Pairing symmetry from in-plane torque anisotropy in $Tl_2Ba_2CuO_{6+\delta}$ thin films

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The in-plane torque anisotropy of high-quality epitaxial $Tl_2Ba_2CuO_{6+\delta}$ thin films patterned into disks has been investigated. We have found that the angular dependence of the reversible torque displays a clear fourfold symmetry added to a twofold one. Excluding all experimental artifacts due to geometry or magnetic-field misalignment, we propose in the frame of a model by Beal-Monod and Maki that this is real bulk evidence for a $d+s$ pairing state allowed by the possible breaking of the tetragonal symmetry at low temperature. Identical measurements on a NbN thin film and a $NbSe_2$ single crystal show no anisotropy, in agreement with the expected symmetry for these classical superconductors. [S0163-1829(98)05610-0]

I. INTRODUCTION

In recent years there has been a large amount of experimental evidence favoring a $d_{x^2-y^2}$ symmetry for the pairing state of the high-temperature superconductors;[1] nevertheless there still is a large debate on the possible mixing of d wave and s wave especially in the orthorhombic $YBa_2Cu_3O_{7-\delta}$ (YBCO). Among the bulk of experiments, results from angular-resolved photoemission,[2,3] nuclear-spin-relaxation rate,[4] or magnetic penetration depth[5] have inferred the presence of nodes in the superconducting gap of the high-T_c cuprates. Furthermore quantum phase-interference experiments have also confirmed the presence of nodes and sign changes of the gap function over the Fermi surface.[6–8] A particularly elegant experiment favoring d-wave symmetry is that of the YBCO tricrystal demonstrating the spontaneous generation of half integer flux quanta in rings interrupted by an odd number of Josephson junctions.[9–11] Several groups have also discussed the influence of d-wave symmetry on the transport properties through tilt boundary junctions.[12,13] However, most of the data were taken on YBCO, where the presence of CuO chains and the orthorhombic distortion of the CuO_2 planes naturally induce an anisotropy in the pairing interaction. Beal-Monod, Maki, and co-workers[14] have shown that the orthorhombic distortion leads necessarily to an admixture of s-wave component in a $d+s$ superconductivity model. In a band-structure model by Combescot and Leyronas[15] the coupling between chains and planes in YBCO was also proposed to lead to an anticrossing of the plane and chain bands, and thus to blend s- and d-wave features. Recently Müller[16,17] proposed for the high-T_c cuprates the possible coexistence of two condensates with different symmetry (s and d wave) but having the same superconducting transition temperature T_c. The mixing of d and s wave is thus still largely debated, as several experiments cannot be explained by a pure d-wave pairing only. For example, tunneling data on Pb/YBCO Josephson junctions indicate the presence of a significant s-wave component,[18] whereas phase-sensitive measurements on YBCO tricrystal microbridges also show evidence of a $d+s$ pairing symmetry.[19]

The problems raised by orthorhombicity and interplane coupling can, in principle, be avoided by investigating the $Tl_2Ba_2CuO_{6+\delta}$ (Tl2201) compound, which has a tetragonal structure with a single CuO_2 layer per unit cell and no CuO chains. Using thin films of Tl2201, the tricrystal experiment was repeated by Tsuei *et al.*[20] in order to confirm the half integer flux quantum effect observed earlier with YBCO.

In this paper we present in-plane torque anisotropy measurements $\tau(\theta)$ performed on epitaxial Tl2201 films patterned into disks in order to gain information on the symmetry of the pairing state in this material.[21] The films are of the same manufacture as those reported in Ref. 20. Our results are compared with similar data taken on the classical superconductors NbN and $NbSe_2$ with known s-wave symmetry. The torque measurement has the advantage of being a true bulk experiment independent of the quality of grain boundaries and interfaces in general, in contrast to the tunneling and phase-sensitive experiments. We expect that in a tetrag-

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onal structure the d-wave state manifests itself by a pure fourfold symmetry in the angular dependence of the torque as the magnetic field B is rotated within the CuO_2 planes.

A simple model for the angular dependence of the in-plane torque anisotropy was proposed earlier by Won and Maki[22] for orthorhombic YBCO. Based on Ginzburg-Landau (GL) theory with d-wave pairing interaction and Coulomb repulsion in the s channel, they calculated the free energy ΔF in the vicinity of the upper critical field H_{c2}. From the expression of ΔF an expression for the in-plane torque angular dependence was derived as

$$\tau(\theta,t)=-\frac{\partial\Delta F}{\partial\theta}\cong-\frac{B}{4\pi\kappa_2^2\beta_{\mathrm{A}}}\ln\left(\frac{H_{c2}(\theta)}{B}\right)H_{c2}\left(\frac{\pi}{4},t\right)\times[a_2\sin(2\theta)+a_4\sin(4\theta)], \qquad (1)$$

where θ is the angle between the applied field B and the a axis, and $t=T/T_c$ is the reduced temperature.

In this equation, the twofold term a_2 describes in an *ad hoc* manner the anisotropy due to orthorhombicity, and the fourfold term $a_4=\Delta H_{c2}/H_{c2}(\pi/4,t)$ reflects d-wave symmetry. The GL and Abrikosov parameters κ_2 and β_{A} have a weak temperature and angle dependence assumed to be negligible.

In-plane torque anisotropy measurements on a rectangular untwinned YBCO single crystal were recently reported by Ishida *et al.*[23] to exhibit a fourfold symmetry attributed to $d_{x^2-y^2}$ symmetry with a twofold contribution claimed to be due to geometrical effects. In this experiment no particular attention was paid to an exact field alignment. Earlier measurements of the a-b plane magnetization in the Meissner state of $LuBa_2Cu_3O_7$ by superconducting quantum interference device (SQUID) magnetometry were dominated by geometric demagnetization factors as well as trapped flux, and were not conclusive about the anisotropy of the pairing state.[24] From resistive measurements along the c axis, a fourfold symmetry of $H_{c2}(\theta)$ in the a-b plane was reported in $La_{1.86}Sr_{0.14}CuO_4$ by Hanaguri *et al.*[25] and more recently by Koike *et al.*[26] in $Pb_2Sr_2Y_{0.62}Ca_{0.38}Cu_3O_8$ twinned single crystals. However such measurements are affected by geometrical and structural artifacts, which might render their conclusions on pairing symmetry questionable. In a recent paper by Aubin *et al.*[27] the presence of a fourfold symmetry in the angular dependence of the thermal conductivity in a YBCO detwinned single crystal was reported. The results were explained by d-wave superconductivity with possible mixing of up to 10% s-wave component. To our knowledge, only angular dependence of the c-axis normal-state magnetoresistance has been reported in Tl2201 (Ref. 28) and exhibits an anisotropy with fourfold symmetry.

