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A study of positron distribution and annihilation characteristics in $YBa_2Cu_3O_{7-x}$

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Abstract. The positron distribution and lifetimes have been computed for the model structures of orthorhombic $YBa_2Cu_3O_7$, tetragonal $YBa_2Cu_3O_{6.5}$ and tetragonal $YBa_2Cu_3O_6$, which consist of different ordered arrangements of oxygen vacancies. The positron potential was obtained as a sum of the full lattice electrostatic potential and the correlation potential in the local density approximation. The positron wavefunction and the eigenvalue of the lowest-lying itinerant positron state was obtained by solving the Schrödinger equation in the finite-difference scheme. The positron wavefunction displays maxima at the oxygen vacancy positions and it is seen that the positron probes predominantly the oxygen vacancies in the basal plane. By computing the overlap of the positron density with the core and valence electron densities, the positron lifetimes for $YBa_2Cu_3O_7$, $YBa_2Cu_3O_{6.5}$ and $YBa_2Cu_3O_6$ are estimated to be 190 ps, 222 ps and 234 ps, respectively. Calculation of the positron wavefunction and lifetime has also been carried out for a positron localised at an isolated oxygen vacancy along the chain in orthorhombic $YBa_2Cu_3O_7$. The calculated values of lifetimes for different arrangements of vacancies have been compared with the experimental values of positron lifetimes in $YBa_2Cu_3O_{7-x}$ measured after various heat treatments.

In the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ (YBCO), the superconducting properties are strongly dependent on the oxygen deficiency x which can be controlled by suitable heat treatments (Ganguli *et al* 1987, Cava *et al* 1987, Hariharan *et al* 1988). For small values of x, YBCO is in the orthorhombic phase and is superconducting whereas, for larger values of x, the system is in the tetragonal phase and is semiconducting. The oxygen deficiency x with respect to the O_7 structure gives rise to oxygen vacancies O_v which in turn can be ordered or disordered. Information on the O_v and their ordering has been obtained from neutron scattering (Beech *et al* 1987, Capponi *et al* 1987, Beno *et al* 1987) and transmission electron microscopy (van Tendeloo *et al* 1987).

Positron annihilation spectroscopy (PAS) is an established method for the investigation of electronic structure and defect properties of metals and alloys (Brandt and Dupasquier 1983, Hautorjavi 1979). With the advent of high-temperature oxide superconductors, many experiments have been carried out with a view to investigating the changes in the positron annihilation characteristics across the superconducting transition (Jean *et al* 1987, 1988, Usmar *et al* 1987, Sundar *et al* 1988). Recently, PAS has been used to study the O_v in YBCO (Bharathi *et al* 1988a). A measurement of the positron lifetime and Doppler-broadened lineshape parameter I as functions of quench temperature indicated that the dominant change in the positron annihilation parameters occurred in the temperature range 500–600 °C coinciding with the orthorhombic-to-tetragonal transition. The lifetimes in the orthorhombic and tetragonal phases of YBCO

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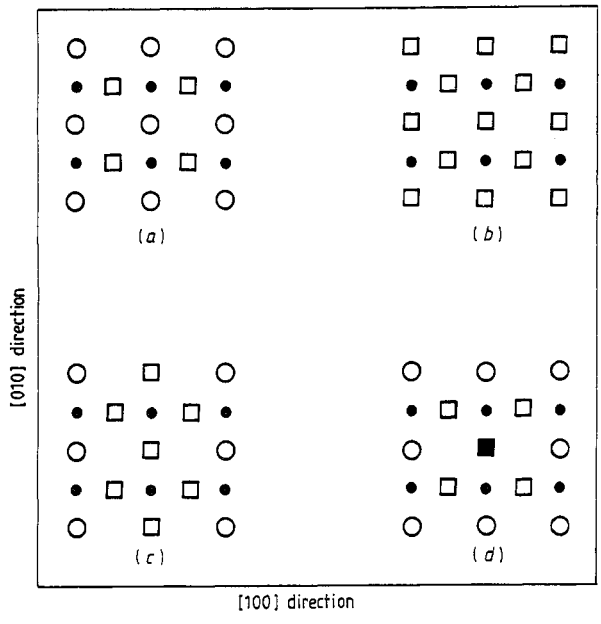

