Respective influences of pair breaking and phase fluctuations in disordered high $T_c$ superconductors

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Electron irradiation has been used to introduce point defects in a controlled way in the CuO$_2$ planes of underdoped and optimally doped YBCO. This technique allows us to perform very accurate measurements of $T_c$ and of the residual resistivity in a wide range of defect contents $x_d$ down to $T_c = 0$. The $T_c$ decrease does not follow the variation expected from pair breaking theories. The evolutions of $T_c$ and of the transition width with $x_d$ emphasize the importance of phase fluctuations, at least for the highly damaged regime. These results open new questions about the evolution of the defect induced $T_c$ depression over the phase diagram of the cuprates.

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 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. The phase fluctuations could explain the occurrence of a direct transition between superconducting and insulating states. An experimental approach which has been used extensively has been to study the influence of the disorder on both the normal and superconducting properties. In plane impurity substitutions induce $T_c$ depression, modification of the superfluid density $n_s$, and local depression of the order parameter. Whether the $T_c$ decrease results from pair breaking effects of the d-wave order parameter, from the inhomogeneity of the order parameter (so called "swiss cheese model"), or from a reduction of the phase stiffness is still highly debated.

In order to bring more accurate information on these issues we have undertaken careful studies of 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 only point defects such as Cu and O vacancies in the CuO$_2$ planes. The fact that a unique single crystal is 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 $T_c = 0$. The results reported in this paper display remarkably simple phenomenological variations. We observe that $T_c$ quite unexpectedly decreases linearly with defect content down to $T_c = 0$, in both underdoped and optimally doped YBCO, at variance with Abrikosov Gorkov based theories. 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 shall discuss whether this approach can describe as well the variation with hole doping of the initial decrease of $T_c$ with increasing disorder.

The single crystals of YBCO are similar to those studied in [11, 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 insure an homogeneous flow of the electrical current throughout the samples. In the case of YBCO$_2$, two different crystals of the same batch ( #1 and #2) have been studied [15]. The irradiations were performed with 2.5MeV electrons in the low temperature facility of the Van der Graaff accelerator at the LSI (Ecole Polytechnique, Palaiseau). 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 during irradiation. 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 [14].

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$_7$ #2. This confirms that even for very high defect content ($x_d \approx 9\%$ in the planes) the hole doping is not significantly modified as was already shown before for low $x_d$ [11, 14].

For low $T_c$ samples upturns of the resistivity are disclosed at low $T$ and increase with increasing $x_d$. These "\ln T" contributions have been analysed in the case of YBCO$_{6.6}$ [18] as being associated with a combination of single impurity scattering and localization effects. The latter become dominant for defect contents for which superconductivity 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 shall see later on, the sharpness of the resistive transition is a good indication that the homogeneity of the damage in the sample is ensured.

The best estimate for $x_d$ is a priori the irradiation fluence [16]. For low $x_d$, data were taken in the irradiation set-up without annealing the samples above 150K. We found that $T_c$ and the normal state resistivity $\rho_{ab}$ (measured at 150K) vary linearly with the irradiation fluence, so that $\Delta \rho_{ab}(150K) - \rho_{ab}^{\text{pure}}(150K)$ 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). Therefore $\Delta \rho_{ab}$ remains a good estimate for $x_d$. However, in YBCO5.6, the variation with irradiation fluence of $\Delta \rho_{ab}$, measured without annealing above 150K, departs from linearity for $\Delta \rho_{ab} > 100\mu\Omega\cdot\text{cm}$, although $T_c$ still decreases linearly with the electron fluence. In this case $\Delta \rho_{ab}$ has then been replaced by $\Delta \rho_{ab}^\ast$, its linear extrapolation with fluence. We have therefore reported in figure 2 the data for $T_c$ versus both $\Delta \rho_{ab}$ and $\Delta \rho_{ab}^\ast$ for YBCO5.6. For YBCO7, the deviation from linearity only occurred for $\Delta \rho_{ab} > 200\mu\Omega\cdot\text{cm}$. 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 that expected from the standard Abrikosov-Gorkov formula which for d-wave superconductors gives $T_c$ as [3, 20]:

$$-\ln(\frac{T_c}{T_{c0}}) = \Psi(\alpha + \frac{1}{2}) - \Psi(\frac{1}{2})$$  \hspace{1cm} (1)

FIG. 1: The resistivity is plotted versus temperature for the single crystal YBCO#2 irradiated at low temperature by 2.5 MeV electrons. Data taken either after annealing at 150K (curve 6) or 300K (curve 7) are shown to coincide.

where $\Psi(x)$ is the digamma function, $\alpha = \hbar/(2\pi k_B T_c \tau)$ is the pair-breaking parameter, and $1/\tau \propto x_d$ is the scattering rate in the normal state. The scale of the $T_c$ reduction is fixed by the ratio of $\hbar/\tau$ and $k_B T_c$ so that the impurity pair breaking becomes more and more efficient when $T_c$ decreases. This yields the well known negative curvature of the AG curve shown in fig 2, which is obviously not observed in the present data [21]. Some published data for impurity substitutions [22] have been fitted with Eq.1. Within the limited accuracy on the impurity content and substitution site they could be fitted as well with a linear variation.

