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MULTI-STATE PAL MODELS FOR INNER FREE-VOLUME STUDY OF SENSOR CERAMICS FOR SOLID- STATE ELECTRONICS

H. Klym [1], O. Shpotyuk [2], I. Karbovnyk [3], R. Kochan [1]

[1] *Lviv Polytechnic National University, 12 Bandera St., UA-79013 Lviv, Ukraine*
klymha@yahoo.com

[2] *Vlokh Institute of Physical Optics, 23 Dragomanov St., UA-79005 Lviv, Ukraine*

[3] *Ivan Franko National University of Lviv, 107 Tarnavsky St., UA-79017 Lviv, Ukraine*

The positron annihilation lifetime models for describing of positron and positronium trapping in inner free-volume structure of solids for example of spinel ceramics are analyzed. It is shown that in fine-grained poorly-nanoporous $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ ceramics there is one defect-related positron annihilation channel. In the case of high-porous MgO-Al_2O_3 ceramics two independent channels of positron annihilation should be considered – the positron trapping and ortho-positronium decaying combined with a so-called "pick-off" annihilation process in nanopores usually filled by water.

Keywords: mathematical model, positron trapping, annihilation channels.

Introduction. Positron annihilation lifetime (PAL) spectroscopy is one of the most powerful experimental methods for studying of structurally inner 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]. The main channels of positron annihilation in these materials could be ascribed to individual positron trapping sites and specific bound states called positronium Ps [1-3]. In the ground state, the Ps exists as singlet para-positronium *p-Ps*, decaying intrinsically (i.e. between *Ps*-forming particles) with two γ-quanta and character lifetime in a vacuum of 124 ps, and triplet ortho-positronium *o-Ps*, decaying with three γ-quanta and lifetime of 142 ns. In matter, since the positron wave function overlaps with electrons outside the *o-Ps*, the annihilation with such electrons having an antiparallel spin decreases lifetime to 0.5-10 ns. The latter process resulting in two γ-rays is commonly called "pick-off" annihilation [1-4].

Early was shown that in the case of porous spinel ceramics, two channels of positron annihilation should be considered – the positron trapping and o-Ps decaying [5]. In general, these processes are independent ones. However, if trapping sites will appear in a vicinity of grain boundaries neighboring with free-volume pores, they can become mutually interconnected resulting in a significant complication of the measured PAL spectra. The aim of this work is the mathematical describing of all PAL processes in porous solids for example of ceramics within multi-channel model, which include positron trapping modes and *Ps* decaying.

Two-state positron trapping model for fine-grained solids. The first results of PAL methods 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 $\tau_1=\tau_b\approx$0.10-0.12 ns were responsible for positron annihilation in undisturbed interior of grains; the second component with $\tau_2=\tau_{gb}\approx$0.25-0.35 ns was responsible for positron trapping at grain boundaries; the third one with $\tau_3=\tau_{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. [6]. 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 $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ ceramics and using experience of works [7,8], we established that the adequate phenomenological description of positron trapping in solids can be developed at the basis of trapping model, 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: κ_d – positron trapping rate of defect; τ_d – positron lifetime in defect, λ_d – positron annihilation rate in defect-free bulk; τ_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 [7], the two-state positron trapping moles we proposed for solids with one-type defect at a very small concentration of nanopores (Fig. 1):

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

$$\begin{cases} \dfrac{dn_n}{dt} = -\lambda_b n_b - \kappa_d n_d = -(\lambda_b + \kappa_d) n_b \\ \dfrac{dn_d}{dt} = \kappa_d n_d - \lambda_b n_b \end{cases}. \quad (1)$$

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

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

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 τ_1 and τ_2 lifetimes defines by the sum [1]:

$$n(t) = n_b(t) + n_d(t) = n_o(I_1 e^{-\frac{1}{\tau_1}} + I_2 e^{-\frac{1}{\tau_2}}) \quad (3)$$

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

$$n(t) = \left[n_o \left(\left(\frac{\lambda_d - \lambda_b}{\lambda_d - \lambda_b - \kappa_d} \right) e^{-(\lambda_b + \kappa_d)t} + \frac{\kappa_d}{\lambda_b + \kappa_d - \lambda_d} e^{-\lambda_d t} \right) \right] \quad (4)$$