Figure 1. Schematic diagrams of the basal plane of (*a*) $YBa_2Cu_3O_7$, (*b*) $YBa_2Cu_3O_6$, (*c*) $YBa_2Cu_3O_{6.5}$ and (*d*) an isolated oxygen vacancy along the Cu–O chain in $YBa_2Cu_3O_7$: ●, Cu; ○, O; □, O_v.

were observed to be 190 ps and 200 ps, respectively. This difference in lifetime indicates that the natures of O_v, which are probed by the positrons, are different in the orthorhombic and tetragonal phases. In order to understand these results more definitively, it is imperative that a first-principles calculation of the positron distribution and annihilation characteristics be carried out. This has been the motivation for the present calculation in which the positron wavefunction and lifetimes have been calculated for the model structures of tetragonal $YBa_2Cu_3O_6$, $YBa_2Cu_3O_{6.5}$ and orthorhombic $YBa_2Cu_3O_7$. A preliminary account of these results has been discussed by Bharathi *et al* (1988b).

Many schemes exist for the first-principles calculation of the positron distribution and annihilation characteristics at vacancies in metals (Brandt and Dupasquier 1983). One of the most widely used methods is due to Puska and Nieminen (1983), which has been applied to a variety of situations such as isolated vacancies, decorated vacancies, vacancy clusters and impurity atom clusters (Nieminen 1983, Bharathi and Chakraborty 1988). In this method, the potential $V_+(\boldsymbol{r})$ experienced by the positron is written as a sum of the Hartree electrostatic potential due to ions and electrons and the electron–positron correlation potential in the local density approximation:

$$V_+(\boldsymbol{r}) = V_{\text{ion}}(\boldsymbol{r}) + V_{\text{e}}(\boldsymbol{r}) + V_{\text{corr}}(n(\boldsymbol{r})) \tag{1}$$

where $V_{\text{ion}}(\boldsymbol{r}) + V_{\text{e}}(\boldsymbol{r}) = \Sigma_i V_{\text{at}}(\boldsymbol{r} - \boldsymbol{R}_i)$ and $n(\boldsymbol{r}) = \Sigma_i n_{\text{at}}(\boldsymbol{r} - \boldsymbol{R}_i)$. Here $\boldsymbol{R}_i$ refers to the atomic positions. In the calculation of $V_+(\boldsymbol{r})$, the atomic potentials are obtained from Herman and Skillman (1963) after subtracting the exchange contribution to the atomic potential. The correlation potential in equation (1) is obtained from the results of the many-body calculation of the correlation energy of the positron in an electron gas of density $n(\boldsymbol{r})$ (Arponen and Pajanne 1979).

The total positron potential given by the above prescription has been evaluated in a three-dimensional grid containing 1625 atoms with a grid size of 0.36 au. The basal plane of the various structures considered are shown in figure 1. To obtain the positron

Table 1. Calculated values of positron lifetime in $YBa_2Cu_3O_{7-x}$.

System	λ_{core} (ns^{-1})	λ_{val} (ns^{-1})	τ (ps)	E (eV)
$YBa_2Cu_3O_6$	0.5389	3.7245	234	−1.7
$YBa_2Cu_3O_7$	0.7269	4.5251	190	−0.85
$YBa_2Cu_3O_{6.5}$	1.0691	3.4414	222	−1.28
Isolated O_v in orthorhombic phase	2.6075	3.3396	168	+3.5

