

**Pair breaking by chain oxygen disorder in light-ion irradiated  $\text{YBa}_2\text{Cu}_3\text{O}_x$  thin films**D. Arias,<sup>1,\*</sup> Z. Sefrioui,<sup>1</sup> G. D. Loos,<sup>1</sup> F. Agullo-Rueda,<sup>2</sup> J. Garcia-Barriocanal,<sup>1</sup> C. Leon,<sup>1</sup> and J. Santamaria<sup>1</sup><sup>1</sup>*GPMC, Departamento de Fisica Aplicada III, Facultad de Fisica, UCM, 28040 Madrid, Spain*<sup>2</sup>*Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), 28049 Cantoblanco, Spain*

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We report on the effect of oxygen disorder in the CuO chains on the superconducting properties of oxygen depleted  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (YBCO). While moderate disorder, induced thermally, depresses the critical temperature as a result of a reduced carrier concentration, strong oxygen disorder and chain fragmentation induced by low energy (80 keV)  $\text{He}^+$  irradiation suppresses the critical temperature beyond the values expected from the reduction of the carrier density. This provides an experimental evidence of pair breaking by chain disorder and outlines the importance of chain states in the pairing mechanism in the YBCO family.

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The effect of disorder in the high  $T_c$  superconductivity has been a topic of longstanding interest. It is well established that the introduction of nonmagnetic impurities in the  $\text{CuO}_2$  planes of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (YBCO) modifies very effectively the superconducting properties. In particular Zn substitution by Cu atoms into the planes<sup>1-4</sup> or Cu displacements within the  $\text{CuO}_2$  planes caused by electron irradiation<sup>5,6</sup> act as nonmagnetic scatterers and depress  $T_c$ . In both scenarios the  $T_c$  depression has been interpreted as due to impurity scattering in a  $d$ -wave superconductor. On the other hand, the effect of scattering centers in the chains has been less explored. In YBCO four bands cross the Fermi level, two correspond to the planes and two to the chains.<sup>7</sup> Defects have been reported to cause mainly intraband scattering assuming absence of hybridization between chain and plane bands,<sup>8</sup> however provided some hybridization exists the situation may be different. CuO chains are unique to the YBCO family, and although in plane optical conductivity measurements suggest strong similarities with other cuprates, the results of various experiments have shown the presence of distinctive features consistent with a significant superfluid density located in the chains.<sup>9-13</sup> These results have produced some theoretical interpretations outlining the importance of chain-plane coupling in the superconductivity of YBCO. Proximity models consider pairing interaction being restricted to the planes but significant coupling to normal electrons in the chains is responsible for a condensate in the chains<sup>14</sup> through hybridization between chain and plane states.<sup>15</sup> Pair tunneling models consider interdependent plane and chain condensates coupled by Josephson pair tunneling processes.<sup>16</sup>

Chains are not continuous but broken into segments of finite length by the fraction of vacant oxygen sites. Oxygen disorder in the chains reduces the average chain length with a direct influence in the hole concentration. Shorter chains yield reduced carrier densities, while chain merging results in increased carrier concentrations. The  $T_c$  increase observed in room temperature annealed bulk samples has been interpreted in terms of an increase in the carrier density resulting from chain ordering.<sup>17,18</sup> Concerning cationic substitution experiments, small amounts of Ni substitution, up to 1% per formula unit, do not cause significant changes in  $T_c$  nor in the optical in-plane conductivity,<sup>19</sup> showing that superconductivity is less sensitive to defects in the chains than in the

planes. Co (Ref. 20) or Ni (Ref. 21) atoms substituted by chain Cu up to amounts of 10% depress  $T_c$  without significantly increasing the residual resistivity, suggesting that carrier concentration is reduced. Chain defects (oxygen disorder or substitution), beside causing a reduction in the hole density for moderate disorder, may play a more active role directly influencing the superconducting properties (as a result of band hybridization), although a higher degree of disorder may be necessary than in the case of plane defects. In fact it has been theoretically proposed recently<sup>15</sup> that, within the hybridization picture, chain disorder can be responsible for pair breaking effects. In this paper we examine the effect of chain oxygen disorder induced by light ion irradiation. At low energies and low doses light ions displace primarily oxygen atoms preferentially from the CuO chains, since this is the lightest and more loosely bound species of the structure and there is a nearly located vacant position in the basal plane along the  $a$  axis.<sup>22</sup> The advantage of light ion irradiation over other procedures (thermally induced disorder) to produce oxygen disorder is its capability of producing considerably larger amounts of disorder. Atomization of the chains produces a significant increase of the residual resistivity and depresses  $T_c$  beyond the values expected from the decrease in the carrier density. This constitutes a direct experimental evidence of the pair breaking effect of chain disorder and strongly supports the importance of coupling between plane and chain states for the mechanism of the superconductivity in the YBCO family.

