LETTER TO THE EDITOR

Positron states in $YBa_2Cu_3O_{7-x}$

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Abstract. We present a series of calculations for positron states and lifetimes in perfect and defected $YBa_2Cu_3O_{7-x}$ using an atomistic model. A simple relationship is found between the lifetime and the oxygen deficiency. The results suggest that the long-lived component resolved in lifetime spectra is associated with metal vacancies and/or metal–oxygen-vacancy complexes, while oxygen vacancies are found to be only shallow positron traps. We give an interpretation of positron lifetime experiments in terms of defects, oxygen-deficient domains and structural changes in the material.

Since the discovery of the class of high-temperature oxide superconductors [1] a vast array of techniques have been employed to study the microscopic characterisation of these materials. The positron annihilation technique (PAT) has substantial potential in this pursuit in two areas. Firstly, the angular correlation of annihilation radiation (ACAR) [2] can yield information on the existence and shape of the Fermi surface. Secondly, the extreme sensitivity of PAT to atomic defects can be used to probe the imperfections in the materials [3, 4]. Furthermore, the early suggestions [5] regarding the response of the positron lifetime to superconductive pairing have been revived [6] for the new materials, which are speculated to have a substantially larger value for the ratio between the gap energy and the carrier Fermi energy than the conventional superconductors.

Positron lifetime studies [3, 4, 6–10] for the sintered ceramics reveal the presence of two components, with lifetime values τ_1 and τ_2 in the ranges 90–170 and 200–250 ps, respectively. Around T_c a clear change in τ_2 is observed: the values below T_c are about 10 ps lower than the values immediately above. Similar effects are observed in ACAR and Doppler-broadening spectra [3, 4, 11]. For single crystals, a one-component lifetime spectrum has been reported [6] with a temperature-dependent value of τ, increasing from 176 ps at and above T_c to 187 ps at 5 K.

The nature of native defects in sintered high-T_c ceramics is an important question, and thus the assignment of the τ-values to bulk and different defect states is highly desirable. Moreover, without unequivocal identification of the lifetime components, interpretation of the temperature- and stoichiometry-dependent features is precluded. This Letter reports the first comprehensive calculations for the annihilation characteristics and offers a general interpretation of the lifetime results.

The calculations are based on the atomistic model [12], in which the effective potential sensed by the positron is first constructed on a three-dimensional grid, after which the positron Schrödinger equation is solved numerically, with proper boundary conditions imposed for either localised (trapped) or delocalised (bulk) states. The positron lifetime

is then calculated from the electron density $n(r)$, positron density $|\psi_+(r)|^2$ and the state-dependent enhancement factors. The positron potential $V^+(r)$ is the sum of the electrostatic Hartree potential $V_c(r)$ and the correlation potential $V_{corr}(r)$. The correlation potential is treated within the local-density approximation, where it becomes a function of $n(r)$ alone. For $V_c(r)$ and $n(r)$ the superposition of electrostatic potentials and charge densities of free atoms at the relevant lattice sites is employed. Detailed comparisons with self-consistent calculations for metals and semiconductors [12, 13] show that the effect of charge self-consistency on the positron lifetimes is of minor importance and does not alter the key conclusions.

In the lifetime calculations we treat the Cu 3d and 4s, the O 2p, the Y 4d and 5s, and the Ba 6s electrons as valence states. These atomic energy levels correspond to one-electron bands in the crystal lying near to or above the Fermi level [14]. The contribution to the annihilation rate from these electrons is calculated in the local-density approximation from

$$\lambda_{val} = \int dr \, |\psi_+(r)|^2 \Gamma(n(r)) \tag{1}$$

where $\Gamma(n)$ is the rate function for a homogeneous system [15]. The contribution of the remaining (core) electrons λ_{core} is calculated using the independent-particle model with a constant enhancement factor of 1.5. The total annihilation rate (the inverse of the lifetime τ) is given by the sum $\lambda_{val} + \lambda_{core}$. The approximations used for V_{corr} and λ_{val} assume metallic positron–electron correlation. An evaluation of the dielectric effects following the recent ideas of Puska and co-workers [16] shows that they have in the present case a minor effect on the positron potential and no effect on the important trends in the lifetimes reported below.