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

$$\tau_1 = \frac{1}{\lambda_b + \kappa_d} = \frac{1}{\tau_b^{-1} + \kappa_d} = \frac{\tau_b}{1 + \tau_b \kappa_d},\ \tau_2 = \frac{1}{\lambda_d} = \tau_d, \tag{5}$$

$$I_1 = \frac{\lambda_d - \lambda_b}{\lambda_d - \lambda_b - \kappa_d} = \frac{\tau_d - \tau_b}{\tau_d - \tau_b + \kappa_d \tau_d \tau_b}, \tag{6}$$

$$I_2 = 1 - I_1 = \frac{\kappa_d}{\lambda_b - \lambda_d + \kappa_d} = \frac{\kappa_d \tau_d \tau_b}{\tau_d - \tau_b + \kappa_d \tau_d \tau_b}. \tag{7}$$

It can be shown that:

$$\tau_b = \left(\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} \right)^{-1} = \frac{\tau_1 \tau_2}{I_1 \tau_2 + I_2 \tau_1},\ \kappa_d = I_2 \left(\frac{1}{\tau_1} - \frac{1}{\tau_2} \right) \tau_{av.} = I_1 \tau_1 + I_1 \tau_1 \tag{8}$$

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 τ_b is greater than the short positron lifetime τ_1 ($\tau_1 < \tau_b < \tau_2$), which sometimes is also called the reduced bulk positron lifetime. The long positron lifetime τ_2 exactly describes the annihilation of positrons captured in open-volume defect.

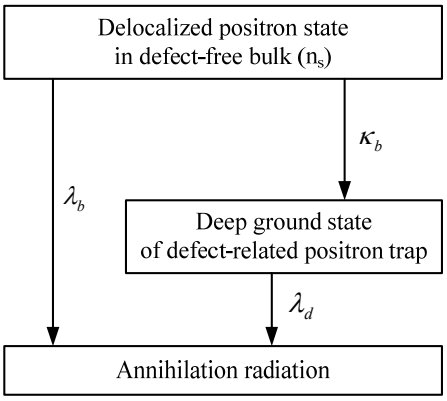

Fig.1. Two-state positron trapping model
(n_s –concentration of positrons in defect-free bulk at time t)

Such two-state positron trapping model can be used to monolithized transition-metal manganite $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics with a small concentration of nanopores [7]. The first component of PAL spectra ($\tau_1 \approx 0.2$ ns) was connected with main spinel structure and the second ($\tau_2 \approx 0.4$ ns) one – with extended defects located near grain boundaries in the vicinity of additional extracted NiO phase. The intensity I_1 corresponds to the amounts of the main spinel phase, while the I_2 intensity – to the amount of NiO phase near grain boundaries. The main changes caused by amount of addition phase and monolithization degree are represented on the positron trapping rate of defect near grain boundaries κ_d [7].

Multi-channel PAL model for nanoporous solids. The main achievement of scientific school of J. Dryzek [9] is the development of the *Ps* trapping. It was shown that PAL spectra have three main components: annihilation of positron in the free state ($\tau_1=\tau_b$ =0.3-0.4 ps); annihilation of *p-Ps* ($\tau_1=\tau_{p\text{-}Ps}$=125 ps) and annihilation of *o-Ps* localized in pores ($\tau_3=\tau_{o\text{-}Ps}$=0.5 ns).

In our previous works at study of nanoporous humidity-sensitive $MgAl_2O_4$ ceramics [9-12], we established that in the case of porous solids with high concentration of nanopores the best fitting are achieved at three- or four-component procedures: the first component is attributed to positron annihilation in the free state and annihilation of *p-Ps* ($\tau_1=\tau_b+\tau_{p\text{-}Ps}$). 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. ($\tau_2=\tau_d$). The third (and fourth) component is attributed to "pick-off" channel of *o-Ps* annihilation in pores ($\tau_3=\tau_{o\text{-}Ps}$). 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. The contribution of positron trapping channels through extended free-volume defects with distinguished PAL parameters will be in the second PAL component. The contribution of *o-Ps* "pick-off" annihilation channels in other phases (such as water) will be in the third and fourth PAL components.