II. EXPERIMENTAL DETAILS

A. Thin films

Tl2201 films of thickness 200 and 500 nm were deposited on thin $SrTiO_3$ (001) substrates by RF magnetron sputtering and then annealed using a two-step process.[29,30] The films investigated here were optimally or overdoped with respective transition temperatures $T_c=82.5$ K (200 nm) and 69 K (500 nm), as measured from dc SQUID magnetization and from the resistive transitions. The crystal structure was checked at room temperature by x-ray diffraction and transmission electron microscopy, and found to be tetragonal, c-axis-oriented, and free of twinning. It has already been shown that the transition temperature of the Tl2201 films can be continuously and reversibly adjusted between 11 and 80 K by annealing in argon or air, with no change in their tetragonal symmetry.[30] The surface topography of the films was further investigated by scanning probe microscopy [scanning tunneling microscopy (STM), atomic-force microscopy (AFM)] and scanning electron microscopy (SEM). The surface appears homogeneous with no preferential orientation of the grown islands. In the thicker films the mean roughness over a 4-μm^2 area was about 15 nm. We have paid special attention to the exact crystallographic orientation of the (001) substrate surface as checked by Laue diffraction. Only substrates with a zero miscut angle ($<0.2°$) were used for our experiment in order to avoid any anisotropy of the flowing currents in the epitaxial films induced by the presence of steps at the substrate surface. For the same films, it has been shown by high-resolution magneto-optical imaging that the flux distribution for the magnetic field applied along the c axis is fractal without measurable anisotropy of the critical current J_c.[31] At larger miscut angles, e.g., at 2.5°, the effective anisotropy of J_c can be as large as 11. For the torque measurement the films were patterned into disks of about 2 mm diameter by conventional photolithographic technique, without any deterioration of the superconducting properties. A perfect disk shape is a stringent prerequisite for a proper in-plane anisotropy measurement without dominant geometrical and demagnetization effects at lower fields ($H\simeq H_{c1}$).

B. Torquemeter

Our capacitive torque magnetometer has been designed to reach the appropriate sensitivity ($\Delta\tau\simeq10^{-12}$ Nm) for our thin-film experiments. It is formed of a flexible 20-μm-thick Si lever located vertically between two electrodes, as shown in Fig. 1(a). The sample is mounted on the ledge of the cantilever at an angle as close to 90° as possible. In a homogeneous magnetic field $\vec{B}$, the lever is bent by the torque $\vec{\tau}=\vec{m}\times\vec{B}$, which acts on the sample with magnetic moment $\vec{m}$. Its deflection is measured by a differential low-noise capacitive technique. The torquemeter with the film positioned horizontally is mounted in a flow cryostat, and the applied field produced by a large-bore NMR electromagnet (field inhomogeneity $\leqslant10^{-4}$) is rotated within the plane of the film with an angular resolution better than 0.01°. The NMR magnet has an additional compensation coil, which allows the remanent field to be cancelled and external field perturbations to be compensated for.

To avoid any artifact due to out-of-plane contributions such as the c-axis pinning component, the field B must remain strictly parallel to the CuO_2 layers during its rotation. We have developed a compensation technique to minimize the precession of $\vec{B}$ with respect to the film plane. This is achieved by applying a small additional field $\vec{b}=\vec{b}_0\sin(\theta-\theta_0)$ along the vertical direction z, with an amplitude modulated in phase with the rotation angle θ of the main field $\vec{B}$

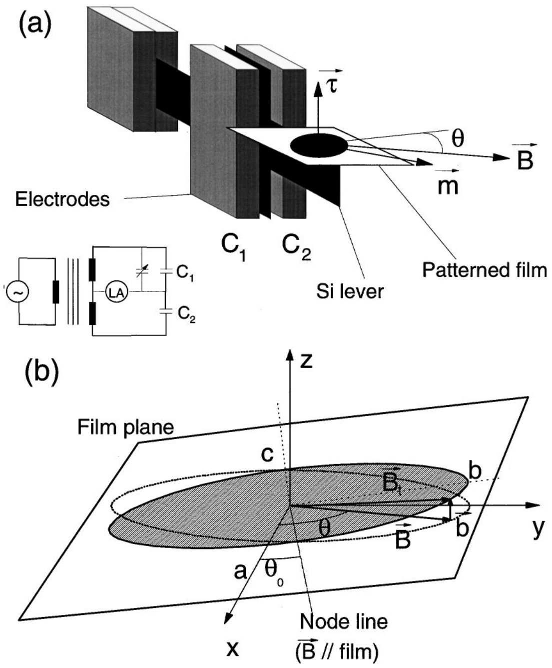

FIG. 1. (a) Schematic view of the capacitive torquemeter with sample geometry. (b) Sketch of the compensation method used to eliminate the misalignment of the rotating field $\vec{B}$ with respect to the film plane by addition of a small field $\vec{b}$ having a variable amplitude along $z[\vec{B}_t=\vec{B}+\vec{b}_0\sin(\theta-\theta_0)]$.

[Fig. 1(b)]. The angle θ is defined with respect to one of the a axes of the film. We have checked by Laue diffraction that these axes are well aligned with the edges of the substrate. After zero-field cooling the sample through T_c, the angular position θ_0 of the node line, where $\vec{B}$ is strictly parallel to the film plane, is found by making successive runs in field until the torque curve $\tau(B)$ becomes zero and well reversible. Once θ_0 is set, the angular torque measurement is performed at a given amplitude B by varying the amplitude b_0 (typically 100–300 G) until $\tau(\theta)$ becomes fully reversible. With this technique the field misalignment is controlled within 0.07°. Usually the experiment is performed by starting the rotation at the node line ($\theta=\theta_0$) in order to avoid any abrupt step Δb, susceptible of generating trapped flux in the sample. Trapped flux, like a fixed moment, would generate a $\sin\theta$ in the anisotropy curve and not a $\sin 2\theta$. Such a $\sin\theta$ component was only observed upon field cooling in a larger field (~0.3 T), but was totally absent after our zero-field-cooling procedure. During a run, the temperature is stabilized within ±5 mK using a Cernox thermometer.