wavefunction ψ_+, the full three-dimensional Schrödinger equation is solved by the finite-difference method (Puska and Nieminen 1983) in the smallest irreducible part of the Wigner–Seitz cell with the appropriate boundary condition, i.e. $(d\psi_+/dr)|_{W\text{-}Scell} = 0$. After ψ_r has been obtained, the positron annihilation rate is determined by the overlap of the positron wavefunction and the electron wavefunction (Brandt and Dupasquier 1983). The annihilation rate λ is obtained as a sum of the valence electron contribution λ_{val} and the core electrons contribution λ_{core}, i.e. $\lambda = \lambda_{val} + \lambda_{core}$. The annihilation rate λ_{val} from the valence electrons is given by the formula of Brandt and Reinheimer (1971) which takes into account the enhancement of the electron density around the positron:

$$\lambda_{val}\ (ns^{-1}) = \int (2 + 134 n_v(r))|\psi_+(r)|^2\ dr. \tag{2}$$

The annihilation rate from the core electrons is calculated in the independent particle approximation (Brandt and Dupasquier 1983) using

$$\lambda_{core}\ (ns^{-1}) = 16\pi \int |\psi_+(r)|^2 n_{core}(r)\ dr. \tag{3}$$

The above-mentioned scheme for the calculation of positron density distribution $|\psi_+(r)|^2$ and the positron lifetime ($\tau = 1/\lambda$) has been carried out for the model structures of $YBa_2Cu_3O_6$, $YBa_2Cu_3O_{6.5}$ and $YBa_2Cu_3O_7$ (cf figure 1). The unit-cell parameters are taken from Beech *et al* (1987) and Sankara Sastry *et al* (1988). The structure for the $O_{6.5}$ phase is taken from the electron diffraction results of Chaillout *et al* (1988). The atomic positions of Y, Ba, Cu and O atoms are known and, on the assumption of neutral atoms at these sites, the total positron potential $V_+(r)$ (cf equation (1)) is calculated as a sum of the atomic potentials (Herman and Skillman 1963) and the correlation potential obtained from electron gas calculations (Arponen and Pajanne 1979). The positron density distribution, obtained as a solution of Schrödinger equation for the various cases are shown in figures 2–5. Using these positron densities, the total annihilation rate in each structure was calculated as a sum of valence and core electron contributions obtained using equations (2) and (3), respectively. In the calculation of valence annihilation rate λ_{val}, the electrons in the outermost orbitals, i.e. $4d^15s^2$ in Y, $6s^2$ in Ba and $4s^2$ in Cu have been taken to contribute to the valence electron density $n_v(r)$. The electrons in the inner orbitals of Y, Ba and Cu and all the electrons in O have been taken as core electrons and the annihilation rate λ_{core} estimated using equation (3). The positron lifetimes for the various structures and the eigenvalues E of the lowest-lying states are presented in table 1.

Figure 2(*a*) shows the positron density in the basal plane of $YBa_2Cu_3O_7$. Figure 2(*b*) shows the corresponding contour plot, plotted at a spacing of one fifteenth of the maximum density. It is seen that the periodic positron distribution has a maximum at

