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Testing the Extended Tao–Eldrup Model. Silica Gels Produced with Polymer Template

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The temperature dependence of *o*-Ps lifetime in the pores calculated from extended Tao–Eldrup model was compared to the experimental data, collected for a set of silica gels synthesized using the polymer template technique. For the sample with average pore radii 2.0 nm rather good agreement between the model and experiment was found. For the sample with narrow pores (near 1.0 nm) the lifetime spectrum was complex. Except the range of highest temperatures the lifetimes are far from model calculations.

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1. Introduction

Positron annihilation lifetime spectroscopy (PALS) is often applied to determine the size of subnanometer free volumes in solids, mainly in polymers. Commonly accepted relation between *o*-Ps lifetime and void radius follows from the Tao–Eldrup model [1]. The decay probability is assumed proportional to the overlap of Ps wave function in zero-point level with the surrounding bulk.

In 1997 our group proposed to take into account the *o*-Ps annihilation from excited states of a particle in the potential well, extending the Tao–Eldrup model toward larger free volumes [2–4]. In the state of equilibrium the observed decay constant is

$$\lambda_{o-\mathrm{Ps}} = \frac{\sum_i \lambda_i g_i \exp(-E_i/kT)}{\sum_i g_i \exp(-E_i/kT)}, \tag{1}$$

where λ_i, g_i, E_i are decay constant, statistical weight and energy for i-th level, respectively. Following Tao–Eldrup approach, for spherical voids

$$\lambda_i = 2 \int_{X_{nl}R/(R+\Delta)}^{X_{nl}} j_l^2(r) r^2 \mathrm{d}r \Big/ \int_0^{X_{nl}} j_l^2(r) r^2 \mathrm{d}r \tag{2}$$

and for capillaries

$$\lambda_i = 2 \int_{Z_{nm}R/(R+\Delta)}^{Z_{nm}} J_m^2(r) r \mathrm{d}r \Big/ \int_0^{Z_{nm}} J_m^2(r) r \mathrm{d}r, \tag{3}$$

where X_{nl} and Z_{nm} are the n-th nodes of the Bessel functions j_l and J_m, respectively. Δ is an empirical parameter related to the penetration of Ps wave function into the bulk and usually assumed 0.18 nm (the value of λ_i is given in ns^{-1}). The free volume can be also approximated by rectangular void [5, 6].

This version of the model (extended Tao–Eldrup model, ETE) allows:

- to apply PALS to relatively large free volumes (e.g. whole range of mesopores),
- to explain the strong temperature dependence of *o*-Ps lifetimes in porous media (decrease with the rise of temperature).

The aim of this paper is to compare the model predictions with experimental results for selected group of silica gels. Below we discuss two examples of silica gel with essentially different pore diameters.

2. Experimental

The samples of mesoporous silica were prepared using the non-ionic triblock copolymer Pluronic PE 10500–$(\mathrm{EO})_{36}(\mathrm{PO})_{56}(\mathrm{EO})_{36}$ (BASF Poland) as a template and tetraetoxysilane (TEOS) as a silica source, according to a procedure being a modification of the method described in the papers [7, 8]. The weighted amount of copolymer was dissolved in HCl solution and stirred for 45 min at 308 K. Then, TEOS was added and the mixture was stirred again for 20 h. In the case of sample A the molar relation of TEOS to copolymer template was 66:1; for sample B it was equal to 53:1. In the case of sample A 1,3,5-trimethyl-benzene (TMB) was added to the reaction mixture as pore expanding agent (the molar proportion of TMB to polymer was equal to 38:1). The aging was conducted for 24 h at elevated temperature 343 K. Finally, the synthesized product was thoroughly washed in bidistilled water, dried and calcined at 870 K for 6 h. All syntheses were performed at the Department of Adsorption, Faculty of Chemistry, UMCS.

