Influence of Pair Breaking and Phase Fluctuations on Disordered High $T_c$ Cuprate Superconductors

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Electron irradiation has been used to introduce point defects in a controlled way in underdoped and optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$ crystals. This technique allows us to perform very accurate measurements of $T_c$ and of the $ab$ plane resistivity in a wide range of defect contents $x_d$ down to $T_c = 0$. The variation of $T_c$ and of the transition width with $x_d$ do not follow current predictions of pair-breaking theories. The data are rather compatible, at least for the highly damaged regime, with the expected influence of phase fluctuations. These results open new questions about the evolution of the defect induced $T_c$ depression over the phase diagram of the cuprates.

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The establishment of the condensed state in high-$T_c$ superconductors (HTSC) is not fully understood. The occurrence of the pseudogap in the underdoped part of the phase diagram [1] has raised the question of the coexistence of competing order parameters, or of the occurrence of preformed pairs, with an eventual condensation of the pairs in a coherent superconducting state at $T_c$. It has been proposed that, in these low carrier concentration systems, $T_c$ could be determined by the phase stiffness of the order parameter [2]. The phase fluctuations could explain the occurrence of a direct transition between superconducting and insulating states. An experimental approach which has been used extensively studied the influence of the disorder on both the normal and the superconducting properties. In-plane impurity substitutions induce $T_c$ depression [3,4], modification of the superfluid density $n_s$ [5,6], and local depression of the order parameter [7]. It is still highly debated whether the $T_c$ decrease results from pair-breaking effects of the $d$-wave order parameter [8,9], from the inhomogeneity of the order parameter (the so-called "Swiss cheese model" [5]), or from a reduction of the phase stiffness [10].

In order to acquire more accurate information on these issues we have undertaken careful studies on the influence of controlled disorder in single crystals of HTSC cuprates. This can be achieved by high energy electron irradiations performed at low temperatures which introduce point defects, in particular, Cu and O vacancies in the CuO$_2$ planes [11–13]. The fact that one single crystal can be progressively damaged allows us to study the influence of disorder with an accuracy impossible to attain with chemical substitutions. This gives us the opportunity to study precisely the properties of samples with highly reduced $T_c$, as we can indeed control the irradiation fluence to reach $T_c = 0$. We observe that $T_c$ quite unexpectedly decreases quasilinearly with defect content down to $T_c = 0$, in both underdoped and optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO), at variance with theories of pair breakings [9]. The analysis of the variation of $T_c$ and of the transition width $\delta T_c$ reveals that the resistivity at $T_c$ is the relevant parameter which determines the $T_c$ depression when $T_c$ approaches zero. This agrees with the expected influence of quantum phase fluctuations. We discuss whether this approach can describe as well the variation with hole doping of the initial decrease of $T_c$ with disorder.

The single crystals of YBCO are similar to those studied in [14]. In-plane resistivities were measured by the van der Pauw method. Special care has been taken to put the electrical contacts on the edges of the samples to ensure a homogeneous flow of the electrical current through the samples. In the case of YBCO$_7$, two different crystals of the same batch (No. 1 and No. 2) have been studied [15]. The irradiations were performed with 2.5 MeV electrons in the low $T$ facility of the Van de Graaff accelerator at the Laboratoire des Solides Irradiés (Ecole Polytechnique, Palaiseau, France). The samples were immersed in liquid H$_2$ and the electron flux was limited to $10^{14}$e/cm$^2$/s to avoid heating of the samples. The sample thicknesses ($\approx 20$ $\mu$m) were much smaller than the penetration depth of the electrons, which ensured a homogeneous damage throughout the samples [16].

For all samples we have found that Matthiessen’s rule is well verified at high temperature, as the high $T$ parts of the $\rho(T)$ curves shift parallel to each other. This is exemplified in Fig. 1, which displays the $T$ dependences of the in-plane resistivity $\rho_{ab}$ for YBCO$_7$ No. 2. This confirms that even for very high defect content ($x_d \sim 9\%$ in the planes [14]) the hole doping is not significantly modified as was already shown for low $x_d$ [11,14].

