

## Universal $T_c$ depression by irradiation defects in underdoped and overdoped cuprates?

F. RULLIER-ALBENQUE<sup>1(\*)</sup>, P. A. VIEILLEFOND<sup>1</sup>, H. ALLOUL<sup>1(\*\*)</sup>,  
A. W. TYLER<sup>2(\*\*\*)</sup>, P. LEJAY<sup>3</sup> and J. F. MARUCCO<sup>4</sup>

<sup>1</sup> *Laboratoire des Solides Irradiés, CEA, CNRS UMR 7642, Ecole Polytechnique  
91128 Palaiseau cedex, France*

<sup>2</sup> *IRC in Superconductivity, University of Cambridge  
Madingley Road, Cambridge CB3 0HE, UK*

<sup>3</sup> *CRTBT, CNRS, BP 166X - 38042 Grenoble cedex, France*

<sup>4</sup> *LEMHE, Université Paris-Sud - 91405 Orsay cedex, France*

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**Abstract.** – We report on a study of the influence of defects introduced in the  $\text{CuO}_2$  planes of cuprates in a wide range of hole dopings  $x$ .  $T_c$  and electrical resistivity  $\rho(T)$  measurements have been performed on electron-irradiated  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+x}$  single crystals. A universal scaling between the decrease in  $T_c$  and  $\Delta\rho_{2D} \times n$ , where  $\Delta\rho_{2D}$  is the increase of the 2D resistance induced by the defects and  $n$  is the carrier concentration equal to  $x$ , is found for all the samples investigated here. This demonstrates that the hole content is the relevant parameter to describe the transport properties all over the phase diagram, in contradiction with a recent suggestion of a change in the number of carriers from  $x$  to  $1-x$  at the optimal doping. Moreover, the analysis of our data suggests that strong scattering persists on the overdoped side.

It is well established that defects introduced in the  $\text{CuO}_2$  planes of cuprates alter very effectively the properties of these materials in both their normal and superconducting states. In particular, the large  $T_c$  depression induced by Zn, a “non magnetic” scatterer, has been extensively studied [1–8]. NMR and susceptibility measurements [2, 3, 8] in Zn-substituted YBCO samples have shown that Zn induces localized moments on neighbouring Cu sites. The size of these moments is tightly related to the hole doping, decreasing from  $S \sim 1/2$  in underdoped samples to a very small value in optimally doped ones. Concerning transport properties, Fukuzumi *et al.* [6] have used Zn substitution in single crystals of YBCO and  $\text{LaSrCuO}$  to probe the evolution of the electronic state of high- $T_c$  cuprates with doping. Their results show a critical change in the normal-state transport properties from the underdoped to optimal or overdoped regime, with the carrier density being identified with the density of doped holes in the former regime and with the density of electrons in the latter one. Nagaosa and Lee [9] were able to account for these resistivity data in the framework of spin-charge separation

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(\*) Present address: Service de Physique de l’Etat Condensé, CEA Saclay, 91191 Gif-sur-Yvette cedex, France.

(\*\*) Present address: Laboratoire de Physique des Solides, Université Paris XI, 91405 Orsay cedex, France.

(\*\*\*) Present address: School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK.

theory. They proposed that the crossover in Zn-induced residual resistivity increases should be due to a Kondo screening effect —screening of localized spins by conduction electron spins— which increases as the hole concentration increases and the local moment disappears.

Electron irradiation is another practical way to introduce in-plane defects in a controllable manner in high- $T_c$  cuprates [10–12]. More precisely, it has been previously shown in YBCO $_{\sim 7}$  that the irradiation defects relevant to explain the  $T_c$  decrease are related to oxygen and copper displacements in the CuO $_2$  planes. They induce a  $T_c$  depression quantitatively similar to Zn substitution [10]. The great advantage of electron irradiation is to allow transport measurements on the same sample with an increasing concentration of in-plane defects ranging from 0 to several % without changing the hole doping.

