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Study of α -Particle Injection Effect on Superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Type

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ABSTRACT

The exposure of nuclear materials, surrounding the nuclear reactor core, to a high intensity neutron flux leads to effects such as swelling and embrittlement. The embrittlement occurs due to the (n, α) reactions combined with high temperature, that lead to helium gas formation and migration to certain regions of lower energy inside the bulk material (crystal lattices). Other similar effect also occurs, and in the specific case of superconductors, the formation of voids, the electronic distribution rearrangement and phase transformation are critical.

Various techniques exist to qualify and quantify this radiation damage effect. The methods are based on destructive methods such as TEM(1), SEM(2), CREEP(3) and others. This work is intended to be a starting point to the application of nondestructive techniques to study radiation damage in superconductors in nuclear application, and a creation of a nuclear data bank for different type of materials. The first scheduled nondestructive technique to be applied is positron annihilation, more specifically positron lifetime measurements.

This work is based on the implementation of a technique, widely used to simulate neutron radiation effects on materials. This simulation is obtained by the injection of charged particles (ions), from an accelerator, and a beam line equipped with some special experimental arrangement to get a homogeneous distribution of injected particles in the sample.

After the ion injection, or neutron damage simulation, the nuclear data are collected by different experimental setups: conventional gamma spectrometer for activation analysis, X-ray diffraction for phase change analysis, and "zero detector" for magnetic permeability measurements.

The behavior of the magnetic permeability with temperature of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconducting ceramics was studied as a function of the amount of He^{++} implanted into the sample. With fluence varying from 1.2 to $6.0 \times 10^6 \text{ He}^{++} \text{ cm}^{-2}$, the results show that the superconducting temperature $T_c(\text{onset})$ stays nearly constant up to $2.5 \times 10^6 \text{ He}^{++} \text{ cm}^{-2}$, decreasing afterwards for higher fluencies. An almost linear decrease is observed for $T_c(\text{offset})$. The magnetic permeability curves show structures whose shapes and relative positions to $T_c(\text{onset})$ change with the fluence. Although this might indicate a mixture of phases coexisting inside the sample, X-ray diffraction shows no clear evidence for such a pattern. A large percentage of the damage recovers after annealing the He -implanted sample at 673 K.

INTRODUCTION

In 1986 Berdnorz and Müller [1] reported superconductivity in LaBaCuO compounds above 30 K. In 1987 Wu et al. [2] raised this value to about 93 K in compounds of YBaCuO . These discoveries prompted a major research effort attempting to find other compounds with even higher temperatures. Such a possibility attracted the attention of different research areas such as nuclear science [3], electronics [4], and aero-

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space [5]. In nuclear science, particularly in fission reactor technology, the discovery and the development of new superconductors are of the utmost importance. Understanding their properties is therefore very important to explain how these properties might change under the influence of present agents. Radiation is one of these agents and it may drastically change some superconductor ceramic properties, such as the critical temperature T_c . It may also change the compound capacity for conducting high density currents and it may affect its stability to high magnetic fields. Therefore, to use such materials in nuclear applications, it is urgent to analyze their behavior under high irradiation doses. This task has been accomplished during the last few years by irradiating superconducting samples with neutrons [7-15], light charged particles [5, 6, 16-22], ion implantation or soft ions [15, 21, 23-28], and energetic heavy ions [22, 29-37].

Overall, the fore-mentioned works report a decrease in the critical temperature T_c and a broadening of the superconductivity transition ΔT_c , although some differences are noted which can be attributed to different qualities of the intergrain material. However, a substantial increase in T_c was observed by Atobe et al. [11], by irradiating a sample of $YBa_2Cu_3O_{7-x}$ simultaneously with thermal neutrons ($7.0 \times 10^{17} \text{ n cm}^{-2}$), fast neutrons ($5.9 \times 10^{17} \text{ n cm}^{-2}$), and γ -rays ($1.3 \times 10^9 \text{ R}$). The improvement of T_c was also observed by Groult et al. [29], by irradiating samples of La_2CuO_4 with 2.9 GeV-Kr with fluence up to $4 \times 10^{12} \text{ ion cm}^{-2}$. Moreover, structures have been observed in the superconducting transition curves of both irradiated and non irradiated samples [5, 8, 11, 19, 21, 25, 28]. This latter result is difficult to understand unless a model is assumed where the sample consists of regions with slightly different oxygen composition, but for which there is no structural phase change [5, 25]. This could explain the large recovery in the superconducting characteristics observed by annealing the damaged samples in O_2 atmosphere [15, 16, 19, 21, 28].