The sandwich of grained samples and positron source (^{22}Na) was placed in a vacuum chamber in order to prevent the *ortho-para* conversion of positronium due to oxygen in air. The chamber was viewed by two scintillation counters coupled to a standard fast-slow delayed coincidence spectrometer. Time base was 1 μs, resolution 0.35 ns. The spectra (containing 1.5×10^6 coincidences each) were processed using the LT programme [9], fitting the function

$$N(x) = \int_0^\infty P(x-t) \sum I_i F_i(t) \mathrm{d}t, \tag{4}$$

where P is the instrumental resolution function, I_i — relative intensity of i-th component in the spectrum, F_i can be in the form of discrete component, $F_i = \lambda_i \exp(-\lambda_i t)$, or continuous λ distribution in log-Gaussian form

$$F_i(t) = \frac{1}{\sigma_i \sqrt{2\pi}} \int_0^\infty \exp\left[-\frac{\ln^2(\lambda \tau_{\mathrm{p}i})}{2\sigma_i^2}\right] \exp(-\lambda t) \mathrm{d}\lambda. \tag{5}$$

In the spectrum processing some components were assumed discrete: p-Ps decay, annihilation of free positrons, decay of o-Ps trapped in small silica imperfections (≈ 1.5 ns). The o-Ps component in the pores was in the form of distribution, as there is certain distribution of pore radii. The LT programme gives in such a case the lifetime at the peak of distribution τ_{p}. The distribution in log-Gaussian form is not symmetric, thus one can calculate also the average lifetime $\langle\tau\rangle$, according to the equation

$$\langle\tau\rangle = \tau_{\mathrm{p}} \exp(\sigma^2/2). \tag{6}$$

Both τ_{p} and $\langle\tau\rangle$ are shown in Figs. 1 and 3.

The sample chamber was placed at the tip of copper rod which could serve as a cold finger of a cryostat; just below the sample container there was a coil, connected to a power supply controlled by Shimaden FP 21 regulator and the thermocouple inside the sample chamber. The temperature could be set in the limits 110–480 K with the accuracy of 0.5 K.

3. Results and discussion

In this paper we were interested in the long-lived part only, in its changes with temperature. Therefore, we have analysed the tail of distribution only, from the delay 40 ns upwards, fitting to it one component with λ distribution (plus random background). This way we omitted all short-lived components and also neglected the range of delays in which the distortion of spectrum can appear due to non-completed thermalization process.

3.1. Sample A

Figure 1 shows the experimental data from LT fit for the sample A for which the liquid nitrogen (LN) adsorption data (Fig. 2) give the pore radius at the peak of distribution $R = 2.0$ nm. Experimental data are shown in two versions: lifetime value at the peak of distribution τ_{p} and mean value $\langle\tau\rangle$. For comparison, the ETE model curves are drawn assuming cylindrical geometry and $\Delta = 0.18$ nm as

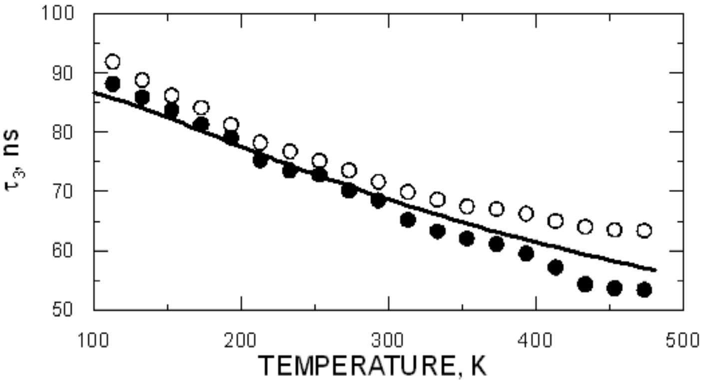

Fig. 1. Sample *A*. The lifetime in the peak of distribution τ_p (full circles) and average lifetime $\langle\tau\rangle$ (open circles) as a function of temperature. Solid line shows the expected lifetime calculated using ETE model for $R = 2.0$ nm.

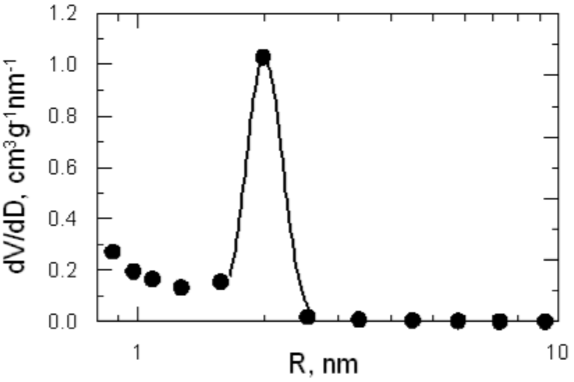

Fig. 2. The distribution of pore radii in sample *A* obtained from liquid nitrogen adsorption.

proposed in Ref. [6]. The solid line corresponds to R as found in LN measurements, 2.0 nm. It is seen that the model curve runs between τ_p and $\langle\tau\rangle$ data or very close to them. It means that the model fits rather well to the data. Let us note that the LT programme does not fit the real λ distribution, but assumes *a priori* the log-Gaussian shape. However, there is a general feature, seen in other experiments of this kind, to observe the slope $\partial\tau_\mathrm{p}/\partial T$ (or $\partial\langle\tau\rangle/\partial T$) greater than expected. The picture is very similar to that obtained earlier [3] for commercial Si40 silica gel (Merck) whose pore diameter is close to that in our sample.

