Doping and Magnetic Field Dependence of In-Plane Tunneling into $YBa_2Cu_3O_{7-x}$: Possible Evidence for the Existence of a Quantum Critical Point

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We present tunneling measurements into $(1,1,0)$ $YBa_2Cu_3O_{7-x}$ films at various doping levels around the optimum. We find that, above a certain doping level near optimum doping, a spontaneous zero bias conductance peak splitting, δ, appears. It increases with doping. It also increases with magnetic field applied along the c axis, for both underdoped and overdoped films. The low field susceptibility $\chi = \frac{d\delta}{dH}|_{H\to 0}$ is maximum, possibly diverging when the spontaneous value of δ goes to zero. These results suggest a transition from a pure $d_{x^2-y^2}$ to a $d + id_{xy}$ or $d + is$ order parameter.

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Recent tunneling experiments, performed on films of the high T_c cuprate $YBa_2Cu_3O_{7-x}$ having the $(1,0,0)$ or $(1,1,0)$ orientations (in-plane tunneling), have shown a change of the order parameter symmetry when a magnetic field is applied parallel to the surface and perpendicular to the CuO_2 planes. An additional component develops, which removes the nodes of the dominant d-wave order parameter [1–3] In a tunneling experiment, these nodes produce a zero bias conductance peak (ZBCP), which reflects the existence of Andreev surface bound states that are formed at and near the Fermi level [4,5]. Removal of the nodes appears as a split of the ZBCP. In addition to the field induced splitting, a spontaneous (zero field) splitting of the ZBCP was also reported in several works [1–3]. It was qualitatively related to overdoping in $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-x}$ films in Refs. [6,7].

In this Letter, we report on a comprehensive study of the ZBCP splitting as a function of oxygen doping and magnetic field for $YBa_2Cu_3O_{7-x}$ films having the $(1,1,0)$ orientation. We show that a spontaneous splitting devlops progressively above a certain doping level, near optimum doping. At this point χ, the initial slope of the field-induced splitting seems to diverge. As the doping is either increased in overdoped samples or decreased in underdoped samples χ decreases. In the last case, no spontaneous splitting is seen. The implications of these results are discussed in the context of current theories, in particular in reference to the possible existence of a quantum critical point (QCP) where time reversal symmetry breaking would occur.

$(1,1,0)$ oriented thin $Y_1Ba_2Cu_3O_{7-x}$ films of various doping levels near the optimal doping were grown on $(1,1,0)$ $SrTiO_3$ substrates, using rf and dc off-axis sputtering. A $Pr_1Ba_2Cu_3O_{7-x}$ template was used in order to reduce the $(1,0,3)$ orientations, following the method used by Poelders *et al.* [8] Garcia Lopez *et al.* [9] showed that the amount of oxygen loaded in the $YBa_2Cu_3O_{7-x}$ film during the growth can be controlled by changing the oxygen pressure and the amount of atomic and ionic oxygen in the plasma. In addition, they showed that the film remains oxidized if quenched at room temperature. We used this method of Garcia Lopez *et al.* to grow overdoped ($T_c = 85.6$–90 K down set) samples, with the doping level controlled by the amount of water vapor added to the plasma. This affects the amount of atomic oxygen in the plasma [10]. By increasing the amount of water vapor, we obtained a reduction of T_c and of Δ_d, the position of the d-wave gap feature. To make sure that we have indeed obtained overdoped films, we have annealed them in a low oxygen pressure environment at 650 °C; a T_c of 90 K was then retrieved as expected. In addition, we have found the resistance characteristics, $R(T)$, in overdoped samples to show the expected positive curvature [11]. Underdoping ($T_c = 83.6$–90 K down set) was achieved by annealing the film in a low oxygen pressure. These films exhibit the downwards deviation of $R(T)$ from linearity, signaling the pseudogap temperature [12], at $T > T_c$.

The junction is an In/insulator/$YBa_2Cu_3O_{7-x}$ contact. Film characterization, junction preparation, junction characterization, and the measurements technique are the same as in Refs. [13,14]. The films are in-plane oriented, the $[1,\bar{1},0]$ direction can be easily distinguished from the $[0,0,1]$ direction using a resistivity measurement as shown in Ref. [13]. The magnetic field can be therefore applied parallel to the surface of the film along either of these directions.