For low $T_c$ samples upturns of $\rho_{ab}$ are disclosed at low $T$ and increase with increasing $x_d$. These “ln$T$” contributions have been analyzed in YBCO$_{6,6}$ [17] as due to a combination of single impurity scattering and localization effects. The latter becomes dominant for defect contents for which $T_c$ is fully suppressed.
To compare our results with pair-breaking theories, it is useful to study the variation of \( T_c \) with defect content \( x_d \). The \( T_c \) values reported hereafter were measured at the middle point of the resistive superconducting transition and the error bars were determined from the 10\%–90\% values of the extrapolated normal state resistivity. As we see later, the sharpness of the resistive transition indicates the homogeneity of the damage in the sample.

The best estimate for \( x_d \) is \textit{a priori} the irradiation fluence. For low \( x_d \), data were taken in the irradiation setup without annealing the samples above 150 K. We found that \( T_c \) and \( \rho_{ab} \) (measured at 150 K) vary linearly with the irradiation fluence, so that \( \Delta \rho_{ab} = \rho_{ab}(150 K) - \rho_{ab}(0) \) represents \( x_d \). In many cases the samples had to be taken to room \( T \) between irradiation runs. Although part of the defects were annealed in such processes, the \( \rho(T) \) curves were found to superimpose to those obtained before annealing (e.g., curves 6 and 7 in Fig. 1). Thus \( \Delta \rho_{ab} \) remains a good estimate for \( x_d \). However, in YBCO_{6.6}, the variation with irradiation fluence of \( \Delta \rho_{ab} \) (without annealing above 150 K) increases slightly faster than linear for \( \Delta \rho_{ab} > 100 \mu \Omega \text{cm} \), although \( T_c \) still decreases linearly. In this case \( \Delta \rho_{ab} \) has then been replaced by \( \Delta \rho_{ab}^{*} \), its linear extrapolation with fluence. We have therefore plotted in Fig. 2 the data for \( T_c \) versus both \( \Delta \rho_{ab} \) and \( \Delta \rho_{ab}^{*} \) for YBCO_{6.6}. For YBCO_{7} the deviation from linearity occurred only for \( \Delta \rho_{ab} > 200 \mu \Omega \text{cm} \). The corresponding correction, which did not exceed 10\%, has not been performed in Fig. 2.

The linear variation of \( T_c \) with defect content, down to \( T_c = 0 \), is the most striking feature of the data displayed in Fig. 2. This result contrasts with the AG formula which for \( d \)-wave superconductors gives \( T_c \) as \([9,18]\)

\[
-\ln\left(\frac{T_c}{T_{c,0}}\right) = \Psi\left(\frac{1}{2}\right) - \Psi\left(\frac{1}{2}\right),
\]

where \( \Psi(x) \) is the digamma function, \( \alpha = \hbar/(2\pi k_B T_c \tau) \) is the pair-breaking parameter, and \( 1/\tau \approx x_d \) is the scattering rate in the normal state. The well-known negative curvature of the AG curve shown in Fig. 2 is \textit{obviously not observed in the present data}. Some published data for impurity substitutions \([19]\) have been fitted with Eq. (1). Within the limited accuracy on the impurity content they could be fitted as well with a linear variation.