III. RESULTS

A. Tl2201 films

The angular dependence of the in-plane torque $\tau(\theta)$ was measured over 360° in two different Tl2201 films of thicknesses 200 nm ($T_c=82.5$ K) and 500 nm ($T_c=69$ K). Data were taken in clockwise $[\tau^+(\theta)]$ and counterclockwise $[\tau^-(\theta)]$ directions of rotation at constant speed. Without correction for the slight misalignment of the film with respect to the rotating field $\vec{B}$, the torque curves $\tau(\theta)$ display a large hysteresis with two peaks due to pinning contributions along the c axis [Fig. 2(a)]. The peaks, i.e., the irreversibility maximum, occurs when $\vec{B}$ crosses the film plane. After optimizing the field alignment, $\tau(\theta)$ becomes fully reversible, as shown in Fig. 2(b), with zeroes as $\vec{B}_t$ becomes parallel to the a axes ($\theta=n\pi/2$, $n=0,1,2,\ldots$). Full reversibility confirms the cancellation of all pinning contributions. Adjustment of the two parameters b_0 and θ_0 is rather critical owing to the thinness of the sample but can be done in a very reproducible way. We have checked that the measured torque is independent of the rotation speed when reduced from 110°/min to 10°/min. This proves the negligible role of eddy currents. Through simulations we also found that the sensitivity of the lever to a torsion around its main x axis is seven orders of magnitude smaller than to that around its z axis. Thus, such a torsion does not affect our torque results.

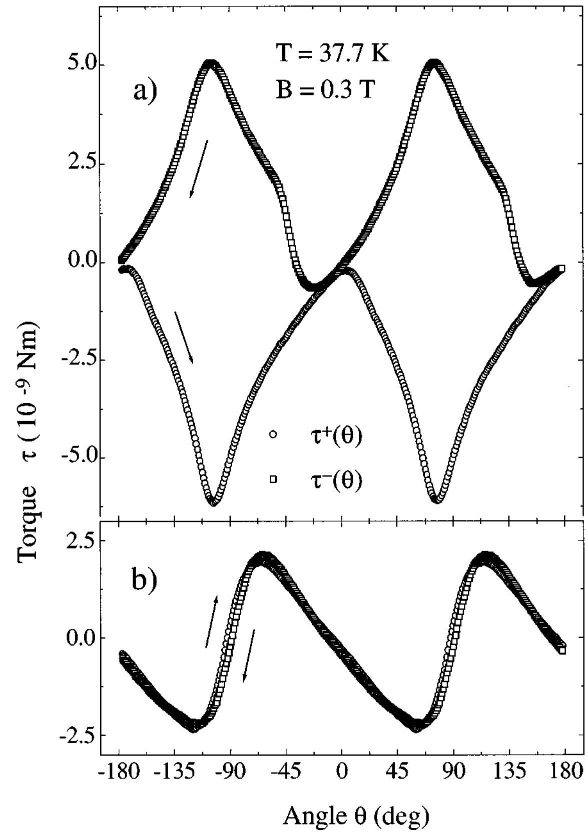

FIG. 2. In-plane torque angular dependence of the 500-nm Tl2201 film at $T=37.7$ K obtained by rotation of the field $B=0.3$ T around the vertical z-axis clockwise (τ^+) and counterclockwise (τ^-): (a) before adjusting for the slight film misalignment with respect to B, (b) after optimized alignment.

Under these conditions the reversible torque given by $\tau_{\mathrm{rev}}(\theta)=\frac{1}{2}[\tau^+(\theta)+\tau^-(\theta)]$ is expected to reflect the intrinsic in-plane properties of the film. For both Tl2201 films $\tau_{\mathrm{rev}}(\theta)$ exhibits a twofold and fourfold symmetry as shown in Fig. 3 for the thicker film (500 nm) at $T=37.7$ K and $B=0.3$ T. After subtraction of the background measured above T_c, which is mainly due to the $SrTiO_3$ substrate, $\tau_{\mathrm{rev}}(\theta)$ can be fitted by the expression

$$\tau(\theta)=\tau_0+\tau_2\sin 2(\theta-\theta_2)+\tau_4\sin 4(\theta-\theta_4), \tag{2}$$

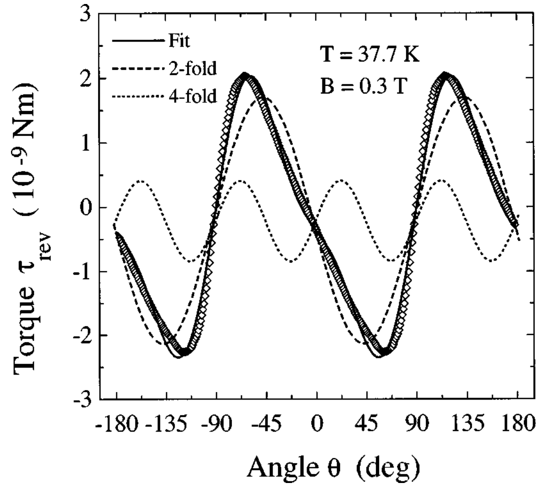

FIG. 3. In-plane reversible torque $\tau_{\mathrm{rev}}(\theta)$ of the 500-nm Tl2201 film at $T = 37.7$ K upon rotation of the field $B = 0.3$ T. The solid line represents the fit to the data using Eq. (2), which is the addition of the twofold (dashed line) and the fourfold component (dotted line).

where τ_2, τ_4 are the amplitudes and θ_2, θ_4 the phases of the two- and fourfold components, respectively. In this particular case, $\tau_2 = 1.92\times 10^{-9}$ Nm, $\theta_2 = 87.3°$, and $\tau_4 = 6.25\times 10^{-10}$ Nm, $\theta_4 = -0.6°$.

