Field induced and spontaneous sub-gap in [110] and [100] oriented YBCO films: indication for a $d_{x^2-y^2} + id_{xy}$ order parameter

G. Deutscher, Y. Dagan, A. Kohen and R. Krupke

School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, Tel Aviv 69978

Tunneling experiments on [110] and [100] oriented YBCO films show that a sub-gap can be induced either by applying a magnetic field parallel to the in-plane c-axis, or by overdoping it with partial Ca substitution for Y. This time reversal symmetry breaking is best described by an id component that is both doping and field dependent. It appears that this component appears in zero field above a well defined doping level. This suggests the existence of a quantum critical point.

1. INTRODUCTION

Spontaneous time reversal symmetry breaking (STRSB) has been one of the most intriguing experimental observations concerning the order parameter of the High Tc cuprates. It was first seen by the tunneling experiments of Covington et al (1) on optimally doped YBCO films grown in such a way that the normal to the CuO planes has a component parallel to the film surface. STRSB, which manifests itself by a splitting of the Zero Bias Conductance Peak (ZBCP), is however not always observed. For instance, no STRSB was seen in the grain boundary tunneling experiments of Alfè et al. (2).

We confirm in this communication that overdoping does systematically increase this sub-gap, as first reported by Krupke and Deutscher (3). We also show that, in the absence of STRSB at or very near optimum doping, the field induced splitting varies as $\sqrt{H}$, and not linearly as originally reported in Ref.(1) and by Krupke and Deutscher (4) for films showing a zero field splitting. This square root behavior is in favor of a symmetry breaking that involves boundary currents, as proposed by Laughlin (5), rather than with the Doppler shift model proposed by Fogelstrom et al. (6), which predicts a linear field splitting. A modification of Laughlin's theory is proposed to explain the doping dependence of the symmetry breaking, both the spontaneous and the field induced ones.

2. EXPERIMENTAL

2.1 Film preparation

Oriented thin films of YBCO, optimally doped and Ca overdoped, were grown onto two different kinds of substrates to obtain the [100] or the [110] orientation. For the [100] orientation, the substrates used were tetragonal [100]-LaSrGaO$_4$ crystals, and for the [110] orientation [110] oriented SrTiO$_3$ crystals were used. In both cases, a PrBa$_2$Cu$_2$O$_y$$_y$ template was first deposited on the substrate following the method of Poelders et al. (7). It allows the growth of a-axis films at temperatures normally used to grow c-axis films. For [110] films, it allows to reduce the growth of [103] grains.

For both film orientations, the c-axis is in plane oriented. It is of some importance that this axis should have the same in-plane orientation throughout the sample. We checked that this was the case using X-ray diffraction, by studying the film morphology, and also by checking the in plane anisotropy of the normal state conductivity. We found that the conductivity along the c-axis was lower by a factor of about 20 to 30 compared to the conductivity in the perpendicular direction.

2.2 Junction preparation

Junctions were formed by pressing an In pad onto the fresh films surface. The area of the contacts was typically of the order of a mm$^2$, and their normal state resistance of the order of 10 $\Omega$ for the optimally doped films, and less than 1$\Omega$ for overdoped films.
It is believed that formation of the dielectric barrier takes place by diffusion of oxygen from the YBCO film, and formation of an In oxide.

In order to check the junctions quality, we measured their characteristic below the critical temperature of the In counter-electrode, at about 1.8K. For [100] oriented films, we estimate a leakage current around 40 to 50%, and for the [110] films, around 10% only.

The junctions are fairly stable, they can undergo several thermal cycles without damage.

3. RESULTS

3.1 Optimally doped films

We obtained similar results for both orientations, albeit with some interesting differences.

General features of the characteristics include:

a) a ZBCP
b) a conductance peak at about 17 mV
c) splitting of the ZBCP under a field applied along the c-axis.

Differences between the two orientations include:

a) a zero field (spontaneous) split of the ZBCP at 4.2K for the [100] oriented films
b) no spontaneous split of the ZBCP at 4.2K for the [110] oriented films. Below the Tc of In, the existence of a spontaneous split cannot be ascertained because it takes a finite field to quench superconductivity in the In counter-electrode.
c) The splitting is linear in the applied field for [100] films, but varies as $\sqrt{H}$ for the [110] films.
d) The 17 mV peak is somewhat more pronounced in the [110] films.

The 17 mV peak is a very reproducible feature. Its amplitude decreases with an applied magnetic field, but its position remains unchanged in fields up to 6T (8). We believe that 17 mV is a good estimate for the value of the d-wave gap.

The origin of the ZBCP is now generally ascribed to Andreev bound states of zero energy at the surface of a d-wave superconductor, when it has an orientation different from [100] (9). Yet, we also observe it for our [100] films. A possible explanation is that, in the presence of surface roughness, there is in fact little difference between the ZBCP for different orientations (6).

This is borne out by our more local Point Contact measurements (10). Another possibility would be that the peak is in fact due to scattering by magnetic impurities. But this is ruled out by the very strong field splitting, discussed below.

The splitting rises rapidly at small fields, reaching typically a few mV at fields of the order of 1T. At higher fields, it grows more slowly, and is also hysteretic.

In most [100] films, a finite zero field split is followed by a linear variation with a slope of about 1 mV/T. In [110] films, it starts from zero in zero field, but rises more quickly, as already mentioned, and reaches a value of several mV already at 0.5T (Fig.1 and 2). The difference between the two kinds of behavior may be due to slightly different doping levels.

Splitting of the ZBCP shows that the zero energy Andreev bound states have been removed, and pushed up to higher energies. This implies that the amplitude of the gap is now finite everywhere on the Fermi surface. The gap symmetry is not anymore pure d-wave, but must include an imaginary component, presumably is or id, which removes the low energy states (a s component would change the position of the nodes, without removing them).