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

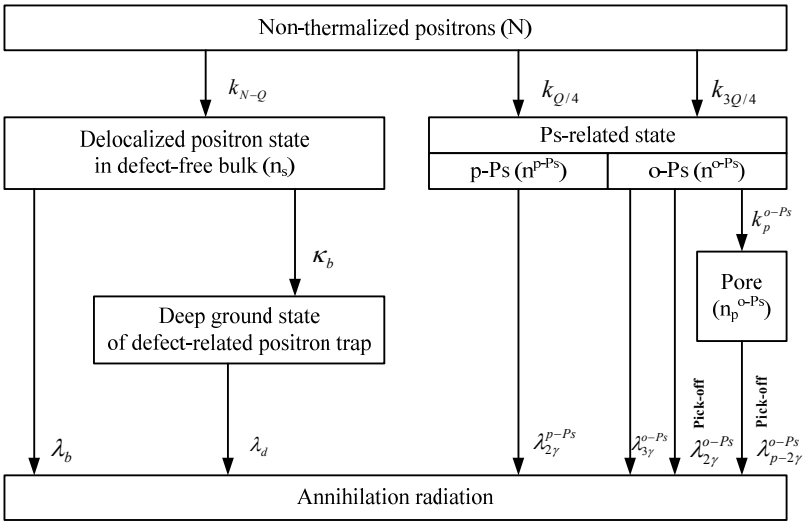

Fig.2. Multi-channel PAL model for porous solids

The first component is attributed to $\lambda_b + \lambda^{p\text{-}Ps}$ – channel. The second component is well distinguished from the first one and is attributed to trapping in more extended free-volume defects (the λ_d –channel). The third component is attributed to "pick-off" $\lambda_p^{o\text{-}Ps}$ channel.

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

$$\begin{cases} \dfrac{dn_b}{dt} = -\lambda_b n_b - \kappa_d n_b = -(\lambda_b + \kappa_d) n_b \\ \dfrac{dn_d}{dt} = \kappa_d n_b - \lambda_d n_d \\ \dfrac{dn^{p=Ps}}{dt} = -\lambda_{2\gamma}^{o-Ps} n^{p-Ps} \\ \dfrac{dn^{o-Ps}}{dt} = -(\lambda_{3\gamma}^{o-Ps} + \lambda_{2\gamma}^{o-Ps} + k_p^{o-Ps}) n^{o-Ps} \\ \dfrac{dn_p^{o-Ps}}{dt} = k_p^{o-Ps} n^{o-Ps} - \lambda_{p-2\gamma}^{o-Ps} n_p^{o-Ps} \end{cases}, \quad (9)$$

where n_b – number (concentration) of positrons in defect-free bulk at time t; λ_b – positron annihilation rate in defect-free bulk ($\lambda_b = 1/\tau_b$); n_d – number (concentration) of positrons trapped in defect at time t; κ_d – positron trapping rate of defect; λ_b– positron annihilation rate in defect ($\lambda_d = 1/\tau_d$); $n^{p\text{-}Ps}$ – number (concentration) of *p-Ps* at time t; $\lambda_{2\gamma}^{p\text{-}Ps}$ – 2γ-quanta annihilation rate of *p-Ps* ($\lambda_{2\gamma}^{p\text{-}Ps} = 1/\tau_{2\gamma}^{p\text{-}Ps} = 0.125$ ns); $n^{o\text{-}Ps}$ – number (concentration) of *o-Ps* at time t; $\lambda_{3\gamma}^{o\text{-}Ps}$ – 3γ-quanta annihilation rate of o-*Ps* ($\lambda_{3\gamma}^{o\text{-}Ps} = 1/\tau_{3\gamma}^{o\text{-}Ps}$); $\lambda_{2\gamma}^{o\text{-}Ps}$ – annihilation rate of *o-Ps* in "pick-off" process ($\lambda_{2\gamma}^{o\text{-}Ps} = 1/\tau_{2\gamma}^{o\text{-}Ps}$); $n_p^{o\text{-}Ps}$– number (concentration) of pores, where *o-Ps* is formed; $\lambda_{p\text{-}2\gamma}^{o\text{-}Ps}$ – *o-Ps* annihilation rate in "pick-off" process through pores ($\lambda_{p\text{-}2\gamma}^{o\text{-}Ps} = 1/\tau_{p\text{-}2\gamma}^{o\text{-}Ps}$); $\kappa_d^{o\text{-}Ps}$ – positron trapping rate of pore.