At different fields up to 1.5 T, $\tau(\theta)$ was measured as a function of temperature. Two typical curves $\tau(\theta)$ taken at 23.7 and 43.2 K for the same Tl2201 film (Fig. 4) clearly show a modification in their shape with changing temperature. During one set of measurements the phases θ_2 and θ_4 remained almost unchanged, within experimental errors. Upon warming up and cooling down through T_c in zero field, we have occasionally observed a simultaneous shift in θ_2 and θ_4 of 90° and 45°, respectively. This demonstrates that the two- and fourfold components are locked to each other. The general trend is a progressive dominance of the twofold component at lower temperature. This behavior is clearly seen in Fig. 5, where the two coefficients $\tau_2^* = \tau_2/B$, $\tau_4^* = \tau_4/B$ and their ratio $R = \tau_4/\tau_2$ are plotted vs reduced temperature T/T_c for both films. The normalization caused by the measuring field B is used to determine a_2 and a_4, which can be derived from Eqs. (1) and (2) as $a_2 = c\tau_2^*$ and $a_4 = c\tau_4^*$ with $c = 1/(4\pi\kappa_2^2\beta_A)\ln(H_{c2}(\theta)/B)H_{c2}(\pi/4,t)$. The general agreement between the data of the two Tl2201 films having different thicknesses and critical temperatures is a good proof of the generality of our observation. The temperature dependence can be described by a $(1-T/T_c)^n$ law with the exponent $n = 2.5$ for τ_4 and 4.5 for τ_2.

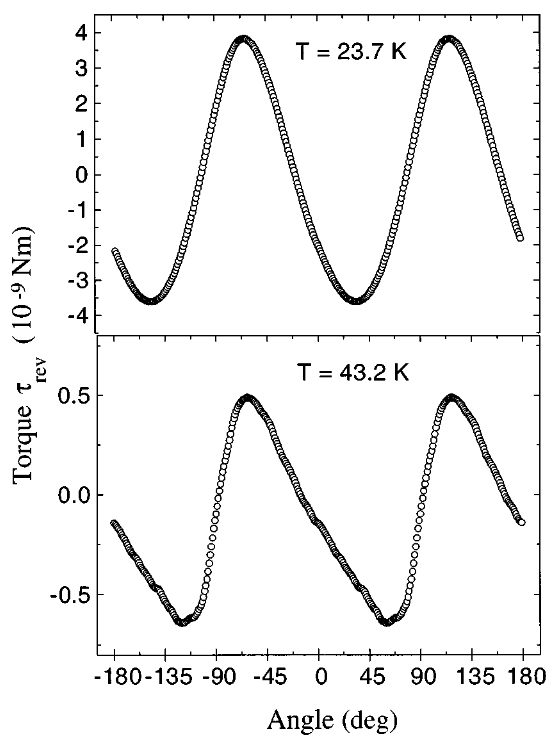

FIG. 4. Examples of angular dependence of the in-plane reversible torque in the 500-nm Tl2201 film measured at two different temperatures 23.7 and 43.2 K. The change in shape is evident.

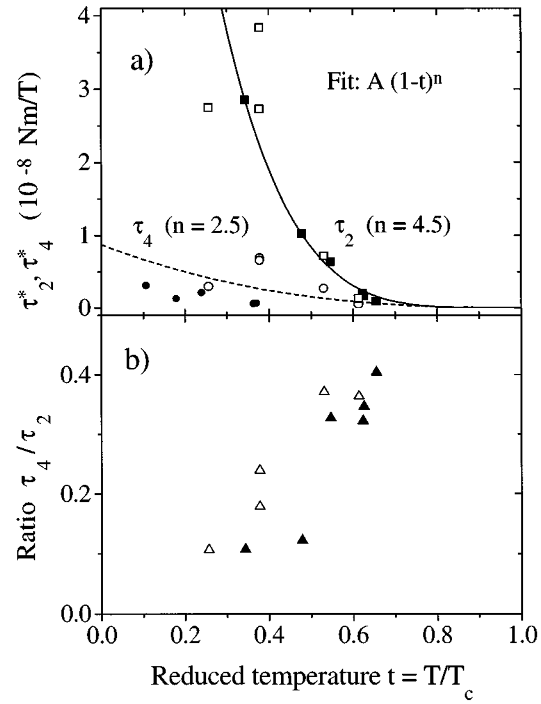

FIG. 5. (a) Normalized twofold ($\tau_2^* = \tau_2/B$) and fourfold ($\tau_4^* = \tau_4/B$) coefficients vs reduced temperature obtained by fitting Eq. (2) to $\tau_{\mathrm{rev}}(\theta)$ curves of two different Tl2201 films (open symbols: 200-nm thick, $T_c = 82$ K; filled symbols: 500-nm thick, $T_c = 69$ K). The factor B is the specific measuring field at each temperature. The two lines are the respective fits with the power law $(1-t)^n$. (b) Corresponding ratio $R = \tau_4/\tau_2$.

B. Classical superconductors NbN and $NbSe_2$

In order to further validate our torque measurements on Tl2201 films and exclude experimental artifacts, we have performed exactly the same measurements on a NbN film and a $NbSe_2$ single crystal. NbN has a fcc cubic (B1) structure and can easily be grown by sputtering on a Si(001) wafer. Its surface structure checked by STM is granular (grain size≃20–30 nm) but very homogeneous. The 200-nm-thick films with a sharp superconducting transition at $T_c = 15.7$ K were patterned into a disk of the same size as the Tl2201 films. Without a perfect in-plane alignment of $\vec{B}$, the

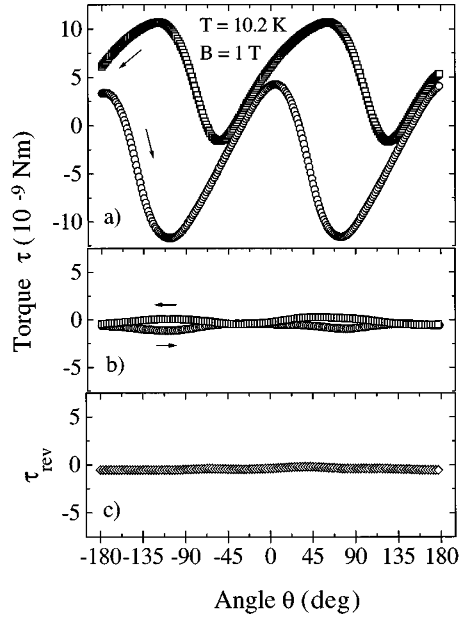

FIG. 6. Angular-dependent torque of a NbN film (200 nm) patterned into a 2-mm-diameter disk, measured at 10.2 K upon rotation of $B=1$ T around the z axis: (a) before proper in-plane alignment of B and (b) after alignment correction. (c) Corresponding reversible torque $\tau_{\mathrm{rev}}(\theta)$.