Let us also consider the width of the superconducting transition, which should reflect the inhomogeneities of the sample. The initial transition width $\delta T_c \simeq 0.7K$ increases roughly linearly with $x_d$ but never exceeds 5K, and then decreases when $T_c$ approaches zero, as can be seen in fig.3. Inhomogeneities due to the irradiation process, such as electron energy losses through the sample, or a divergence of the electron beam at the level of the sample, etc... result in a macroscopic distribution of $x_d$ with the full width $\delta x_d = ax_d$. Within the AG theory the transition width $\delta T_c$ should scale with the derivative of the AG function. A large increase of $\delta T_c$ would then be expected when $T_c$ reaches zero, contrary to the experimental observation. From the observed quasi linear variation of $\Delta T_c$ with defect content one should expect a linear increase of $\delta T_c$ down to $T_c = 0$. The fact that $\delta T_c$ goes through a maximum rather indicates that superconductivity becomes less sensitive to the distribution of defect content. Such a possibility will be further consid-
erated in the discussion hereafter.

Let us point out at this stage that the observation in underdoped pure compounds of a linear relation between \( T_c \) and \( n_s \), has led some authors to consider that this relation applies as well for impure samples. The present observation of a linear decrease of \( T_c \) definitely contradicts this simple guess.

In a totally different approach, Emery and Kivelson (EK) 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 \( T_{\rho}^{\text{max}} \) which is proportional to \( n_s/m^* \) can be much lower than the mean field critical temperature 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 that their magnitude is determined by the value of \( \rho(T_c) \), and that superconductivity disappears for a critical value \( \rho_Q \), so that

\[
\ln(\frac{T_{\rho}^{\text{max}}}{T_c}) = \frac{\rho(T_c)}{\rho_Q} \ln(\epsilon/T_c) \tag{2}
\]

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

Although AG theory is not applicable when localization corrections to the conductivity occur, the experimental deviations are already evident for a range of \( T_c \) values for which these effects are negligible. A quantitative discrepancy with AG theory has been also evidenced, as the initial decrease of \( T_c \) is much slower than predicted \[5, 12, 13\]. For YBCO\(_7\) for instance, theoretical estimates of \( \Delta T_c/\Delta \rho_{ab} \) range from 0.7 to 1.2 \( K/\mu\Omega . \text{cm} \), a factor 2 to 4 higher than the experimental value found here (\( \sim 0.35 \ K/\mu\Omega . \text{cm} \)). It has been shown that this difference can be taken into account in the framework of the AG model for a d-wave order parameter if one assumes an anisotropic impurity scattering \[22\]. With appropriate parameters, one can explain the initial decrease of \( T_c \) but with a similar dependence with \( x_d \) 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 in the high \( T_c \) cuprates, which does not allow to assume a uniform gap averaged over the disorder. This might allow to explain as well the variation of the superfluid density \( n_s \) with \( x_d \) as proposed by Franz et al \[24\]. Such a possibility is reinforced by the recent STM data \[7\] which reveal that the large depression of the DOS peaks, and therefore of \( n_s \), found nearby Zn impurities disappears on a lengthscale comparable to the coherence length \( \xi \).

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 noticed by various authors \[3, 6\].

The fact that we have access in our experiment to \( T_c \) values near zero allows us to test this dependence very precisely 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 \( T_{\rho}^{\text{max}} = 103 K \) and \( \rho_Q = 600 \mu\Omega . \text{cm} \) for YBCO\(_7\) (76.6K and 1380\( \mu\Omega . \text{cm} \) for YBCO\(_6\)\(_6\)). Whatever the value chosen for \( \epsilon \) we always found a value of \( \rho_Q \) roughly two times larger in YBCO\(_6\)\(_6\) than in YBCO\(_7\) as it is mainly given by the value of \( \rho(T_c) \) corresponding to \( T_c = 0 \).

**FIG. 3**: Width of the superconducting \( \delta T_c \) defined as shown in the insert as a function of \( \Delta \rho_{ab} \) for the two crystals of YBa\(_2\)Cu\(_3\)O\(_7\). The maximum of \( \delta T_c \) corresponds to a \( T_c \) of \( \sim 40 K \). The variation expected from AG, EK and linear dependence of \( T_c \) with \( \delta x_d/x_d \sim 7% \) are also plotted (see text).

