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POSITRON ANNIHILATION AT DEFECTS IN SINTERED HIGH Tc PEROVSKITE
SUPERCONDUCTORS

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ABSTRACT

We report positron lifetime measurements in sintered superconducting $Ba_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$ oxides. It is shown that the thermal behaviour of the positron lifetime spectra strongly depends on the preparation of the ceramics. A lifetime of 196 ± 3 ps is attributed to oxygen deficient regions. Two lifetimes of 251 ± 7 ps and 225 ± 5 ps are attributed to a cation vacancy presenting a temperature dependent atomic arrangement. The lifetime transition ($251 \rightarrow 225$ ps) occurs during decreases in temperature across the resistivity superconducting transition. This lifetime change indicates that the volume of the cation vacancy decreases in the superconducting state.

1. INTRODUCTION

Positrons are well known to be a useful and unique probe of atomic vacancy type defects in metals, semiconductors and insulators [1-4].

Because the nature of the native defects in the sintered high Tc ceramics is still an open question, it is useful to investigate positron annihilation in such compounds. It is particularly important to determine how the preparation of the ceramics may control native vacancy defects. Recently, several authors have reported positron annihilation measurements in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics [5-14]. The temperature dependence of the positron annihilation parameters varies widely from an author to another. Positron lifetimes have not yet been attributed to well defined positron annihilation states, although Jean et al. [6] have proposed that the lifetime of 220 ps may be due to positron trapping in oxygen vacancies.

In this paper, we report positron lifetime measurements in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics obtained from various laboratories and prepared under different conditions. The aim of this work is to find the positron lifetimes common to the various ceramics. It is shown that various annihilation states may exist in sintered high Tc superconductive ceramics. We find that at least three lifetime values are reproducible in the various samples and arise from three

different positron annihilation states. We propose that two types of defects are responsible for these lifetimes.

2. EXPERIMENTS

The superconducting ceramics were provided by different laboratories belonging respectively to the Nuclear Center of Saclay (SAC), Thomson (THO), the University of Orsay (ORS) and the Helsinki University of Technology (HEL). The THO, ORS and HEL specimens were $YBa_2Cu_3O_{7-x}$ ($x=0.10$ - 0.20) ceramics. The SAC specimen was a $GdBa_2Cu_3O_{7-x}$ ceramic. All the ceramics showed a resistivity superconducting transition with a width of a few degrees centered at 91 ± 2 K depending on the specimens. The HEL specimens were sintered at 950°C for 30 h in oxygen and then successively annealed at 700°C for 6 h, at 550°C for 12 h, at 430°C for 12 h in oxygen before cooling at room temperature. The THO specimens were sintered at 950°C for 6 h in oxygen, then annealed at 600°C for 9 h and finally slowly cooled to room temperature. The SAC were sintered in air at 950°C for 12 hours and the ORS specimens were sintered in oxygen at 950°C .

The lifetime spectra were recorded with a fast-fast lifetime spectrometer with a time resolution of 275 ps full width at half maximum (FWHM). A second lifetime spectrometer with a resolution of 220 ps was also used for some lifetime spectra measurements. About

10^6 counts were accumulated for each spectrum. After source component and background subtraction, the lifetime spectra were analyzed with one or two exponential decay components. Annihilations in the source were taken into account with a two component lifetime spectrum (233 ps, 4%) and (505 ps, 2%). The same source was used for all the measurements made in situ in a cryostat between 15 K-300 K. A second source (233 ps, 2.4%) and (505 ps, 1.2%) was also used to duplicate room temperature measurements.

3. RESULTS

3.1 Lifetime spectra at room temperature

The lifetime spectra at room temperature given in Table I are reproducibly measured in samples having undergone the same preparation. Table I shows that the average positron lifetimes τ are very different in the three $YBa_2Cu_3O_{7-x}$ ceramics at room temperature. The HEL ceramic displays the shortest lifetime at 173 ps. The lifetime τ in the THO ceramic exceeds that of the HEL ceramic by about 50 ps, whereas the lifetime τ in the ORS ceramic exceeds that of the HEL ceramic by only 20 ps.