Theoretical arguments have been proposed for both kinds of components. Fogelstrom et al. (6) have shown that Meissner screening currents at the surface of the sample induce a Doppler shift of the Andreev states by an energy of the order of $v_f \cdot p_F$, where $v_f$ is the superfluid velocity, proportional to the applied field at low field, and $p_F$ is the Fermi momentum. This shift is equivalent to a field induced is component.

The minimum angle between the two vectors, which gives the largest possible shift, is determined by the width of the tunneling cone. Fitting the data for the [100] films gives a tunneling cone of a few degrees, typical of many tunnel junctions. The hysteretic splitting at high fields has been explained in terms of vortex penetration (4).

We are lead to question this interpretation due to the results obtained on the [110] films. As mentioned, these films, that do not show a spontaneous split of the ZBCP, display a field splitting that varies as $\sqrt{H}$. Such a behavior is strongly suggestive of the existence of a boundary current $j_s$, proportional to the induced gap $\Delta$. 
which creates a magnetic moment interacting with the induction in such a way that the free energy of the sample is lowered by an amount $j_s \cdot B$, proportional to $\Delta \cdot B$. Because the induced gap increases the free energy by an amount proportional to $\Delta^3$, minimization of the free energy leads to the $\sqrt{H}$ variation of the induced gap, as shown by Laughlin (5). Note that in this interpretation, the field induced gap is a bulk, not a surface effect.

### 3.2 Overdoped films

We used a relatively high level of Ca substitution (20% of the Y content in pure YBCO). In bulk samples, this level of substitution decreases Tc down to about 60K (10). For our films, it is down to 65 to 70K. Transitions are significantly broader than in pure YBCO films (several degrees instead of less than 1K).

For both kinds of orientation, the main experimental features are as follows:

- **a)** the conductance peak that we associate with the d-wave gap is moved from 17 mV down to 11 to 12 mV.
- **b)** the ZBCP is no longer observed. It is replaced by a dip that persists up to around 15K.
- **c)** the energy width of the conductance dip is of several mV, larger than the zero field splitting in the pure [100] films and than that reported by Covington et al. (1).
- **d)** Upon application of a field parallel to the c-axis, the width of the dip increases, but not very fast.

We attach some importance to the decrease, upon overdoping, of the peak position that we associate with the d-wave gap. This shows that the peak position is a characteristic of the bulk of the film, and not just of its surface. If the relatively small 17 mV value, measured in the pure film, reflected a gap reduction at the surface because of a reduced Tc (due for instance to a loss of oxygen), the peak position should increase rather than decrease upon overdoping.

But the main observation on the overdoped films is the disappearance of the ZBCP, replaced by a spontaneous sub-gap.

**Fig.1 Split peak field dependence, [100] film. Full symbols H/c, empty symbols: field oriented in plane and perpendicular to c.**

**Fig.2 Split peak field dependence, [110] film**

**Fig.3 Gap and sub-gap in overdoped [110] film**
One cannot anymore describe the shape of the characteristic at small bias as a split ZBCP. This distinction is important. While a split ZBCP may be, at least qualitatively, understood as a Doppler shift of the zero energy Andreev bound states, its absence means that such states are simply not present. This, together with the $\sqrt{H}$ splitting seen in the pure [110] films, brings us to the conclusion that a bulk $id$ component, induced by the applied field, by overdoping, or impurity states (11),(12) is a more likely interpretation of the data than a surface $is$ component.

From the width of the conductance dip, we infer that the sub-gap in our overdoped films is of the order of a few meV. This is already a significant fraction of the $d$-wave gap. It may be that the smaller spontaneous "split" seen in our [100] films (about 05 mV) is due to a slight overdoping. More work is necessary to determine how the spontaneous sub-gap varies with overdoping, but it would seem that it does increase continuously. One can note that, if that trend continues up to stronger doping levels, the decreasing $d$-wave component and the increasing $id$ one will eventually become of the same order of magnitude. At that stage, the amplitude of the gap is in fact constant around the Fermi surface.

4. THEORETICAL MODELING

The available data suggests that optimum doping is a special concentration, above which a spontaneous sub-gap appears. We propose a form of the free energy based on the assumption that this concentration $x_c$ is a quantum critical point. At $T=0$:

$$F = a\Delta^2 + b\Delta^3 - c\Delta B$$  \hspace{0.5cm} (1)

where $\Delta$ is the sub-gap, the coefficients $b$ and $c$ have been calculated by Laughlin, and $a$ is of the form:

$$a = a_0(x - x_c)$$  \hspace{0.5cm} (2)

where $a_0$ is a negative constant.

Minimization of the free energy with respect to $\Delta$ gives the equilibrium value:

$$\Delta_0 = \frac{-a + \sqrt{a^2 + 3bcB}}{3b}$$  \hspace{0.5cm} (3)

At the quantum critical point, $\Delta_0$ varies as $\sqrt{B}$ as proposed by Laughlin. For $x > x_c$ there is a finite subgap in zero field; it increases linearly at low fields, with a slope $c/|2a|$, which decreases as overdoping is increased. At $x < x_c$, there is no subgap in zero field; it increases linearly at low fields with a slope $c/|2a|$, which decreases as the underdoping is more pronounced. At higher fields, the $\sqrt{B}$ dependence is again dominant. These properties are in agreement with all known data.

This work was supported in part by the Oren Family Chair of Experimental Solid State Physics and by the Heinrich Hertz Minerva Center for Superconductivity.

5. REFERENCES

10) Y. Dagan et al., see these proceedings.