This work presents the results that we have obtained by irradiating $YBa_2Cu_3O_{7-x}$ samples with alpha particles of 28 MeV maximum energy. The purpose of this work was twofold: first, to study the superconducting behavior of samples homogeneously implanted with a high concentration of He, which simulates the effect caused by He diffusion that appears in nuclear reactors because of (n, α) reactions [38]. Secondly, to try to shed some

light on the origin of the structures previously observed in the magnetization curves of irradiated and non irradiated samples. An advantage of this simulating technique is a reduction of the time scale, i.e., in a few hours of irradiation is possible to implant He with concentration that would take years in nuclear power reactors [39].

2. MATERIALS AND METHODS

2.1. SAMPLE PREPARATION AND CHARACTERIZATION

The samples were prepared from the compounds Y_2O_3 , $Ba(NO_3)_2$ and CuO , following the conventional procedure [40]. A mixture of Y, Ba and Cu in 1: 2: 3 proportion was heated in a crucible porcelain with 5.6 ml s^{-1} oxygen flux at 1223 K for 20 hours. After pressing, we obtained 350 μm thin pellets whose density was about 5.89 g cm^{-3} .

The ignition, made under the same conditions that were used for the preparation, lasted for 18 hours. At that point the temperature was slowly reduced (1.7 K min^{-1}) until it went down to 673 K. The samples were kept at this temperature for two hours, before being brought to room temperature. Then, one sample, referred to as 1S, was withdrawn from the pellet. This sample had its mass weighed (5.867 mg) and a size compatible with the limitations imposed by the size of the probe used to measure the magnetic permeability, namely $2 \times 1 \times 1 \text{ mm}$ [41].

The remaining pellet was ground again in an agate mortar, pressed and ignited under the same conditions as before, for another 18 hours. At that point, another sample (1DS) was withdrawn with a mass of 8.260 mg.

2.2. IRRADIATION PROCEDURE

The samples were fixed to a water-cooled, copper target holder [42], which is pictured in Fig. 1. Metallic indium was used to fix the samples, since it increases heat dissipation and it prevents the temperature during the irradiation procedure from reaching its 429 K fusion temperature. In earlier work [20], we showed that no measurable amount of Indium adsorption and/or absorption was observed in similar samples.

The irradiations were carried out at the IEN/CNEN CV-28 Cyclotron, at room temperature. Beams of 28 MeV α -particles were periodically degraded by a rotating disc [43], in which several aluminum sheets of various thicknesses were mounted. This device, which is shown in Fig. 1, allows to implant particles uniformly throughout the irradiated volume of the sample. The 28 MeV α -particle range, as calculated by the RANGETAB code [44] for these ceramic materials, is 183 μm thin. In order to have a uniform He^{++} implantation throughout its bulk volume, the 350 μm thick samples were irradiated in both faces.

The beam current was kept constant at nearly 500 μA . This value corresponds to a flux of $1.64 \times 10^{12} \alpha \text{ cm}^{-2} \text{ s}^{-1}$. Charge integration in the target was controlled in all irradiations so that the 1S and the 1DS samples got cumulative fluence corresponding to 1.2, 2.4, 3.6, 4.8, and $6.0 \times 10^{16} \alpha \text{ cm}^{-2}$. After a time delay of 24 to 48 hours from the end of each irradiation, the samples had their mass weighed, to control any measurable amount of material loss, and had their magnetic permeability measured as a function of temperature.

3. RESULTS AND DISCUSSION

The measurements of the magnetic permeability as a function of temperature were carried out using a conventional zero detector (lock-in amplifier 124 PAR), in the temperature range between 66 K and 94 K [41], with the sample immerse in a nitrogen dewar.

Prior to any irradiation, both samples had their magnetic permeability measured as a function of the temperature. We obtained identical results for $T_c(\text{offset})$ and $\Delta T_c(10-90\%)$, which ensures the standardization of the samples (see Figs. 2 and 3).

As the amount of fluence increases, we can observe that $T_c(\text{onset})$ stays nearly the same for sample 1S, while varying by a few K in sample 1DS. However, for fluencies exceeding $2.4 \times 10^{16} \alpha \text{ cm}^{-2}$ a large downward shift is observed in $T_c(\text{offset})$ for both samples, but now it stays almost the same in 1DS, while varying a little in 1S. This pattern is better observed in Figs. 4 and 5, which shows extracted values of $T_c(\text{onset})$ as a function of the irradiation dose received by each sample (see below).