The $GdBa_2Cu_3O_{7-x}$ ceramic gives the same lifetime as the ORS $YBa_2Cu_3O_{7-x}$ ceramic. This result is interesting because both ceramics have undergone only one thermal annealing at 950°C and

therefore have undergone somewhat similar preparation.

As seen from Table I, the decomposition of the lifetime spectra is also dependent how and where the ceramics were prepared. Only one lifetime component is resolved in the spectra measured in the HEL, ORS $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ samples. Three lifetime components are found in the THO $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ samples. The long lifetime τ_3 of about 2000 ps in the THO $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic is obviously due to positronium formation but it has a rather low intensity (<1%) and so will be not further discussed. The average lifetime arising from the two shorter components τ_1 and τ_2 is 214 ps, higher than the single lifetimes of 173 ps, 189 ps and 198 ps respectively found in the other ceramics. The long lifetime τ_2 in the THO $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic is about 251 ± 7 ps and therefore much higher than the single lifetimes found in the other ceramics. The short lifetime τ_1 is about 165 ± 10 , lower than the single lifetimes found in the other ceramics.

3.2 Temperature effects

In Figure 1, the variation of the average lifetime with temperature is shown to depend on the origin of the ceramics. When the temperature decreases from 300 K to 77 K, the average lifetime varies in opposite ways in the THO and HEL $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ samples. The positron lifetime decreases in the THO sample while it increases in the HEL sample. The ORS $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and SAC $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ have a similar behaviour as a function of temperature: both show no

temperature variation in the positron lifetime . Again it is noted that the positron behaviour is similar in those samples which have undergone similar preparation.

The decompositions of the lifetime spectra remain the same over the range 77-300 K. One lifetime component is resolved in the HEL and ORS $YBa_2Cu_3O_{7-x}$ and in the SAC $GdBa_2Cu_3O_{7-x}$ samples. Three components are present in the THO $YBa_2Cu_3O_{7-x}$ sample over the range 17-300 K. Figure 2 shows that the long lifetime τ_2 decreases with decreasing temperature in a rather abrupt way between 120 K and 80 K. The lifetime drops from 251 ± 7 ps to 225 ± 5 ps. The lifetime transition 251/225 ps occurs in the temperature range where the superconducting resistivity transition takes place . The intensity I_2 has a non-monotonic variation decreasing from 55 % at 300 K to 20% at 120 K. Then I_2 increases to 60 % when the lifetime decreases to 225 ps at 80 K and reaches 70 % at 15 K. The short lifetime τ_1 seems to remain unchanged with an average value of 170 ps over the range 15-300 K.

In spite of the presence of the 251 ps long component in the THO ceramics, the superconducting transition occurs at about 93 K as shown in Figure 3.

4. POSITRON TRAPPING IN SINTERED CERAMICS

The positron lifetime we have measured in the $YBa_2Cu_3O_{7-x}$ ceramics are hereafter discussed in the framework of the trapping model [1-3, 15-16 and refs. therein]. This model is used to describe the positron behaviour in crystals containing defects. In a perfect crystal, positrons annihilate from a delocalized Bloch state with a lifetime constant τ_b depending on the electron density in the crystal bulk. In a crystal containing defects, positrons may be trapped in localized states. Positrons annihilate from these localized states with lifetimes τ_d characteristic of the electron density in the vicinity of the defect.

Due to their positive charge, positrons are trapped very efficiently in the potential wells arising from vacancy type defects. This trapping is easily detected because when trapped in vacancy type defects, positrons annihilate with lifetime constants longer than when delocalized in the perfect lattice, typically $\tau_b/\tau_d \gg 1.2$.

It has been shown in alloys that positrons may also annihilate from localized states arising from small precipitates or zones where the chemical composition is different from that in the matrix [17-19]. In this case, the states extend over the precipitates and so are much less localized than in vacancy type defects. The size of the precipitates necessary to obtain localisation depends on the matrix and on the nature of the precipitates. In the precipitates,

positrons may annihilate with lifetime constants longer or shorter than in the perfect lattice of the matrix depending on the structure and composition of the precipitates relative to the matrix.