The structural parameters for orthorhombic ($x \leqslant 0.5$) and tetragonal ($x > 0.5$) $YBa_2Cu_3O_{7-x}$ have been taken from [17] and [18], respectively. The former structure is also used for the defect calculations. In the $x = 0$ ($x = 1$) structure all the O(1) sites at $(0, \frac{1}{2}, 0)$ are occupied (empty). For $x = 0.5$ we take all the O(1) sites in every second Cu–O chain to be empty.

The calculated positron wavefunctions for the perfect structures ($x = 0, 0.5$, and 1) show the attraction towards the region between the Cu–O chains [11], the effect being most pronounced for $x = 1$. The positron lifetime and the affinity (with respect to the $x = 0$ structure) as a function of oxygen concentration are shown in figure 1. There is a clear correlation between x and the positron response: the lifetime and the affinity will *increase* with oxygen deficiency. The calculated lifetime for perfect $YBa_2Cu_3O_7$ is 159 ps, which compares well with the lowest mean lifetimes (151 to 173 ps) reported in literature [3, 7, 8]. The experimental spectra typically show more than a single lifetime component, indicative of defect trapping. Thus the experimentally quoted values are upper limits to the bulk lifetime: our results suggest that the higher values (>176 ps) reported for single-crystal $YBa_2Cu_3O_{7-x}$ must be, at least partially, due to trapping. Figure 1 also includes experimental [8] mean lifetimes from a series of sintered samples with varying oxygen content, which confirm the predicted relationship. Finally, our calculations for different bulk oxides show essentially no sensitivity to Y substitution by other rare-earth elements, in accord with experiments [8].

The conclusion from the calculations for bulk states is that in real crystals positrons will favour oxygen-deficient areas. There is substantial recent evidence [19, 20] that regions of ordered oxygen vacancy structures do exist in real single crystals. The dimensions of such domains have been reported to be ≈ 200 Å in the longitudinal direction
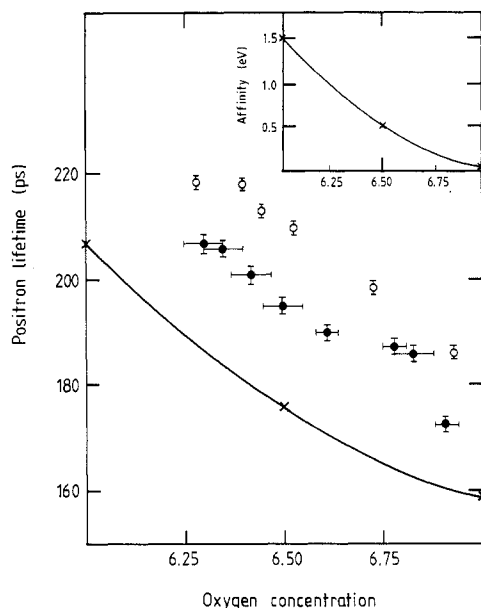
Figure 1. The positron lifetime and affinity (with respect to the $x = 0$ system) in bulk $YBa_2Cu_3O_{7-x}$. The crosses denote the present theoretical results. The full and open circles are the experimental results [8] of Nyberg and co-workers and Smedskjær and co-workers, respectively.

(parallel to the Cu–O chains) and $\simeq 20$ Å in the transverse direction. Positron localisation in such domains is analogous to the well known phenomenon of trapping into coherent precipitates in alloys (Guinier–Preston zones) [21].