Samples used were high quality YBCO samples epitaxially grown  $c$ -oriented on  $\text{SrTiO}_3$  by a high pressure (3.4 mbar) dc sputtering system in pure oxygen atmosphere. Film thickness was fixed at 500 Å for all samples. Samples were deoxygenated *in situ*, adjusting the oxygen content by following a stability line of the pressure-temperature phase diagram during sample cool down.<sup>23</sup>  $\text{He}^+$  irradiation was conducted at room temperature by using a commercial ion implanter for microelectronic applications. Beam currents were smaller than  $0.1 \mu\text{A cm}^{-2}$  to minimize heating effects. Samples were tilted  $7^\circ$  away from the beam direction to avoid channeling. Energy was 80 keV, and doses were varied between  $10^{14}$  and  $10^{15} \text{cm}^{-2}$ . The projected ion range calculated using the SRIM 96 software was larger than 3000 Å in all cases ensuring that  $\text{He}^+$  ions go through the film and

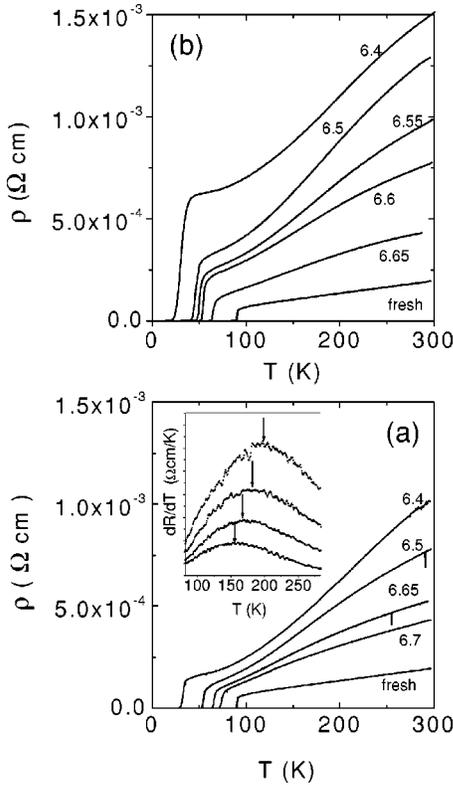


FIG. 1. Resistivity curves of oxygen depleted samples with an ordered (a) and a disordered (b) chain oxygen distribution. Oxygen contents are nominal. Note that disordered samples have a slightly smaller  $T_c$  that the corresponding ordered samples with the same nominal composition. Inset: first derivative of the normal state resistivity curves.  $T_0$  is determined at the maximum.

embed into the substrate. Resistivity was measured immediately after irradiation to minimize the influence of the defect annealing at room temperature. Raman spectra were taken with a Renishaw Ramascope microspectrometer and an  $\text{Ar}^+$  laser (wavelength 514.5 nm). Light power density on the sample surface was kept below  $500 \text{ W/cm}^2$  to avoid photo-induced changes in the spectra. Despite the relatively high power density, most of the light was absorbed in the substrate due to the small sample thickness. Experiments at different power densities and as a function of time showed spectra to be free of unwanted laser heating effects.

In the first step, oxygen ordering was controlled during the oxygenation sequence (*in situ*) after film growth. Pressure and temperature were simultaneously controlled to follow a stability line of the oxygen content phase diagram during sample cool down. Very ordered oxygen distributions were attained for low cooling speeds (1 K/min), which yielded resistance curves with small values of the residual resistivity [see Fig. 1(a)]. These samples will be termed *ordered* samples hereafter. However, higher cooling speeds (10 K/min), yielded samples with much higher residual resistivity values [see Fig. 1(b)], characteristic of a disordered oxygen distribution in the CuO chains (*disordered* samples hereafter). In fact disordered samples showed slightly smaller values of the critical temperature than the corresponding ordered samples with the same nominal oxygen content. Resis-