In the high T_c ceramics we have studied, the wide dispersion of the average lifetimes measured at room temperature gives direct evidence that the sintered ceramics contain defects able to localize positrons. Our primary task is to identify the lifetime constants which arise from annihilation in localized states. We will then discuss the origin of the states and whether localization occurs in vacancy type defects or in other imperfections.

We attribute the long lifetime of 251±7 ps to a well defined annihilation state. The following experimental facts support this view. First, the 251 ps lifetime remains unchanged over the temperature range 100-300 K while its intensity decreases. Second, such lifetimes have been previously observed by other authors in $YBa_2Cu_3O_{7-x}$ ceramics, e. g. by Smedskjaer et al. [13]. The 251 ps lifetime is much longer than the shorter average lifetime measured in the $YBa_2Cu_3O_{7-x}$ ceramics, 1.4 times longer. This high value strongly suggests that the 251 ps lifetime is due to a vacancy type defect which contains at least one vacancy. This is strongly suggested by comparing the value 251 ps to the other lifetimes found in the ceramics. And last, we note that the 251 ps lifetime is found in the normal conducting state and disappears in the superconducting state.

In the superconducting state, positrons are still trapped in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics. However the characteristics of the trapped state have clearly changed and the long lifetime τ_2 is 225 ± 5 ps over the range 15-85 K. Again it seems likely that this lifetime is due to a well-defined vacancy defect containing at least one vacancy. It is 1.3 times longer than the shorter average lifetime that we have measured in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics. Other authors have measured lifetimes in the same range of 225 ± 10 ps [6-7,12] but it must be pointed out that they have measured them at room temperature in the normal state.

It is striking to observe that the ORS and SAC sample give nearly the same lifetime of 190 ± 3 ps at room temperature and that this lifetime remains constant over the range 80-300 K. In addition, it is clear that between 80-120 K the HEL ceramics give rise to the same lifetime 187 ± 3 ps as do the ORS and SAC ceramics. This behaviour may indicate that the 190 ps lifetime corresponds to a well-defined annihilation state. As average lifetimes shorter than 190 ps are measured in the ceramics, it is likely that the 190 ps lifetime corresponds to a defect rather than to the crystal bulk. We shall assume defects for its origin and examine below their properties.

The 190 ps lifetime has the four following characteristics. First, the 190 ps defect is observed in the normal state as well as in the superconducting state. Second, the positron trapping is more or less saturated in this defect depending on the samples. In the ORS

and SAC samples, the positron trapping in the 190 ps is complete even at room temperature. In the HEL sample, the positron trapping becomes to be complete below 120 K. Third, the positron trapping in the 190 ps defect appears to be temperature dependent. In the HEL sample, positron trapping in the 190 ps defect disappears gradually above 150 K. Fourth, in the THO sample, the annihilation state from which trapping into the 225 ps and 250 ps defects occurs seems to correspond to the 190 ps state. If we apply the trapping model with one defect to the spectra measured in the THO samples and calculate the lifetime τ_0 given by the expression

$$\tau_0 = (I_1 \tau_1^{-1} + I_2 \tau_2^{-1})^{-1}$$

we find a value of 195 ± 4 ps for τ_0 over the temperature range 15-150K and a value of 201 ± 5 ps at 300 K. If we apply the same calculation to the spectra measured by Ishibashi et al. [12] or by Smedskjaer et al. [13] at room temperature in $YBa_2Cu_3O_{7-x}$ ceramics, the values of τ_0 are 188 ps and 194 ps, respectively.