Such multi-channel PAL model can be used to porous humidity-sensitive MgO-Al_2O_3 ceramics [11]. Two independent channels of positron annihilation should be considered – the positron trapping with short-live τ_1 and τ_2 lifetimes and *o-Ps* decaying ("pick-off" annihilation in water) with long-live τ_3 and/or τ_4 lifetimes. The shortest lifetime component (the first channel of positron annihilation) in the studied ceramics reflects mainly the microstructure specificity of the spinel with character octahedral and tetrahedral cation vacancies. The τ_2 lifetime can be treated as defect-related one, these positron trapping defects being located near grain boundaries with addition MgO phase [12]. The third and the fourth longest (τ_3, I_3) and (τ_4, I_4) components in the resolved lifetime spectra are due to "pick-off" annihilation of *o-Ps* atoms in the intergranual pores [15]. These components are owing to predominant nanopores filled with absorbed water [12]. It was shown in [10] that with sintering temperature of ceramics the *o-Ps* "pick-off" decaying occurs preferentially in the nanopores filled by absorbed water, while the ceramic samples sintered at relatively low temperature show this process in both water-filled and water-free nanopores. The water-sorption processes act on positron trapping, which is close to the saturation independently on their structural perfectiveness of ceramics [8].

Conclusion. The PAL spectroscopy can be adequately used to free-volume study of solids. Two-state positron trapping model (two PAL components) should be applied to characterization of extended defects in temperature-sensitive fine-grained $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ ceramics with a very small concentration of nanopores. Two independent channels (three or four components) of positron annihilation within multi-channel model should be considered in porous humidity-sensitive MgO-Al_2O_3 ceramics: positron trapping and *o-Ps* decaying within "pick-off" annihilation in nanopores filled by water.

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REFERENCES

1. *Krause-Rehberg R.* Positron Annihilation in Semiconductors. Defect Studies / R. Krause-Rehberg. – Berlin-Heidelberg-New York: Springer-Verlag, 1999. – 378 p.
2. *Shpotyuk O.* Free volume in vitreous chalcogenide semiconductors: possibilities of positron annihilation lifetime study / O. Shpotyuk, J. Filipecki. – Częstochowa: Ed. WSP w Częstochowie, 2003. – 114 p.
3. *Kansy J.* Positronium trapping in free volume of polymers / J. Kansy, G. Consolati, C. Dauwe Radiation Physics and Chemistry. – 2000. – Vol. 58. P. 427-431.
4. *Consolati G.* Investigation of nanostructures in ordinary cement through positron annihilation lifetime spectroscopy / G. Consolati, G. Dotelli, F. Quasso // Journal of Applied Physics. – 1999. – Vol. 86, No 8. – P. 4225-4231.
5. *Shpotyuk O.* PAL spectroscopy in application to humidity-sensitive $MgAl_2O_4$ ceramics / Shpotyuk O., Ingram A., Klym H., Vakiv M., Filipecki J. // Journal of European Ceramic Society. – 2005. – Vol. 25. – P. 2981-2984.
6. *Langhammer H.T.* On the crystal and defect structure of manganese-doped barium titanate ceramics / H.T. Langhammer // *Mater. Lett*. – 1996. – Vol. 26. – P. 205–210.
7. *Klym H.* Structural studies of spinel manganite ceramics with positron annihilation lifetime spectroscopy / H. Klym, A. Ingram, O. Shpotyuk, J. Filipecki, I. Hadzaman // Journal of Physics: Conf. Ser. – 2011. – Vol. 289. – P. 012010-1-5.
8. *Klym H.* Extended positron-trapping defects in insulating $MgAl_2O_4$ spinel-type ceramics / H. Klym, A. Ingram, O. Shpotyuk, J. Filipecki, I. Hadzaman // Physica Status Solidi (c). – 2007. – Vol. 4, No 3. – P. 715-718.
9. *Dryzek J.* Calculations of annihilation rate of o-Ps in pick-off process / J. Dryzek // Acta Physica Polonica A. – 1999. – Vol. 95, No 4. – P. 539–545.
10. *Klym H.* Extended defects in insulating $MgAl_2O_4$ ceramic materials studied by PALS methods / H. Klym, A. Ingram, O. Shpotyuk, J. Filipecki, I. Hadzaman // IOP Conference Series: Materials Science and Engineering. – 2010. – Vol. 15. – P. 012044-1-5.
11. *Klym H.* Evolution of porous structure and free-volume entities in magnesium aluminate spinel ceramics / H. Klym, A. Ingram, I. Hadzaman, O. Shpotyuk // Ceramics International. – 2014. – Vol. 40. – P. 8561–8567.
12. *Filipecki J.* Water-sensitive positron-trapping modes in nanoporous magnesium aluminate ceramics / J. Filipecki, A. Ingram, H. Klym, O. Shpotyuk, M. Vakiv // Journal of Physics: Conf. Ser. – 2007. – Vol. 79. – P. 012015-1-4.