The conductance characteristics of an underdoped sample [having a zero resistance temperature (down set), $T_c = 86.7$ K] at various magnetic fields applied parallel to the c direction at 4.2 K is presented in Fig. 1. The d-wave gap feature is strongly marked at the positive bias side, with a conductance maximum at 16.7 mV. As is common to all our underdoped samples ($T_c = 83.6$–90 K down set), no splitting of the ZBCP is seen at zero magnetic field. A focus on the low bias behavior is shown in the inset of Fig. 1, the ZBCP splits as the magnetic field is increased. We define δ as the position of the maximum of the split ZBCP at the positive bias side. δ and the amplitude of the split peak both rapidly increase as the field is increased from zero to

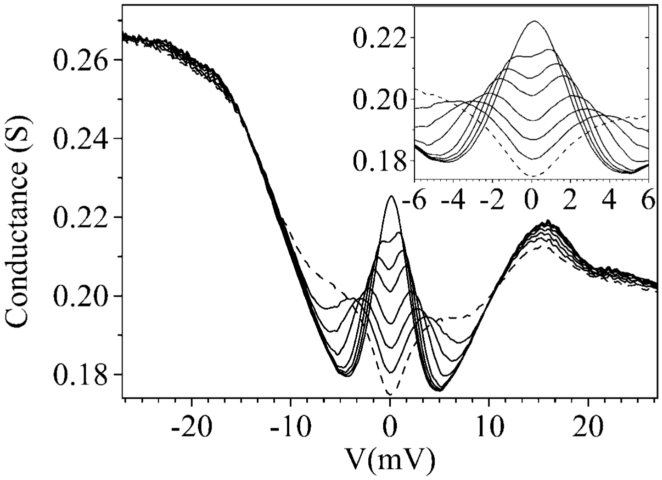

FIG. 1. The conductance versus voltage characteristics for an underdoped sample ($T_c = 86.7$ K down set) at 4.2 K at various magnetic fields: 0, 0.2, 0.3, 0.4, 0.6, 1, 2, and 4 T (dashed) applied parallel to the surface of the film along the c direction. We note the gap feature at 16.7 mV and a ZBCP, which splits as the field is increased. Inset: A focus on the conductance behavior at low biases and at the same applied fields.

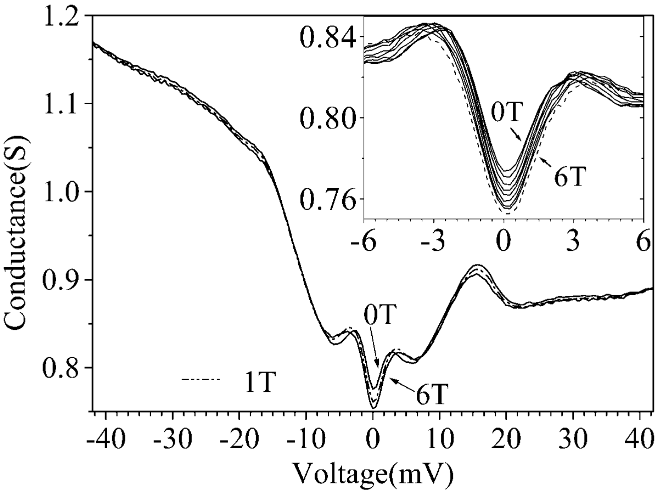

FIG. 2. The conductance versus voltage characteristics for an overdoped sample ($T_c = 85.6$ K down set) at 4.2 K at various magnetic fields: 0, 1 (dashed), and 6 T applied parallel to the surface of the film along the c direction. We note a sharp gap feature at 15.6 mV and a zero field splitting with a conductance maximum at 2.6 mV; this splitting increases with increasing magnetic field. Inset: A focus on the junction behavior at low biases and at various magnetic fields: 0, 0.1, 0.2, 0.3, 0.4, 0.7, 1.5, 4, and 6 T.

0.6 T; they both increase moderately from 0.6 to 2 T. At fields higher than 2 T, the peak is suppressed while δ keeps increasing. We have also applied the magnetic field parallel to the $\mathrm{CuO_2}$ planes (along the $[1,\bar{1},0]$ direction). No splitting is observed up to a field of a few telsa. Beyond that field a small splitting appears, possibly due to a small angle between the magnetic field and the $[1,\bar{1},0]$ direction. The d-wave gap feature, which appears at 16–16.7 mV in the underdoped samples, is sensitive to the magnetic field applied parallel to the $\mathrm{CuO_2}$ planes, as well as to the magnetic field applied parallel to the c direction.

The conductance versus voltage characteristics for an overdoped sample ($T_c = 85.6$ K down set) at 4.2 K, and in various magnetic fields applied parallel to the surface of the film along the c direction, are presented in Fig. 2. The gap feature is at 15.6 mV on the positive bias side. The magnitude of the gap feature is sensitive to the magnetic field (measured up to 6 T), but its position is not. A focus on the conductance behavior at low bias and at various magnetic fields applied parallel to the c direction is presented in the inset of Fig. 2. One can observe a splitting (or a subgap) already at zero magnetic field. Here, at zero field $\delta(0) = 2.6$ mV. The presence of the zero field splitting is common to all the overdoped samples, while its value, $\delta(0)$, is doping dependent. When the field is applied parallel to the $[1,\bar{1},0]$ direction, no effect on the ZBCP is seen up to a field of few tesla. By contrast, the d-wave gap feature is more sensitive to a magnetic field applied in this direction than in the $[0,0,1]$ direction. The magnetic field behavior of the conductance characteristics described above is common to all our overdoped samples. The main modifications that occur upon increasing the degree of overdoping are an increase in $\delta(0)$, a decrease of χ, and a decrease of the d-wave gap value.