In the HEL ceramics at a temperature of about 250 K, the low values of the single lifetime component suggests that positrons may annihilate from the delocalized bulk states. However, measurements above room temperature are needed to determine the level of the bulk lifetime. Lifetime spectra with a single component of 176 ps have been measured in $YBa_2Cu_3O_{7-x}$ single crystals by [10-11]. This value is quite close the average lifetime we measure in the HEL sintered $YBa_2Cu_3O_{7-x}$ ceramics. But, surprisingly, the lifetime of 176 ps in

single crystals exhibits a different temperature variation from the one observed in the HEL ceramics. Figure 4 shows that in the single crystals the 176 ps lifetime remains constant down to the superconducting transition temperatures. This may indicate that the 190 ps defect is related to the polycrystalline character of the sintered ceramics.

5. NATURE OF THE POSITRON TRAPS

The picture which emerges from our analyses of the lifetime spectra in the ceramics may be summarized as follows. In the ORS and SAC samples, the 190 ps defects dominate positron trapping up to room temperature. In the HEL ceramic, the concentration of the 190 ps defects is lower than in the ORS and SAC samples and positron annihilation takes place partly in bulk at room temperature. In the THO ceramic, the 190 ps defects exist in addition to the defects 225 ps and 251 ps, in which positrons are more strongly localized.

The HEL ceramic a priori contains less defects than the other ceramics we have studied. If we examine the details of the preparation of the samples, the HEL samples were cooled very slowly in pure oxygen with several annealings performed during several hours at decreasing temperature. Such careful annealing stages were not performed during the preparation of the other ceramics. On the other hand, extended regions, over which the oxygen concentration varies have been observed in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystals [20 - 22]. Moreover, oxygen-vacancy ordered domains have been recently

observed by dark-field transmission electron microscopy in oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ single crystals [22]. In the sintered ceramics we studied, the oxygen concentration may present smaller fluctuations in the HEL sample than in other samples. We can suppose that in this sample, the oxygen deficient regions over which oxygen is lacking are reduced in size and/or density. Oxygen deficient regions may be able to localize positrons in the same way as do small phases of coherent precipitates in alloys [18]. Assuming that positron localization in the oxygen deficient regions are able to localize positrons and give rise to the lifetime of 190 ps, we can explain why the HEL ceramic appears to be of better quality. Fewer zones able to localize the positrons are available and it is only below 150 K that trapping in these zones become efficient. These regions of low oxygen concentration may be enhanced near the grain boundaries, which would explain why they are still present in the HEL sintered ceramics in spite of the careful preparation and are not observed in single crystals (Figure 4).

The idea that oxygen deficient regions, in peculiar oxygen-vacancy ordered domains, are able to localize positrons is strongly supported by recent calculations of Jensen et al. [23]. Keeping the orthorhombic structure constant and varying the stoichiometry from 7 to 6.5, the authors found that the positron lifetime increases by 16 ps and the positron zero point energy decreases by 0.5 eV. When the stoichiometry is reduced to 6, the lifetime increase is 47 ps and the energy decrease is 0.8 eV. These changes should be compared with the changes induced by trapping at oxygen and cation vacancies.

According to the authors [23], trapping at any of the oxygen vacancies give at the best a binding energy of 0.2 eV and a lifetime 10 ps longer than τ_0 . The lifetime and the binding energy at a metal atom vacancy depend on the type of vacancies. We list the results obtained by Jensen et al. for the copper vacancies, the yttrium and barium vacancies in the order of increasing lifetimes. Trapping at $V_{Cu}(2)$ vacancies (Cu vacancy in the pyramid CuO5) gives 19 ps for the lifetime increase and 0.7 eV for the binding energy. Trapping at a V_Y vacancy or at a $V_{Cu}(1)$ vacancy (copper vacancy in the square plane CuO4) increases the lifetime by 45 ps. However, the binding energy is much higher for V_Y (2.7 eV) than for $V_{Cu}(1)$ (1 eV). Trapping at a VBa vacancy gives the maximum effect of 104 ps for the lifetime increase and of 3.5 eV for the binding energy. On the basis of these calculations, localisation in regions of low oxygen concentration with stoichiometry about 6.5 appears to be more effective than trapping at an oxygen vacancy and to be as effective as trapping at a $V_{Cu}(2)$ vacancy. Localization in oxygen deficient regions is therefore a process which can compete with trapping at metal atom vacancies. The localization in the oxygen deficient regions provides a distribution of positron lifetimes which may vary from the bulk lifetime to values 50 ps longer depending on the oxygen stoichiometry in the region.

