

Pore size determination by positron annihilation lifetime spectroscopy

BOŻENA JASIŃSKA¹, ANDRZEJ L. DAWIDOWICZ², TOMASZ GOWOREK¹, JAN WAWRYSZCZUK¹

¹Institute of Physics, Maria Curie Skłodowska University, pl. Marii Curie-Skłodowskiej 1, 20–031 Lublin, Poland.

²Department of Chemical Physics, Faculty of Chemistry, Maria Curie Skłodowska University, pl. Marii Curie-Skłodowskiej 3, 20–031 Lublin, Poland.

Two Vycor glasses were investigated using PALS method. The model of pick-off annihilation in cylindrical free volume was applied to evaluate the pore radii. The o-Ps mean lifetime value in the pores changed from 6.5 to 40 ns in one glass, while from 13 to 51 ns in the other (softer) one. The determined pore radii, using a cylindrical shape model, were from 0.5 to 1.4 nm and from 0.7 to 1.6 nm, respectively.

Keywords: positron annihilation, positronium, porous glass, porosimetry.

1. Introduction

In recent years positron annihilation lifetime spectroscopy (PALS) has become a popular tool in investigations of free volumes in solids, particularly in polymers [1]. A simple relation between ortho-positronium lifetime and void radius was proposed by TAO [2] and ELDRUP *et al.* [3].

Positron entering a substance can annihilate directly as a free particle, or it can create a bound state with one of the electrons of the medium-positronium (singlet state – para-Ps, or triplet state – ortho-Ps) which locates in the regions of low electron density, called free volume. In vacuum para-Ps decays with a mean lifetime value $\tau_S = 125$ ps, and ortho-Ps – with $\tau_T = 142$ ns. In the matter the decay rates are altered by the pick-off process (*e.g.*, annihilation of positron bound in positronium with one of the electrons of the surroundings). The pick-off process can shorten the o-Ps mean lifetime even by two orders of magnitude, depending on the free volume size. The model mentioned above [3] gives the possibility to determine the free volume size from the o-Ps lifetime value, if one assume a spherical void shape with radius R . Ps atom is trapped in the potential well whose depth is equal to Ps work function. However, for convenience of calculations it is commonly accepted to substitute that potential by the infinitely deep one with radius $R_0 = R + \Delta R$, where $\Delta R = 0.17$ nm is

an empirically fitted parameter representing the overlap of Ps wavefunction with those of the electrons of the medium. It means that inside the void (below R value) the electron density is assumed zero, and in the layer of ΔR thickness it is constant. The total o-Ps decay constant is

$$\lambda_{\text{o-Ps}} = \frac{1}{\tau_{\text{o-Ps}}} = \lambda_{\text{po}} + \lambda_{\text{T}}, \quad (1)$$

where λ_{po} is the pick-off constant and λ_{T} – the intrinsic decay constant of triplet state.

In the great number of papers related to the positron annihilation in solids, the volume radii of several angstroms in size are observed, and the respective o-Ps mean lifetimes lie in the range from 1 to 3 ns.

2. Cylindrical model

A void of spherical shape with an infinite potential well is only a rough approximation of the real free space in the material. Vacancies, natural free volumes between the molecules existing in perfect crystal, or free spaces in the vicinity of admixtures, are not spherical. As it was shown earlier, even small deformations in the shape of voids change significantly the relationship between $\tau_{\text{o-Ps}}$ and the free volume size [4], [5]. The same tendency is observed in the case of pores produced in amorphous materials. Elongation of the third dimension of the holes by 5–10 times gives values of o-Ps lifetime approaching these of infinitely long channels [6], so it is justified to assume that the pores of the infinite length take a cylindrical shape. The concept of an ΔR layer surrounding a channel of radius R , as in paper [3], can therefore be maintained. The infinitely long capillary model is commonly accepted in physical chemistry.

Another important modification of the Tao–Eldrup model is needed for pores with a radius over 1 nm. This modification is based on the possibility to populate the levels above the ground state in the potential well. The set of levels for a particle in the potential well is characterized by the energies:

$$E_{nl} = \frac{\hbar^2 X_{nl}^2}{2m R_0^2} = 1.90 \times 10^{-2} \frac{X_{nl}^2}{R_0^2} \quad (2)$$

for spherical voids E_{nl} in eV for R_0 in nanometers, and

$$E_{nm} = \frac{\hbar^2 Z_{nm}^2}{2m R_0^2} + E_{\parallel} \quad (3)$$

for cylindrical ones.

