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 $YBa_2Cu_3O_{7-\delta}$ 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 $YBa_2Cu_3O_{7-\delta}$ (YBCO), at variance with theories of pair breakings [9]. The analysis of the variation of T_c and of the transition width δT_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 $10^{14} e/\mathrm{cm}^2/\mathrm{s}$ to avoid heating of the samples. The sample thicknesses ($\simeq 20\ \mu$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 ρ_{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 ρ_{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.

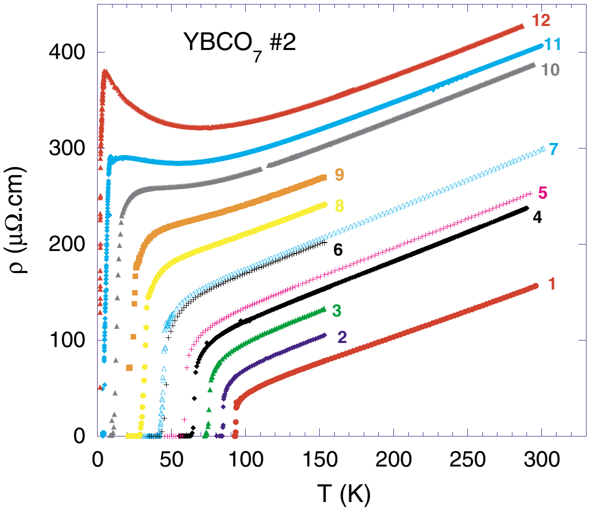

FIG. 1 (color online). The resistivity is plotted versus temperature for the single crystal YBCO$_7$ No. 2 irradiated at low temperature by 2.5 MeV electrons. Data taken either after annealing at 150 K (curve 6) or 300 K (curve 7) are shown to coincide. The initial increase of ρ_{ab} (without annealing at room T) is equal to 18 $\mu\Omega$ cm per $10^{19} e/\mathrm{cm}^2$.

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 *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 ρ_{ab} (measured at 150 K) vary linearly with the irradiation fluence, so that $\Delta\rho_{ab} = \rho_{ab}(150\ \mathrm{K}) - \rho_{ab}^{\mathrm{pure}}(150\ \mathrm{K})$ 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 $\Delta\rho_{ab} > 100\ \mu\Omega$ 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 $\Delta\rho_{ab} > 200\ \mu\Omega$ 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]

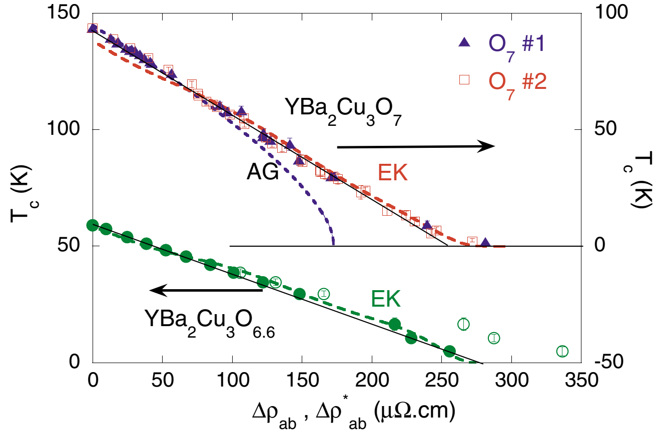

FIG. 2 (color online). Decrease of T_c versus defect content x_d. The latter is proportional to $\Delta\rho_{ab}$ measured at 150 K for YBCO$_7$. For YBCO$_{6.6}$ the data are plotted versus $\Delta\rho_{ab}$ (empty circles) and $\Delta\rho_{ab}^*$ (full circles) which is a best estimate of x_d as explained 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.

$$-\ln\left(\frac{T_c}{T_{c0}}\right) = \Psi\left(\alpha + \frac{1}{2}\right) - \Psi\left(\frac{1}{2}\right), \tag{1}$$

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 well known negative curvature of the AG curve shown in Fig. 2 *is 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 δT_c, which should reflect the inhomogeneities of the defect distribution in the sample. As can be seen in Fig. 3, δT_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 *macroscopic* distribution of x_d with a full width $\delta x_d = a x_d$. Therefore, if $T_c = f(x_d)$, one obtains $\delta T_c - \delta T_c^0 = a x_d f'(x_d)$. While an upward curvature of $\delta T_c - \delta T_c^0$ will be expected from the AG function, the experimental decrease of δT_c indicates that T_c must approach zero with an upward curvature. Thus the measurement of δT_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 δT_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