In the presence of zones of different oxygen stoichiometry, positrons are expected to annihilate with a distribution of close lifetimes. Experimentally, it is then difficult to resolve the spectra into the various lifetime components. The spectra give only

a single lifetime which is the average of the lifetime distribution. This single lifetime reflects therefore the inhomogeneity of the oxygen stoichiometry. Boileau et al. [18] have shown that positron localization occurs in a precipitate when the size of the precipitate exceeds a critical size. In our case, taking a difference in positron affinity of 0.5 eV, one can roughly estimate that the zones of oxygen stoichiometry 6.5 must extend over a volume of about $(14 \text{ \AA})^3$ to localize positrons, i. e. over the length of the unit cell in the c direction. Otherwise, positrons are not sensitive to the size of zones. Chen et al. [22] proposed that the oxygen-vacancy-ordered domains that they observed in the $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ single crystals correspond to a stoichiometry of 6.5. It is therefore interesting that these ordered domains extend over a volume of average dimensions $(26 \times 200 \times 10) \text{ \AA}^3$ in the axis direction a,b,c, i. e. over a volume sufficient for positron localization.

The positron trapping in the 225 ± 5 ps defect observed in the superconducting state decreases when the temperature increases. The 225 ± 5 ps lifetime is replaced by another well-defined lifetime in the normal state, the lifetime 251 ± 7 ps. This lifetime transition reflects either (i) a property of the positron trapping or (ii) the disappearance of the 225 ps defect itself as a function of temperature. The possibility (i) implies that the positron trapping is temperature dependent. The positron trapping may vary with the temperature because the specific trapping rate in the defect is temperature dependent and/or because there is a detrapping from the defect. In $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics which have a

metallic character, one expects positron trapping to occur in vacancies via a electron-hole creation mechanism and consequently expects the specific trapping rate into the 225 ps and 251 ps defects to exhibit no temperature dependence. Detrapping from the 225 ps defects is unlikely: high binding energy (1 eV) is expected since the lifetime is already 50 ps longer than 173 ps. Therefore, we rule out the possibility of a temperature dependent positron trapping property for the 225 ps and 251 ps defects. This means that the possibility (i) is excluded and we are left with the possibility (ii): the 225 ps defect itself disappears when the temperature increases and the 251 ps defect appears.

The appearance of the 225 ps lifetime below T_c in the THO ceramics seems to be connected with the superconducting transition. However, further experiments are needed to verify that the lifetime transition 251 \rightarrow 225 ps is in fact due to the superconducting transition. The transition 251 \rightarrow 225 ps is a smooth transition compared to the resistivity transition which occurs within a few degrees as seen in Figure 3. The lifetime transition has already started above 120 K, temperature at which the positron trapping at the 251 \pm 7 ps defect disappears to the benefit of one (or more) annihilation state(s) with shorter lifetimes. This transition, as discussed above, is difficult to explain in terms of positron trapping properties. We propose that the 225 ps and 251 ps lifetime arise from the same vacancy defect. The 251 \rightarrow 225 ps transition occurs because the defect undergoes a configuration change when the temperature decreases below 120 K. The defect has a more open

structure in the normal state than in the superconducting state. Cation vacancies associated with the region of low oxygen concentration are likely to be the origin of the 251-→225 ps lifetime transition. Cation vacancies have been reported as possible native defects in these ceramics. Cation displacements and vacant cation sites have been observed by using high-resolution electron microscopy [21]. X-ray diffraction experiments have shown that $V_{Cu(1)}$ vacancies are present in single crystals and the estimated concentrations are rather high 4-8% at⁻¹ [24]. It has not been observed that other cationic sites were vacant [24].