In this paper, we present results of resistivity measurements on single crystals of optimally and underdoped YBCO $_{7-\delta}$  and optimally and overdoped Tl $_2$ Ba $_2$ CuO $_{6+\delta}$  (Tl-2201) irradiated at low temperatures by 2.5 MeV electrons. This allows us to study the interplay between in-plane defects and hole doping for a wide range of hole dopings. The remarkable result of this paper is to show that the relevant parameter to describe the changes in  $T_c$  and resistivity induced by in-plane defects is the concentration of doped holes, in contradiction with the analysis proposed in ref. [6] and [9].

Single crystals of YBCO $_{7-\delta}$  were grown using the standard flux method as described elsewhere [13]. Some optimally doped crystals were subsequently annealed in air at different temperatures and quenched at room temperature to adjust their oxygen content. The evaluation of oxygen content in our crystals was made by comparing  $T_c$  values —taken as the middle of the superconducting transition— with published data [14]. Three different crystals were studied with  $\delta$  values of 0.07, 0.2 and 0.4.

Tetragonal single crystals of Tl $_2$ Ba $_2$ CuO $_{6+\delta}$  were grown using a Cu-rich flux. Good electrical contacts are made by evaporating gold pads onto the as-grown samples. Furthermore, the crystals are annealed using various combinations of annealing temperature, atmosphere and time in order to obtain  $T_c$  values ranging from  $\sim 2$  K to 83 K [15]. Four different crystals with  $T_c$  values of 80 K, 54 K, 33 K and 31 K have been used.

The electron irradiations were performed in the low-temperature facility of the Van de Graaff electron accelerator at the LSI. During irradiation, the samples are immersed in liquid H $_2$  (21 K) and the irradiation flux is limited to  $2 \times 10^{14}$  e $^-$ /cm $^2$  s in order to avoid heating of the samples. *In situ* resistivity measurements have been performed between 20 K and 300 K.

Figures 1a and b show the temperature dependence of the *in-plane* resistivity  $\rho_{ab}$  for two single crystals of YBCO $_{7-\delta}$  with  $\delta \sim 0.07$  and  $\sim 0.4$  irradiated at 20 K in the same run and annealed up to 300 K for increasing electron fluences. One observes the same tendencies as usually found when defects are introduced into CuO $_2$  planes:  $T_c$  shifts downwards and the absolute value of the resistivity increases. For both optimal and underdoped compounds, the  $\rho(T)$  curves are perfectly parallel showing that the irradiation defects induce a temperature-independent contribution to resistivity, *i.e.* Matthiessen's rule is very well verified. This also indirectly confirms that the hole doping is not modified under irradiation in agreement with Hall effect data on electron-irradiated YBCO $_7$  [10]. Therefore one can determine the increase of residual resistivity  $\Delta\rho$  due to in-plane defects with high accuracy as the vertical shift of the  $\rho(T)$  curves. In underdoped crystals we can note that defects do not affect the characteristic temperature below which the pseudo gap starts to open, as already observed [2, 4, 12]. Moreover a metal-insulator transition is visible once resistivity values are around 300  $\mu\Omega$  cm. We have also observed this transition in optimally doped YBCO crystals at about the same resistivity value but for much higher electron fluences [16].

Intermediate measurements have been carried out without warming the samples above 100 K. In such conditions we have previously shown the absence of defect annealing [10]. Very

