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Positron states in pure and Fe doped polycrystalline $YBa_2Cu_3O_{7-\delta}$ superconductors

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Abstract. The temperature dependences of bulk positron annihilation parameters for pure and Fe doped $YBa_2Cu_3O_{7-\delta}$ are considered in the context of temperature dependent positron trapping. Data for samples of composition $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ with $x = 0.0$, 0.005, 0.01, 0.02 and 0.03 are reported. Shallow traps with positron binding energies of 0.06 ± 0.01 eV and 0.16 ± 0.01 eV were identified for samples with $x \leqslant 0.01$ and $x = 0.02$ respectively. It is demonstrated that the data in the literature can be explained qualitatively by the presence of such traps and that the initial observation of a correlation between bulk positron annihilation parameters and superconductivity was coincidental.

1. Introduction

The advent of high-temperature superconductors [1,2] has stimulated research in many areas of solid state physics, positron annihilation spectroscopy (PAS) being no exception. The first results were reported by Jean *et al* [3], who observed a sharp change in the positron annihilation parameters at the superconducting transition temperature (T_c). Following this initial publication a plethora of work has appeared [4–24] in the literature.

With some notable exceptions [12, 15, 23] it has been generally observed that both positron line shape parameter S [26] and lifetime decrease below T_c, Usmar *et al* [12, 23] reported no temperature dependence, below T_c, in the S parameter for several samples of polycrystalline pure and Fe doped $YBa_2Cu_3O_{7-\delta}$. Further, Usmar *et al* [12] have reported *both* types of behaviour in nominally identical samples of $YBa_2Cu_3O_{7-\delta}$.

Here a detailed analysis of the results reported by Usmar *et al* [12, 23] and additional data for Fe doped $YBa_2Cu_3O_{7-\delta}$ are reported. The results are discussed in the context of temperature dependent positron trapping into traps whose depths depend on some, as yet, unknown detail of sample preparation. Furthermore, it is demonstrated that the published results [3–24] can, at least, be qualitatively accounted for by the presence of such traps.

2. Experimental details

$YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ samples with $0.0 \leqslant x \leqslant 0.03$ were prepared and characterized using a variety of techniques including electron microprobe, x-ray, neutron diffraction and

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TEM [27]. Microprobe analysis showed the samples to have compositions close to those prepared, i.e. $x = 0.0$, 0.005, 0.01, 0.02 and 0.03. The variation of T_c and structural parameters, including Fe site occupancy and microstructure, have been reported by Xu *et al* [27]. In particular twin widths in these samples were observed to vary from ~0.2 μm in $YBa_2Cu_3O_7$ to ~0.02 μm in $YBa_2(Cu_{0.98}Fe_{0.02})_3O_{7-\delta}$. The additional positron results presented here were obtained concomitantly with previously published data [23] so details of both line shape and lifetime measurements utilized here have been reported elsewhere [12, 23].

3. Results and discussion

The temperature dependence of the positron line shape parameter S for samples of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ are shown in figure 1. Despite the low-temperature (below ~140 K) differences, which have also been reported for pure $YBa_2Cu_3O_{7-\delta}$ by Usmar *et al* [12] and will be discussed later, all samples exhibit a decrease of S above some threshold temperature. This threshold temperature is ~100 K for samples A, B and C and ~240 K for sample D. A threshold temperature of ~240 K was also apparent for samples of pure $YBa_2Cu_3O_{7-\delta}$ [12] and $YBa_2(Cu_{0.985}Fe_{0.015})_3O_{7-\delta}$ [23]. It should be noted that the onset of the decrease in S is not necessarily associated with the superconducting transition of the sample material. To emphasize this point data for $YBa_2(Cu_{0.97}Fe_{0.03})_3O_{7-\delta}$ ($T_c = 83$ K), with a much reduced temperature dependence of S, have been included in figure 1. These data will not be discussed further. The characteristic high-temperature behaviour of the line shape parameter, for all but the aforementioned sample E, is indicative of thermal detrapping of positrons from shallow traps. Such traps have been considered previously [9, 22, 23] and have been observed in some metals (see, e.g. [28, 29]).