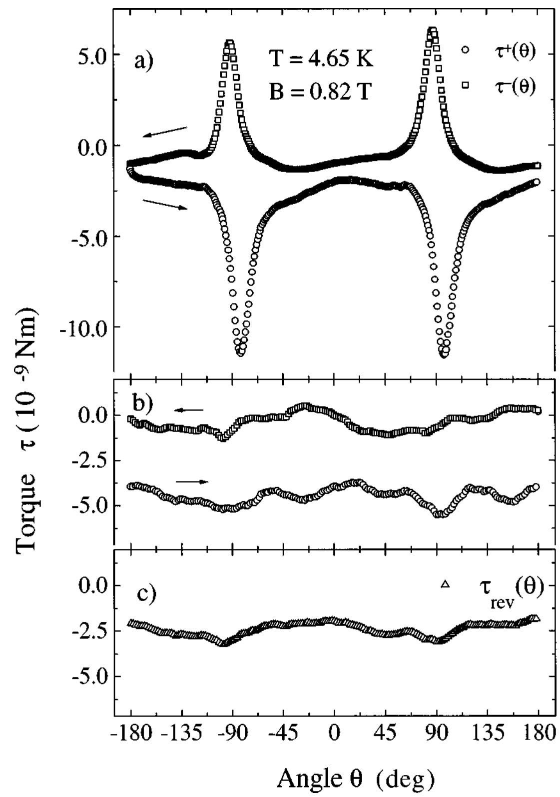

FIG. 7. Angular-dependent torque of a triangular 2H-NbSe$_2$ single crystal upon rotation of the field $B=0.82$ T around the z axis at 4.65 K: (a) before proper in-plane alignment of B and (b) after alignment correction. (c) Corresponding reversible torque $\tau_{\mathrm{rev}}(\theta)$.

torque signal displays a large hysteresis between $\tau^{+}(\theta)$ and $\tau^{-}(\theta)$, characterized by two large maxima and minima around $\pm 90°$ [Fig. 6(a)]. After proper adjustment of the parameters b_0 and θ_0, the torque amplitude is largely reduced compared to the initial uncompensated one, with negligible angular dependence [Fig. 6(b)]. The derived reversible torque $\tau(\theta)_{\mathrm{rev}}$ itself is almost completely flat and shows no anisotropy [Fig. 6(c)]. This holds true at the different temperatures and fields used in the measurements. This result confirms that in an isotropic material with very strong pinning, the out-of-plane magnetization effects can be fully cancelled with our technique and that, as expected, no in-plane torque anisotropy remains.

A better comparison to the layered Tl2201 is made with 2H-NbSe$_2$, which is a clean type-II superconductor with a transition temperature $T_c=7.2$ K and a charge-density-wave transition at 33 K. This material has a layered hexagonal structure formed by stacking triple layers of SeNbSe on top of each other. The superconducting gap and its temperature dependence are known to follow the BCS predictions.[32] The first observation of the Abrikosov vortex lattice using an STM was made by Hess *et al.*[33] on this material. We shaped the single crystal into an equilateral triangle having 2.5-mm-long sides, expecting to observe a three- or sixfold symmetry in the in-plane torque anisotropy. This is not the case. In fact, prior to exact field alignment [Fig. 7(a)], the $\tau^{+}(\theta)$ and $\tau^{-}(\theta)$ curves again display a large hysteresis with peaks located around $\pm 90°$ because of the pinning contribution along the c-axis. After proper alignment the out-of-plane components are reduced by a factor up to ~ 15, leaving two parallel lines with minimal structures and, in contrast to the Tl2201 films, no evidence of any specific symmetry [Fig. 7(b)]. The offset between $\tau^{+}(\theta)$ and $\tau^{-}(\theta)$ is believed to originate from in-plane pinning, which produces a frictional torque on the vortex lines during rotation. This also explains the small angle shift ($\sim 6°$) between the peaks in $\tau^{+}(\theta)$ and $\tau^{-}(\theta)$ in Fig. 7(a).

We note here that the torque amplitude $\tau(\theta,t)$ at a given field B is mainly determined by the ratio $H_{c2}(t)/\kappa^2$, see Eqs. (1) and (3) of the sample and by its volume V. For Tl2201 and NbSe$_2$, which are both in the clean limit, this ratio can be estimated at $T=0$ to be $H_{c2}(0)/\kappa^2 \approx 4-5\times 10^{-3}$ T for both compounds. Now, as the volume of the NbSe$_2$ crystal is about 100 times larger than that of the Tl2201 film, it appears that the normalized reversible torque amplitude τ_{rev}/BV of the former is effectively 1000 times smaller than that of the latter, at approximately the same t. Thus, plotted on the same scale as for Tl2201, the normalized angular torque of NbSe$_2$ would be absolutely flat.

IV. DISCUSSION

The striking result of our experiment is the presence of the twofold ($\sin 2\theta$) component in the in-plane torque anisotropy of Tl2201, which is unexpected for a tetragonal symmetry. A possible origin in the microstructure of the film can *a priori* be excluded, as confirmed by the absence of any preferential growth structure in the film in the AFM/STM and SEM images. If stacking faults were to occur, they would run along both crystallographic axes and thus contribute more to a fourfold symmetry. The measurements performed on 2H-NbSe$_2$ and NbN, which show no anisotropy, are a strong proof that all non-in-plane pinning contributions due to field misalignment and geometrical effects can be fully cancelled. The argument that flux pancakes could be trapped during the cooling along one direction and remain in this configuration during the entire rotation does not hold, as such trapped flux would mainly generate a $\sin\theta$ component. Several tests have been done to exclude this effect. Finally, by turning the film/substrate on the cantilever by 45°, we have observed a shift of the torque signal by the same angle. All these tests substantiate our view that the observed twofold term is not artifactual but must be related to the superconducting state.