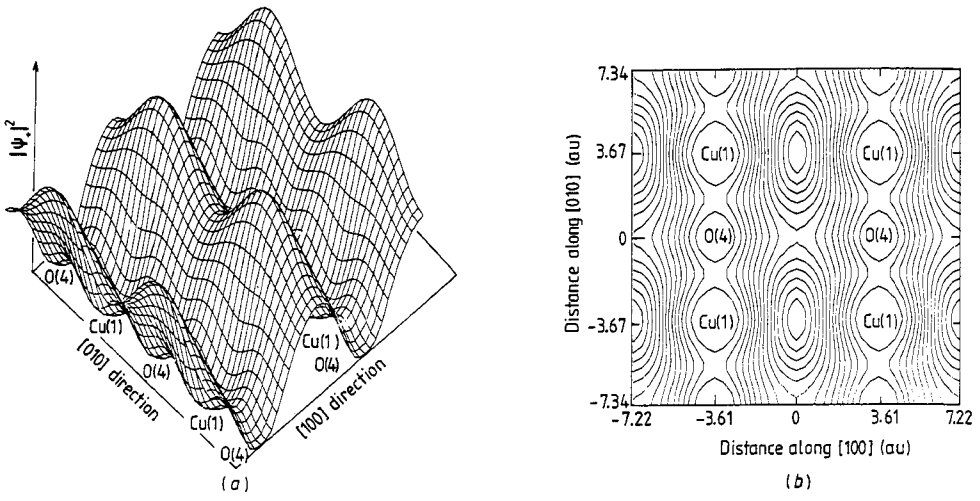

Figure 2. (*a*) Positron density distribution in the basal plane of $YBa_2Cu_3O_7$; (*b*) contour plot of positron distribution plotted at a spacing of one fifteenth of the maximum value which occurs at the oxygen vacancy between the Cu(1) atoms.

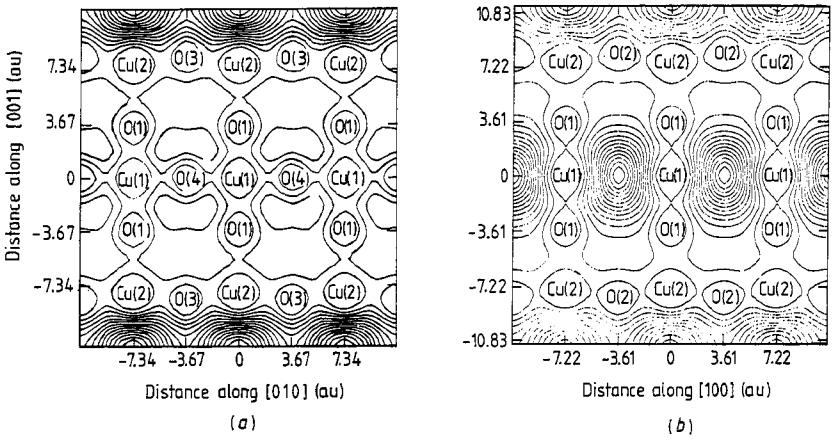

Figure 3. Contour plots of the positron distribution (*a*) in the (100) plane and (*b*) in the (010) plane in $YBa_2Cu_3O_7$. The maxima of the positron density at O_v between the Cu(1) atoms is 33% larger than that in the open space between Cu(2) atoms along the [001] direction.

the O_v between the Cu(1) atoms along the [100] direction. Figures 3(*a*) and 3(*b*) show the contour plots of the positron distribution on the (100) and (010) planes. The atomic positions, following the notation of Beech *et al* (1987), are marked. It is seen that the maxima of the positron distribution occur both at the O_v between the Cu(1) atoms and at the open space between the Cu(2) atoms along the [001] direction. However, the amplitude of the maxima between the Cu(1) atoms is about 33% larger than that between the Cu(2) atoms. This clearly indicates that the positron samples predominantly the O_v in the basal plane of YBCO. By computing the overlap of the positron density with the core electron densities of the various constituent atoms of the unit cell of YBCO, as obtained from Herman and Skillman (1963), the annihilation rate with the core electrons is estimated to be 0.7269 ns^{-1}. The annihilation rate with the valence electrons was estimated using equation (2) to be 4.5251 ns^{-1}. The total annihilation rate is thus

