken with the angle increasing (decreasing), respectively. The lowest line was obtained at $T=90$ K. Proceeding upwards in the figure, the sequence of measurement temperatures was $T=85$, 80, 75, 70, and 65 K, with the uppermost line in the figure corresponding to data taken at $T=62$ K. Units of torque, τ, are dyn cm.

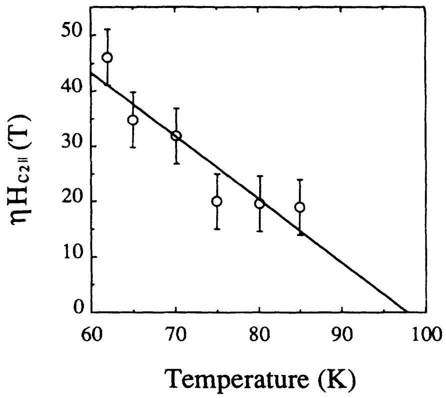

FIG. 4. The temperature dependence of $\eta H_{c2\parallel}$, calculated from the plots in Fig. 3.

terest to see how these affect the applicability of the three-dimensional (3D) theory. To that end, a number of torque measurements were made in the range $90 < T < 105$ K. In this region, it was found that the apparent value of η increased with increasing temperature. At $T=95$ K, for example, it had risen to a value of 2.5. Note that this is much smaller than the value of 24 reported for the thin film at $T=90$ K, suggesting that there is no simple association between anomalous η values and fluctuations. Of more interest, for all temperatures at which a torque was detectable we found that *the drop at high angles remained extremely sharp.* Figure 5 shows examples of such high-angle data. The angular-resolution problem mentioned previously is compounded at high temperatures by a diminished signal-to-noise ratio. However, the data continued to give γ estimates of a few hundred, even at the highest temperature examined ($T=105$ K).

There are two additional points of interest. First, for $YBa_2Cu_3O_{7-\delta}$ it has been reported[8] that the angular dependence of the torque below $0.9T_c$ is anomalous. For $YBa_2Cu_3O_{7-\delta}$, the best available estimates suggest[9] that the Ginzburg-Landau coherence length becomes less than the spacing of the Cu-O planes below a cross over temperature of $\sim 0.9T_c$. For this and other reasons it was suggested[7] that the anomalous behavior in $YBa_2Cu_3O_{7-\delta}$ is associated with such a dimensional crossover. Because of the extreme anisotropy of $Tl_2Ba_2CaCu_2O_x$, any such crossover would be expected to occur much closer to T_c. In this work we have shown that the angular dependence of the torque is well described by Eq. (1) all the way down to $\sim 0.6T_c$. However, there is no direct conflict between these two observations. The anomalous behavior for $YBa_2Cu_3O_{7-\delta}$ was confined to the angular region where the torque falls rapidly with increasing angle. In the case of $Tl_2Ba_2CaCu_2O_x$, this situation is only realized for $\theta > 89.9°$. With our present angular resolution, an anomaly with similar characteristics to the one reported in $YBa_2Cu_3O_{7-\delta}$ would be impossible to resolve. We are presently constructing a torque magnetometer with improved angular resolution so that we can address this question experimentally.[10]

Finally, we consider the huge discrepancy between our mass-anisotropy value for this material, 10^5, and the value of about 10 reported in two investigations[3,4] that used grain-aligned samples of the closely related thallium compound $Tl_2Ba_2Ca_2Cu_3O_x$. We suggest that this discrepancy results from a substantial amount of misaligned material in the grain-aligned samples. In both those investigations, the narrow angular half-width ($\sim 1°$) of an x-ray rocking curve was used as an indication of good alignment. However, a rocking-curve half-width can be a misleading measure if the sample contains grains which are misaligned by many degrees. Some sort of pole analysis[11–13] is then required to properly characterize the alignment. If suitable precautions are taken, such work confirms that aligned samples of $YBa_2Cu_3O_{7-\delta}$ can be prepared containing a very small amount of unaligned material. No such detailed analysis has been reported for the thallium materials. An elementary consideration of the magnitude of the aligning torque indicates that misalignment by many degrees is impossible if the starting grains are homogeneous single crystals. The thallium superconductors are known to have many more defects than $YBa_2Cu_3O_{7-\delta}$, and single crystals are harder to grow.[5] It is therefore possible that the problem lies in defects that result in a significant proportion of the grains having polycrystalline regions. To explain the low anisotropy values obtained in Refs. 3 and 4 would require that of the order of half of the material sample was unaligned.[3] Quantitative evidence that such a degree of misalignment is possible for grain-aligned $Tl_2Ba_2Ca_2Cu_3O_x$ samples comes from the work of Halperin *et al.*[14] They have made use of the ^{205}Tl Knight-shift anisotropy to determine the misaligned fraction, finding values in the range from $\frac{1}{2}$ to $\frac{3}{4}$ for a number of samples prepared in the usual way. The x-ray rocking-curve widths for the same samples were all of the order of 1°. As an additional cautionary comment, we note that the difficulties mentioned are almost certainly also present with 2:2:1:2 and 2:2:2:3 bismuth material. Torque experiments on grain-aligned 2:2:1:2 bismuth samples[6] give mass anisotropies of the order of 10, a value which is also known to be much too low.[15]

In summary, we have confirmed that $Tl_2Ba_2CaCu_2O_x$ is

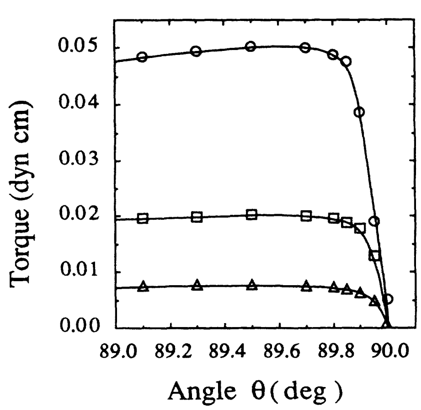

FIG. 5. Angular dependence of the torque in the high-angle region. The magnetic field was held constant at $H=1$ T. Circles, squares, and triangles represent data taken at $T=95$, 100, and 105 K, respectively. The curves through the data sets are drawn to guide the eye.

the most anisotropic of all the high-T_c materials. Our results provide an estimated lower bound of 10^5 for the superconducting effective-mass anisotropy. Comparison with work on grain-aligned samples suggests that individual grains of the thallium high-T_c superconductors prepared by using conventional ceramic processing contain substantial polycrystalline regions.

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