In Equations (2) and (3) m is the particle mass, $m_{\text{Ps}} = 2m_{\text{e}}$; X_{nl} and Z_{nm} are the nodes of the respective J_l and J_m Bessel functions; E_{\parallel} is the energy of longitudinal particle motion, not quantized, $E_{\parallel} \approx 0.5kT$. The level diagram for cylindrical and spherical wells is shown in Fig. 1. The longitudinal velocity component does not

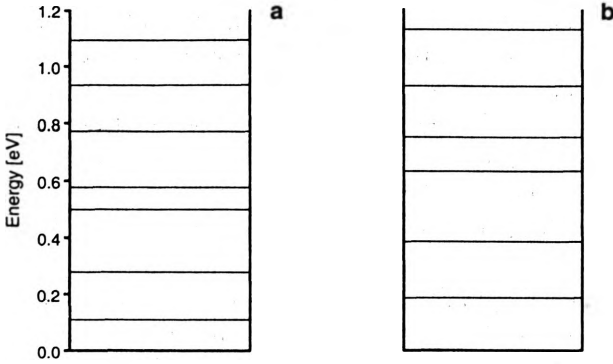


Fig. 1. Energy levels in the potential wells: cylindrical well (a), spherical one (b). A well radius in both cases is equal 1 nm.

influence the overlap of Ps wavefunction with the bulk, thus for an infinitely deep potential and an infinitely long cylinder the decay rate for nm level is

$$\lambda^{nm}(R) = \lambda_b \left(\frac{\int_0^{Z_{nm}R/R_0} J_m^2(r)r dr}{\int_0^{Z_{nm}} J_m^2(r)r dr} \right), \quad (4)$$

where $\lambda_b = 2 \text{ ns}^{-1}$ represents the o-Ps decay rate in the bulk. If thermal equilibrium is achieved, one should observe a single decay rate averaged over populated states

$$\lambda_{po} = \frac{\sum_{i=1}^N \lambda_i(R) g_i \exp[-E_i(R)/kT]}{\sum_{i=1}^N g_i \exp[-E_i(R)/kT]}. \quad (5)$$

Energy E_i can be limited to the quantized part only, E_{\parallel} is the same for all levels, thus it enters into the exponent as a constant, eliminated at normalization.

For example, for radius $R = 1.5 \text{ nm}$ the population of the second level reaches about 10% at room temperature; for such radius R next levels can be assumed empty, and the sum (5) is reduced to two terms only. The larger radius R is, the more levels should be taken into consideration in Eq. (5). With an increasing number of states engaged, for a very large pore cross-section one can try to apply another geometry, *e.g.*, rectangular one. In such a case the wave functions have a simple form of sine waves. The equation for a pick-off rate in a cuboid was given by us [5] for the ground state

and it can be easily extended to higher states by substituting $1/n\pi\sin(nx)$ for $1/\pi\sin x$ and summing the terms like in Eq. (5) up to infinity. This approach used recently intensively by GIDLEY *et al.* [7] shows, however, its advantages at very large transversal dimensions of pores, when the λ_{po} becomes weakly dependent on these dimensions, and one needs to find the relationship between the square side and equivalent pore diameter to compare the PALS results with the classic chemical methods. A full discussion of the modifications introduced in the proposed model is given in papers [8], [9].

In order to test in detail the proposed cylindrical model, a few series of samples with well-controlled pore dimensions have been prepared. For comparison, selected samples were also analysed using liquid nitrogen (LN) desorption and small angle X-ray scattering (SAXS) methods.

3. Experimental

Two initially nonporous Vycor glasses, composed of 7, 23, 70 per cent of Na_2O , B_2O_3 and SiO_2 (first one) and 10, 35, 55 per cent of respective oxides (second one) were investigated. Two stages of treatment were used in order to produce pores: liquation (annealing) in the temperature range from 725 K to 950 K and leaching (etching) in 3N solution of sulphuric acid; the procedure is described in [10].

The positron source, ^{22}Na , was sandwiched between two layers of grained Vycor glass (fraction 70–100 μm), placed into a vacuum chamber and kept under pressure of ~ 0.5 Pa. All measurements were performed at room temperature using a conventional fast-slow lifetime spectrometer with Pilot U scintillators. The time spectrum was recorded in the range 1 μs (4000 channels), the time resolution of the spectrometer was $2\tau_0 \approx 0.300$ ns. The data were processed by LT programme [11].

4. Results and discussion

The time spectrum consisted of several components: $\tau_1 \approx 0.45$ ns due to p-Ps decay and free annihilation (not resolved because of high channel definition), $\tau_2 \approx 1.3$ –1.5 ns due to o-Ps decay in small interatomic voids in the glassy bulk, and the longest-lived τ_3 changing from 6.5 to 50 ns due to o-Ps annihilation in the pores (the lifetime value of this component depends on the glass thermal treatment conditions). The respective intensities I_i are not discussed in this paper.