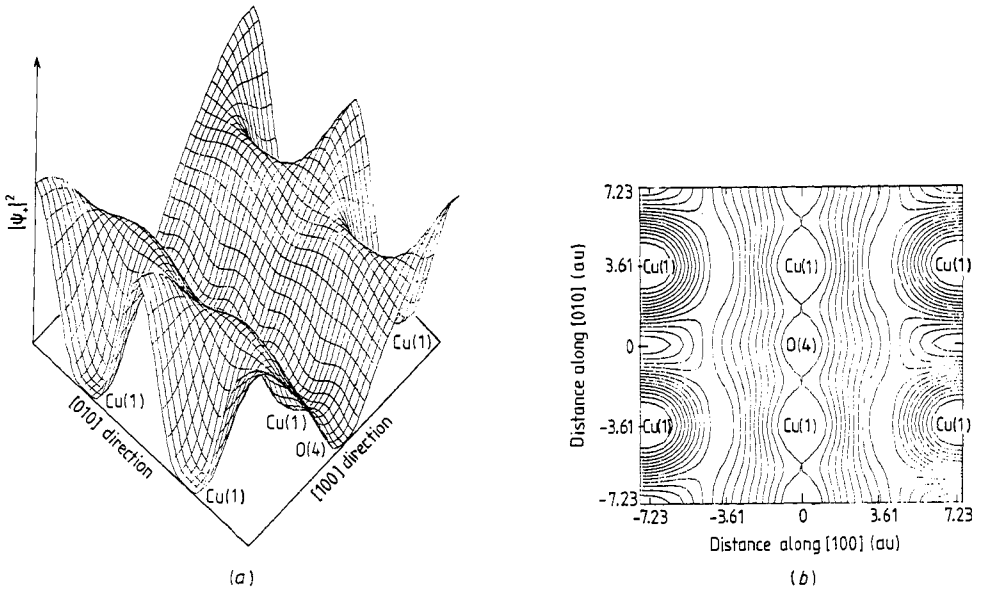

Figure 4. (*a*) Positron density distribution in the basal plane of tetragonal $YBa_2Cu_3O_{6.5}$; (*b*) contour plot of the positron density indicating the maxima at O_v between Cu(1) atoms along the [010] direction.

5.2520 ns^{-1}, yielding a positron lifetime of 190 ps in the orthorhombic phase.

Recently, Turchi *et al* (1988) have computed the positron wavefunction in $YBa_2Cu_3O_7$ by using the variational procedure of Chiba and Tsuda (1974) and Chiba (1976). From a plot of the positron density in the various planes, they conclude that positrons wrap around the Cu–O chains and in particular the Cu(1)–O(4) and Cu(1)–O(1) positions. The region where the probability of finding the positron is a maximum is seen to lie between the two Cu–O chains and runs parallel to the chain direction. In this respect the positron distribution obtained by Turchi *et al* (1988) using a different formalism bears a strong resemblance to the present results (cf figures 2 and 3).

In figures 4(*a*) and 4(*b*) are shown the positron density distribution and the contour plot in the basal plane of tetragonal $YBa_2Cu_3O_{6.5}$. The positron distribution shows maxima at the O_v vacancy positions between the Cu(1) atoms along the [010] direction. Using this $|\psi_+(\boldsymbol{r})|^2$, the positron lifetime in this structure is estimated to be 222 ps. Figures 5(*a*) and 5(*b*) show the positron density distribution and the contour plot in the basal plane of tetragonal $YBa_2Cu_3O_6$. It is seen that the periodic positron distribution has maxima at the O_v between the Cu(1) atoms. Using the $|\psi_+(\boldsymbol{r})|^2$, the lifetime in the tetragonal phase was estimated to be 234 ps.

In addition to the calculation of the positron distribution and lifetimes for various ordered arrangements of vacancies in different stoichiometric compositions of YBCO, calculations have also been performed for an isolated oxygen vacancy along the chain in $YBa_2Cu_3O_7$ (cf figure 1(*d*)). The Schrödinger equation has been solved numerically for the boundary condition that ψ_+ vanishes at a large distance of 14.4 au from the vacancy (in contrast with the periodic boundary condition for the previous case of ordered vacancies). The positron density distribution and contour plot, shown in figures 6(*a*) and 6(*b*), respectively, clearly indicate that the positron density is peaked at the chain oxygen vacancy. When the overlap of the positron density was computed using the electron density, the lifetime of the positron localised at O_v was estimated to be

