Transition from a Mixed to a Pure *d*-Wave Symmetry in Superconducting Optimally Doped $YBa_2Cu_3O_{7-x}$ Thin Films Under Applied Fields

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We have probed the Landau levels of nodal quasiparticles by tunneling along a nodal direction of (110) oriented $YBa_2Cu_3O_{7-x}$ thin films with a magnetic field applied perpendicular to the CuO_2 planes, and parallel to the film's surface. In optimally doped films and at low temperature, finite energy nodal states are clearly observed in films thinner than the London penetration depth. Above a well defined temperature, the order parameter reverts to a pure *d*-wave symmetry.

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The pairing interaction responsible for superconductivity in the high temperature superconductors is still under debate. There is much experimental evidence showing that the order parameter has a dominant $d_{x^2-y^2}$ symmetry [1,2], but important questions such as the nature of quasiparticle states in the under-doped region and the existence of a minority component of the order parameter are still under debate [3]. Studying the density of states when a magnetic field is applied along the *c* axis can lend important information on both of these questions.

Gor'kov and Schrieffer [4] have remarked that in a *d*-wave, superconductor nodal quasiparticles undergo in their orbital motion a series of Andreev—Saint-James reflections from nearby lobes of the order- parameter, resulting in finite energy states. These states, as noted by Anderson [5], carry a current around the Fermi surface. Each time an electron, say, is reflected as a hole, the missing pair reappears as a Cooper pair in the condensate. Such currents can be described by an id_{xy} component which, as shown by Laughlin [6], lowers the free energy of the superconducting state under the applied field because of the moment they produce. Minimization of the free energy with respect to the amplitude, δ_{xy}, of the minority component, lends at $T = 0$ the law: $\delta_{xy} = aH^{1/2}$ with $a = \hbar v\sqrt{\frac{2e}{\hbar c}}$. Here $v = \sqrt{v_1 v_2}$, where v_1 is the Fermi velocity, $v_2 = \frac{1}{\hbar}\frac{\partial\Delta}{\partial k}$ at the node direction, and Δ is the main $d_{x^2-y^2}$ superconducting gap. A weak first order phase transition to a pure *d*-wave symmetry was predicted to occur at a temperature $k_B T_{\mathrm{CF}} = b\delta_{xy}(H)$, where b is a universal constant equal to 0.52. It was however pointed out that in the mixed state, Meissner currents would cause a large Doppler shift of the nodal states energy, making their observation difficult if not impossible [7].

In this Letter, we show how this difficulty can be resolved by taking measurements on films thinner than the London penetration depth and conclude that a field induced minority component exists below a well defined temperature T_{CF}. Our results are in semiquantitative agreement with Laughlin's theory [6] with proportionality constant, $b = 0.34$, smaller than the predicted one.

One of the most powerful tools for probing the order parameter is tunneling spectroscopy. For conventional superconductors, the tunneling spectrum is directly proportional to the superconductor's density of state and exhibits two peaks at biases corresponding to $\pm\Delta$, where Δ is the superconducting gap [8]. For a *d*-wave order-parameter symmetry, zero energy surface states are formed when quasiparticles undergo successive Andreev—Saint-James reflections from order parameters whose phase differ by π, as occurs upon reflection at a surface perpendicular to a nodal direction. Tunneling along a node direction, i.e., the (110) direction, shows a zero bias peak in the tunneling spectrum [9] due to these states [10]. An additional minority id_{xy} component would show up as peaks of the junction's conductance at biases equal to δ_{xy}, replacing the zero bias peak [9].

According to theoretical predictions [4,6], tunneling spectral peaks should thus appear when the field is applied perpendicular to the CuO_2 planes in films having a nodal orientation. The presence of such peaks was noted previously, but received a different interpretation [11–13], which is that Meissner screening currents will Doppler shift the zero energy surface states. It was shown [14] that the split of the zero bias conductance peak is always larger in increasing fields than in decreasing ones, a behavior that can be understood on the basis of the hysteretic behavior of screening currents. These currents are of two kinds: Meissner currents on the scale of the London penetration depth, and Bean currents due to vortex pinning. Meissner currents are large in increasing fields, due to the Bean Livingston barrier that retards the penetration of vortices, and small in decreasing fields because there is no barrier against vortex exit. As for Bean currents, they reverse sign upon field reversal and are typically weak compared to Meissner currents in increasing fields. In experiments performed on $YBa_2Cu_3O_{7-x}$ thick films having the (110) orientation, Beck *et al.* [15] have reported on finite bias conductance peaks that follow the $H^{1/2}$ law in decreasing fields where screening currents are weak, and attributed them to a field induced id_{xy} component. This conclusion has however remained controversial as the intensity of screening currents is not known with certainty.