**FIG. 4**: The decrease of \( T_c \) as a function of \( \rho(T_c) \) as defined in the insert of fig.3 is compared to Eq.2. The best fits are obtained for \( \rho_Q \) equal to 600 and 1380 \( \mu\Omega . \text{cm} \) respectively for YBa\(_2\)Cu\(_3\)O\(_7\) and YBa\(_2\)Cu\(_3\)O\(_6\)\(_6\).
We can as well determine the expected evolution of the transition width $\delta T_c$ assuming $\delta x_d = ax_d$. We have done this for YBCO$_7$, taking the derivative of Eq.2 with an analytical fit of the data for $\rho(T_c)$ versus $\Delta \rho_{h}$. 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 conclusively be done solely from the data near $T_c = 0$ and allows to explain jointly the variation of $T_c$ and of $\delta T_c$, while all the alternative possibilities examined so far did not. So this emphasizes the importance of quantum phase fluctuations and of $\rho(T_c)$ 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 [28] ($\rho_{Q}^{2D} = 10 k\Omega/\square$ and $25 k\Omega/\square$ for YBCO$_7$ and YBCO$_{6,6}$) are much smaller than those observed in ion irradiated thin films [ref.12 in [1]]. This is probably related to the fact that irradiation damage in thin films usually induces much larger increase of resistivity than in single crystals. However the large variation of $\rho_{Q}^{2D}$ with hole doping found here is not anticipated by EK. This might stem from the fact that the analysis of EK is a priori more appropriate to describe underdoped cuprates with low superfluid density. One expects a behaviour completely different for overdoped materials for which $T_c$ should be determined by the mean-field transition temperature and disorder should be mainly pair breaking.

This leads us as well to consider that our fits are not a proof that the analysis of EK applies for the initial decrease of $T_c$ particularly in optimally doped YBCO$_7$ which is at the borderline between underdoped and overdoped behaviour. It is interesting at this stage to remind the results obtained for the initial decrease of $T_c$ in cuprates with different hole dopings $n_h$. We have shown that $\Delta T_c/\Delta \rho_{ab}$ increases steadily with $n_h$ [14]. Obviously the initial slope of Eq.2 that is $\Delta T_c/\Delta \rho = -(T_c/\rho_{Q}) \ln(e/T_c)$ cannot explain this behaviour unless one introduces a large non physical reduction of $\rho_{Q}$ with increasing hole content. If the number of carriers is taken as the number of holes $n_h$, the initial slope is such that $\Delta T_c$ scales as $n_h^\gamma / \tau$ all over the phase diagram [14], which indicates that pair breaking in the $d$-wave superconducting state might still contribute to the initial decrease of $T_c$. This possibility is favored by the STM observation, in optimally doped Bi-2212, of quasiparticle states around Zn impurities, as expected from strong scattering theories [6]. A reasonable explanation of the data would then be the occurrence of a crossover from pair breaking to phase fluctuations regime for high disorder. Such a crossover should progressively shift towards increasing disorder with increasing doping.

In conclusion the possibility to create very homogeneous disorder and well controlled defect contents $x_d$ has allowed us to study carefully the depression of $T_c$ down to $T_c = 0$ in underdoped and optimally doped YBCO. We have shown that $T_c$ which decreases quasi linearly with $x_d$, does not scale with the reported variation of $n_s$. The observation of the narrow transition width in YBCO$_7$ for large $x_d$ allowed us to suggest that $\rho(T_c)$ is the relevant scattering rate which controls $T_c$ for high damage, as expected from quantum phase fluctuations. The present experiments provide sufficiently detailed information to stimulate further theoretical calculations which should take into account both the amplitude and phase variation of the order parameter.

As for the highly damaged samples, we might anticipate that their superconducting properties should strongly differ 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 superconductor-insulator and the metal-insulator transition observed in other 2D structures.

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The 2D sheet resistance $\rho^{2D}$ is determined as $\rho^{2D} = n \cdot \rho_{ab}/c$ where $c$ is the $c$-axis parameter and $n$ is the number of CuO$_2$ planes per unit cell. The values found here have an order of magnitude comparable to the value $\hbar/4e^2 = 6.45\,\text{k}\Omega/\square$ usually quoted for the superconducting to insulator transition in 2D metals [24]. One can notice in fig.2 that $T_c$ vanishes for both hole contents for $\Delta \rho^{2D}_{ab}$ of the order of $6.4\,\text{k}\Omega/\square$ as also seen for Zn substitution [4], although $\rho(T_c)$ is much larger.
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