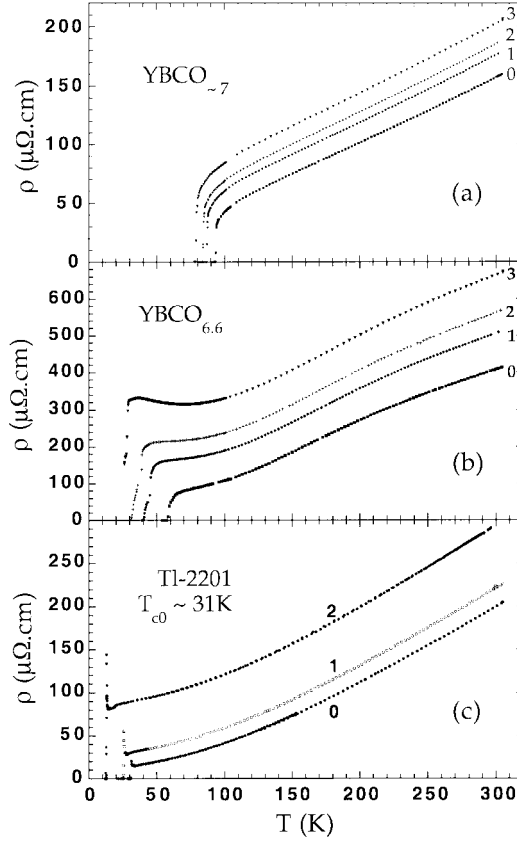


Fig. 1 – Temperature dependences of the in-plane resistivity in YBCO<sub>7</sub> (a), YBCO<sub>6.6</sub> (b) and over-doped Tl-2201 (c). The  $\rho(T)$  curves have been recorded after systematic annealing at 300 K. The two YBCO crystals have been irradiated in the same run with fluences of 0, 2.5, 3.8 and  $6 \times 10^{19}$  e/cm<sup>2</sup>, respectively for curves 0 to 3. In the case of over-doped Tl-2201, the electron fluences were 0, 0.8 and  $3.4 \times 10^{19}$  e/cm<sup>2</sup>. In the case of irradiated Tl-2201, the appearance of an anomalous  $\rho(T)$  peak just above the transition probably results from a non-uniform current density distribution in this specific crystal [17].

good linear dependences of the residual resistivity and the critical temperature *versus* electron fluences are found (fig. 2). Similarly to the case of Zn substitution, the decrease rate of  $T_c$  is faster on the underdoped side, increasing by a factor  $\sim 2$  from O<sub>7</sub> to O<sub>6.6</sub> as reported in the inset of fig. 2.

In the case of YBCO<sub>7</sub>, the threshold energies necessary to displace oxygen and copper atoms have been previously determined to be equal, respectively, to 10 and 15 eV [10]. The number of defects created per CuO<sub>2</sub> plane is  $n_d^i = \sigma_d^i \varphi t$ , where  $\sigma_d^i$  is the cross-section for displacing the atom  $i$  from its site and  $\varphi t$  is the electron fluence. Calculations of  $\sigma_d^i$  [18] lead to a total number of displaced O and Cu atoms per CuO<sub>2</sub> plane  $n_d \simeq 3.7 \times 10^{-3}$  for an electron fluence of  $10^{19}$  e/cm<sup>2</sup>. Even if this absolute value of  $n_d$  is not very accurate, one does not expect a variation with the oxygen content. This allows the precise comparison between the three different crystals studied here which is illustrated in fig. 2. The rate of increase of the 2D resistivity  $\Delta\rho_{2D}$  increases from 0.6 to 1.9 k $\Omega$ /‰ defects with decreasing oxygen content from O<sub>7</sub> to O<sub>6.6</sub> [19].

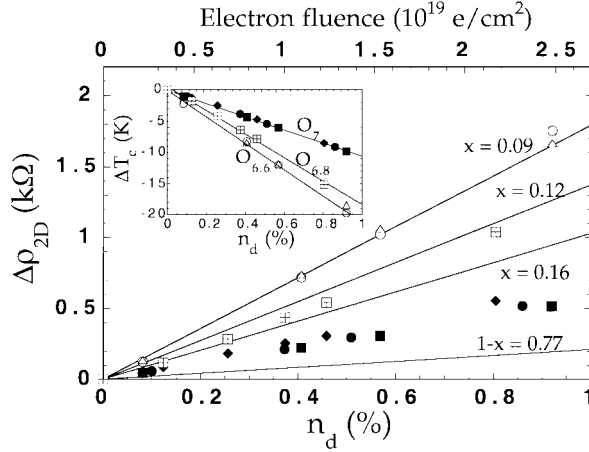


Fig. 2 – Increase of the 2D resistance measured at 100 K (without warming the samples above 100 K) for the different YBCO<sub>7-δ</sub> single crystals (closed symbols: O<sub>7</sub>, full symbols: O<sub>6.6</sub>, □: O<sub>6.8</sub>), as a function of the electron fluence and the in-plane defect concentration  $n_d$ . The solid lines indicate the fit using eq. (1) in the unitarity limit with the indicated values for the carrier concentration  $n$ . Inset: corresponding decreases of the critical temperature *vs.*  $n_d$ .