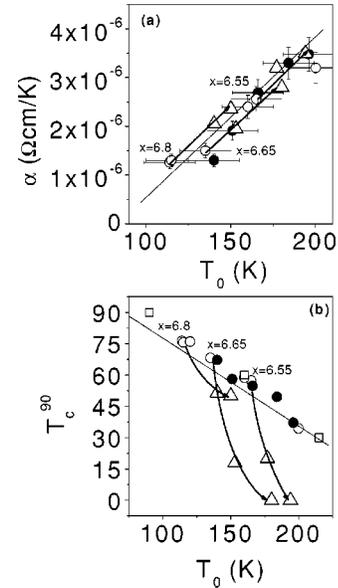


FIG. 2. (a) High-temperature slope  $\alpha$  of the resistance curves vs  $T_0$  for oxygen depleted ordered (open circles) and disordered (solid circles) samples. Irradiated samples are denoted with open triangles. Arrows connect the starting sample with the changes resulting from  $4 \times 10^{14}$  and  $6 \times 10^{14} \text{ cm}^{-2}$  irradiation experiments (triangles) for three different nominal oxygen contents. (b)  $T_c$  vs  $T_0$  for oxygen depleted ordered (open circles), disordered samples, (solid circles) and irradiated samples (open squares). Open squares show the effect of Co substitution into the chains from Ref. 20. Arrows connect the starting sample with the changes resulting of  $4 \times 10^{14}$  and  $6 \times 10^{14} \text{ cm}^{-2}$  irradiation experiments (triangles) for three different nominal oxygen contents.

tance curves of the oxygen depleted samples show the well known S-shape. The high-temperature slope,  $\alpha$ , is inversely proportional to the carrier concentration. The temperature  $T^*$  at which resistance curves depart from linearity at high temperatures have been related to the onset of in-plane antiferromagnetic correlations and is a precursor of the pseudogap.<sup>24</sup> This temperature approximately coincides with twice the temperature  $T_0$  at the inflexion point (maximum of the first derivative),<sup>25</sup> i.e.,  $T^* = 2T_0$ . It is worth noting the increase of  $T_0$  with oxygen depletion for ordered [see inset of Fig. 1(a)] and disordered samples (not shown).  $T_c$  has been determined from the onset (90% resistivity criterion) of the superconducting transition to make results independent of extrinsic transition broadening. We have found a linear correlation between  $\alpha$  and  $T_0$  and between  $T_c$  and  $T_0$  for ordered oxygen depleted samples (see open circles in Fig. 2). This correlation is determined by the carrier concentration. Interestingly disordered oxygen depleted samples follow exactly the same correlation (solid circles in Fig. 2). This shows that moderate thermally induced oxygen disorder does not depress the critical temperature for other reasons that a reduction of the carrier concentration as a result of chain fragmentation. We have also included in this figure data of Co substituted YBCO taken from Ref. 20, which also follow the same trend. This shows that the substitution of magnetic impurities in the chains up to 9% reduces the carrier concentration in accordance with the conclusions of the same

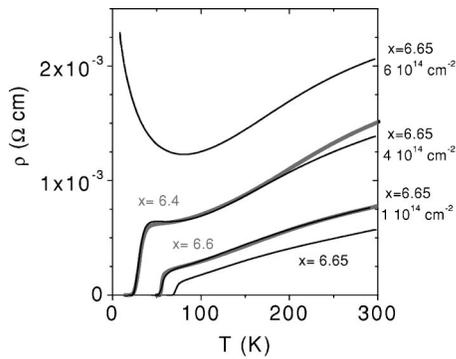


FIG. 3. Effect of  $\text{He}^+$  irradiation on an ordered sample with nominal oxygen content  $x=6.65$  (bottom curve) at 80 keV and doses of  $1 \times 10^{14}$ ,  $4 \times 10^{14}$ , and  $6 \times 10^{14} \text{ cm}^{-2}$  (Thin black lines from bottom to top). Thick gray lines correspond to disordered oxygen depleted samples with nominal oxygen contents  $x=6.6$  and  $x=6.4$  (from bottom to top).

reference. Therefore we have shown that *moderate* thermally induced disorder in the chains does reduce the carrier density and depresses  $T_c$  accordingly. In the following we examine how light ion irradiation induces *strong* oxygen disorder in the  $\text{CuO}$  chains.