If a sample contains positron traps from which the positron has a finite probability of escape prior to annihilation, the line shape parameter S can be written [26, 30, 31]

$$S = \frac{\lambda_t \kappa S_t + \lambda_b(\lambda_t + \Delta)S_b}{\lambda_b\lambda_t + \lambda_t\kappa + \lambda_b\Delta} \tag{1}$$

where S_b and S_t are the characteristic values of S for the bulk and trapped states respectively; the annihilation rates from the bulk and trapped states are λ_b and λ_t respectively; κ is the trapping rate and Δ the detrapping rate. The temperature dependence of Δ has been evaluated theoretically by several authors. Here the expression

$$\frac{\Delta}{\kappa} = \frac{1}{\sigma_v}\left(\frac{m^*kT}{2\pi\hbar^2}\right)^{3/2} \exp\left[-\left(\frac{E_b}{kT}\right)\right] \tag{2}$$

of Manninen and Nieminan [31] was adopted. In (2) E_b is the binding energy of the positron to the trap, m^* is the effective mass of the positron and σ_v is the density of traps. All other symbols take their usual meanings.

Combining equations (1) and (2) results in an expression that can be fitted (solid lines in figure 1) to the monotonically decreasing part of $S(T)$. Thus the binding energy and trap density for any particular sample can be obtained. Here the previously published low-temperature lifetime results [12, 23] for which the standard trapping model [26] ($\Delta = 0$ in (1)) applies were used in evaluating S_t, λ_t, λ_b and κ while S_b was taken as the high-temperature asymptote of $S(T)$ (cf. figure 1). Where the data were insufficient, fitting was extended to κ. For sample C this procedure resulted in a fitted value of κ the same as that

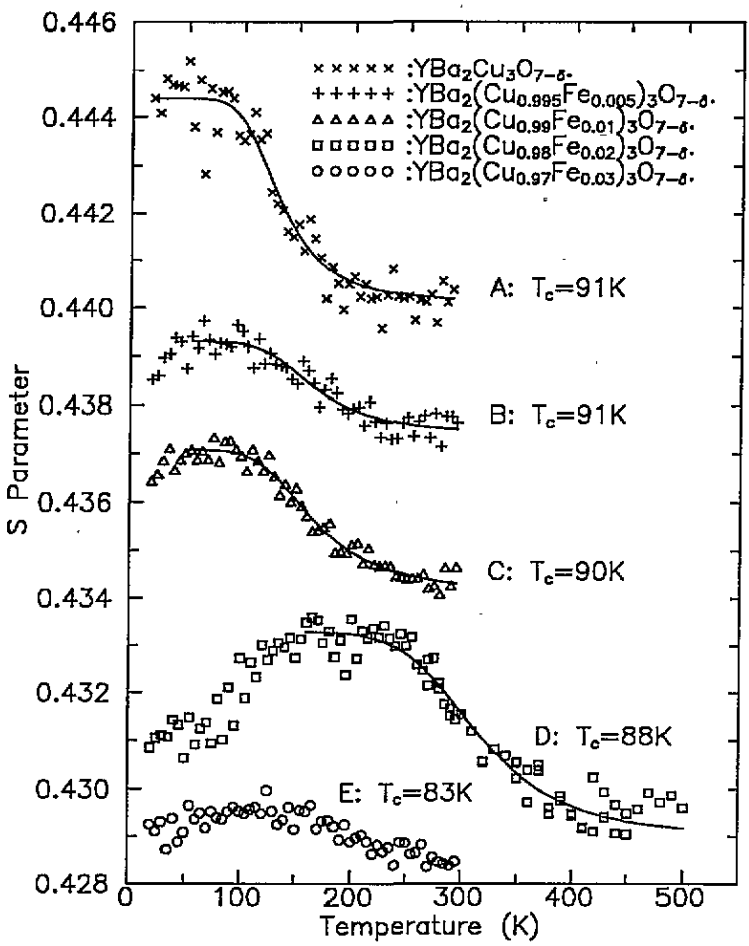

Figure 1. The positron line shape parameter S versus temperature for pure and Fe doped $YBa_2Cu_3O_{7-\delta}$. The solid lines are fitted curves for the shallow-trapping model described in the text. Note that for clarity and ease of presentation data have been offset by varying degrees along the y axis.

obtained from experimental data and had no effect on the values of E_b and σ_v returned by the fitting program. Values of E_b, σ_v and trap lifetimes for samples A, B, C and D are given in table 1. Interestingly the onset of detrapping for the samples studied here and elsewhere [22] occurs at $T_1 \approx E_b/7k$. The high-temperature limit (T_h) above which trapping is undetectable is less well defined but occurs between $\sim E_b/3k$ and $\sim E_b/4k$. Further, the annihilation rate λ_t ($= 1/\tau_t$) also provides a measure of the binding energy of the positron in the trap.