As pointed out by Annett,[1] group-theory arguments do not allow the mixing of the four singlet pairing states in a single plane with square symmetry unless fluctuation effects are dominant. Thus, in order to explain our data it is reasonable to expect that the mixing can be generated by an orthorhombic distortion of the Tl2201 film occurring at low temperature. One possibility could be the presence of defects in the Tl films. Jorgensen *et al.*[34] have recently shown that interstitial oxygen between the Tl-O plane as well as Cu substitution on the Tl sites affects the properties of Tl2201. In particular the latter defect is found to correlate with orthorhombic strains: samples with less Cu on the Tl sites have larger orthorhombic strains. The breaking of the local symmetry could also arise from thermal fluctuations and other disorder effects. This point still has to be clarified by low-temperature x-ray or neutron-diffraction analysis.

In order to develop the idea of a single $d+s$ pairing state further, we should note that the formal separation into a twofold and fourfold component does not really make sense. In general the $d+s$ wave function retains the shape of a four-leaf clover with two large and two small leaves until the amount of s character becomes equal to or larger than the d component. Thus we tried to fit our torque data with an expression proposed by Maki and Beal-Monod[14,35] in a two-dimensional (2D) model for mixed $d+s$ wave superconductivity for an orthorhombic superconductor and characterized by a gap function of the form $\Delta(\vec{k})=\Delta\cdot[\cos(2\phi)+r]$, ($|r|<1$). Here ϕ is the angle the wave vector $\vec{k}$ makes with the a axis, and r measures the amount of s-wave contribution and vanishes in the absence of an orthorhombic distortion. In this model the normal-state anisotropy is also taken into account through an elliptical Fermi surface with a density of states $N_0(\phi)$ and an effective mass ratio $\varepsilon=(m_b-m_a)/(m_b+m_a)$. From the calculation of the free energy and of $H_{c2}(\theta)$ for B parallel to the a-b plane, the following angular dependence for the torque is derived:

$$\tau(\theta,t)=-\frac{BH_{c2}(\pi/4,t)}{8\pi\kappa^2\beta_A}\ln\left(\frac{\eta H_{c2}(\theta,t)}{B}\right)\frac{X\sin(2\theta)}{[1+X\cos(2\theta)]^{3/2}}. \quad (3)$$

Here η is a constant of order unity, κ and β_A are the GL and the Abrikosov parameters, respectively. The quantity X is essentially a function of the anisotropy ε, of the s-wave admixture r, and of a coefficient g measuring the orthorhombic distortion. Thus, the in-plane anisotropy of the upper critical field can be written as $H_{c2}^b/H_{c2}^a=\sqrt{(1+X)/(1-X)}$.

We found that the fit of our torque data with Eq. (3) is in fact much better than with Eq. (2). An example is shown in Fig. 8 for the same experimental curve of Fig. 3 taken at 37.7 K and $B=0.3$ T. In this case the fitting parameter is $X=0.427$. From the measurements done on both Tl2201 films at different temperatures, one observes a monotonic increase of $X(t=T/T_c)$ as displayed in Fig. 9(a). The anisotropy ratio $R_{ab}(t)=H_{c2}^b/H_{c2}^a$ plotted in Fig. 9(b) is found to increase continuously from about 1.1 to 1.7 in the given temperature range, $0.25\leq t\leq 0.65$. A value for r can only be derived in a given limit, for example, in the case of an isotropic Fermi surface, i.e., $\varepsilon=0$. In this case $X=-(r+2g)/(1+4rg)$. Close to T_c, the coefficient g depends on the effective at-

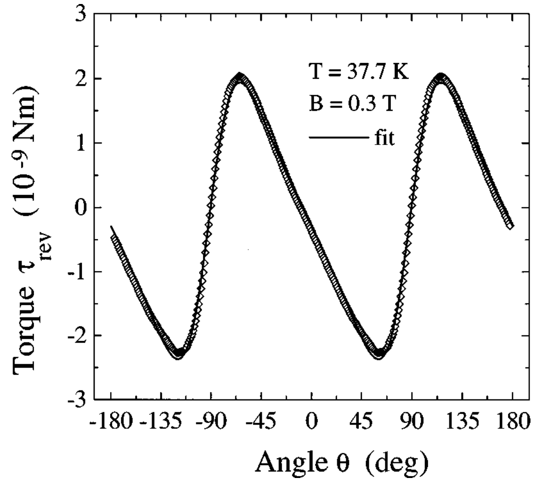

FIG. 8. Fit of the reversible torque of the 500-nm-thick Tl2201 film using the angular dependence [Eq. (3)] proposed for a superconductor with mixed $d+s$-wave symmetry.

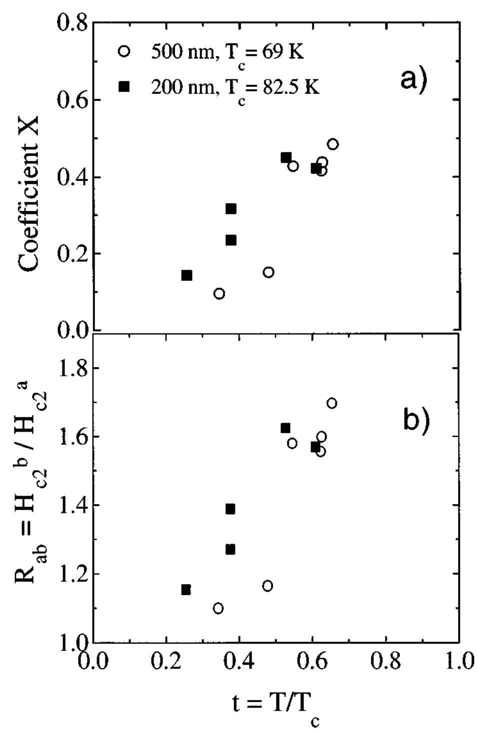

FIG. 9. Temperature dependence (a) of the fitting coefficient X and (b) of the corresponding upper critical field anisotropy ratio, H_{c2}^b/H_{c2}^a.