The third component appeared in the material after liquation only, it means that the raw material was not porous for both glass compositions. Figure 2 shows the τ_3 values as a function of the liquation time and temperature, while Fig. 3 presents the pore radii obtained from Eqs. (4), (5), if one assumes that a parameter $\Delta R = 0.19$ nm according to [8], [9]. Surfaces in the Figs. 2 and 3 were spread over 60 experimental points for both glasses. The experimental uncertainty for each point in Fig. 2 is below 0.5 ns, which means that the pore radii are determined with an uncertainty below 0.1 nm. Comparing these two figures one can see that the radii of the pores change in

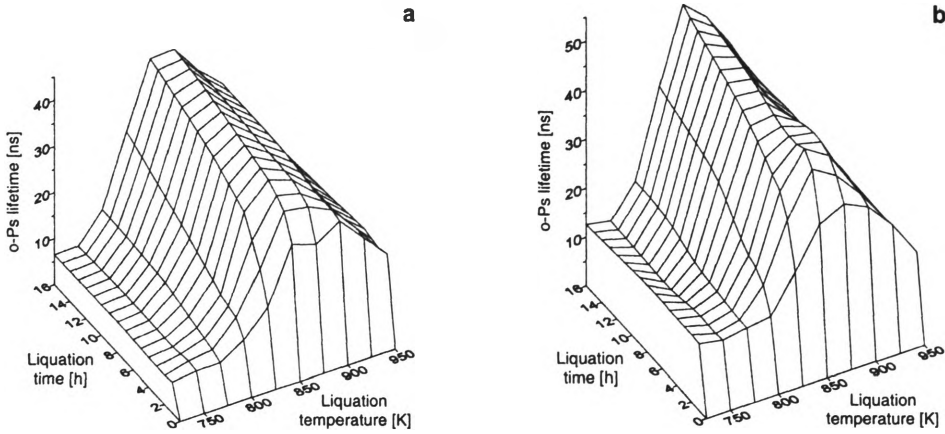


Fig. 2. Mean o-Ps lifetime in the pores vs. the time and temperature of liquation; glass composed of: 7% Na₂O, 23% B₂O₃ and 70% SiO₂ (a), 10% Na₂O, 35% B₂O₃ and 55% SiO₂ (b).

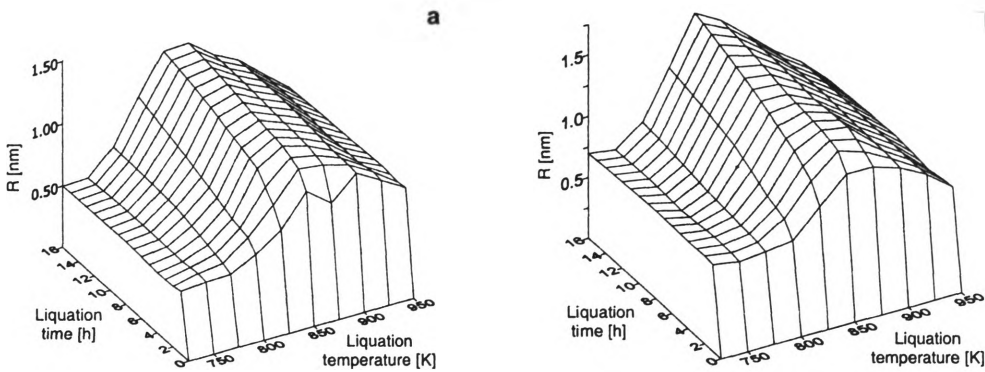


Fig. 3. Pore radius vs. the time and temperature of liquation; the radii values were obtained using the data from Fig. 2 and Eqs. (2) and (3); a, b – the same as in Fig. 2.

a narrower range than the mean lifetime values. For the pores with radii up to 10 nm the PALS method is very sensitive to their cross-section dimension. Doubling of the pore radius from 1 to 2 nm corresponds to the lifetime increase from 26 to 58 ns. Using the measured τ_{o-Ps} values we can examine the tendencies in the pore radius changes with time and temperature of the thermal treatment. The data presented in this paper together with component τ_2 and respective intensity I_i allow us to study a variety of processes occurring in the investigated materials during that treatment, and their rates. A detailed discussion of all processes in 7/23/70 Vycor glass was presented elsewhere [10].

Several glass samples were investigated using LN and SAXS methods. The radii of the pores obtained by these two methods agree rather well with those determined from PALS data. For example, in the harder glass liquated during 16 h at 875 K the average pore radius determined by PALS was 1.15 nm, while it was 1.06 nm by LN;

the SAXS method gave a slightly lower value – 0.83 nm. For a sample liquated 16 h at 925 K we obtained values of $R = 0.95$ nm and 0.91 nm from PALS and LN, while for a sample processed 8 h at 950 K – 0.91 nm and 0.83 nm, respectively. The LN method gives slightly lower values, which can be ascribed alternatively to two factors:

- the measurements done at lower temperature than PALS, or
- LN can see only “open” pores, well accessible for liquid, while positrons can also annihilate in the closed pores. It is also seen that the differences between both presented methods grow with lowering the pore radius. A 1 nm radius is at the limit to the low range of specifying the LN method; the lower limit for the SAXS method is about 0.5 nm. PALS is then the only experimental method which can be used for investigations up to the angstroms-size voids in the material.

5. Conclusions

Taking into account the population of the upper levels in the potential well, the cylindrical model allows us to determine correctly the pore radius. It is to be noted that the contribution of these levels changed with the void radius (discussed in this paper) and with temperature of the sample during the measurements. Thus, one can observe the temperature variations of lifetime, while the classic Tao–Eldrup model does not predict the temperature effects.

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