A comparison of the binding energies in table 1 reveals that the active trap in samples A, B and C is approximately one-third of the depth of that in sample D. The lifetime results of Moser and Henry [15] for $YBa_2Cu_3O_{6.9}$ are consistent with a trap whose binding energy is similar to that (0.06 eV) for samples A, B and C. Hentrich *et al* [22] reported a positron trap in $YBa_2Cu_3O_{7-\delta}$, similar to that for sample D, with a binding energy of 0.16 ± 0.01 eV and a lifetime of 192 ± 6 ps. The form of $S(T)$ and lifetime results for sample B in [12] also

Table 1. Positron binding energies and trap concentrations obtained from fitting the $S(T)$ curves (A, B, C and D) in figure 1 with the model of positron trapping at shallow traps.

Sample	Binding energy (eV)	Defect concentrations per cell	τ_b (ps)	τ_t (ps)	Label
$YBa_2Cu_3O_{7-\delta}$	0.055±0.002	1.7×10^{-6}	163	184	A
$YBa_2(Cu_{0.995}Fe_{0.005})_3O_{7-\delta}$	0.061±0.004	10.6×10^{-6}	163	184	B
$YBa_2(Cu_{0.99}Fe_{0.01})_3O_{7-\delta}$	0.057±0.002	7.1×10^{-6}	163	184	C
$YBa_2(Cu_{0.98}Fe_{0.02})_3O_{7-\delta}$	0.17±0.01	3.8×10^{-6}	166	190	D

suggests a trap with a similar binding energy. Somewhat deeper traps can be inferred from the initial results of Jean *et al* [3] and Usmar *et al* [4] (cf. table 4). None of these traps can be definitively identified. Further it is unclear whether the different binding energies are a consequence of a single trap site whose environment (and therefore E_b) changes from sample to sample, or of as many as three different sites.

Positron lifetimes in the traps lie in the range ~180 ps to ~120 ps (at 100 K), which is at most 50 ps greater than the bulk lifetime (163 ± 3 ps). The consequence of this small difference for the analysis of positron lifetime spectra is of real importance. As has been pointed out by Usmar *et al* [23] the reliable separation of lifetimes in such close proximity to each other is only possible with spectrometer resolutions of $\leqslant$ 200 ps FWHM. The majority of the published data have been derived from lifetime spectra measured with instruments of considerably worse ($\geqslant$ 225 ps FWHM) resolution. The data of Ishibashi *et al* [24] for Fe doped $YBa_2Cu_3O_{7-\delta}$ and those presented in tables 3 and 4 illustrate this point. Ishibashi *et al*, whose data is in qualitative agreement with those published here, found, using a resolution in the range 190–210 ps FWHM, that separation of lifetime spectra into two components 'was subject to large scatter'.

Table 2. Room- and low-temperature positron lifetime parameters for $YBa_2(Cu_{0.99}Fe_{0.01})_2O_{7-\delta}$. The numbers in parenthesis are the standard deviations that result from numerical analysis. (F) means the parameter was fixed during the analysis.

Temperature	RSF FWHM (ps)	τ_1 (ps)	τ_2 (ps)	I_2 (%)	Variance
292	165	163(1)			0.977
200	201(4)	168(1)			0.983
	198(F)	57(13)	170(2)	90(2)	0.884
160	203(4)	171(1)			1.177
	198(F)	101(16)	184(7)	79(7)	1.111
120	199(4)	175(1)			0.914
	198(F)	80(13)	182(4)	86(3)	0.915
100	202(5)	178(1)			1.078
	198(5)	114(33)	186(9)	84(3)	0.915
80	203(5)	177(1)			1.106
	198(5)	98(37)	181(6)	90(7)	1.095

Data shown in table 2 are results of lifetime measurements, made with a spectrometer resolution of 200 ps FWHM, in the temperature range 80–292 K for sample C. Evidently one- or two-component analysis was possible throughout this temperature range and both provide acceptable fits to the measured spectra. Two-component analysis does, however, result in a large scatter of τ_1 and a temperature dependence of I_2 inconsistent with that of S. The data presented in table 3 were derived from lifetime spectra simulated using a computer program and subsequently analysed using POSITRONFIT [35]. Spectra were

Table 3. Positron lifetime parameters resulting from the numerical analysis of simulated positron lifetime spectra. The input parameters of the simulation are included and the numbers in parenthesis are the standard deviations that result from numerical analysis.