Figure 2 displays the localised positron wavefunction corresponding to the case of a single O(1) vacancy in $YBa_2Cu_3O_7$. The significant result is that the localisation is very weak, i.e. the wavefunction extends far from the vacancy especially within the *ab* plane. This is also reflected in the lifetime which is only 10 ps longer than the bulk lifetime, and in the low binding energy ($\simeq 0.2$ eV) for binding to the trap. The results for the four types of oxygen vacancies show no essential differences. The results clearly suggest that it is unreasonable to assign the τ_2-component in the lifetime spectra to oxygen vacancies.

Metal vacancies and metal–oxygen-vacancy complexes, on the other hand, are strong traps with binding energies of 1 eV and above and with substantially longer lifetimes (see table 1). Figure 3 shows the positron wavefunction in a Cu(1) vacancy, displaying the strong degree of localisation. The results in table 1 show the different types of defect that give rise to lifetimes in the range of the observed τ_2-values. Although we cannot make an unamibugous assignment of τ_2, it seems to be associated with metal vacancies, either isolated or in conjunction with oxygen vacancies. The PAT results thus demonstrate the presence of such defects in sintered samples. A recent neutron diffraction study [22] also indicates that a considerable fraction of Cu(1) sites may be empty.

The picture that emerges from the calculations is that the observed lifetime spectra reflect the competition between (weak) localisation in oxygen-deficient regions and (strong) trapping in metal vacancies. This explains the apparent variations between differently prepared samples, as well as hysteresis and aging effects, as the different preparation and annealing processes can easily alter the defect populations.

The observed temperature dependences of τ_1 and τ_2 at and below T_c deserve further comment. As for τ_2, it is highly unlikely that any direct influence of the formation of the superconducting state on the annihilation characteristics would only manifest itself when metal vacancies are present. Thus the positron results imply that changes in the atomic
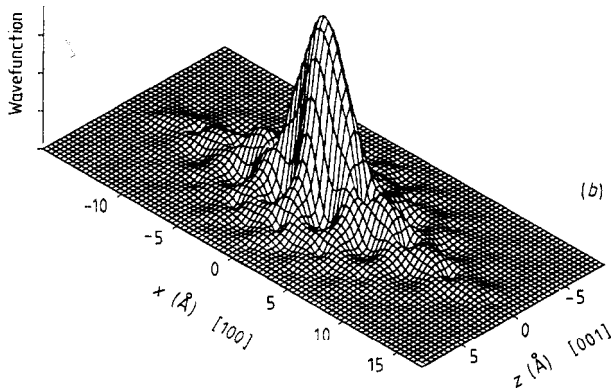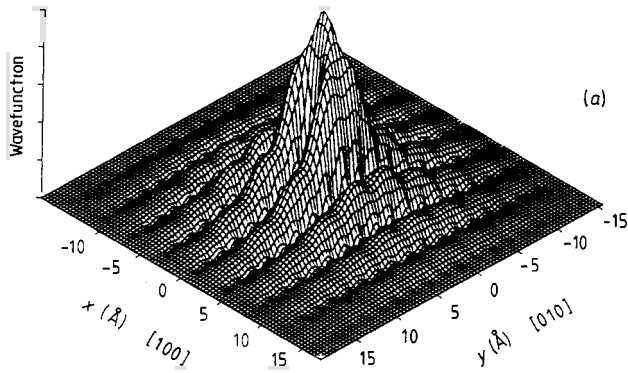
Figure 2. The wavefunction of a positron trapped at a single O(1) vacancy in the $YBa_2Cu_3O_7$ crystal, drawn in (*a*) the *ab* plane, (*b*) the *ac* plane.
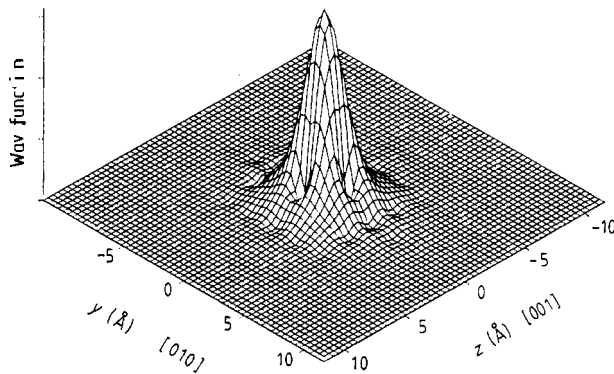
Figure 3. The wavefunction of a positron trapped at a single Cu(1) vacancy in the $YBa_2Cu_3O_7$ crystal drawn in the *bc* plane.