Figure 3 shows the effect of irradiation on a sample of nominal oxygen content  $x=6.65$  (bottom curve of Fig. 3). Resistance curves with thin dark lines in the figure correspond to irradiation fluences of  $1 \times 10^{14}$ ,  $4 \times 10^{14}$ , and  $6 \times 10^{14} \text{ cm}^{-2}$  from bottom to top. The first observation is that the resistivity curves of irradiated samples are not parallel, indicating that the carrier density is being reduced upon irradiation. Accordingly, there is a clear shift of the inflexion point to higher temperatures. Interestingly, irradiation at small doses produces an effect which is strikingly similar to slight deoxygenation plus thermal disorder. Note that the resistance curve of a sample with oxygen content  $x=6.65$  irradiated at  $1 \times 10^{14} \text{ cm}^{-2}$  exactly coincides with that of a disordered deoxygenated sample with a slightly smaller oxygen content of  $x=6.6$  (with thick gray line in the figure). *This is a strong indication that the effect of light ion irradiation is located primarily in the  $\text{CuO}$  chains.* Furthermore, the threshold dose to appreciably depress  $T_c$  decreases when oxygen content is decreased, again pointing to disorder being located in the chains. Irradiation at larger doses of  $4 \times 10^{14} \text{ cm}^{-2}$  also produces a sample which is similar to a disordered deoxygenated sample with a lower nominal oxygen content of 6.4 (also with thick gray line in Fig. 3); however significant differences appear in the high-temperature portion of the resistivity curve. The question arises if irradiation is reducing the oxygen content. This can be definitely discarded from Raman-scattering experiments. Figure 4 shows Raman spectra of fresh and irradiated samples. It is well known that the line at  $500 \text{ cm}^{-1}$  associated to stretching mode of the apical oxygen is very sensitive to the oxygen content, shifting to lower frequencies when the oxygen content is reduced.<sup>26</sup> While a clear shift can be observed for the oxygen depleted sample, it stays at the same position for fresh and irradiated samples even at a much higher dose ( $1 \times 10^{15} \text{ cm}^{-2}$ ) than those used in this work. The slight broad-

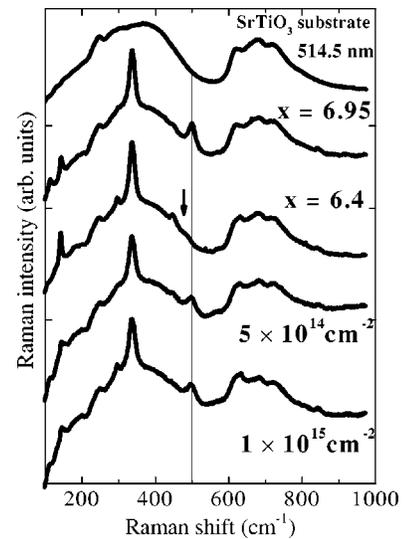


FIG. 4. Raman spectra of (from top to bottom)  $\text{SrTiO}_3$  substrate, a fresh fully oxygenated sample, an oxygen depleted sample with  $x=6.4$ , and fully oxygenated samples irradiated at  $5 \times 10^{14} \text{ cm}^{-2}$  and  $1 \times 10^{15} \text{ cm}^{-2}$ . The vertical line marks the position of the  $500 \text{ cm}^{-1}$  line.

ening of the  $500 \text{ cm}^{-1}$  line in the irradiated samples may arise from induced chain oxygen disorder. This excludes that irradiation is reducing the oxygen content and supports the picture that carrier concentration is being reduced as a result of oxygen disorder in the chains. Moreover, as far as the relation between  $\alpha$  and  $T_0$  is concerned [see Fig. 2(a)], irradiated samples follow the same behavior as oxygen depleted (ordered and disordered) samples. The effect of irradiation for given oxygen contents [indicated in Fig. 2(a)] produces a displacement along the correlation line. Arrows in Fig. 2(a) connect the starting sample with the changes resulting from  $4 \times 10^{14}$  and  $6 \times 10^{14} \text{ cm}^{-2}$  irradiation experiments (triangles) for three different nominal oxygen contents. This indicates that the carrier concentration is being reduced upon irradiation. However there is a strong disruption in the correlation between  $T_0$  and  $T_c$  for irradiated samples. Curved lines in Fig. 2(b) connect the starting sample with the changes resulting of  $4 \times 10^{14}$  and  $6 \times 10^{14} \text{ cm}^{-2}$  irradiation experiments (triangles) for three different nominal oxygen contents. We have found that irradiation produces samples with much smaller  $T_c$  than that corresponding to the  $T_0$  values (carrier concentration). *This is a strong indication of pair breaking by the strong oxygen disorder introduced by light ion irradiation.* Note that this effect is more pronounced when oxygen content is reduced [see Fig. 2(b)] indicating that disorder is occurring in the chains. It is well known that ion irradiation generates pinning centers and one would expect the critical current to increase accordingly. However we find a reduction of the critical current density down to  $5 \times 10^5 \text{ A/cm}^2$  for an irradiation dose of  $4 \times 10^{14} \text{ cm}^{-2}$ , below the values in excess of  $10^6 \text{ A/cm}^2$  found in fresh samples of this thickness (50 nm). In addition, we have previously reported<sup>27</sup> a decrease in the activation energy for vortex motion in the liquid state by almost one order of magnitude in 1 T field, upon the same irradiation fluence.

