Ortho-positronium localization in pores of Vycor glass at low temperature

Radosław Zaleski

Maria Curie-Skłodowska University, Institute of Physics, Pl. M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland

E-mail: radek@zaleski.umcs.pl

Abstract. An explanation of a discrepancy between the Extended Tao-Eldrup model and experimental lifetimes observed in some porous materials at low temperatures is presented. The discrepancy is expected in pores with a varying thickness. In such pores thermalized ortho-positronium (o-Ps) could locate in the widest parts, between potential barriers formed by a higher ground energy levels in the narrower parts of the pore. Such an effect can occur, if the energy, which o-Ps can obtain from thermal excitation, is not sufficient enough to pass the energy barrier (i.e., at low temperatures). As a consequence, the lifetime of a localized o-Ps is characteristic for the widest part of the pore only, and not to the averaged width, which can be observed when o-Ps has the ability to move freely along a pore. The problem is discussed basing on the temperature dependence of the results for Vycor glass obtained by o-Ps annihilation lifetime spectroscopy. Additionally to the mean lifetimes, the width of the lifetime distribution in the component is taken into account in the discussion.

1. Introduction

Positronium (Ps) is an exotic atom, similar to hydrogen, where a positron plays the role of a proton. This antiparticle-particle system is unstable due to intrinsic (with its own electron) or pick-off (with an electron from a surroundings) annihilation [1]. This second process concerns mostly long-lived ortho-positronium (i.e., state of Ps, where a positron and an electron have parallel spines) and it makes o-Ps interesting for material studies. However, in order to correctly interpret the data obtained from o-Ps used as a probe, its behavior in the material has to be known as well as it is possible.

A relatively new method of material study is positron porosimetry based on positron annihilation lifetime spectroscopy (PALS) [2-6]. This method is dedicated to the reconstruction of pore size distributions from the PALS spectra. The extended Tao-Eldrup model [7] is used to transform o-Ps lifetimes to pore sizes. An additional calculation scheme based on a simple model [8,9] is used for the transformation of o-Ps component’s intensities to the volume of the pores of a particular size. The main advantage of this technique is the possibility to perform measurements in various conditions (e.g., a wide temperature range [10-13], various mechanical pressures [14] or in the presence of a gas [15-17]). Nevertheless, positron porosimetry still requires testing until it can be established as commonly used technique for the characterization of porous material.

The most disturbing discrepancy from the predictions of the models used in positron porosimetry is the elongation of the o-Ps lifetime at low temperatures [11,12,18]. This effect is not common for every porous material (e.g., it is not observed for porous polymers [9], polymer-silica composites [19] and is also negligible for most of the ordered porous silica materials [20]). It suggests that it is not a problem
with the model assumptions, but it is the result of a specific o-Ps behaviour caused by the properties of the materials. Among the possible sources of uncommon o-Ps lifetime are chemical bounds of positronium (which need to be verified in the future) or physical effects influencing the observed lifetimes.

One of the physical effects, which can distort the expected o-Ps lifetime is positronium migration observed, particularly, in relatively large free volumes, such as mesopores [21-24]. However, o-Ps migration, besides distorting positron porosimetry results, can also be beneficial, if it is fully understood and described. The migration of o-Ps from open pores makes positron porosimetry results complementary to standard sorption techniques [6], which are sensitive only to open pores. Moreover, in experiments like AEGIS or GBAR production of positronium dedicated for antihydrogen creation relies on the migration of o-Ps outside the open mesopores [25,26].

An explanation of the unexpected low temperature o-Ps lifetime elongation, using assumption that this effect is connected with the migration of o-Ps, will be presented in this paper.