Input parameters for simulation			Output parameters from least-squares fitting routine			
Resolution function parameters						
FWHM (ps)		Relative intensity (%)	Resolution function parameters			
230		90	Fixed at values of input parameters for simulation			
310		10				
Lifetime parameters ($\tau_b = 162$ ps)			Lifetime parameters			
τ_1 (ps)	τ_2 (ps)	I_2 (%)	τ_1 (ps)	τ_2 (ps)	I_2 (%)	Variance
159.2	190	10	175(15040)	175(1478)	62.4(60)	0.957
			164(1)			0.964
151.8	190	30	163(5)	1403(662)	0.2(0.2)	0.927
			164(1)			1.035
131.2	190	60	122(29)	183(10)	71(17)	0.875
			168(1)			1.116
67.3	190	90	69(12)	193(2)	87(1)	0.983
			186(1)			1.142

generated, with jitter applied to the time zero, assuming two-state trapping with $\tau_b = 162$ ps and $\tau_i = 190$ ps and a timing resolution of 230 ps FWHM. A source component ($\tau_s = 140$ ps, $I_s = 4.5\%$) was also included. Obviously two-component analysis gave unphysical lifetime parameters for $I_2 \leqslant 30\%$ and single-component analysis was acceptable throughout. With the above discussion in mind the published lifetime data (summarized in table 4) for pure $YBa_2Cu_3O_{7-\delta}$ will be considered.

Lifetimes greater than ~450 ps indicate the presence of voids. Hill *et al* [21] have reported their samples to contain pores of ~50 μm radius. Evidently the lifetimes τ_2 (500 ps) and τ_3 (>1 ns) reported by these authors are associated with pores. Thus one can conclude that the only lifetime reported by Hill *et al* [21] intrinsic to $YBa_2Cu_3O_{7-\delta}$ is τ_1 (= 195–230 ps). The long lifetime ($\tau_2 > 600$ ps) reported by Wang *et al* [5] can be disregarded for the same reason, leaving a lifetime intrinsic to $YBa_2Cu_3O_{7-\delta}$ in the range 195–204 ps.

Now, the references in table 4 can be divided according to the number of intrinsic lifetimes reported. Where two lifetimes were reported [3, 4, 8, 10, 12, 13, 22, 23] τ_2 lies in the range 185–220 ps with $\tau_1 \leqslant 140$ ps. Application of the standard two-state trapping model [26] to the data of Jean *et al* [3] results in temperature independent bulk lifetimes ($\tau_b = (\lambda_b)^{-1} = (\sum_i I_i\lambda_i)^{-1}$) of 165 ± 5 ps [25] and 162 ± 5 ps for $YBa_2Cu_3O_{6.8}$ and $YBa_2Cu_3O_{6.2}$ respectively. The data of Bharathi *et al* [10] give $\tau_b = 163 \pm 5$ ps for $YBa_2Cu_3O_{7-\delta}$ with $0.0 \leqslant \delta \leqslant 0.2$. Further Hentrich *et al* [22] have reported the bulk lifetime for $YBa_2Cu_3O_{7-\delta}$ ($\delta \leqslant 0.05$) to vary linearly with temperature from 155 ps at 80 K to 165 ps at 440 K. Thus the experimental results strongly suggest that the bulk lifetime of positrons in $YBa_2Cu_3O_{7-\delta}$ with $0.0 \leqslant \delta \leqslant 0.8$ is 163 ± 5 ps. Theoretical estimates [32, 34, 37] for the bulk lifetime in $YBa_2Cu_3O_7$ give 157 ps $\leqslant \tau_b \leqslant$ 164 ps depending on the exact prescription used for the calculation. Thus subsequent discussion will assume that $\tau_b = 163 \pm 5$ ps for $YBa_2Cu_3O_{7-\delta}$ with $0.0 \leqslant \delta \leqslant 0.2$, the composition range of interest here.

Single intrinsic lifetimes have been reported by several authors [5, 11, 13, 15, 16]. The lifetimes were found to be in the range (cf. table 4) 175–210 ps. All of these data were measured using lifetime spectrometers with timing resolutions of between 225 ps and 380 ps

Table 4. A summary of the positron lifetime parameters for $YBa_2Cu_3O_{7-\delta}$ that have appeared in the literature. Where possible data pertaining to T_c and other physical properties of the samples studied are included.