If we assume, as is usually done, that the contribution of the *s*-wave channel dominates the scattering processes, the increase in  $\rho_{2D}$  can be written as

$$\Delta\rho_{2D} = \frac{4\hbar}{e^2} \frac{n_d}{n} \sin^2 \delta, \quad (1)$$

where  $\delta$  is the scattering phase shift and  $n$  the carrier concentration. We have plotted in fig. 2 the values of  $\Delta\rho_{2D}$  obtained in the unitarity limit ( $\delta = \pi/2$ ) assuming that the carriers are the doped holes (with concentration  $x$ ), that is  $n = x$ . We find that the lower the hole doping, the closest the experimental data with these unitarity limit estimates. Here we have taken  $x$  to be equal to 0.16, 0.12 and 0.09, respectively, as the oxygen content decreases, using the relationship between  $T_c/T_{c0}$  and  $x$  proposed by Tallon *et al.* [20]. These values are somewhat low compared to those usually assumed in the literature. Nevertheless, our experimental result for YBCO<sub>7</sub> cannot be accounted for by using eq. (1) with  $n = 1 - x$  as proposed in ref. [6] and [9] for Zn-substituted crystals even with the value of  $x = 0.23$  taken by Fukuzumi *et al.* [6]. One can see in fig. 2 that our data lie well above the straight line obtained in this limit. We shall perform hereafter an analysis of  $\Delta T_c$  *vs.* residual resistivity which suggests that  $x$  is indeed the relevant carrier number.

Let us consider now the low-temperature irradiation defects in Tl-2201 crystals. Contrary to the case of YBCO, the response of Tl-2201 strongly depends on the doping level of the samples. The optimally doped crystals behave similarly to YBCO<sub>7</sub>: defects introduced at 20 K are stable up to  $\sim 130$  K and the resistivity above  $T_c$  exhibits a linear  $T$ -dependence obeying Matthiessen's rule. However, in overdoped crystals irradiation at 20 K induces a very fast decrease of  $T_c$  whose major part is recovered after warming up the samples to 80 K. Meanwhile, the irradiation-induced increase of the normal-state resistivity exhibits no thermal recovery. We think that this might be associated with a change of hole doping induced by oxygen displacements in the charge reservoir planes which are reversible after annealing above 80 K. A detailed analysis of these effects will be reported elsewhere [21]. Nevertheless, after systematic annealing at 300 K, one can see in fig. 1c that Matthiessen's rule is also very well verified for the most overdoped Tl-2201 crystal studied here. This is for us the indication

that the residual defects remaining in the samples after this thermal treatment do not modify the hole doping. One can therefore conclude that the prime cause of  $T_c$  suppression after annealing at 300 K is again due to the presence of defects in the  $\text{CuO}_2$  planes. As for YBCO, the increase of  $\Delta\rho$  due to these defects can be determined very precisely by the parallel shift of the  $\rho(T)$  curves.

In this condition the actual value of  $n_d$  in the  $\text{CuO}_2$  planes cannot be estimated reliably. However, in order to compare the effect of irradiation in Tl-2201 and YBCO, we have plotted in fig. 3 the decreases in  $T_c$ ,  $\Delta T_c$ , as a function of  $\Delta\rho_{2D}$  (a) and  $\Delta\rho_{2D} \times n$  (b) with  $n = x$  for all the samples studied here. We have used the same approach as described above to estimate the hole doping in Tl-2201 [22], which leads to  $x = 0.16$  for the optimally doped sample and to 0.22 and 0.25 for the overdoped ones with initial  $T_c$  of 54 and 31 K, respectively. Data obtained on the crystal with initial  $T_c$  of 33 K give similar results to the one with  $T_c = 31$  K and has not been reported in fig. 3. The striking result displayed in fig. 3b is that, irrespective of the compound or of the hole doping, the data are located on the same pair-breaking curve. It is worth mentioning that such a scaling is also followed for irradiation defects in single crystals of two other compounds displaying a large optimal value for  $T_c$ : Bi-2212 [23] and lightly underdoped Hg-1223 [24].