2. Experimental

2.1. Experimental methods

The conventional fast-slow delayed coincidence spectrometer was used for the PALS measurements. Its detectors were equipped with BaF$_2$ scintillators. The energy windows covered both photopeak and energies of about 150-200 keV below Compton edge in order to obtain a high overall coincidence rate and, first of all, highest possible contribution of three gamma annihilation events in the spectrum. The positron source, made of $^{22}$Na (0.4 MBq) enclosed in a Kapton envelope, was surrounded by two layers of the sample. A sample holder was placed on the copper rod, which could be cooled by liquid nitrogen when necessary. The main temperature regulator was a heater placed inside the rod, just below the sample holder. The current flowing through the heater was controlled by a Shimaden FP 21 unit, which allowed us to obtain temperature stability ±0.1 K. A vacuum below 0.1 Pa was maintained in the sample chamber by a turbo-molecular pump. It allowed the preventing of both the o-Ps to p-Ps conversion in the presence of oxygen and the contamination of the pore surface.

The total count number in each spectrum slightly exceeded $10^7$. The lifetime spectra were initially analysed numerically by Bayesian methods using the MELT routine [27], which allowed us to find the total number of components in the spectrum as well as the lifetime distributions. Thereafter, fitting of the coefficients of a spectrum model (assumed basing on the MELT results) was performed by the LT programme [28]. This second type of analyses diminished the scatter of the results. The time resolution function was approximated by two Gaussian functions giving together FWHM ~ 280 ps. Except the o-Ps components described later, para-positronium $\tau_1 = 120-140$ ps and free positrons $\tau_2 = 400-600$ ps components were found.

Independent from PALS, a material characterization was performed by measuring the nitrogen adsorption/desorption isotherms at 77 K with the use of AUTOSORB-1CMS adsorption analyser (Quantachrome Instruments). The specific surface area ($S_{BET}$) of the sample was found using the BET method in the relative pressure $p/p_0$ range of 0.05 to 0.3. The total pore volume ($V$) was estimated from the amount of nitrogen adsorbed at the relative pressure of 0.99. The mesopore diameter at the maximum of the distribution was found using the Barrett-Joyner-Halenda method ($D_{B,H}$) and alternatively using the Density Functional Theory equilibrium model for cylindrical pore geometry ($D_{DFT}$).

2.2. Material

The initial Vycor glass was prepared by melting NaNO$_3$, Na$_2$B$_4$O$_7$ and SiO$_2$ (from Brazilian quartz) at 1725 K. The homogenous mixture was then rapidly cooled in water resulting in solid material, which was then grinded to a fine powder. The glass obtained was composed of 7% Na$_2$O, 23% B$_2$O$_3$ and 70% SiO$_2$. Afterwards, the material was heated at 770 K in order to demix its components (liquation process). The structure of pores was created by leaching the cooled glass in an acidic bath, which
removed alkali-borate phase from the material leaving empty spaces (i.e. mesopores) surrounded by walls made mostly of SiO$_2$ [29].

Characterization of the obtained Vycor glass by the nitrogen sorption method showed that its specific surface area $S_{BET} = 297$ m$^2$/g and total pore volume $V = 0.207$ cm$^3$/g. Depending on the method used for the determination of the most probable pore size $D_{BJH} = 2.3$ nm or $D_{DFT} = 3.1$ nm.

3. Results and discussion

Numerical analysis of the positron lifetime spectra of the Vycor glass revealed three o-Ps components. The origin of the shortest-lived one ($\tau_3 = 1.7$-2.2 ns, $I_3 = 4$-7%) are undoubtedly free volumes in the glass structure, between the atoms of amorphous SiO$_2$. Likewise, the presence of the medium-lived component with a lifetime scattered around 14 ns and a low intensity ($I_4 = 1$-3%) is probably caused by the existence of micropores (e.g., microcracks) in the material. The most interesting, from the point of view of the present study, is the long-lived component reflecting the annihilation of o-Ps in the mesopores produced by leaching.