and electronic structure occur near T_c. Calculations for defects in semiconductors [13] indicate that even a major readjustment of the electronic structure (such as a change in the defect charge state) without atomic relaxation has little influence on the lifetime value. It therefore appears that the positron results around T_c must be interpreted in terms of *structural* changes, i.e. the rearrangement of atomic positions around the defect. To investigate the magnitude of this effect, we have varied the positions of the two O(1) atoms near a Cu(1) vacancy. A relaxation of $\simeq 0.2$ Å of the O(1) atoms towards the vacant Cu(1) site reproduces the observed 10 ps change in the lifetime. The qualitative

Table 1. Calculated positron lifetimes τ and binding energies E_b (with respect to the bulk positron state) for various defects in $YBa_2Cu_3O_7$.

	τ (ps)	E_b (eV)
Bulk $YBa_2Cu_3O_7$	159	—
O vacancy	$\simeq 170$	$\simeq 0.2$
Cu(1) vacancy	207	1.1
Cu(2) vacancy	182	0.7
Y vacancy	206	2.7
Ba vacancy	263	3.5
Cu(1)–O(1) divacancy	236	1.5

conclusion is that associated with the superconductivity transition there are movements of the order of 0.1 Å in the oxygen subsystem, which manifest themselves in the lowering of the defect (metal vacancy) lifetime below T_c.

Neutron diffraction [23] and EXAFS [24] measurements show that any structural relaxations in the bulk occurring around T_c are less than 0.1 Å, while anomalies in the lattice parameters have been observed [23, 25]. Modifications of the vibrational properties below T_c have been seen in investigations based on Raman scattering [26], Mössbauer spectroscopy [27], and EXAFS [24]. However, none of these techniques are defect-sensitive (as the positrons are). Thus the indicated structural changes at T_c provide new information about the processes leading to the superconducting transition.

Finally, the reported temperature dependence of τ (the bulk lifetime) has tentatively been associated [6] with superconductive pairing. We find such an explanation very unlikely for the following reason. In metals and semiconductors, short-range screening effects lead to a simple relation between a change in the ambient electron density Δn and the change in the annihilation rate $\Delta\lambda$ [15]:

$$\Delta\lambda = 134\,\Delta n \qquad (2)$$

where Δn is in au and $\Delta\lambda$ in units of ns^{-1}. Thus the observed increase of about 10 ps in the lifetime implies a change in the electron density near the Cu–O chains of the order of 1.5×10^{22} cm^{-3}, which is substantially larger than estimates [28] for the total carrier density in the materials.

Another explanation for the increase of τ below T_c is that in terms of structural changes in the oxygen subsystem. It has been reported [23] that the displacement amplitudes of the O(1) atoms, in particular in the direction perpendicular to the Cu–O chain axis, remain anomalously large even at low temperatures. At high temperatures, the off-centre oxygen atoms are likely to be disordered, with little effect on the lifetime as discussed for isolated oxygen vacancies above. At low temperatures, the off-centre atoms may arrange themselves into ordered ('zig-zag') patterns, with associated vacancies for non-zero x. The ordered structure leads to stronger localisation *along* the Cu–O chains, with a concomitant increase in the lifetime. However, as the reported displacement amplitudes are small ($\simeq 0.05$ Å), the calculated effect on the lifetime is small ($\simeq 1$–2 ps) and does *not* explain the reported change. Our conclusion then is that the temperature dependence of the lifetime is due to competition between trapping into oxygen-deficient areas and thermal detrapping from them.