traction λ, on the Coulomb repulsion μ, and on r in the following way:[14,36] $g=(\lambda+\mu)r/[\lambda(1-2r^2)]$. A relation between r and X can then be derived from these two equations. Taking the reasonable values $\lambda=0.5$ and $\mu=0.2$ and our experimental $X=0.427$, one obtains two solutions for the s-wave contribution, namely $r=-0.12$ and $r=-0.97$ in the range $|r|\leq 1$. According to the model, a pure d-wave state corresponds to $X=0$ and $R_{ab}=1$. As the s-wave contribution increases, these two quantities increase correspondingly. Thus the temperature dependence of X and R_{ab} derived from our data suggests that the s-wave component rises continuously with temperature up to T_c. A question that naturally arises is whether Eq. (3) is appropriate to analyze our torque data. If one assumes Tl2201 to be a conventional anisotropic s-wave superconductor, a natural way to proceed would be to solve the London equations for an anisotropic superconductor using the effective mass anisotropy $\gamma=\sqrt{m_b/m_a}$. Following the procedure of Kogan,[37,38] we would get an expression for the torque resembling Eq. (3), but with a term proportional to $\alpha\sin(2\theta)[1+\beta\cos(2\theta)]^{-1/2}$, where α and β are functions of γ. Analyzing our data with this term did not yield as good a fit as the above expression for the mixed $d+s$ state. This is in fact expected as quantum phase-interference experiments exclude the anisotropic s wave owing to the sign change of the order parameter. Thus the interpretation of our data with a mixed $d+s$ state seems the most reasonable approach mainly because we do not observe the single fourfold term expected for a pure d wave. Estimating the relative weight of the s wave with respect to the d wave is nevertheless difficult mainly because the GL equation for the free energy is a nontrivial function of the order parameter chosen as $\Psi=|\Psi_d|\cos 2\theta+|\Psi_s|$, owing to the terms in $|\Psi|^2$, $|\Psi|^4$ in addition to the mixed terms due to gradients and field. Thus, trying to fit the free energy F obtained by integrating the experimental torque $\tau(\theta)$ over θ in order to get the ratio $|\Psi_s|/|\Psi_d|$ is not easy except if one considers only the first term in $|\Psi|^2$, which is not quite realistic. We can simply emphasize that the angular torque curve $\tau(\theta)$ has only four zeroes over 2π rather than eight, which corresponds to an energy angular dependence with two maxima and two minima. This can be explained only in a picture in which the ratio of d- to s-wave component is approximately $(|\Psi_s|/|\Psi_d|)\simeq 1$. Now, how does this conclusion agree with the tricrystal results of Tsuei *et al.*[20] on Tl2201? One element of the answer is proposed in Ref. 17. Because of the strongly layered structure of the cuprate, experiments that probe physical quantities along given crystallographic directions might be sensitive to the combination of s and d wave to a different extent. For example, because of the short coherence length in the a-b plane, tunneling and interface experiments through grain boundaries can be influenced by the gap reduction at the interface and by the relative crystallographic orientation in such a way that the s-wave component is partly filtered out. As suggested by Müller and Keller,[17] the fact that the critical current of a bicrystal tunneling junction decreases with increasing misorientation angle ϕ between two adjacent grains[39] can be understood by the relative orientation of the $d_{x^2-y^2}$ lobes. Indeed close to $\phi=45°$, the d-tunneling current is suppressed because the contributions of the positive and negative lobes cancel out, and thus only the small s component of the current prevails. Therefore the faceting, which is always present at the grain boundaries,[12] might explain why the d-wave component dominates in most phase-sensitive experiments. On the other hand, the torque experiment, which probes the entire bulk of a single-domain sample, does not discriminate between s and d wave, and therefore sees the mixture of both components.

V. CONCLUSIONS

The in-plane torque anisotropy measured on Tl2201 thin films, patterned into disks, do not exhibit a simple fourfold symmetry as would be expected for a purely tetragonal superconductor, but is consistent with a mixed $d+s$-wave pairing state. The most plausible candidate seems to be an admixture of a $d_{x^2-y^2}$ component with a fairly large amount of s^+. In the temperature range measured, we observe that the ratio of s- over d-wave character continuously increases with temperature. The mixed pairing state is only allowed by a breaking of the tetragonal symmetry, possibly an orthorhombic distortion occurring at low temperature. The validity of our results, especially the absence of artifacts due to geometrical effects or out-of-plane pinning contributions, has been confirmed by performing the same torque experiment on NbN films and $NbSe_2$ single crystals. In both of these classical superconductors no anisotropy is observed. The advantages of torque magnetometry, which is truly a bulk experiment, have to be further tested on other high-T_c superconductors, in particular single crystals with cylindrical geometry.

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[1] For a review see J. Annett, N. Goldenfeld, and A. J. Leggett, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1996), Vol. 5, pp. 375–461.

[2] Z.-X. Shen, D. S. Dessau, B. O. Wells, D. M. King, W. E. Spicer, A. J. Arko, D. Marshall, L. W. Lombardo, A. Kapitulnik, P. Dickinson, S. Doniach, J. DiCarlo, A. G. Loeser, and C. H. Park, Phys. Rev. Lett. **70**, 1553 (1993).

[3] H. Ding, J. C. Campuzano, A. F. Bellman, T. Yokoya, M. R. Norman, M. Randeria, T. Takahashi, H. Katayama-Yoshida, T. Mochiku, K. Kadowaki, and G. Jennings, Phys. Rev. Lett. **74**, 2784 (1995).