A striking feature emerges from Figs. 2 and 3: the presence of structures ("bumps") in the magnetic permeability curves of the irradiated samples.

Beginning with Fig. 2b, which corresponds to a fluence of $1.2 \times 10^{16} \alpha \text{ cm}^{-2}$, the presence of a "bump" located close to 90 K is easily observed. This sample, under twice as much fluence (Fig. 2c) shows the appearance of two others structures, located close to 88 and 85 K, respectively. After successive irradiations, with constant increments of fluence (see Figs. 2d and 2e), we notice an evolution of the "bumps" downwards to lower temperatures, and again reaching a smooth behavior at the highest fluence (Fig. 2f).

Figure 3 shows the results obtained with the sample doubly sintered, 1DS. Although presenting a general pattern similar to the one observed in sample 1S, we may notice some difference, as for example, the nonexistence of a "bump" close to 85 K, for $F = 2.4 \times 10^{16} \alpha \text{ cm}^{-2}$ (Fig. 3c), which was observed in sample 1S (Fig. 2c). Yet, the two subsequent irradiations at 3.6 and $4.8 \times 10^{16} \alpha \text{ cm}^{-2}$ (Figs. 3d and 3e) give values of $T_c(\text{onset})$ roughly equal to the one for $F = 6.0 \times 10^{16} \alpha \text{ cm}^{-2}$ (Fig. 3f).

In an attempt to extract some quantitative relationship between these results, we have plotted the numerical values obtained for $T_c(\text{onset})$, $T(\text{offset})$, $T(\text{bump \#1})$, and $T(\text{bump \#2})$ as a function of the fluence received by the samples 1S (Fig. 4) and 1DS (Fig. 5), respectively. From these figures, it can be observed that: (1) the temperature $T_c(\text{onset})$ remains nearly constant for fluencies up to $2.4 \times 10^{16} \alpha \text{ cm}^{-2}$, decreasing afterwards by 5 or 6 K for higher fluencies the temperature $T(\text{bump \#1})$ presents linear behavior (with a negative slope) for sample 1S; however, such a pattern is less clear in sample 1DS; (3) the temperature $T(\text{offset})$ shows an almost linear decrease in both samples, and might present a plateau for fluence values corresponding to the shift observed in $T_c(\text{onset})$ (Figs. 4 and 5). These conclusions suggest that the dependence of $T_c(\text{onset})$ on the fluence appears to be due to a definite quantity of implanted ions. Therefore, it seems that a given He-concentration threshold is needed in order to lead to a significant change on $T_c(\text{onset})$. This hypothesis might be justified on the grounds that each "bump" indicates the beginning of a different domain of oxygen concentration, as a result of the amount of implanted He^{++} . Therefore, when a definite quantity of superconducting

material undergoes such a transformation, a definite variation in $T_c(\text{onset})$ occurs, without necessarily provoking a structural phase transformation within the sample. Further, it explains results in X-ray diffraction that show that the lattice parameters are not altered much by irradiation, in agreement with the results we have found in standard X-ray diffraction performed on sample 1S.

Other authors [5, 8, 19] have also observed a "bump-like" structure in measurements of resistivity as a function of temperature, in YBaCuO, but the presence of a different phase has also been eliminated by X-ray diffraction experiments. Nevertheless, according to Maish et al. [5], a complete characterization needs the determination of the phase and the identity of the ions displaced by the irradiation, including techniques such as MET [45], enhanced X-ray diffraction [46, 47], positron annihilation (PAT) [48], and Rutherford Backscattering (RBS) [49].

Although these samples have an overall similarity, generally speaking, a careful analysis of the results presented in Figs. 4 and 5 show that they do not behave exactly in the same way. These differences could be, for instance, related to the nonhomogeneous ion distribution of the beam. As a result, the actual values of the fluence could differ from the nominal values. In addition, these differences are also related to the preparation of the samples, since sample 1DS underwent a different preparation than sample 1S (see 2.1 above).

In order to evaluate the similarities, the values of $\Delta T_c(10 - 90\%)$ for the samples' 1S and 1DS as a function of fluence F they've been plotted in Fig. 6. We notice minima at $F = 0$ and at $F = 3.6 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$ and a maximum at $F = 2.4 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$. For the maximum peak at $F = 2.4 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$, it is reasonable to suppose that the "bumps" are at the end of their "evolution" (see Figs. 2c and 3c). On the other hand, the minimum at $F = 3.6 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$ can be explained by the downward shift in $T_c(\text{onset})$ observed at this fluence (see Figs. 3d and 4d).