In summary, comparison of detailed calculations for the positron states in $YBa_2Cu_3O_{7-x}$ with experimental results points to the presence of metal vacancies in

sintered samples. Oxygen vacancies are only weak traps and cannot account for the observed long lifetimes. It is also shown that positrons will have a strong affinity to oxygen-deficient areas, and consequently will favour those present in real single crystals. The observed temperature dependence of the lifetime components below T_c is associated with thermal detrapping from shallow traps in the oxygen subsystem.

References

[1] Bednorz J G and Müller K A 1986 *Z. Phys.* B **64** 189
[2] Hoffmann L *et al* 1988 *Europhys. Lett.* **6** 61
[3] Jean Y C *et al* 1987 *Phys. Rev.* B **36** 3994
[4] Usmar S G, Sferlazzo P, Lynn K G and Moodenbaugh A R 1987 *Phys. Rev.* B **36** 8854
[5] Dresden M 1954 *Phys. Rev.* **93** 1413
    Stump R and Talley H E 1954 *Phys. Rev.* **96** 904
[6] Harshman D R *et al* 1988 *Phys. Rev.* B **38** 848
[7] Ishibashi S *et al* 1988 *Phys. Lett.* **128A** 387
[8] Smedskjær L C *et al* 1988 *Physica* B **150** 56
    Nyberg P, Hautojärvi P and Härkönen K 1989 unpublished
[9] Corbel C, Bernede P, Pascard H, Rullier-Albenque F, Korman R and Marucco P 1989 unpublished
[10] Smedskjœr L C *et al* 1988 *Phys. Rev.* B **37** 2330
[11] von Stetten E C *et al* 1988 *Phys. Rev. Lett.* **60** 1069
[12] Puska M J and Nieminen R M 1983 *J. Phys. F: Met. Phys.* **13** 333
[13] Puska M J, Jepsen O, Gunnarsson O and Nieminen R M 1986 *Phys. Rev.* B **34** 2695
[14] Mattheiss L F and Hamann D R 1987 *Solid State Commun.* **63** 395
    Herman F, Kasowski R V and Hsu W Y 1987 *Phys. Rev.* B **36** 6904
[15] Puska M J, Mäkinen S, Manninen M and Nieminen R M 1989 *Phys. Rev.* B at press
[16] Corbel C and Puska M J 1989 *Phys. Rev.* B at press
[17] Beno M A *et al* 1987 *Appl. Phys. Lett.* **51** 57
[18] Renault A *et al* 1987 *J. Physique* **48** 1407
[19] Domengues B, Hervieu M, Michel C and Raveau B 1987 *Europhys. Lett.* **4** 211
[20] Chen C H *et al* 1988 *Phys. Rev.* B **38** 2888
[21] Dlubek G, Brummer O, Yli-Kauppila J and Hautojärvi P 1981 *J. Phys. F: Met. Phys.* **11** 12
[22] Roth G *et al* 1988 *Physica* C **152** 329
[23] Francois M *et al* 1988 *Solid State Commun.* **66** 1117
[24] Crozier E D *et al* 1987 *Phys. Rev.* B **36** 82888
    Zhang Ke *et al* 1987 *Phys. Rev.* B **37** 3375
[25] Horn P M *et al* 1987 *Phys. Rev. Lett.* **59** 2772
[26] Wittlin A *et al* 1987 *Solid State Commun.* **64** 477
    Macfarlane R M, Rosen H and Seki H 1987 *Solid State Commun.* **63** 831
[27] Boolchand P *et al* 1988 *Phys. Rev.* B **37** 3766
    Yuen T *et al* 1988 *Phys. Rev.* B **37** 3770
[28] Gottwick U *et al* 1987 *Europhys. Lett.* **4** 1183
    Cheong S-W *et al* 1987 *Phys. Rev.* B **36** 3913