Above 220 K, the long-lived component’s lifetime agree very well with predictions of the ETE model (Fig.1), which were calculated assuming a cylindrical pore shape of diameter $D = 2.8$ nm and the value of the empirical parameter (required by the model) $\Delta = 0.193$ nm [30]. The deviation from the curve predicted by the model is visible below 220 K. Instead of diminishing changes of the lifetime with decreasing temperature, it increases very fast, reaching a value 30% larger than expected at the lowest achieved temperature of 106 K. This value of lifetime according to the ETE model corresponds to $D = 3.4$ nm, a diameter 20% larger than the one calculated at temperatures above 220 K. A change of the material structure leading to such growth of the pores is highly improbable, and it was not observed in the results of the nitrogen sorption method at an even lower temperature of 77K. Therefore, the effect should be ascribed to special o-Ps behavior in the Vycor glass.

The intensity of the longest-lived component increases with temperature from 19% to 28% allowing us to determine the lifetime of this component with a sufficient accuracy. The increase of the intensity reflects the changes of the positron mobility, which rises with temperature, causing a higher

Figure 1. Temperature dependence of the o-Ps components lifetime and intensity. Lines represent predictions of the ETE model for cylindrical pores with diameter 2.8 nm (solid) and 3.4 nm (dashed).

Figure 2. The distribution of lifetimes (a) in the longest-lived component obtained by MELT and the relative distribution of pore sizes (b) calculated using the ETE model form the presented distribution of lifetimes at 106 K (dashed line), 223 K (dashed-dotted line) and 463 K (solid line).
probability of a positron encountering a mesopore, which is then followed by o-Ps creation [31]. The deviation from this dependence is observed below 220 K, in the same temperature range where the lifetime disagrees with the ETE model. However, almost constant intensity in this region is most likely a consequence of different detection efficiencies of three-gamma and two-gamma annihilation. Much longer lifetime, observed at low temperature, is accompanied with increased ratio of three-gamma to two-gamma annihilation. Wide energy window in the stop detector results in more efficient registration of three-gamma events comparing to two-gamma ones. Therefore an intensity is dependent not strictly on number of o-Ps formed in a particular free volume, but also, to a lesser extent, on their lifetime. This is probably a reason of the intensity distortion at low temperatures, where large changes of lifetime are detected. Elongation of the lifetime with temperature decrease causes artificial increase of the intensity, which seems to be constant instead of the continuation of its decrease.

A more detailed investigation of the longest-lived component was performed using Bayesian methods, which give a quasi-continuous intensity distribution over a dense lifetime grid (Fig.2a). The distributions in the spectra above 220 K are both quite wide (FWHM ≈ 7 ns), while a 2-3 times narrower peak (FWHM ≈ 2 ns) is observed at 106 K. Positron porosimetry calculation schemes [9] allow the reconstruction of a pore size distribution at chosen temperatures (Fig. 2b). As it was found before, the pore size at the maximum of the distribution is in very good agreement with each other for temperatures above 220 K, while at low temperatures the maximum is definitely shifted towards larger pore size. Moreover, the width of a pore size distribution is similar for larger temperatures. The difference between the width of the lifetime distribution obtained at 203 K and 463 K is most likely cause by an inaccuracy of the MELT analysis rather than a result of a physical effect. However, the width of the distribution is undoubtedly much narrower for 106 K. Moreover, it is significant that low temperature distribution is located within the tail of the distributions found for temperatures above 220 K. It would suggest, that o-Ps annihilates only in the largest pores at low temperature, while it can annihilate in pores of various sizes at higher temperatures.

Figure 3. Several lowest energy levels of a particle (e.g., positronium) in a rectangular potential well of depth 3 eV (dotted lines). A cylindrical shape of the potential well with a diameter of 2.8 nm (left) and 3.4 nm (right) is assumed. Filled parts of the lines show the probability of energy levels occupation by the thermalized particle at 106 K (down), 223 K (middle) and 463 K (top).