The calculations of the trapping rate within the one defect trapping model indicate that positron trapping into the 225/251 ps occurs from the 190 ps lifetime (see chapter 4). Assuming a specific trapping rate per vacancy of $2 \times 10^{14} \text{ s}^{-1}$ [1-3], the cation vacancy concentration in the low oxygen deficient regions is calculated to be of the order of $10E-5 \text{ at}^{-1}$.

6. CONCLUSION

In conclusion, the sintered ceramics we studied were found to contain defects able to localize positrons. All of them appear to contain regions of low oxygen concentration with which we associate the lifetime of 190 ps. Cation vacancies are observed. They appear to be associated with the oxygen deficient regions. The open volume in these cation vacancies decreases when the temperature decreases below the superconducting transition. The atomic

rearrangement of the cation vacancies is reflected by the lifetime transition $251 \pm 7 \rightarrow 225 \pm 5$ ps. Even the ceramics with the highest defect concentration show the superconducting transition at 93 K in the resistivity.

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Table I. Lifetime spectra at room temperature in sintered high T_c $YBa_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$ ceramics prepared in different laboratories: Thomson (THO), University of Orsay (ORS), Helsinki University of Technology (HEL), Centre d' Etudes Nucléaires de Saclay (SAC).

SAMPLES	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	$\bar{\tau}$ (ps)
$YBa_2Cu_3O_{7-x}$ THO	165 ± 18	43 ± 13	251 ± 7	57 ± 15	2000 ± 400	0.5 ± 0.1	224 ± 2
$YBa_2Cu_3O_{7-x}$ HEL	173 ± 2	-	-	-	-	-	173 ± 2
$YBa_2Cu_3O_{7-x}$ ORS	190 ± 2	-	-	-	-	-	190 ± 2
$GdBa_2Cu_3O_{7-x}$ SAC	190 ± 3	-	-	-	-	-	189 ± 2