In an effort to establish more firmly the origin of the field induced finite bias conductance peaks, we have made a series of tunneling measurements as a function of field and temperature on films thinner than the London penetration depth. Both the Bean Livingston and the Bean currents must then be quite weak, since screening currents generated on opposite faces of the film cancel each other. If the origin of the finite bias peaks seen in thick films is a Doppler shift of zero energy surface bound states, they should not occur at all in thin films, either in increasing or in decreasing fields. If, on the other hand, they are basically due to field induced finite energy nodal states, they should persist in the thin films with no field hysteresis and follow the $H^{1/2}$. As we now describe in detail, this is indeed what we have found.

We fabricated (110) oriented $YBa_2Cu_3O_{7-x}$ thin films by dc off-axis sputtering on (110) $SiTrO_3$ substrates with one of the surface edges parallel to the c axis. A $PrBa_2Cu_3O_{7-x}$ buffer layer was first deposited by off-axis rf sputtering in order to reduce the growth of (103) oriented grains [16]. The thickness of the samples is less than 500 Å. X-ray diffraction reveals peaks corresponding to the (110) orientation, the T_C of the samples ranged from 84 K to 89 K down-set. The films' surface is relatively smooth, having an average surface roughness of a few tens of angstroms according to atomic force microscope measurements. We verified the in-plane orientation by comparing the normal state resistance along the two different directions and found the expected anisotropy [16].

The tunneling junctions are produced by pressing Indium thin pads on fresh samples, as described elsewhere [14,17]. The configuration of the sample and the field orientation is shown in Fig. 1. The Indium-Oxide layer, which is created in the area of contact, results in junction resistances in the range of 1–15 Ω. This process may reduce the oxygen concentration in the junctions' area, especially in very thin samples. In order to alleviate this effect, we grew our films in the presence of a reduced vapor pressure of water, which results in increased oxygen content in the film [18]. The junctions are stable under thermal cycles, and the junctions' resistance remains unchanged if kept in a helium gas environment. This allows us to measure the temperature dependence of their tunneling characteristic, if necessary by performing successive cooling runs under various applied fields. The planar junction technique averages the tunneling conductance at a macroscopic length scale in contrast to scanning tunneling microscopy measurements which give sharper peak features [19]. However, its stability over thermal and magnetic fields cycles is of great advantage for the present work.

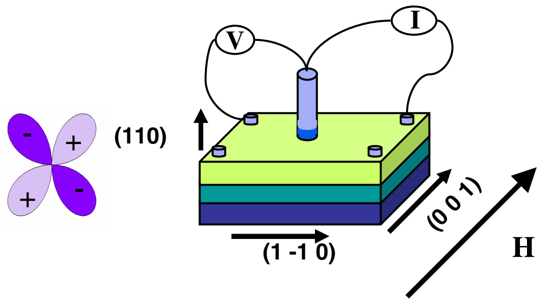

FIG. 1 (color online). A scheme of the samples' configuration. The samples' surface is in the (110) direction, and one of the surface edges is parallel to the c axis. The magnetic field is applied parallel to the surface and to the c axis.

In Fig. 2(a), we show the differential conductance obtained on a thin film at 4.2 K, measured at magnetic fields $H = 0$, 6, and 12 T, in increasing and decreasing fields. At zero magnetic field, there is a clear peak at zero bias, as expected for a (110) oriented film [9]. This peak splits into two spectral peaks in the presence of a finite magnetic field. The conductance spectra in increasing and decreasing fields are almost identical as opposed to the high hysteretic behavior of the spectral peaks in thicker samples as shown in Fig. 2(b) and in Ref. [14,17]. This highly hysteretic