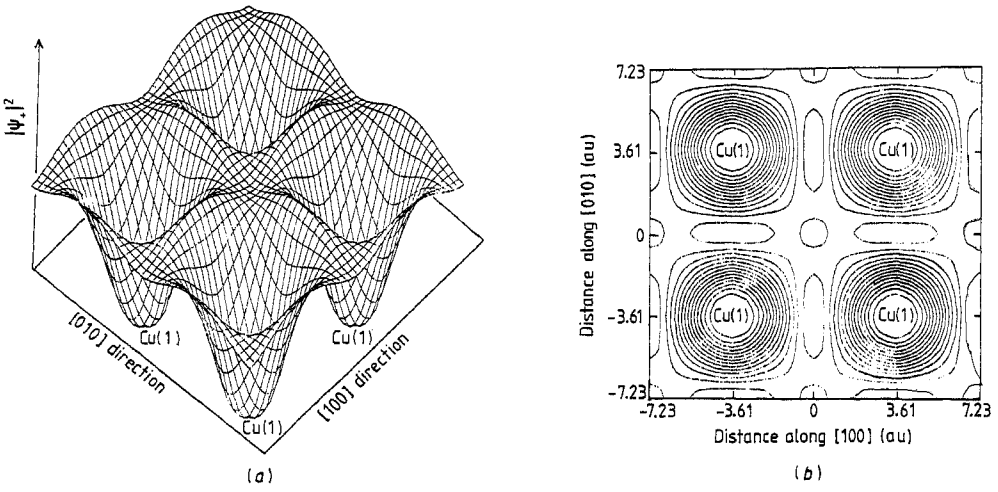

Figure 5. (*a*) Positron density distribution in the basal plane of tetragonal $YBa_2Cu_3O_6$. (*b*) Contour plot of the positron density indicating the maxima at the O_v between Cu(1) atoms.

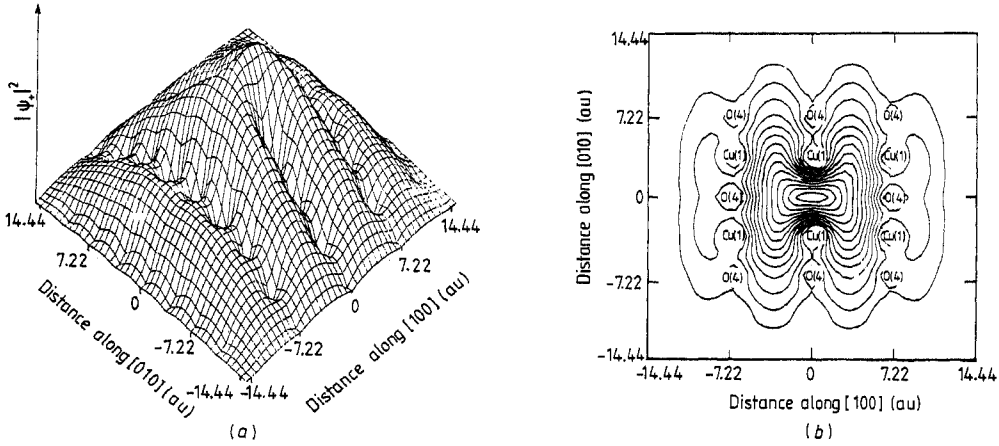

Figure 6. (*a*) Localised positron density distribution at an isolated O_v along the chain in $YBa_2Cu_3O_7$. (*b*) Contour plot of the positron density distribution.