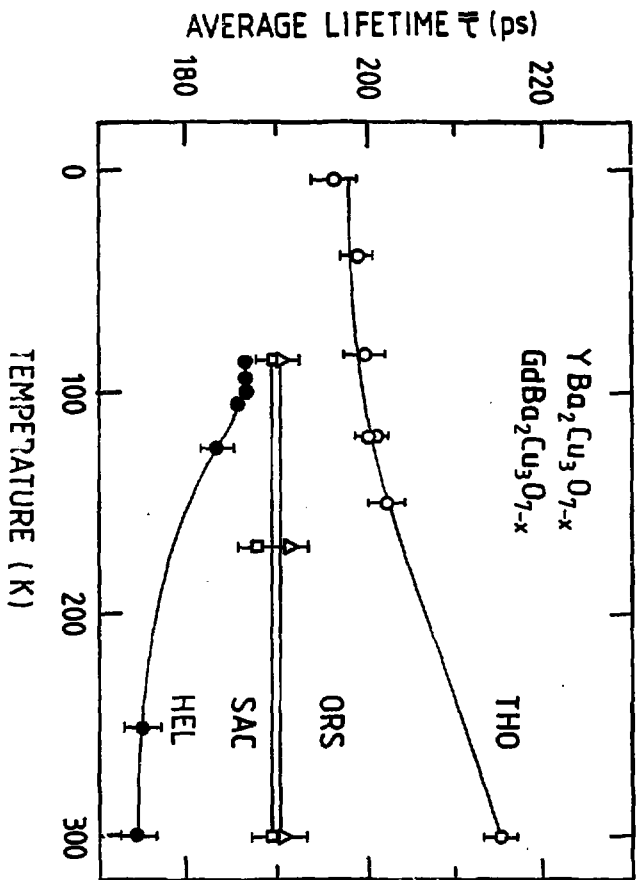
FIGURE CAPTIONS

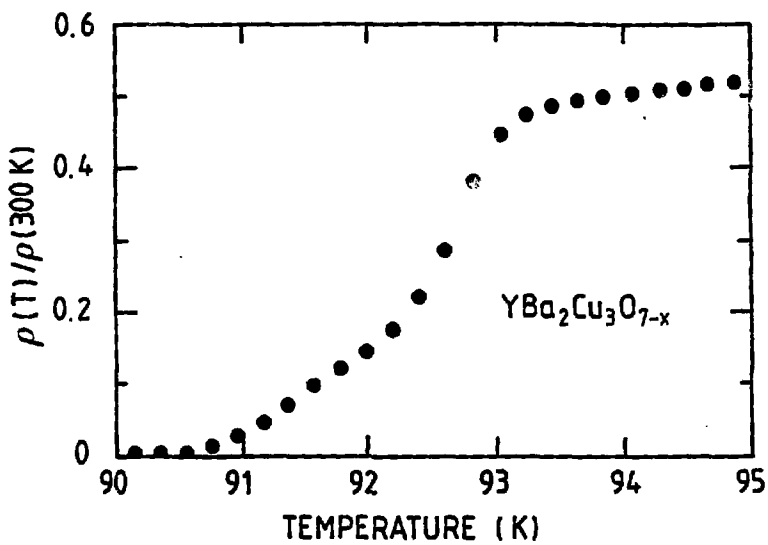
Figure 1. Positron average lifetime as a function of temperature in sintered high- T_c $YBa_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$ ceramics.

Figure 2. Long lifetime τ_2 and its intensity I_2 in the sintered high- T_c $YBa_2Cu_3O_{7-x}$ prepared in Thomson.

Figure 3. Superconducting resistivity transition in the sintered high- T_c $YBa_2Cu_3O_{7-x}$ prepared in Thomson.

Figure 4. Positron lifetime as function of temperature in the sintered high- T_c $YBa_2Cu_3O_{7-x}$ prepared at the Helsinki University of Technology (this work) compared to the average lifetime in a single crystal prepared in AT&T Bell Laboratories (after [10]).





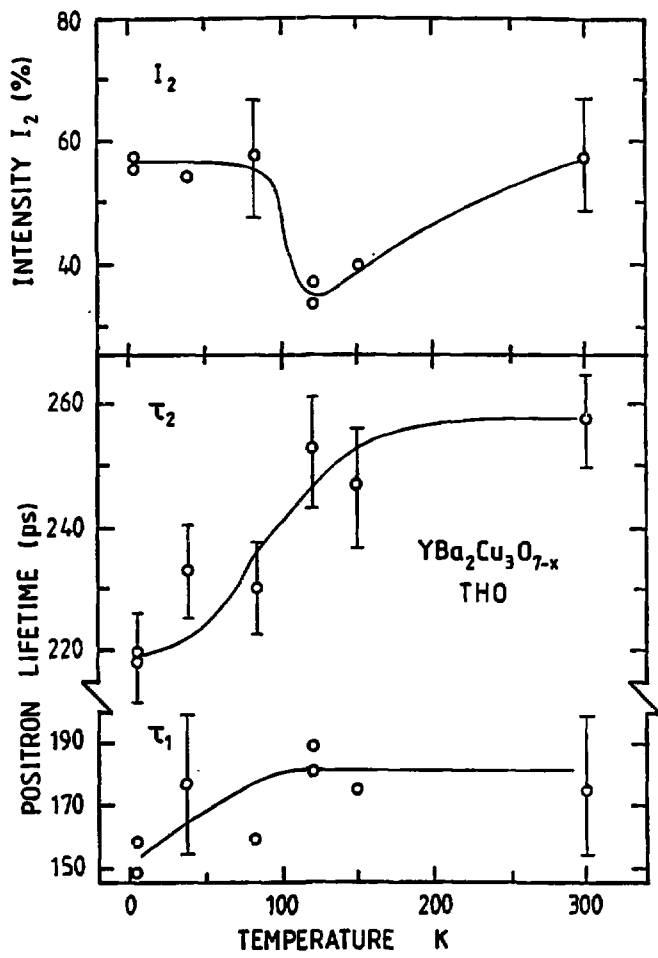


Fig 2

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