3.2. Sample B

In the case of very narrow pores the LN adsorption porosimetry gives only a rough estimate of radii; for our sample *B* it is 0.9–1.2 nm. At the radius 1 nm the spacing of levels in the well almost excludes the population of upper levels, the situation resembles the classic Tao–Eldrup one-level model. Expected change of *o*-Ps lifetime from lowest to highest temperature is by 2 ns only. The experimental temperature dependence of τ_{p} and $\langle\tau\rangle$ (analysed this time from 20 ns delay upwards) does not fit to the model. As one can see in Fig. 3 the model curve (assuming $R = 0.9$ nm) approaches the experimental data in the highest temperature region only. The variance of the fit is for all points rather bad, like 1.12–1.25. Therefore, one can suppose that more than one component is present. Two component fit is shown in Fig. 4. One of components resembles the model curve, however the change of τ_{p} from 110 K to 470 K is still 6 ns. The other, long-lived, is not easy to

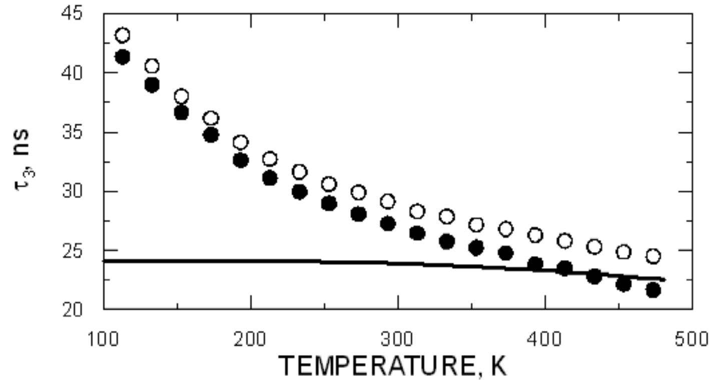

Fig. 3. Sample *B*. The lifetime in the peak of distribution τ_{p} (full circles) and average lifetime $\langle\tau\rangle$ (open circles) as a function of temperature. Solid line shows the expected lifetime calculated using ETE model for $R = 0.9$ nm.

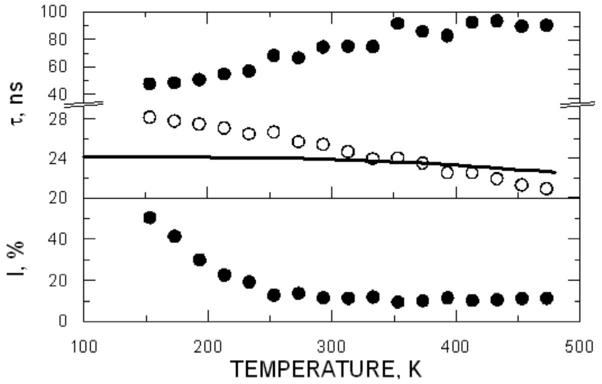

Fig. 4. Sample *B*. Two-component fit to the long-lived part of the spectrum. Solid line is the ETE model curve for $R = 0.9$ nm. Upper part — lifetimes of both components; lower part — relative intensity of longest-lived component.

explain. It dominates at low temperatures, thus one could suppose that it follows from the pre-thermalization effects. However, an excess of positronium in high levels should give an opposite effect — shortening of τ.

4. Conclusions

In the case of sample with the pore diameter about 2 nm the model gives rather good estimate of *o*-Ps lifetime. In the sample with small pores we observe an additional component which has no simple explanation. It is not a unique exception from ETE model, similar effect was observed earlier in some Vycor glass samples [10]. The ETE model takes into account two processes only: pick-off and self-annihilation. There are some other processes which can influence the final value of lifetime. One of them is *ortho-para* conversion, which was eliminated by us by performing the measurements in vacuum, however, chemical reactions and in particular adsorption of residual gases on the pore surface, as well as adsorption of positronium itself can lead to the changes of annihilation probability. A drastic example of such distortions is given in the paper by Uedono et al. [11].

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