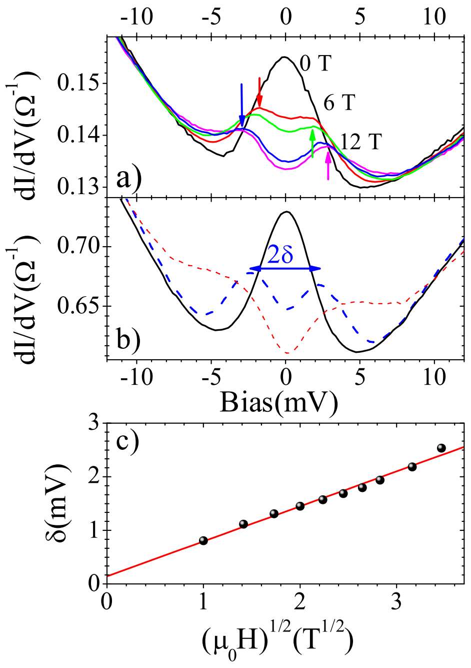

FIG. 2 (color online). (a) The conductance spectrum of a thin sample obtained when increasing and decreasing the magnetic field. Full black line: $H = 0$ T. Arrows facing up(down) represent increasing(decreasing) field. (b) The conductance spectrum obtained on a thick sample. Full black line: $H = 0$, thin dashed line: $H = 4$ T increasing field, thick dashed line: $H = 4$ T decreasing field. (c) Spectral peak value versus the square root of applied field in decreasing fields measured on a thin sample at 4.2 K. The solid line is a linear fit with a slope of 0.65 $mV/T^{1/2}$. We note that the slope found here is slightly smaller than that found for thicker films (see text).

behavior has been ascribed to strong screening currents in increasing fields and much weaker ones in decreasing fields as discussed above [15,20]. The negligible hysteresis observed in our thin samples implies that the screening currents are very low even in increasing fields and that the two finite bias peaks cannot be due to a Doppler shift of the zero energy bound states. The difference between the behavior of thin and thick films is particularly dramatic in increasing fields, where the spectral peaks cannot be identified anymore at all in thick samples. This is because the Doppler shift, due to Meissner currents, widens the peaks and pushes them into high bias where they are merged with the background and the main gap structure [Fig. 2(b)].

We define the minority gap peak value, δ, as half the distance between the positive and negative bias conductance peaks [see Fig. 2(b)]. In our thin films, $\delta(H)$ follows the $H^{1/2}$ behavior as shown in Fig. 2(c). This is in agreement with measurements performed earlier on thick films in decreasing fields [15,20] and confirms the assumption that Meissner currents are weak in that case, but may be not negligible in view of the smaller slope obtained here.

Measuring the tunneling spectrum at various magnetic fields and temperatures, we find that in a fixed magnetic field, the minority gap peak value disappears above a well defined temperature. For example, we show in Fig. 3(a) the measured conductance in a field of 7 T at various temperatures. At 1.6 K, there are two clear peaks at ±1.75 mV. As the temperature rises, the conductance at zero bias increases until the finite bias peaks completely disappear at 8.5 K. The conductance at high biases is independent of temperature as expected for tunneling, assuring us that the junction characteristics remain intact.

However, in order to be able to properly assert if there is a temperature induced modification of the density of states at low bias, one must take into account the effect of thermal smearing on the tunneling spectra [8]. Therefore, we have convoluted the tunneling spectra measured at the lowest temperature (below 1.6 K) with the derivative of the Fermi-Dirac distribution function at the desired temperature. Previous scanning tunneling measurements showed that the density of states hardly changes at such low temperatures [21]. Therefore, using our procedure, we have calculated a thermally smeared curve for higher temperatures and thus estimated the effect of thermal smearing on the low energy spectrum. Figure 3(b) shows the measurement taken at 8.5 K (red solid line) and the result of smearing the 1.6 K measurement to 8.5 K (black dashed line). While the smeared curve still shows two distinct peaks, the measurement does not, but rather exhibits a peak at zero bias. It is therefore clear that temperature induces a change in the density of states. At biases higher than 5 mV, the two curves are identical.

A representative graph of the minority gap value versus temperature for various values of the applied field is shown in Fig. 4(a). The minority gap value is approximately constant at low temperatures and disappears abruptly at a temperature, which we define as T_{CF}. The minor initial rise in the sub gap peaks' value is an effect of thermal smearing.

The value of T_{CF} increases with the applied field and the resulting low temperature conductance peak value. We find that they obey the universal linear relation $k_B T_{\mathrm{CF}} = 0.34\delta$ as shown in Fig. 4(b). The data points in the graph were taken from five different samples with different characteristics (one of the points was measured on a thick sample in decreasing field), which implies the universality of the proportionality constant. The measured slope is smaller than Laughlins' prediction $k_B T_{\mathrm{CF}} = 0.52\delta$. Laughlins' calculation was performed for bulk materials, while our measurements were done on very thin films, which are highly susceptible to surface effects. Laughlin did not mention the length scale of the currents responsible for the dipole moments. If the thickness of the film is comparable to the aforementioned length scale, interaction between the currents resulting in a partial cancellation of the opposite currents should be considered. This might contribute to the disagreement between the theoretical ratio and our experimental result.