Let us also consider the width of the superconducting transition \( \delta T_c \), which should reflect the inhomogeneities of the defect distribution in the sample. As can be seen in Fig. 3, \( \delta T_c \) increases linearly with \( x_d \) from \( \delta T_c^0 = 0.7 \) K never exceeds 5 K, and then decreases when \( T_c \) approaches zero. Inhomogeneities of the irradiation process, such as electron energy losses through the sample, or a divergence of the electron beam, etc., result in a \textit{macroscopic} distribution of \( x_d \) with a full width \( \delta x_d = ax_d \). Therefore, if \( T_c = f(x_d) \), one obtains \( \delta T_c - \delta T_c^0 = ax_d f'(x_d) \). While an upward curvature of \( \delta T_c - \delta T_c^0 \) will be expected from the AG function, the experimental decrease of \( \delta T_c \) indicates that \( T_c \) must approach zero with an upward curvature. Thus the measurement of \( \delta T_c \) gives us a more accurate determination of the actual shape of \( T_c = f(x_d) \) than the data of Fig. 2. Let us point out that the maximum of \( \delta T_c \) coincides with the occurrence of low \( T \) upturns of resistivity, as shown in the inset of Fig. 4, where \( \rho(T_c) \) has been plotted versus \( \Delta \rho_{ab} \). As discussed hereafter, this observation is found compatible with expectations from phase fluctuation theories.

Although AG theory is not applicable when localization and/or Kondo-like corrections to the conductivity

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**FIG. 1** (color online). The resistivity is plotted versus temperature for the single crystal YBCO_{7} No. 2 irradiated at low temperature by 2.5 MeV electrons. Data taken either after annealing at 150 K (curve 6) or 300 K (curve 7) are shown to coincide. The initial increase of \( \rho_{ab} \) (without annealing at room \( T \)) is equal to 18 \( \mu \Omega \text{cm} \) per 10\(^{19} \) e/cm\(^2\).

**FIG. 2** (color online). Decrease of \( T_c \) versus defect content \( x_d \). The latter is proportional to \( \Delta \rho_{ab} \) measured at 150 K for YBCO_{7}. For YBCO_{6.6} the data are plotted versus \( \Delta \rho_{ab} \) (full circles) and \( \Delta \rho_{ab}^{*} \) (empty circles) which is a best estimate of \( x_d \) as explained in the text. The Abrikosov-Gorkov (AG) curve (dotted line) is represented in the top part. Linear fits (full lines) are also displayed together with those for Emery and Kivelson (EK) theory (dashed lines) as explained in the text.
explain the initial decrease of $T_c$ but with a similar dependence on $x_d$ as the AG curve, which does not solve the contradiction with our results.

A major reason for a breakdown of the AG theory might result from the very short coherence lengths $\xi$ in the high $T_c$ cuprates, which does not allow one to assume a uniform gap averaged over the disorder. This might explain as well the variation of the superfluid density $n_s$, with $x_d$ as proposed by Franz et al. [22]. Such a possibility is reinforced by the recent scanning tunneling microscopy (STM) data [7] which reveal a depression of the density of states peaks near Zn impurities on a length scale comparable to $\xi$. As these regions of depressed superconductivity overlap for large $x_d$, a simplistic all-or-nothing model (so-called "Swiss cheese") might explain the negative curvature of $n_s(x_d)$ which has been reported [5,6]. The observation in underdoped pure compounds of a linear relation between $T_c$ and $n_s$ [23] has led some authors to consider that this relation applies as well for impure samples [24,25]. The present observation of a quasilinear decrease of $T_c$ definitely contradicts this simple guess.

In a totally different approach, EK [2] argue that in low $n_s$ superconductors $T_c$ might be determined by phase fluctuations of the order parameter. The temperature of the classical phase ordering $T_{\theta}^{\text{max}}$, which is proportional to $n_s/m^*$, can be much lower than the mean-field $T_c$ and is therefore an upper bound on the true $T_c$. In that case the influence of disorder is to increase quantum phase fluctuations. They propose [10] that their magnitude is determined by the value of $\rho(T_c)$ and that superconductivity disappears for a critical value $\rho_Q$, so that

$$\ln(T_{\theta}^{\text{max}}/T_c) = \rho(T_c)/\rho_Q \ln(\epsilon/T_c)$$

in which $\epsilon$ is the energy scale of pairing interactions.