After all irradiations, sample 1S underwent a thermal treatment at 673 K, in 1.5 atm O_2 flux during 2.5 hours. The results obtained for the magnetic permeability after this treatment can be seen in Fig. 2g. A clear tendency to return to the initial state (prior to the irradiation procedure) can be observed. This result is

highlighted by plotting the values of $T_c(\text{onset})$, $T(\text{offset})$, $T(\text{bump\#1})$ after annealing (empty symbol in Fig. 4), and $\Delta T_c(K)$ (empty square in Fig. 6) as a function of the fluence received by each sample.

4. CONCLUSIONS

The effects of He^{++} implantation in samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconducting ceramics have been studied. The results obtained show that the critical temperature T_c presents a two-regime behavior as a function of the dose: a fluence-independent pattern, for fluencies below $2.5 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$, and a shift of about 5 K to low temperatures at higher fluencies. Our results are not in agreement with the shift to below 4.2 K observed by Antonenko et al. [18] for fluencies greater than $2 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$. However, it is in agreement with most of the results obtained with neutrons, charged particles or heavy ions irradiations in superconducting samples.

The existence of previously observed structures [5, 8, 11, 19, 21, 25, 28] appears to be confirmed by our work. Although this might indicate a mixture of phases coexisting inside the bulk of the sample, X-ray diffraction shows no evidence for such a pattern. A reasonable explanation for the origin of such structures supposes different domains of oxygen concentration within the sample, whose boundaries' scale with a definite amount of implanted He^{++} concentration. Nevertheless, further characterization needs to be done, in order to determine the validity of such a hypothesis. We leave this characterization (MET, PAT, RBS, and enhanced X-ray diffraction) as future work. Finally, a large recovery of the superconductor properties is obtained by annealing the damaged sample in an O_2 atmosphere. This recovers indicate that nuclear reactions occurring within the irradiated sample [20] are not the leading factor responsible for the degradation of the superconducting properties of the irradiated sample. As stated above, further characterization has to be done in order to find reasonable explanations of the effects observed in this work.

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REFERENCES

- [1] J.C. Bednorz and K.A. Muller, *Z. Phys.* B64 (1986) 189.
- [2] M.K. Wu et al, *Phys. Rev. Lett.* 58 (1987) 908.
- [3] R.R. Hasiguti, *Trans. Jap. Inst. of Metals* 22 (1981) 831.
- [4] D.R. Clark, *Int. J. Mod. Phys.* B1 (1987) 169.
- [5] W.G. Maish et al, *IEEE Transaction on Nuclear Science*, 34 (1987) 1782.
- [6] D.B. Chrisey et al, *App. Phys. Lett.* 53 (1988) 1001.
- [7] H. Kpfer et al, *Z. Phys.* B69 (1987) 167.
- [8] A. Umezawa et al, *Phys. Rev.* B36 (1987) 7151.
- [9] J.R. Cost, J.O. Willis, J.D. Thompson, and D.E. Peterson, *Phys. Rev.* B37 (1988) 1563.
- [10] H. Yoshida, and K. Atobe, *Physica* C153-155 (1988) 337.
- [11] K. Atobe and H. Yoshida, *Phys. Rev.* B36 (1987) 7194.
- [12] B.A. Aleksashin et al, *Physica* C153-155 (1988) 339.
- [13] P. Mller et al, *Solid State Commun.* 65 (1988) 223.
- [14] P. Przyslupski et al, *Physica* C153-155 (1988) 345.
- [15] K.V. Rao et al, *Physica* C153-155 (1988) 347.
- [16] A. Hofmann et al, *Physica* C153-155 (1988) 341.
- [17] F. Rullier-Albenque et al, *Solid State Commun.* 66 (1988) 417.
- [18] S.V. Antonenko et al, *Physica* C153-155 (1988) 336.
- [19] G.C. Xiong, H.C. Li, G. Linker, and O. Meyer, *Phys. Rev.* B38 (1988) 240.
- [20] J. Barreto et al, *J. Matt. Sci. Lett.* 8 (1989) 689.
- [21] O. Meyer et al, *Nucl. Instr. and Meth.* B39 (1989) 628.
- [22] B. Hensel et al, *Phys. Rev.* B42 (1990) 4135.
- [23] G.J. Clark, A.D. Marwick, R.H. Koch, and R.B. Laibowitz, *App. Phys. Lett.* 51 (1987) 139.
- [24] G.J. Clark et al, *Nucl. Instr. and Meth.* B32 (1988) 405.
- [25] A.E. White et al, *Phys. Rev.* B37 (1988) 3755.
- [26] J.M. Valles Jr., et al, *Phys. Rev.* B39 (1989) 11599.
- [27] A.D. Marwick et al, *Phys. Rev.* B39 (1989) 9061.
- [28] S. Matsui et al, *Nucl. Instr. and Meth.* B39 (1989) 635.
- [29] D. Groult et al, *Europhys. Lett.* 6 (1988) 151.
- [30] D. Bourgault et al, *Phys. Rev.* B39 (1989) 6549.
- [31] L. Civale et al, *Phys. Rev. Lett.* 67 (1991) 648.
- [32] M. Konczykowski et al, *Phys. Rev.* B44 (1991) 7167.
- [33] W. Gerhuser et al, *Phys. Rev. Lett.* 68 (1992) 879.
- [34] V. Hardy et al, *Physica* C191 (1992) 85.
- [35] V. Hardy et al, *Rad. Effec. Defec. Sol.* 126 (1993) 137.
- [36] M. Kraus et al, *Rad. Effec. Defect. Sol.* 126 (1993) 147.
- [37] A. Legris et al, *Rad. Effec. Defec. Sol.* 126 (1993) 155.
- [38] H. Schroeder and P. Batfalsky, *J. Nuc. Mater.* 117 (1983) 287.

