On the Mathematical Approaches to Multi-state PAL Models for Porous Solids

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Abstract - **The mathematical approaches for all positron annihilation processes in porous solids for electronics are performed within multi-channel model, which include positron trapping modes and positronium decaying.**

Keywords – **Mathematical model**, **Positron trapping**, **PAL channels**

I. INTRODUCTION

Positron annihilation lifetime (PAL) spectroscopy is one of the most powerful experimental methods for studying of structurally intrinsic voids in solids: vacancy-like defects and some their extended modifications (clusters, agglomerates, micro- and nanovoids, etc.) in "traditional" single-crystal semiconductors and insulators [1]. However, this method was rarely used to porous materials through complication in interpretation of the obtained results and deficiency of mathematical models describing processes in such solids. The aim of this work is the mathematical describing of all PAL processes in porous solids (nanoporous ceramics, polymers, etc.) within multi-channel model, which include positron trapping modes and positronium (Ps) decaying.

II. POSSIBLE POSITRON TRAPPING MODELS FOR FINE-GRAINED SOLIDS

The first results of PAL methods using for fine-grained solids were presented by scientific school of Krause-Rehberg R. [1]. The best fitting was achieved at three-component mathematical procedure: the first component with $t_1=t_b\approx$0.10-0.12 ns were responsible for positron annihilation in undisturbed interior of grains; the second component with $t_2=t_{gb}\approx$0.25-0.35 ns was responsible for positron trapping at grain boundaries; the third one with $t_3=t_{surf}\approx$0.5-0.6 ns was responsible for positron trapping in pores.

The other results in respects to PAL application for fine-grained materials were presented by group of Langhammer H.T. [2]. The Mn-doped $BaTiO_3$ ceramics were investigated, the best fitting being achieved if two-component procedure with arbitrary lifetimes is used.

At studying of temperature-sensitive spinel ceramics and using experience of previous works [1-2] we established that the adequate phenomenological description of positron trapping in solids can be developed at the basis of so-called trapping models, which gives quantitative correlation between physically real parameters of positron trapping sites or defects and experimentally determined PAL spectra. The next parameters are usually chosen to describe positron trapping in defect: k_d – positron trapping rate of defect; t_d – positron lifetime in defect, l_d– positron annihilation rate in defect-free bulk; t_b – bulk positron lifetime.

In general, since the defect-related annihilation channels are additional ones to direct annihilation of positrons from delocalized state in defect-free bulk, the above models are conveniently considered as the multi-state positron trapping models. The simple set of differential rate equations are used in order to obtain the total amount of annihilated positrons at time *t* or. The main prerequisites for this procedure are as follows: positrons are not significantly trapped before thermalization (1); defects, which can capture positrons, are distributed throughout the whole structural network (2); there is no interaction between different positron traps.

Take into account our previous results [3], the two-state positron trapping moles we proposed for solids with one-type defect at a very small concentration of nanopores (Fig. 1):

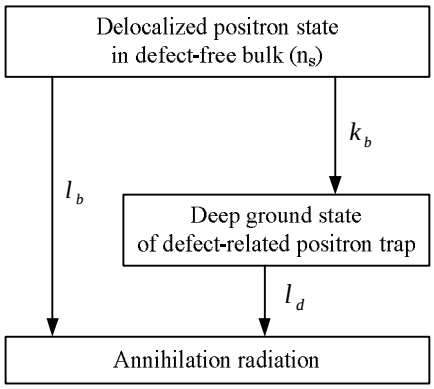

Fig.1 Two-state positron trapping model:
n_s –concentration of positrons in defect-free bulk at time *t*

The set of rate equations for positron capture by one defect (a single open-volume defect):

$$\begin{cases} \dfrac{dn_n}{dt} = -l_b n_b - k_d n_d = -(l_b + k_d) n_b \\ \dfrac{dn_d}{dt} = k_d n_d - l_b n_b \end{cases} . \qquad (1)$$

Its solutions $n_b(t)$ and $n_d(t)$ satisfy the following starting conditions:

$$\begin{cases} n_b(0) = n_0 \\ n_d(0) = 0 \end{cases} \qquad (2)$$

The total amount of annihilated positrons at time *t* (which gives the whole decay spectrum of annihilated positrons) in the case of two fitting components with I_1 and I_2 intensities $(I_1 + I_2 = 1)$ and t_1 and t_2 lifetimes defines by the sum:

$$n(t) = n_b(t) + n_d(t) = n_o(I_1 e^{-\frac{1}{t_1}} + I_2 e^{-\frac{1}{t_2}}) \qquad (3)$$

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After mathematical manipulation, the total amount of annihilated positrons at time *t* is equal to

$$n(t)=\left[n_o\left(\left(\frac{l_d-l_b}{l_d-l_b-k_d}\right)e^{-(l_b+k_d)t}+\frac{k_d}{l_b+k_d-l_d}e^{-l_d t}\right)\right] \quad (4)$$