A way to distinguish between the Doppler shift effect and the minority component induced by the applied field, is by their respective temperature dependence. A first order phase transition that leads to the abrupt disappearance of

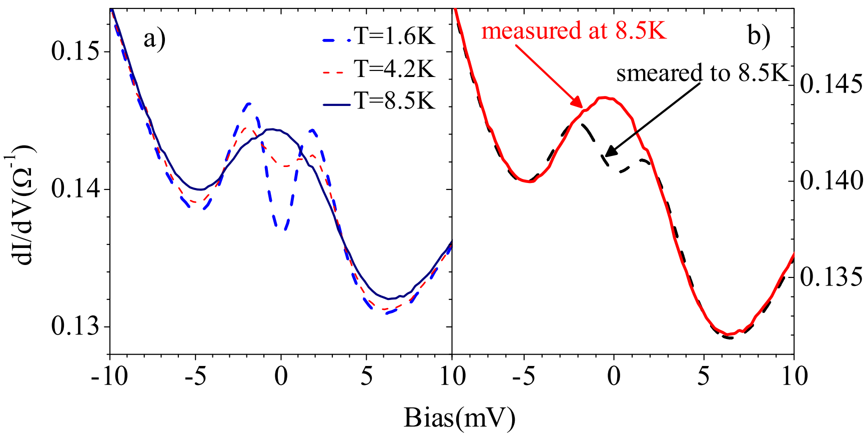

FIG. 3 (color online). (a) Conductance measured under a field of 7 T at various temperatures. (b) Comparison between the measured data at $T = 8.5$ K, $H = 7$ T (full line) and the result of smearing the data measured at $T = 1.6$ K, $H = 7$ T to $T = 8.5$ K (dashed line).

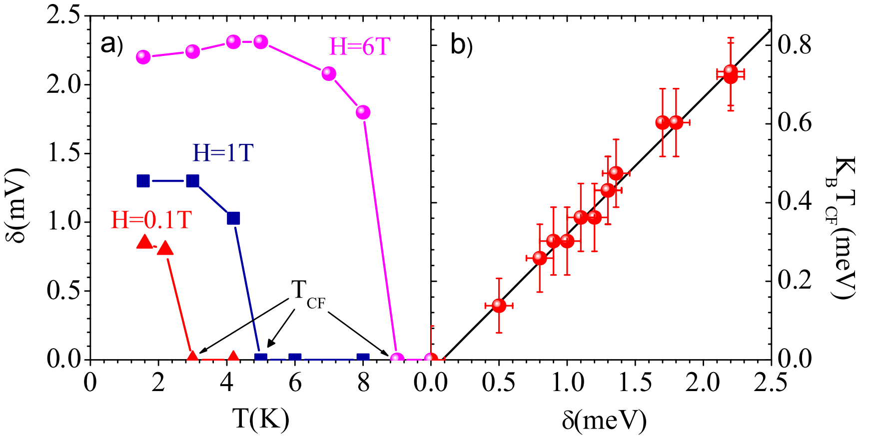

FIG. 4 (color online). (a) The spectral peak values versus temperature obtained from different applied magnetic fields. (b) The temperature at which the spectral peak disappears versus the peak value at low temperatures.

the minority order parameter at high temperatures has been predicted [6]. On the other hand, screening currents and the accompanying Doppler shift should persist at high temperatures since the superfluid momentum is independent of temperature at temperatures significantly lower than T_C [22]. In addition to the small field hysteresis in the position of the finite bias peaks, their sharp disappearance at a well defined temperature rules out that a Doppler shift of the zero energy surface bound states is at their origin.

The proposed interpretation of the experiments that we have described requires that the scattering time of nodal quasiparticles be long compared to the time it takes them to complete a Saint-James cycle. This appears to be true at optimum doping, but not away from it as we show in a separate publication [23].

In conclusion, we claim that the field induced spectral peaks seen in nodal tunneling in very thin films result from the formation of a minority order parameter, and cannot be attributed to a Doppler shift of the zero energy states due to Meissner screening currents. The square root dependency of the spectral peak positions in the magnetic field strength, the absence of field hysteresis and their abrupt disappearance with temperature are all in favor a field induced id_{xy} minority imaginary order parameter at low temperatures and a transition to a pure d-wave order parameter at high temperatures, as predicted by Laughlin. Our findings are in general agreement with his model, but a comparison of the way in which the tunneling density of states evolves with temperature would require a more detailed theory than is now available. The absence of a minority order parameter inferred from the heat capacity square root field dependence [24] is not in contradiction with our conclusions because these measurements were performed on much thicker crystals where superfluid currents are strong (and at the origin of the square root dependence) and predicted to render the minority component unobservable [7].

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