[f]

Sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	I_1 (%)	I_2 (%)	τ_b (ps)	Reference and comments
$YBa_2Cu_3O_{6.8}$	139	200(10 K)			35(10 K)	165	[3] RSF 255 ps FWHM (80%)
$T_c = 90$ K		220(300 K)			25(300 K)		290 ps FWHM (20%)
$YBa_2Cu_3O_{6.2}$	139	228(10 K)			36(10 K)		
$T_c < 1$ K		240(300 K)			36(300 K)		
$YBa_2Cu_3O_{7-\delta}$		194(15 K)			94		[4] RSF 210 ps FWHM
$T_c = 90$ K		210(120 K)					$\delta < 0.01::\tau_1$ no reported
$YBa_2Cu_3O_{7-\delta}$	202(50 K)	600(50 K)			4(50 K)		[5] RSF 330 ps FWHM
$T_c = 87.5$ K	195(90 K)	460(90 K)			8(90 K)		$\delta = 0.18$ deduced from δ
	204(300 K)	870(300 K)			4(300 K)		dependence of $T_c(\delta(T_c))$
$YBa_2Cu_3O_{7-\delta}$	~ 98	196(21 K)			60(21 K)		[8] RSF 270 ps FWHM
$T_c = 85$ K		228(206 K)			45(206 K)		$\delta = 0.2$ deduced from $\delta(T_c)$
$YBa_2Cu_3O_7$	~ 50	190			94		[10] RSF not reported.
$YBa_2Cu_3O_{6.95}$	~ 50	190			94		RT measurements
$YBa_2Cu_3O_{6.5}$		200			100		on quenched samples
$YBa_2Cu_3O_{7-\delta}$		188(60 K)			100		[11] RSF 300 ps FWHM
$T_c = 87.5$ K		194(90 K)			100		$\delta = 0.18$ from $\delta(T_c)$
$YBa_2Cu_3O_{7-\delta}$	87	202		93		176	[12] RSF 163 ps FWHM
92 K > T_c > 89 K	111	186		76		161	$\delta < 0.15$ from $\delta(T_c)$
	163			100		163	twin densities reported
$YBa_2Cu_3O_{7-\delta}$	175(5 K)					as τ_1	[18] RSF 260 ps FWHM
$T_c = 94$ K	190(100 K)						$\delta < 0.10$ from $\delta(T_c)$
$YBa_2Cu_3O_{7-\delta}$	185	280			0(50 K)	185	[19] RSF 215 ps FWHM
					30(300 K)	210	$\delta = 0.15$, 0.24, 0.67
$YBa_2Cu_3O_{7-\delta}$	190(80 K)						[20] RSF 375 ps FWHM
93.5 K > T_c > 89.5 K	194(100 K)						$0.1 \leqslant \delta \leqslant 0.2$
$YBa_2Cu_3O_{6.91}$	195	500(30 K)	1500(30 K)	91(30 K)	8(30 K)		[21] RSF 225 ps FWHM
$T_c = 90$ K		460(300 K)	3000(300 K)	85(300 K)	12(300 K)		samples contained 50 μm
$YBa_2Cu_3O_{6.75}$	200(30 K)	450(30 K)		81(30 K)			pores
$T_c = 65$ K	230(300 K)	500(300 K)		86(300 K)			
$YBa_2Cu_3O_{7-\delta}$	80(50 K)	187			70(50 K)		[22] RSF 190 ps FWHM
$T_c > 90$ K from $\delta(T_c)$	160(450 K)				0(450 K)		$\delta \leqslant 0.05$

FWHM. Thus in the light of the previous discussion it is suggested that the reported lifetimes are unresolved mixtures of lifetimes associated with annihilations from the bulk and a trapping site. However, the range of lifetimes reported probably cannot be dismissed as an analytical artefact and is likely to reflect real differences between samples.