168 ps. On comparison with the lifetime value of 190 ps for $YBa_2Cu_3O_7$, it is seen that the lifetime of the positron in the itinerant state in YBCO is larger than in the localised state. This trend is opposite to what is conventionally observed for vacancies in metals in which the positron lifetime at vacancies is larger than in the Bloch state. This opposite behaviour in YBCO can be understood if we note that in this case the itinerant state is on a vacancy lattice and the localisation of the positron at O_v results in an increase in the overlap of the positron density with the core electrons of the neighbouring atoms. This can be seen by comparing the positron distribution shown in figures 2(*b*) and 6(*b*). The larger annihilation rate of the localised positron with the core electrons is indicated in table 1. Further, the eigenvalue of the positron localised at an isolated O_v along the Cu–O chain is seen to be larger than for the positron of the itinerant state in $YBa_2Cu_3O_7$. This implies that the isolated O_v along the chain is a shallow trap. The presence of such shallow traps, which become effective at low temperatures, may be of relevance in explaining the temperature dependence of annihilation parameters in YBCO (Jean *et al*

Table 2. Experimental values of positron lifetimes in $YBa_2Cu_3O_{7-x}$.

System	Lifetime (ps)	I_2 (%)	Reference
Tetragonal $YBa_2Cu_3O_{6.5}$	200 ± 2	100	Bharathi *et al* (1988a)
Orthorhombic $YBa_2Cu_3O_{7.0}$	190 ± 2	92	Bharathi *et al* (1988a)
Tetragonal $YBa_2Cu_3O_{6.0}$	235	35	Jean *et al* (1987)
Orthorhombic $YBa_2Cu_3O_{6.8}$	220	30	Jean *et al* (1987)
Orthorhombic $YBa_2Cu_3O_7$	210 ± 2	94	Usmar *et al* (1987)
Orthorhombic $YBa_2Cu_3O_7$ single crystal	176 ± 2	100	Jean *et al* (1988)

1987, 1988).

There have been several experimental measurements of positron lifetime in $YBa_2Cu_3O_{7-x}$. Some of the results are given in table 2. While there is some scatter in the lifetime values measured by various groups, the common feature is that the lifetime in the tetragonal phase is larger by about 5% than the lifetime in the orthorhombic phase. For example, our measurements (Bharathi *et al* 1988a) indicate a value of 190 ps for $YBa_2Cu_3O_7$ and 200 ps for tetragonal $YBa_2Cu_3O_{6.5}$. Jean *et al* (1987) have measured a value of 220 ps for orthorhombic $YBa_2Cu_3O_{6.8}$ and 235 ps for tetragonal $YBa_2Cu_3O_{6.5}$. On comparison with the calculated values of the lifetimes shown in table 1, it is seen that there is a good agreement with the experimental results. In particular, the calculated lifetimes reproduce the experimentally observed feature that the lifetime increases with increase in oxygen deficiency. It may be remarked that the observed difference between the lifetimes in the orthorhombic and tetragonal phases cannot be explained from the conventional viewpoint of positron trapping at vacancies acting as independent trapping centres. If the vacancies were to act as independent trapping centres, then, since the difference between the orthorhombic and tetragonal phases is only that they have different concentrations of O_v, there should not have been any difference in lifetime. As a result of the present analysis of positron states in ordered vacancies, it can be stated that the difference between the lifetime of the orthorhombic and the tetragonal phases arises because of the difference between the ordered arrangements of vacancies in the two phases.

To summarise, the present calculations provide a definitive evidence for the fact that positrons probe the ordered O_v in the basal plane of YBCO. Further, different ordered arrangements of O_v in the orthorhombic and tetragonal phases lead to a difference in the positron distributions and lifetimes. The calculated values of lifetimes in the orthorhombic and tetragonal phases are seen to be in good agreement with the experimental results. The isolated O_v along the Cu–O chain acts as a shallow trap characterised by a lifetime smaller than that of a positron annihilating from the itinerant state. The main result of the present calculation, i.e., that positrons are sensitive to an ordered arrangement of O_v assumes significance in the light of recent findings that there exists different ordered arrangements of O_v (de Fontaine *et al* 1987) which can be obtained by suitable heat treatments and that the ordering of vacancies have considerable influence on the physical properties of YBCO (Batlogg and Cava 1987).

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