By comparing expressions (3) and (4), the following two-component fitting parameters can be defined for this two-state positron trapping model:

$$t_1=\frac{1}{l_b+k_d}=\frac{1}{t_b^{-1}+k_d}=\frac{t_b}{1+t_b k_d},\ t_2=\frac{1}{l_d}=t_d, \quad (5)$$

$$I_1=\frac{l_d-l_b}{l_d-l_b-k_d}=\frac{t_d-t_b}{t_d-t_b+k_d t_d t_b}, \quad (6)$$

$$I_2=1-I_1=\frac{k_d}{l_b-l_d+k_d}=\frac{k_d t_d t_b}{t_d-t_b+k_d t_d t_b}. \quad (7)$$

It can be shown that:

$$t_b=\left(\frac{I_1}{t_1}+\frac{I_2}{t_2}\right)^{-1}=\frac{t_1 t_2}{I_1 t_2+I_2 t_1}, \quad (8)$$

$$k_d=I_2\left(\frac{1}{t_1}-\frac{1}{t_2}\right),\ t_{av.}=I_1 t_1+I_1 t_1. \quad (9)$$

If two-state positron trapping model is valid and two-component fitting procedure is applied for mathematical treatment of the experimentally obtained PAL spectra, then the bulk defect-free positron lifetime t_b (8) is greater than the short positron lifetime t_1 ($t_1 < t_b < t_2$), which sometimes is also called the reduced bulk positron lifetime; the long positron lifetime t_2 exactly describes the annihilation of positrons, captured in open-volume defect.

III. Multi-channel PAL model

The main achievement of scientific school of J. Dryzek [4] is the development of the Ps trapping. It was shown that PAL spectra have three main components: annihilation of positron in the free state ($t_1=t_b$ =0,3-0,4 ps); annihilation of para-positronium (p-Ps) ($t_1=t_{p\text{-}Ps}$=125 ps) and annihilation of orto-positronium (o-Ps) localised in pores ($t_3=t_{o\text{-}Ps\text{-}p}$=0,5 ns).

In our work at studying of nanoporous humidity-sensitive $MgAl_2O_4$ ceramics [5] we establish that in the case of porous solids with high concentration of nanopores the best fitting are achieved at three-component procedure: the first component is attributed to positron annihilation in the free state and annihilation of p-Ps ($t_1=t_b+t_{p\text{-}Ps}$); the second component is distinguished from the first one is attributed to trapping in more extended free-volume defects, such as multi-atom vacancy-like clusters, grain boundaries, etc. ($t_2=t_d$); the third component is attributed to "pick-off" channel of o-Ps annihilation in pores ($t_3=t_{o\text{-}Ps}$). Alternatively, the following positron trapping model is possible: the contribution of positron annihilation on defects (single- or double-atom vacancies, dislocations, etc.) will be in the short-time defect-related PAL component (1); the contribution of positron trapping channels through extended free-volume defects with distinguished PAL parameters will be in the second PAL component (2); the contribution of o-Ps "pick-off" annihilation channels in other phases, such as H_2O) will be in the third PAL component (3).

The most possible channels of positron annihilation in fine-grained porous solids are shown on Fig.2.

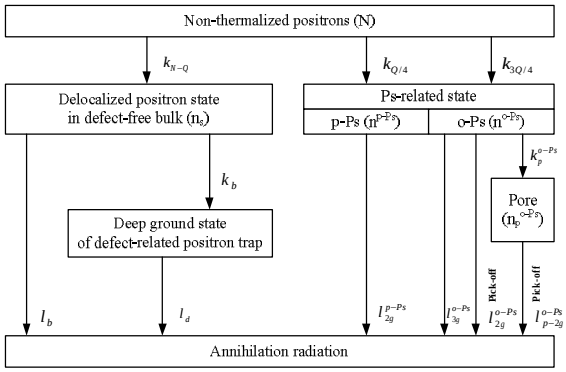

Fig.2 Multi-channel PAL model for porous solids

The set of rate equations for multi-channel PAL processes is:

$$\begin{cases}\dfrac{dn_b}{dt}=-l_b n_b-k_d n_b=-(l_b+k_d)n_b\\ \dfrac{dn_d}{dt}=k_d n_b-l_d n_d\\ \dfrac{dn^{p=Ps}}{dt}=-l_{2g}^{o-Ps}n^{p-Ps}\\ \dfrac{dn^{o-Ps}}{dt}=-(l_{3g}^{o-Ps}+l_{2g}^{o-Ps}+k_p^{o-Ps})n^{o-Ps}\\ \dfrac{dn_p^{o-Ps}}{dt}=k_p^{o-Ps}n^{o-Ps}-l_{p-2g}^{o-Ps}n_p^{o-Ps}\end{cases} \quad (10)$$

IV. Conclusion

The approach to modelling of PAL processes in porous solids for electronics was presented. It is shown, that PAL model in poorly-nanoporous solids is described by positron trapping channel. In the case of high-porous solids unifies the channels of positron trapping and positronium decaying.

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