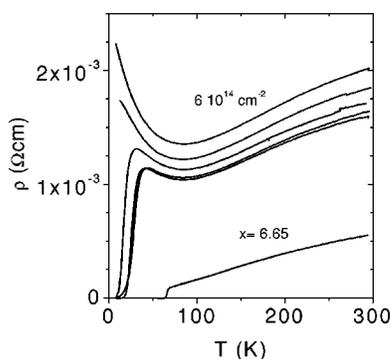


FIG. 5. Time evolution of the resistance curves of a sample with an oxygen content of  $x=6.65$  (bottom curve) after irradiation at a fluence of  $6 \times 10^{14} \text{ cm}^{-2}$  (upper curve). Remaining curves from top to bottom show the effect of room temperature annealing in two week steps.

These results are consistent with pair breaking effects in light ion irradiated samples. Further support for pair breaking originating in chain oxygen disorder can be drawn from the time evolution of irradiated samples. Figure 5 shows the time evolution of the resistance curves of a sample with an oxygen content of  $x=6.65$  (bottom curve) after irradiation at a fluence of  $6 \times 10^{14} \text{ cm}^{-2}$ . The upper curve has been measured immediately after irradiation, remaining curves from top to bottom show the effect of room-temperature annealing in 2 week steps. It is important to note that resistance curves are nearly parallel to each other upon time recovery, indicating that  $T_0$  and  $\alpha$  are not changing substantially, and thus that the carrier concentration is not increasing significantly. On the other hand,  $T_c$  increases sharply and insulating (irradiated) samples become superconducting. The increase of the critical temperature saturates after a 2 month period. Since irradiated fully oxygenated ( $x=6.95$ ) samples did not show  $T_c$  recovery we can exclude this effect arising from disorder induced in the CuO planes, whose structure is the same for oxygenated and deoxygenated samples. This, on the contrary,

indicates that irradiation is causing a strong atomization of the chains, most likely, via the occupancy of the vacant position along the  $a$  axis. It is well established that only chains longer than four or five Cu-O elements are effective in supplying holes to the planes while shorter chains keep holes localized. Therefore, if the chain length of the irradiated deoxygenated samples is small enough, significant reordering can occur (with room-temperature annealing) without substantially increasing the average chain length, thus keeping carrier concentration unaltered but increasing the critical temperature.

The suppression of the critical temperature by disorder in the chains outlines the importance of the chains in the superconductivity of the YBCO family in agreement with recent theoretical studies.<sup>14–16</sup> The observed pair breaking effect might be an expression of the importance of the coupling of normal electrons of the CuO chains into the superconducting state.<sup>14</sup> Within this frame, chain disorder might increase the scattering rate through a reduction of the density of states at the Fermi level of hybridized plane-chain bands crossing the Fermi level as proposed recently.<sup>15</sup> Our results would be also consistent with recently proposed pair tunneling models,<sup>16</sup> which consider the importance of the chains condensate in the superconductivity of YBCO, and where oxygen disorder in the chains would certainly depress (if not suppress) chain superconductivity.

In summary, we have shown that light ion irradiation induces strong oxygen disorder in the CuO chains. A substantial depression of the critical temperature has been found which cannot be explained as resulting from a reduction in the carrier density. This is a strong indication of pair breaking by chain oxygen disorder. These results outline the importance of chains in the superconductivity of YBCO family in agreement with recent theoretical studies.

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