This “universal” scaling strongly suggests that  $\Delta T_c$  is due to impurity scattering in a  $d$ -wave superconductor as first suggested by Radtke *et al.* [25]. It is then given by the standard Abrikosov-Gork’ov formula which for small  $n_d$  is written as

$$\Delta T_c = -\frac{\pi}{4k_B}\Gamma_n, \quad (2)$$

where  $\Gamma_n = \frac{n_d}{\pi N(E_F)} \sin^2 \delta$  is the scattering rate in the normal state and  $N(E_F)$  the density of states at the Fermi level [26,27]. With a cylindrical Fermi surface, eq. (2) transforms into

$$\Delta T_c = -\frac{\pi e^2 \hbar}{8k_B m^*} \Delta\rho_{2D} \times n. \quad (3)$$

As comparable values of the effective mass  $m^*$  are found for YBCO and Tl-2201 [28], our experimental results give strong support to eq. (3) and to a  $d$ -wave symmetry of the pairing state all over the phase diagram. It is worth noting here that an analysis in terms of anisotropic  $s$ -wave superconductors would lead to a similar expression as eq. (3) with the degree of anisotropy  $\chi$  ( $0 \leq \chi \leq 1$ ) as a proportionality coefficient in eq. (3) [12,29]. Such an analysis would be unlikely as this parameter  $\chi$  can hardly be the same for the two compounds studied here whatever their hole dopings.

The correlation of eq. (3) should be independent of the nature of the defects. We have therefore considered the data for Zn in YBCO and LSCO. The values of ref. [6] for YBCO<sub>6.6</sub> has been reported in fig. 3b as has been determined by the parallel shifts of the  $\rho(T)$  curves. For YBCO<sub>7</sub>, the data of ref. [1] and [6] display an apparent breakdown of Matthiessen’s rule which introduces some difficulty in the determination of the residual resistivity. We rather reported here the data of Semba *et al.* [30] for which Matthiessen’s rule is well obeyed. As can be seen in fig. 3b, these results for Zn in YBCO are in a very good agreement with the scaling found for irradiation defects [31]. This result does not apply for the Zn-substituted LSCO system [6] for which Matthiessen’s rule applies as well. We attribute this difference to the fact that the 124 compound has an anomalously low optimal  $T_c$  (35 K) when compared to other one-layer compounds such as Tl-2201 or Hg-1201. This low  $T_c$  could be associated with intrinsic defects which are detected by NMR measurements [32], and might also influence thermopower data [22].

Let us point out now that the interest of eq. (3) is that it allows to eliminate the actual scattering rate. It is then insensitive to the nature of the point defects. If the relevant carrier