Of the remaining publications in which single lifetimes were reported or discussed some criterion is appropriate. As was noted earlier in this work and, although not specifically commented upon, was evident as long ago as 1988 [12] the initial correlation of changes in positron annihilation parameters [3, 4, 6–9] with T_c for $YBa_2Cu_3O_{7-\delta}$ was coincidental. Nevertheless several authors [18, 37] have continued to make this association. In particular the initial results of Jean *et al* [3] revealed a temperature independent bulk lifetime [25] of 163 ± 3 ps for $YBa_2Cu_3O_{6.9}$ while in later work [18] a temperature dependent bulk lifetime, 185 ps $\leqslant \tau_b \leqslant$ 195 ps was reported. The latter work utilized an argument involving variations of local charge density associated with superconductivity to explain $\tau_b(T)$. In fact the magnitude of the lifetime and its temperature dependence [18] are consistent with it being a mixture (cf. the previous discussion) of annihilations from the bulk and a trap site with binding energy ~0.16 eV. Thus, although the low-temperature behaviour of $\tau(T)$ may result from changes in local charge density, the argument presented by Jean *et al* [18], which associates features of $\tau_b(T)$ with superconductivity, is probably incorrect.

Thus far it has been established, using the data published here, that in pure and Fe doped $YBa_2Cu_3O_{7-\delta}$ ($0.0 \leqslant \delta \leqslant 0.2$) there exist positron trapping sites with binding energies of ~0.06 eV and ~0.17 eV. Further, as was mentioned earlier, the results of Moser and Henry [15] are consistent with a positron trap with binding energy of ~0.06 eV while Hentrich *et al* [22] have reported a trap with binding energy of 0.16 eV. Moreover, bearing in mind the previous discussion pertaining to spectral analysis, the lifetime data reported in the literature [3–14, 16–21] can also be explained, at least qualitatively, by the presence of positron traps of similar ($E_b \leqslant 0.2$ eV) depth. Identification of all of these trapping sites poses a problem for, although a comparison of the binding energies and lifetimes presented in table 1 with those arrived at via theoretical calculations for O(1) site vacancies [32] shows surprisingly good agreement for samples A, B and C, other authors (notably Szotek *et al* [33]) have concluded on the basis of band structure calculations that the O(1) vacancy will not trap positrons. Further, neutron scattering results [39–45], to be discussed later, indicate that the densities of O(1) site vacancies in $YBa_2Cu_3O_{7-\delta}$ are of the order of 10^{-1} per cell, some four to five orders of magnitude greater than those reported in table 1. In fact as was noted earlier, it is unclear whether the different binding energies should be associated with different trapping sites or a single site whose environment changes from sample to sample. In either case the low-temperature differences in $S(T)$ observed by Usmar *et al* [12] for different samples of pure $YBa_2Cu_3O_7$ must be accounted for. These differences indicate the presence of both shallow ($E_b \approx 0.06$ eV) and deep ($E_b \approx 0.16$ eV) traps in *nominally identical* samples. Some authors [19] have argued that the variability of positron annihilation parameters is due to varying degrees of phase separation in samples. The results of Usmar *et al* [12] belie this argument, while other results [10] strongly suggest that the trap lifetime (and therefore depth) depends on δ (increases with δ). Thus the available data pertaining to the structure of pure and Fe doped $YBa_2Cu_3O_{7-\delta}$ will be considered. The structure will be discussed in the context of its relationship with positron wave functions for these materials.

Positron wave functions for $YBa_2Cu_3O_7$ have been calculated by various authors [9, 32, 34, 36]. For the bulk state the general consensus is that more than 95% of the positron charge resides between the basal and Cu–O planes. Here the presence of Ba ions at seem to play an important role, effectively confining better than 70% of the positron

charge between the Ba ion and basal planes. Thus the positron is delocalized in the a–b plane and primarily annihilates with electrons from bands associated with the O(1), Cu(1) and O(4) sites. Even in the O(1) vacancy trapped state the positron wave function [32, 34] extends over three to four unit cells in the a–b plane but is confined to a layer ~5 Å deep, centred on the basal plane, in the c direction. Again the Ba ion seems to play an important role in localization of the positron in the c direction.

The structure of $YBa_2Cu_3O_{7-\delta}$ ($\delta \leqslant 0.63$) has been established by x-ray [38, 45, 46] and neutron [39–44] diffraction to be orthorhombic. In the composition range $0.0 \leqslant \delta \leqslant 0.2$ variations in the lattice parameters are dominated by a more or less linear increase in c of ~0.15%. In this same composition range the distances (z) of the O(4) (O(4)(z)) and Ba (Ba(z)) sites from the basal plane decrease and increase respectively by ~0.5%. Also, it has been found [42–44] that, in practice, $YBa_2Cu_3O_{7-\delta}$ always contains a finite concentration of O(1) site vacancies. The concentration of these vacancies increases [42] from $\sim 10^{-1}$ per cell at $\delta = 0.07$ to $\sim 2 \times 10^{-1}$ per cell at $\delta = 0.2$. Further, the evidence in the literature [47–50] suggests that O(1) site vacancies may be ordered and to some extent [50] attracted to twin boundaries.