In Fig. 3, we present the magnetic field dependence of the ZBCP splitting δ for samples having various doping levels. A spontaneous splitting appears above the doping level at which the d-wave gap is maximum ($\Delta_d = 17.1$ mV, down triangles). We note that χ is then at its maximum.

We show in Fig. 4 how δ (squares) and χ^{-1} (circles) vary as a function of $[\Delta_d(\max) - \Delta_d]^{1/2}$ on the overdoped side. It is known that the critical temperature and the value of the d-wave gap follow the same variation as a function of doping, as it increases beyond its optimum value [15]: $T_c(\max) - T_c \propto \Delta_d(\max) - \Delta_d$. Since $T_c(\max) - T_c \propto [p(\max) - p]^2$, where p is the oxygen content per unit cell, $[\Delta_d(\max) - \Delta_d]^{1/2}$ is a parameter representing the doping of the sample. We prefer to use gap values, determined as shown in Ref. [13], rather than T_c values, as an indication of the local level of doping. This is because the doping level at the junction may be somewhat affected by the way in which it is produced, which involves some diffusion of oxygen to form the tunnel barrier [16]. For the sample having the maximum d-wave gap value, $\Delta_d(\max)$, there is no spontaneous measurable zero field splitting, $\delta(0) = 0$. Beyond the unknown, but close to optimum, doping level of this sample, it can be seen that $\delta(0) \propto [\Delta_d(\max) - \Delta_d]^{1/2}$. This indicates that there is a change of symmetry of the order parameter beyond a well-defined doping level, which involves the removal of

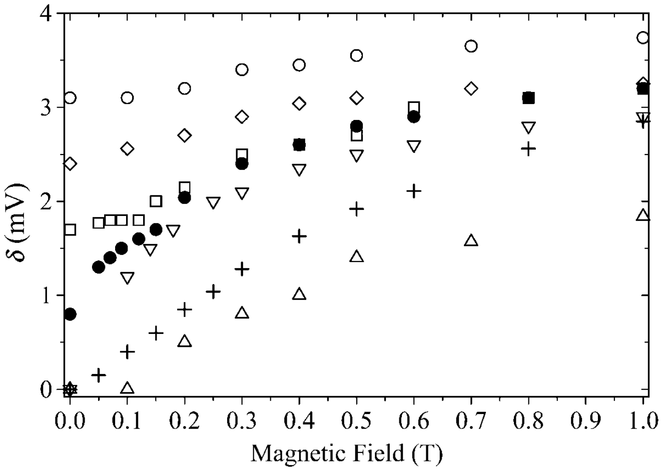

FIG. 3. The magnetic field dependence of the subgap peak position δ for various YBCO samples of various doping levels. Hollow circles: overdoped, $T_c = 85.6$ K down set, $\Delta_d = 15.6$ meV; hollow diamonds: overdoped, $T_c = 85.9$ K, $\Delta_d = 16.1$ meV; hollow squares: overdoped, $T_c = 86.2$ K down set $\Delta_d = 16.6$ meV; solid circles: overdoped, $T_c = 86.2$ K down set, $\Delta_d = 16.8$ meV; down triangles: optimally doped, $T_c = 90$ K down set, $\Delta_d = 17.1$ meV; crosses: underdoped, $T_c = 86.7$ K down set, $\Delta_d = 16.7$ meV; up triangles: underdoped, $T_c = 83.6$ K, $\Delta_d = 16$ meV. Δ_d is the position at which the d-wave gap feature appears as determined using the procedure of Ref. [13].

the d-wave nodes. In addition, it can be seen that χ^{-1} is also proportional to $[\Delta_d(\max) - \Delta_d]^{1/2}$, i.e., to the doping level.

The change of symmetry may be a surface effect, or a reflection at the surface of a bulk property. Balatsky [17] has shown that the pure d-wave symmetry is unstable in the presence of defects, such as impurities or surfaces, against the formation of an id_{xy} component. Predicted values of this component are, however, small compared to the experimental values of δ that we report here. Besides, this theory does not predict a doping dependence of a surface induced id_{xy} component. Another possibility would be the existence of π junctions near a surface, equivalent to the formation of spontaneous vortices and of their screening currents [18]. Again, there is no prediction thus far that these vortices should exist only in the overdoped regime, and in increasing concentrations as a function of doping.