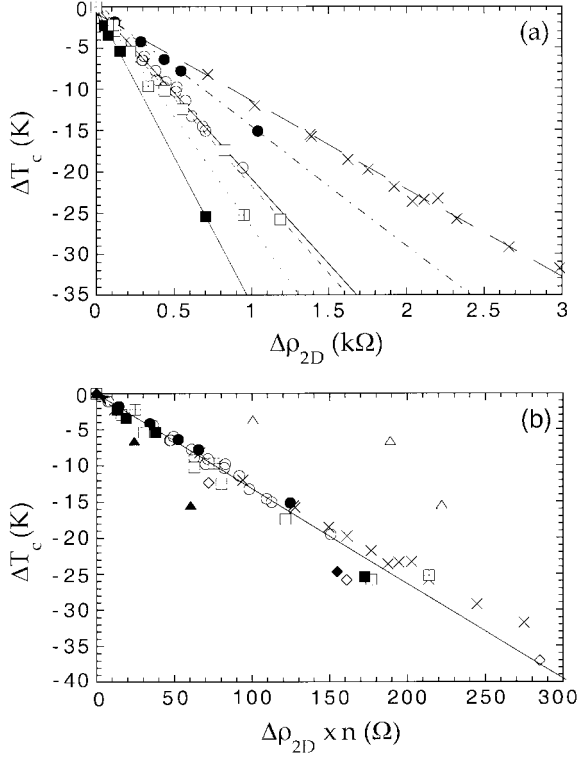


Fig. 3 – The decrease in the critical temperature  $\Delta T_c$  induced by irradiation defects is plotted as a function of: (a) the increase in 2D resistance  $\Delta\rho_{2D}$  (measured at 100 K) and (b) the quantity  $\Delta\rho_{2D} \times n$  for the different samples studied ( $\circ$  YBCO<sub>7</sub>,  $\bullet$  YBCO<sub>6.8</sub>,  $\times$  YBCO<sub>6.6</sub>,  $\square$  optimally doped Tl-2201,  $\boxplus$  and  $\blacksquare$  overdoped Tl-2201 with initial  $T_c$  of 54 and 31 K). In panel (b) the empty and closed diamonds are the corresponding data for Zn-substituted YBCO<sub>7- $\delta$</sub>  crystals with  $\delta = 0.07$  [30] and 0.37 [6]. The empty and closed triangles are for Zn-substituted La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> with  $x = 0.15$  and 0.2 [6].

concentration changed from  $x$  to  $1 - x$  at optimal doping in eq. (2) and eq. (3), this should lead to a breakdown of the scaling reported in fig. 3b. This is for us the *clear indication that  $x$  is the relevant parameter to describe transport properties in the cuprates*. The analysis of Fukuzumi *et al.* was done assuming that the scattering remains in the unitarity limit and attributed the change in residual resistivity with a change of the relevant carrier concentration. Our results of fig. 3b do rather suggest that the carrier concentration is always given by  $x$  while the scattering rate (that is  $\sin^2 \delta$ ) is responsible for the variation of residual resistivity. This is quite compatible with our analysis of  $\Delta\rho_{2D}$  shown in fig. 2. Indeed the decrease of  $\Delta\rho_{2D}/n_d$  with increasing doping can be associated to a decrease of  $\delta$  from the unitarity limit  $\delta = \pi/2$ . On the overdoped side we have no direct estimate of  $\sin^2 \delta$ . Studies of impurities substitution in different overdoped cuprates have shown that  $\Delta T_c/n_d$  decreases up to  $n \sim 0, 2$  and then remains constant [7, 33]. If such a behaviour applies for the Tl-2201 system, the correlation reported in fig. 3 suggests that the phase shift goes on decreasing in the overdoped region. Taking similar values of  $\sin^2 \delta$  for optimally doped YBCO and Tl-2201 leads to a crude estimate  $\sin^2 \delta \sim 0.4$  for  $n \sim 0.25$  which suggests that strong defect scattering persists on the overdoped side. In any case the theoretical analysis of the scattering, and even the applicability of eq. (2) require a good microscopic description of the defects and of the carriers. Zn or Ni

defects might lead to different quantitative variations of the scattering rate with hole doping.

In summary, the analysis of resistivity data in electron-irradiated YBCO and the universal scaling found between  $\Delta T_c$  and the pair-breaking parameter  $\Gamma_n$  for cuprate systems with high optimal  $T_c$  show unambiguously that the number of doped holes is the relevant parameter to describe transport properties in cuprates from the underdoped to the overdoped regime. Moreover, the results suggest that the decrease of the scattering rate with increasing hole doping is real and cannot be ascribed to a change of Fermi surface. More quantitative comparison of the scattering rates for irradiation defects and impurity substitutions depends on their microscopic nature. The use of microscopic probes to characterize the irradiation defects will help in such an analysis, and is left for future investigations.

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