[4] J. A. Martindale, S. E. Barrett, C. A. Klug, K. E. O'Hara, S. M. DeSoto, C. P. Slichter, T. A. Friedmann, and D. M. Ginsberg, Phys. Rev. Lett. **68**, 702 (1992).
[5] W. Hardy, D. A. Bonn, D. C. Morgan, R. Liang, and K. Zhang, Phys. Rev. Lett. **70**, 3999 (1993); D. A. Bonn, P. Dosanjh, R. Liang, and W. N. Hardy, *ibid.* **68**, 2390 (1992).
[6] D. A. Wollman, D. J. Van Harlingen, W. C. Lee, D. M. Ginsberg, and A. J. Leggett, Phys. Rev. Lett. **71**, 2134 (1993).
[7] D. A. Wollman, D. J. Van Harlingen, J. Giapintzakis, and D. M. Ginsberg, Phys. Rev. Lett. **74**, 797 (1995).
[8] D. A. Brawner and H. R. Ott, Phys. Rev. B **50**, 6530 (1994).
[9] C. C. Tsuei, J. R. Kirtley, C. C. Chi, L. S. Yu-Jahnes, A. Gupta, T. Shaw, J. Z. Sun, and M. B. Ketchen, Phys. Rev. Lett. **73**, 593 (1994).
[10] J. R. Kirtley, C. C. Tsuei, J. Z. Sun, C. C. Chi, L. S. Yu-Jahnes, A. Gupta, M. Rupp, and M. B. Ketchen, Nature (London) **373**, 225 (1995).
[11] J. R. Kirtley, C. C. Tsuei, M. Rupp, J. Z. Sun, L. S. Yu-Jahnes, A. Gupta, M. B. Ketchen, K. A. Moler, and M. Bhushan, Phys. Rev. Lett. **76**, 1336 (1996).
[12] J. Mannhart, H. Hildenkamp, B. Mayer, Ch. Gerber, J. R. Kirtley, A. Moler, and M. Sigrist, Phys. Rev. Lett. **77**, 2782 (1996).
[13] Y. Ishimaru, J. Wen, K. Hayashi, Y. Enomoto, and N. Koshizuka, Jpn. J. Appl. Phys., Part 2 **34**, L1532 (1995).
[14] M. T. Beal-Monod and O. T. Valls, Physica C **235-240**, 2145 (1994); M. T. Beal-Monod and K. Maki, Phys. Rev. B **53**, 5775 (1996); Europhys. Lett. **30**, 415 (1995); Physica C **265**, 309 (1996).
[15] R. Combescot and X. Leyronas, Phys. Rev. Lett. **75**, 3732 (1995).
[16] K. A. Müller, Nature (London) **377**, 133 (1995).
[17] K. A. Müller and H. Keller, in *Materials Aspects of High-T_c Superconductivity: 10 Years after the Discovery*, Delphi, Greece, August 1996, Vol. 343 of NATO ASI Series E: Applied Sciences (Kluwer, Dordrecht, 1997), p. 7.
[18] A. G. Sun, D. A. Gajewski, M. B. Maple, and R. C. Dynes, Phys. Rev. Lett. **72**, 2267 (1994).
[19] J. H. Miller, Q. Y. Ying, Z. G. Zou, N. Q. Fan, J. H. Xu, M. F. Davis, and J. C. Wolfe, Phys. Rev. Lett. **74**, 2347 (1995).
[20] C. C. Tsuei, J. R. Kirtley, M. Rupp, J. Z. Sun, A. Gupta, M. B. Ketchen, C. A. Wang, Z. F. Ren, J. H. Wang, and M. Bhushan, Science **271**, 329 (1996).
[21] C. Rossel, M. Willemin, J. Hofer, H. Keller, Z. F. Ren, and J. H. Wang, Physica C **282–287**, 136 (1997).
[22] H. Won and K. Maki, Europhys. Lett. **34**, 453 (1996), and references therein.
[23] T. Ishida, K. Okuda, H. Asaoka, Y. Kazumata, K. Noda, and H. Takei, Czech. J. Phys. **46**, 1217 (1996); Physica C **263**, 260 (1996).
[24] J. Buan, B. P. Stojkovic, N. E. Israeloff, A. M. Goldman, C. C. Huang, O. T. Valls, J. Z. Liu, and R. Shelton, Phys. Rev. Lett. **72**, 2632 (1994).
[25] T. Hanaguri, T. Fukase, Y. Koike, I. Tanaka, and H. Kojima, Physica B **165&166**, 1449 (1990).
[26] Y. Koike, T. Takabayashi, T. Noji, T. Nishizaki, and N. Kobayashi, Phys. Rev. B **54**, R776 (1996).
[27] H. Aubin, K. Behnia, M. Ribault, R. Gagnon, and L. Taillefer, Phys. Rev. Lett. **78**, 2624 (1997).
[28] N. E. Hussey, J. R. Cooper, J. M. Wheatley, I. R. Fisher, A. Carrington, A. P. Mackenzie, C. T. Lin, and O. Milat, Phys. Rev. Lett. **76**, 122 (1996).
[29] Z. F. Ren, J. H. Wang, and D. J. Miller, Appl. Phys. Lett. **69**, 1798 (1996).
[30] C. A. Wang, Z. F. Ren, J. H. Wang, D. K. Petrov, M. J. Naughton, W. Y. Yu, and A. Petrou, Physica C **262**, 98 (1996).
[31] R. Surdeanu, R. J. Wijngaarden, R. Griessen, C. Rossel, Z. F. Ren, and J. H. Wang, Physica C **282-287**, 2219 (1997).
[32] B. P. Clayman and R. F. Frindt, Solid State Commun. **9**, 1881 (1971).
[33] H. F. Hess, R. B. Robinson, R. C. Dynes, J. M. Valles, and J. V. Waszczak, Phys. Rev. Lett. **62**, 214 (1989).
[34] J. D. Jorgensen, O. Chmaissem, J. L. Wagner, W. R. Jensen, B. Dabrowski, D. G. Hinks, and J. F. Mitchell, Physica C **282-287**, 97 (1997).
[35] K. Maki and M. T. Beal-Monod, Phys. Rev. B **55**, 11 730 (1997).
[36] M. T. Beal-Monod and K. Maki (private communication).
[37] V. G. Kogan, Phys. Rev. B **38**, 7049 (1988).
[38] R. A. Klemm (private communication).
[39] D. Dimos, P. Chaudhari, and J. Mannhart, Phys. Rev. B **41**, 4038 (1990).