The fact that we have access in our experiment to $T_c$ values near zero allows us to test this dependence very precisely. This is done in Fig. 4, where the data for $T_c$ are plotted versus $\rho(T_c)$. Reasonable fits of our data can be obtained with a large range of $\epsilon$ values. As suggested by EK, we have therefore chosen a realistic value $\epsilon \sim 1200$ K, the antiferromagnetic exchange energy in YBCO$_7$. As can be seen in Fig. 4, the data can be well fitted by Eq. (2) with $T_{\theta}^{\text{max}} = 103$ K and $\rho_Q = 600 \mu\Omega$ cm for YBCO$_7$ (76.6 K and 1380 $\mu\Omega$ cm for YBCO$_{6.6}$). Whatever the value chosen for $\epsilon$ we always found a value of $\rho_Q$ roughly 2 times larger in YBCO$_{6.6}$ than in YBCO$_7$, as $\rho_Q$ is mainly given by the value of $\rho(T_c)$ corresponding to $T_c = 0$.

Using the analytical fit $\rho(T_c) = g(\Delta \rho_{ab})$ displayed in the inset of Fig. 4, we plotted in Fig. 2 the variation of $T_c$ given by Eq. (2). For YBCO$_7$, recalling that $\Delta T_c - \Delta T_c^0 = ax_d f(x_d)$, we can also determine the expected evolution of the transition width $\Delta T_c$. The variation of $\Delta T_c$ calculated with the parameters deduced from the fit of Fig. 4 reproduces rather well the trend of the experimental data in Fig. 3 with $a = 0.07$. This analysis can be based solely on the measured values.
from the data near $T_c = 0$ and explains both the variation of $T_c$ and of $\delta T_c$, while all the alternative possibilities examined so far did not. This emphasizes the importance of $\rho(T_c)$ and quantum phase fluctuations in determining the actual $T_c$ in this highly damaged region. Let us point out that the values for $\rho_Q$ taken per CuO$_2$ sheet [26] ($\rho_{Q,2D}^{2D} = 10 \, \text{k}\Omega/\square$ and $25 \, \text{k}\Omega/\square$ for YBCO$_7$ and YBCO$_{6.6}$) are much smaller than those observed in ion irradiated thin films (Ref. [12] in [10]). This is probably obtained for the initial decrease of $T_c$ doped behavior. Let us recall at this stage the results variation of $T_c$ of the actual different hole dopings YBCO$_6$.

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As for the highly damaged samples, we might anticipate that their superconducting properties should differ strongly from those observed in weakly disordered compounds. Although this regime occurs near superconductor to insulator transition, further work is clearly needed to understand the relationship with the metal-insulator transition observed in other 2D structures.

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[15] The error on $\rho_{ab}$ ($5\%$) is that on the sample thickness. To compare the two samples, we have thus chosen to impose the same slope of $\rho(T)$ at high $T$. This corresponds to a correction of $3\%$ on the thickness of sample No. 2.
[16] We can estimate the energy loss of 2.5 MeV electrons to be $\sim 1 \, \text{keV}/\mu\text{m}$ in YBCO.
[20] If we naively take into account the fact that $x_d$ at low $T$, this would lead to an even larger deviation of Eq. (1) from the data.
[26] The 2D sheet resistance $\rho^{2D}$ is determined as $\rho^{2D} = n \rho_{ab}/c$, where $c$ is the c-axis parameter and $n$ is the number of CuO$_2$ planes per unit cell. The $\rho^{2D}$ values found here are larger than $h/4e^2 = 6.5 \, \text{k}\Omega/\square$ usually quoted for the superconducting to insulator transition in 2D metals [27]. One can notice that $T_c$ vanishes for both hole contents for $\Delta \rho^{2D}_{ab} = 4.7 \, \text{k}\Omega/\square$ contrary to Zn substitution for which $T_c \to 0$ for $\Delta \rho^{2D}_{ab} = 6.5 \, \text{k}\Omega/\square$ for YBCO$_{6.6}$ and for $\sim 2.3 \, \text{k}\Omega/\square$ for YBCO$_7$ [4].