The effect, on structure, of substituting Cu with Fe in $YBa_2Cu_3O_{7-\delta}$ has been studied using several experimental techniques including electron and neutron diffraction, EXAFS and Mössbauer spectroscopy [27, 51, 52]. General consensus [51, 52] has Fe occupying Cu(1) sites with each Fe added accompanied by 0.5 O per unit cell. The extra O is randomly distributed in empty a (O(5)) and b (O(1)) axis sites. Moreover, in the formula $YBa_2(Cu_{1-x}Fe_x)_3O_{\alpha-\delta}$, $\delta = -3x/2$ but the value that should be assigned to α is not as well known. The results of Dunlap *et al* [52] suggest $\alpha \approx 6.93$. Thus $\alpha - \delta \leqslant 7$ for $x \leqslant 0.046$ so that all of the Fe doped samples studied here contain significant concentrations of O(1) site vacancies.

Lattice parameters for the samples studied here have been reported elsewhere [27]. In the composition range studied c remains constant, a increases by ~0.85% and b decreases by ~0.61%. The variations of both a and b probably reflect disordering of the Cu(1)–O(1) chains resulting from the random distribution of Fe on Cu(1) sites. Finally additions of Fe result in narrower twins. Pure $YBa_2Cu_3O_{7-\delta}$ samples were found [12, 27] to contain broad twins with widths between 0.170 μm and 0.20 μm while $YBa_2(Cu_{0.985}Fe_{0.015})_3O_{7-\delta}$ and $YBa_2(Cu_{0.98}Fe_{0.02})_3O_{7-\delta}$ contained narrow twins with widths of ~0.05 μm and 0.02 μm respectively. $YBa_2(Cu_{0.97}Fe_{0.03})_3O_{7-\delta}$ exhibited [27] a tweed-like structure.

It is evident from the structural parameters that all pure and Fe doped $YBa_2Cu_3O_{7-\delta}$ samples studied here and elsewhere [24, 53] contain O(1) site vacancies ($O(1)_v$). Notwithstanding the apparent discrepancies between the concentrations of $O(1)_v$ arrived at via the positron trapping model used here and neutron diffraction data it is likely that $O(1)_v$ are at least partially responsible for positron trapping in pure and Fe doped $YBa_2Cu_3O_{7-\delta}$. Further, positron annihilation parameters could be affected by other structural parameters (e.g. Ba(z) and $O(1)_v$ concentrations) that depend on the, often poorly known, parameter δ. Several scenarios present themselves as possible explanations for the variability of positron annihilation characteristics reported here and elsewhere [3–24]:

(i) positrons are trapped at $O(1)_v$ with the binding energy (E_v) sensitive to Ba(z) and therefore to δ;

(ii) positrons are trapped at $O(1)_v$ and ${}^nO(1)_v$ clusters (${}^2O(1)_v$ for example) with the relative concentrations of $O(1)_v$ and ${}^nO(1)_v$ sensitive to the degree of $O(1)_v$ ordering and

(iii) diffusion controlled trapping at twin boundaries with the positron diffusion coefficient being sensitive to the degree of order in the Cu–O (basal) plane.

Of these scenarios the first two cannot be reconciled with the results of Usmar *et al* [12] and the third with the theoretical temperature dependence [30] of the annihilation parameters (τ_m or S) reported by several authors [3, 4, 12, 15, 22, 23]. Two more possibilities will be considered.

Ishibashi *et al* [53] has considered $O(1)_v$ and $O(1)_v$ clusters ($^nO(1)_v$) as shallow traps with e.g. $E_v < E_{2v}$. Here E_v and E_{2v} are the positron binding energies to $O(1)_v$ and $^2O(1)_v$ respectively. These authors have suggested that if both types of trap are active in a particular sample then as the sample temperature decreases τ_m (or S) would initially increase as escape from the deeper trap becomes less probable and then decrease again below some threshold temperature for which the same is true of the shallower trap. In the low-temperature limit the standard trapping model (with three states) would pertain and τ_m (or S) should become temperature independent. This limit can be estimated using the empirical relationships ($T_h \approx E_b/3.5k$ and $T_l \approx E_b/7k$) mentioned earlier and is between ~50 K and ~80 K for the data susceptible to this interpretation published here and elsewhere [12, 23, 53]. All of these data have, within experimental error, τ_m (or S) proportional to T for 20 K $\leqslant T \leqslant$ 90 K, casting some doubt on this hypothesis.