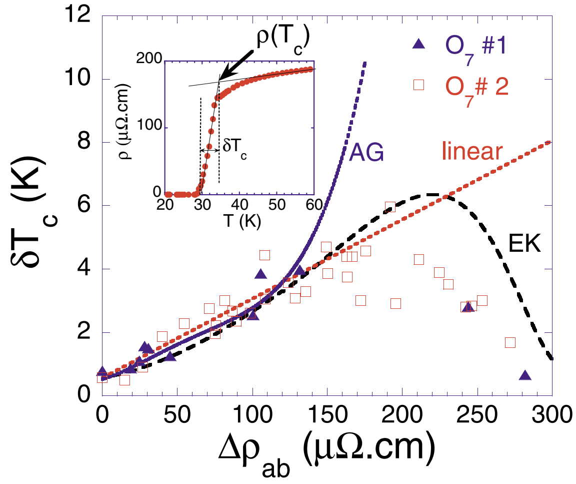

FIG. 3 (color online). Width δT_c of the superconducting transition defined as shown in the inset as a function of $\Delta\rho_{ab}$ for YBCO$_7$. The variations expected from the AG, EK theories and for a linear T_c are plotted for $\delta x_d/x_d \sim 7\%$ (see text).

occur [17], the experimental deviations are already evident for a range of T_c values for which these effects are negligible [20]. A quantitative discrepancy with AG theory has also been evidenced, as the initial decrease of T_c is much slower than predicted [5,12,13]. For YBCO$_7$, for instance, theoretical estimates of $\Delta T_c/\Delta\rho_{ab}$ [8] range from 0.7 to 1.2 K/$\mu\Omega$ cm, a factor of 2 to 4 higher than the experimental value found here ($\sim$0.35 K/$\mu\Omega$ 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 [21]. With appropriate parameters, one can 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.*

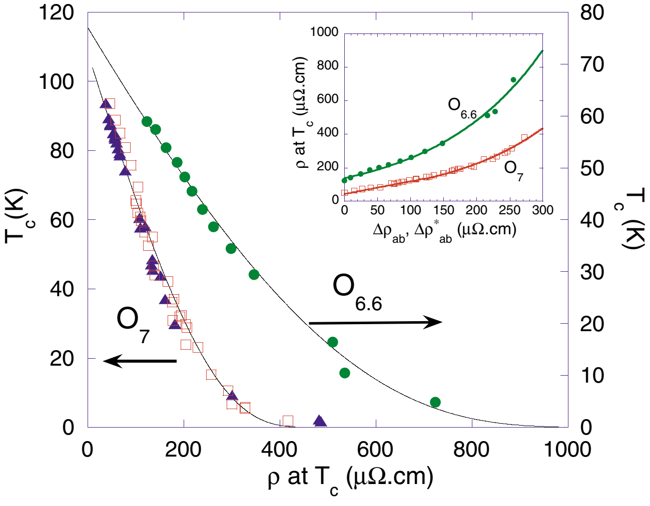

FIG. 4 (color online). The decrease of T_c as a function of $\rho(T_c)$ as defined in the inset of Fig. 3 is compared to EK theory [Eq. (2)]. The best fits are obtained for ρ_Q equal to 600 and 1380 $\mu\Omega$ cm, respectively, for YBCO$_7$ and YBCO$_{6.6}$. The data for $\rho(T_c)$ versus $\Delta\rho_{ab}$ are displayed in the inset together with analytical fits (merely exponential here).

A major reason for a breakdown of the AG theory might result from the very short coherence lengths ξ 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 ξ. 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 $T_\theta^{\max}$, 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 ρ_Q, so that

$$\ln(T_\theta^{\max}/T_c) = \rho(T_c)/\rho_Q \ln(\epsilon/T_c) \qquad (2)$$

in which ϵ 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 ϵ 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 $T_\theta^{\max} = 103$ 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 ϵ we always found a value of ρ_Q roughly 2 times larger in YBCO$_{6.6}$ than in YBCO$_7$, as ρ_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 $\delta T_c - \delta T_c^0 = a x_d f'(x_d)$, we can also determine the expected evolution of the transition width δT_c. The variation of δT_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 from the data near $T_c = 0$ and explains both the variation of T_c and of δT_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 ρ_Q taken per CuO_2 sheet [26] ($\rho_Q^{2D} = 10\ k\Omega/\square$ 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 [10]). This is probably related to the fact that irradiation damage in thin films usually induces a much larger increase of resistivity than in single crystals. However, the large variation of ρ_Q^{2D} with hole doping found here is not anticipated by EK. This might stem from the fact that the analysis of EK is more appropriate to describe underdoped cuprates with low n_s. One expects a different behavior for overdoped materials for which T_c should be the mean-field transition 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 behavior. Let us recall at this stage the results obtained for the initial decrease of T_c in cuprates with different hole dopings n_h. We have shown that $\Delta T_c/\Delta\rho_{ab}^{2D}$ increases steadily with n_h [14]. Obviously the initial slope of Eq. (2), that is $\Delta T_c/\Delta\rho = -(T_c/\rho_Q)\ln(\epsilon/T_c)$, cannot explain this behavior unless one introduces a large nonphysical reduction of ρ_Q with increasing n_h. If the number of carriers is taken as n_h, the initial slope is such that ΔT_c scales as m^*/τ over the entire 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, as expected from strong scattering theories [7]. A reasonable explanation of the data would then be the occurrence of a crossover from pair breaking to a phase fluctuation regime for high disorder. Such a crossover should progressively shift towards increasing disorder with increasing doping.

In conclusion, the use of electron irradiation 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 quasilinearly 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 suggests 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 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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