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БАГАТОСТАНОВІ МОДЕЛІ ПАС ДЛЯ ОПИСУ ВНУТРІШНЬОГО ВІЛЬНОГО ОБ'ЄМУ СЕНСОРНОЇ КЕРАМІКИ ДЛЯ ТВЕРДОТІЛЬНОЇ ЕЛЕКТРОНІКИ

Г. Клим [1], О. Шпотюк [2], І. Карбовник [3], Р. Кочан [1]

[1] Національний університет «Львівська політехніка», вул. С. Бандери, 12, 79013 Львів, Україна
klymha@yahoo.com

[2] Інститут фізичної оптики імені О.Г. Влоха, вул. Драгоманова, 23, 79005 Львів, Україна

[3] Львівський національний університет імені Івана Франка вул. ген. Тарнавського, 107, 79017 Львів, Україна

Проаналізовано моделі позитронної анігіляції для опису внутрішнього вільного об'єму в твердих тілах на прикладі шпінельної кераміки. Показано, що для дрібнодисперсної кераміка із збідненою поруватою структурою $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ характерний один дефектний канал захоплення позитронів. У випадку поруватої кераміки MgO-Al_2O_3 мають місце два незалежні канали – анігіляції позитронів та розпаду атомів орто-позитронію через процес"pick-off" в нанопорах, в тому числі, зволожених водою.

Ключові слова: математична модель, захоплення позитронів, канали анігіляції.

МОДЕЛИ МНОГИХ СОСТОЯНИЙ ПАС ДЛЯ ОПИСАНИЯ ВНУТРЕННЕГО СВОБОДНОГО ОБЪЕМА СЕНСОРНОЙ КЕРАМИКИ ДЛЯ ТВЕРДОТЕЛЬНОЙ ЕЛЕКТРОНИКИ

Г. Клым [1], О. Шпотюк [2], І. Карбовнык [3], Р. Кочан [1]

[1] Национальный университет «Львовская политехника», ул. С. Бандеры, 12, 79013 Львов, Украина
klymha@yahoo.com

[2] Институт физической оптики имени О.Г. Влоха, ул. Драгоманова, 23, 79005 Львов, Украина

[3] Львовский национальный университет имени Ивана Франка ул. ген. Тарнавского, 107, 79017 Львов, Украина

Проанализированы модели позитронной аннигиляции для описания внутреннего свободного объема в твердых телах на примере шпинельной керамики. Показано, что для мелко-дисперсной керамика с обедненной пористой структурой $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ характерен один дефектный канал захвата позитронов. В случае пористой керамики MgO-Al_2O_3 имеют место два независимых канала – аннигиляции позитронов и распада атомов орто-позитрония через процесс "pick-off" в нанопорах, в том числе, увлажненных водой.

Ключевые слова: математическая модель, захвата позитронов, каналы аннигиляции.