- [39] H. Ullmaier, *Trans. Inst. Metals* 34 (1981) 324.
- [40] E. Mattievich et al, *Hyp. Interact.* 42 (1988) 1254.
- [41] R.F.R. Pereira, E. Meyer, and M. F. Silveira, *Rev. Sci. Instrum.* 54 (1983) 899.
- [42] A.S. Abreu, Z.C. Gonçalves, Z.C. Martha, Instituto de Engenharia Nuclear (IEN-Pio) *Annual Tec. Rep.* 4.14 (1984) 64.
- [43] A.S. Abreu,, Instituto de Engenharia Nuclear (IEN) *Annual Tec. Rep.* 4.6.2 (1984) 91.
- [44] D.J. Schlyer, "Program SPARK, (Rangetab)," Chem. Dept., BNL, Upton NY, Private Communication (1985).
- [45] A. Khurana, *Phys. Today*, April 1987, 17.
- [46] R.J. Cava et al, *Phys. Rev. Lett.* 58 (1987) 1676.
- [47] S.J. Hagen et al, *Phys. Rev.* B37 (1988) 7929.
- [48] M.K. Teng, *Phys. Lett.* A124, 6 (1987) 363.
- [49] J.C. Barbour, B.L. Doyle, and S.M. Myers, *Phys. Rev.* B38 (1988) 7005.

Fig. 1. Diagram of He implantation chamber used in this experiments, provided by KFA-Jülich, Germany.

Fig. 2. Magnetic permeability as a function of the temperature, showing curves obtained with sample 1S: (a) for non-irradiated, (b) irradiated with $1.2 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$, (c) irradiated with $2.4 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$, (d) irradiated with $3.6 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$, (e) irradiated with $4.8 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$, and (f) irradiated with $6.0 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$. The result obtained by annealing the sample 1S after irradiated with $6.0 \times 10^{16} \text{ } \alpha \text{ cm}^{-2}$ is shown in (g).

Fig. 3. Magnetic permeability as a function of the temperature, showing curves obtained with sample IDS: (a) for non-irradiated, (b) irradiated with 1.2×10^{16} α cm⁻², (c) irradiated with 2.4×10^{16} α cm⁻², (d) irradiated with 3.6×10^{16} α cm⁻², (e) irradiated with 4.8×10^{16} α cm⁻², and (f) irradiated with 6.0×10^{16} α cm⁻².

Fig. 5. Behavior of $T_c(onset)$ (open triangles), $T(bump1)$ (open circles), and $T(offset)$ (open squares) for sample IDS.

Fig. 4. Behavior of $T_c(onset)$ (open triangles), $T(bump1)$ (open circles), $T(bump2)$ (open diamond), and $T(offset)$ (open squares) for sample IS. The results obtained after annealing (see text) are shown by full symbols.

Fig. 6. Comparing ΔT_c for samples 1S (open circles) and IDS (open squares) at different irradiation doses. The result obtained after annealing sample 1S (see text) is also shown (full square).