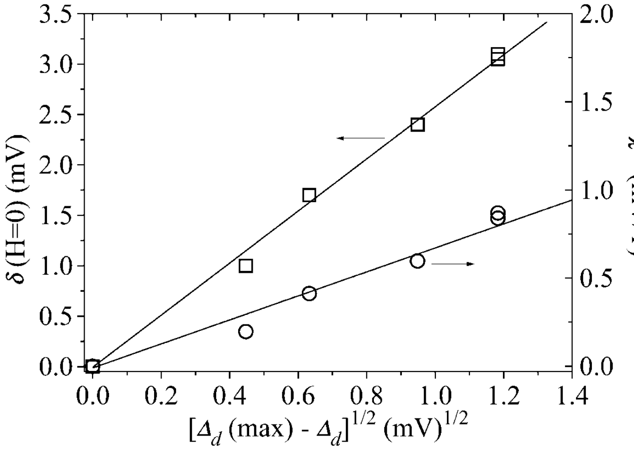

FIG. 4. Squares: The subgap δ at zero field (see Figs. 1 and 3) as a function of $[\Delta_d - \Delta_d(\max)]^{1/2}$, where Δ_d is the position of the d-wave gap feature and $\Delta_d(\max)$ is the position of the d-wave gap feature in the sample at which Δ_d is maximal and the subgap at zero field is zero. The solid line is a linear fit with a slope of 2.6 ± 0.1 (mV)$^{1/2}$. Circles: The inverse susceptibility at low fields $\chi^{-1} = (d\delta/dH)^{-1}$ in Fig. 3 where δ is the subgap as a function of $[\Delta_d - \Delta_d(\max)]^{1/2}$ (see Fig. 3). The straight line is a linear fit with a slope of 0.7 ± 0.1 T/mV$^{3/2}$.

Fogelström *et al.* [19] have shown that a spontaneous is component can be formed at the surface of a d-wave superconductor, if there exists a subdominant s-wave order parameter appearing below a temperature T_s. They have, in this way, interpreted the experiment of Covington *et al.* [1] showing a spontaneous splitting (followed by a field increase, itself explained as a Doppler shift). In its present stage, the theory of Fogelström *et al.* does not make any prediction concerning the field dependence of the ZBCP splitting as a function of T_s (or doping), which we find experimentally to be important and systematic. Moreover, recently, Dagan *et al.* [20] have found δ to be thickness independent for films thinner than the penetration depth. The superconducting carrier velocity is strongly thickness dependent in this case. This implies that the magnetic field splitting is not primarily a Doppler shift effect due to the Meissner screening currents.

Other interpretations of our experiment involve the existence of a QCP. A phenomenological expression for the free energy, that predicts the existence of a spontaneous and of a field induced id_{xy} component, has been recently proposed by Deutscher *et al.* [6]. It includes an additional term giving such a spontaneous, doping dependent component:

$$F = a\delta^2 + b\delta^3 + cB\delta\,, \tag{1}$$

where δ is the amplitude of the id_{xy} component, $a \propto p - p_c$ controls the position of the QCP, b is a consequence of the gapless nodal quasiparticle in the $d_{x^2-y^2}$ superconductor. The coefficients b and c are given in Ref. [21]. For $p > p_c$, and zero applied field, the free energy is at a minimum for δ having the value

$$\delta(0) = \frac{2|a|}{3b}\,. \tag{2}$$

Since, as already mentioned, the d-wave gap has a parabolic variation as a function of doping around its maximum, this expression is in agreement with our data shown in Fig. 4. Additionally, the expression (1) predicts that χ should diverge at the critical point as $(c/|2a|)$, again in agreement with the data shown in Fig. 4.

Laughlin's theory [21] predicts the existence of a field-induced magnetic moment of the sample. According to the proposed extension, a spontaneous moment should also exist in overdoped samples. A weak spontaneous moment has indeed been recently reported in $YBa_2Cu_3O_{7-x}$ films [22], but, thus far, its doping dependence has not been investigated.

Other QCP models [23,24] give similar doping dependences of $\delta(0)$ and χ, presumably because critical fluctuation corrections to the mean field model in Eq. (1) are expected to be small [23].

In conclusion, the data presented here show that time reversal symmetry breaking is strongly doping dependent. The field effect is strongest when the d-wave gap is at is maximum. At higher doping levels, spontaneous time reversal symmetry breaking occurs. The low field susceptibility and the spontaneous subgap (or splitting of the ZBCP) vary in inverse proportions. These results suggest that spontaneous time reversal symmetry breaking occurs beyond a quantum critical point.

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