The fact is that the only common feature in the structure of samples that exhibit similar behaviour in $S(T)$ is their twin widths (or densities). Thus it is suggested that in samples with $S(T)$ having the form observed in samples A, B and C here and D in [12], all of which have broad twins ($\geqslant$ 1200 Å), the active positron trap is either an O(1) site vacancy or vacancy cluster (probably $^2O(1)_v$). The $^2O(1)_v$ would certainly reduce the apparent discrepancy between the densities of trap sites indicated by neutron scattering results and those arrived at here via the analysis of positron data. In fact if $O(1)_v$ ordering occurs then a large range (including those reported in table 1) of $^2O(1)_v$ concentrations are possible. Exact concentrations would depend on the degree to which the $O(1)_v$ were ordered. In samples where $S(T)$ has the form typical of that observed for sample D here and B in [12], both of which have narrow twins ($\leqslant$500 Å), the trap site is at the twin boundary, either the boundary itself or some open volume site defect (probably $O(1)_v$ of $^nO(1)_v$) associated with it. Unfortunately the evidence that supports this hypothesis is largely circumstantial; however, the following can be said.

In general it has been found that even in pure $YBa_2Cu_3O_{7-\delta}$ twins can be as narrow as ~100–200 Å [12, 54] and samples containing broad twins ($\geqslant$1000 Å) are not easily produced. This would explain the propensity of samples for which $S(T)$ has a form similar to that of sample B in [12]. Also data pertaining to the effect of Ni and Zn doping on twin densities in $YBa_2Cu_3O_{7-\delta}$ show [54] that twin widths are significantly reduced by the presence of these dopants. Thus the data of Ishibashi *et al* [53] for Ni and Zn doped $YBa_2Cu_3O_{7-\delta}$ are not inconsistent with trapping at twin boundaries. Here it should be noted that, in contrast to the case of Fe, both Ni and Zn substitute [51, 55] for Cu in the Cu(2) site, i.e. in the O(2)–Cu(2)–O(3) plane, so the changes in $\tau_m(T)$ observed by Ishibashi *et al* [24] cannot be associated with modifications of the Cu(1)–O(1) chain structure. Also since the twin boundaries have structures not found in the bulk, the low-temperature differences in $S(T)$ observed by Usmar *et al* [12] and here in sample D do not necessarily throw up an inconsistency. The low-temperature ($\leqslant$100 K) behaviour of $S(T)$ in sample D here and typical of most results reported for $YBa_2Cu_3O_{7-\delta}$ could be explained by low-temperature structural relaxation at twin boundaries.

4. Conclusion

It is clear from the data presented here and reported elsewhere [12, 15, 22, 23] that the

features observed in the temperature dependence of positron annihilation parameters of pure and doped polycrystalline $YBa_2Cu_3O_{7-\delta}$ are not, as has been suggested by several authors [3–7, 11, 18] associated with superconductivity in these materials. Thus the discussions presented in the literature [3–7, 18, 37] that purport to associate the temperature dependences of positron annihilation parameters ($S(T)$ or $\tau_m(T)$) with superconductivity are not supported by the available data. The underlying reason for the canard that had bulk positron annihilation parameters associated with the superconducting transition is twofold. Firstly some authors failed to realise that experimental results [3, 12, 22] indicated that the bulk lifetime of positrons in $YBa_2Cu_3O_{7-\delta}$ ($0.0 < \delta < 0.2$) is 163 ± 3 ps. Secondly this lack of realization resulted in lifetimes obtained from single-component analysis of spectra containing two components being reported as temperature dependent bulk lifetimes.

Finally it has been clearly demonstrated that the sample to sample variation of positron annihilation parameters in pure [12] and doped [23, 53] $YBa_2Cu_3O_{7-\delta}$ can be accounted for by a variety of positron trapping sites. Results reported here and in the literature [3, 12, 22] indicate that at least two trapping sites are possible. These sites cannot be clearly identified; however, circumstantial evidence strongly suggests one to be associated with O(1) site vacancies (possibly $^2O(1)_v$) and another with twin boundaries. Binding energies of positrons at the above-mentioned sites are 0.06 ± 0.02 eV and 0.16 ± 0.02 eV respectively.

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