In order to find the origin of such an effect, the occupation of energy levels by positronium at various temperatures trapped inside the cylindrical pores of various size was investigated (Fig.3). A square potential well with depth 3eV [32,33] was assumed. It is worth noticing, that the depth of the
well is not a very important parameter, because the difference between the energy levels in a finite well of 3 eV depth and an infinite one is almost constant and less than 8% for the presented energy levels. Two diameters of the well were investigated: 2.8 nm, the mean size found by PALS, which is close to an averaged pore size from nitrogen sorption, and 3.4 nm, the size of pores found at 106 K. The difference between energy levels for these both pore sizes is easy to observe. The ground energy level in the smaller pore is equal to about 70% of the energy in the larger one. Differences between the energies of the excited states are even larger. The probability of energy levels occupation by thermalized positronium at various temperatures can be determined applying the Boltzmann distribution to the energy level structure, in the same way as it was done in the ETE model. Results presented in Fig.3 show, that even at 463 K only several energy levels can be populated by positronium with a significant probability. Only the two lowest energy levels can be populated at 223 K, and practically only the ground level is populated at 106 K. This quantum property of positronium trapped in the well can help in explaining the discrepancy between the ETE model and the experimental results at low temperature.

The wide distribution of pore sizes, like the one observed in the Vycor sample, can be interpreted in two ways for the cylindrical pores: pore width is different in each pore, but uniform along a pore, or pore width varies along a pore (Fig.4). The second case is much more probable for Vycor glass, where pores created during the leeching form an interconnected, disordered structure. The energy levels of positronium trapped in such pores change fluently along a pore between energy level configurations similar to the ones presented in Fig.3. As long as positronium at high temperatures can occupy excited energy levels, a transfer from wider pores to the narrower ones requires gaining some thermal energy form the wall if o-Ps stays on the same level or losing some energy, if o-Ps changes to a lower level. Since it was proven that during its lifetime o-Ps changes the occupied level many times [7], migration of o-Ps along the pore is almost uninterrupted. Therefore, its lifetime is averaged over lifetimes characteristic for the pores with random sizes, which Ps passes during its lifetime. In contrary, o-Ps almost certainly occupies the ground level at low temperatures. There is no thermal energy which can be acquired by o-Ps when it encounters smaller a pore fragment with a higher energy ground level. For that reason o-Ps becomes trapped in the widest part of the pore (Fig.4) and annihilates with a lifetime characteristic for this part of the pore only. According to the explanation presented above, the systematic increase of the longest-lived component lifetime with decreasing temperature observed in Fig.1, would be a result of successive fractions of the narrowest pores getting inaccessible for o-Ps. In other words, it can reflect a diminishing probability of finding o-Ps inside narrower pores, as its movement from the wider part of a pore to the narrower ones is less and less probable comparing to the movement in the opposite direction when temperature decreases.

Figure 4. A schematic representation of the probability of finding o-Ps in the pore of Vycor glass at high (left) and low (right) temperatures.

4. Conclusions

Elongation of the o-Ps lifetime at low temperatures can be attributed to o-Ps localization in the wider parts of the pores. This effect should be observed in the pores which have varying, highly non-uniform width. The temperature below which this effect occurs, should depend on the narrowest pore size (i.e. on both mean pore size and width of pore size distribution), because the distance between the energy levels depend on the pore size. The temperature, below which deviation is observed, should be lower
for larger pores or for narrower pore size distribution. Observation of these relations in various porous materials can verify the presented model.

It is highly unlikely that this effect explains all deviations from the ETE model. Nevertheless, it should be taken into account during the characterization of porous solids. It can provide, or at least verify, some information about material structure, which are the width of pore size distribution and the uniformity of single pore thickness. The property of pores with varying thickness, which consist in letting through only positronium with energy above some threshold could be useful for some applications where energy of positronium emitted from pores is important (e.g. antihydrogen production). A porous material with tailored pore outlets can provide o-Ps with a narrow energy distribution.

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