Mathematical modeling of elementary trapping-reduction processes in positron annihilation lifetime spectroscopy: methodology of Ps-to-positron trapping conversion

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Abstract. Methodological possibilities of positron annihilation lifetime (PAL) spectroscopy in application to nanostructurized substances treated within three-term fitting procedure are reconsidered to parameterize their atomic-deficient structural arrangement. In contrast to conventional three-term fitting analysis of the detected PAL spectra based on admixed positron trapping and positronium (Ps) decaying, the nanostructurization due to guest nanoparticles embedded in host matrix is considered as producing modified trapping, which involves conversion between these channels. The developed approach referred to as x3-x2-coupling decomposition algorithm allows estimation free volumes of interfacial voids responsible for positron trapping and bulk lifetimes in nanoparticle-embedded substances. This methodology is validated using experimental data of Chakraverty et al. [Phys. Rev. B71 (2005) 024115] on PAL study of composites formed by guest NiFe₂O₄ nanocrystals grown in host SiO₂ matrix.

1. Introduction
To be successful in nanomaterial engineering, it is necessary to possess an advanced instrumentation tool that can efficiently explore a nanospace at both atomic-specific (inner space occupied by atoms, atomic groups and molecules) and atomic-deficient (free of electron and atomic densities) levels [1]. The latter is of high importance in view of essential deficit in reliable void-testing probes sensitive to length scales of atomic and subatomic ranges. One of such probes that can fit the gap in methodological resolutions is based on positronics [2-6], i.e. analytical space-time continuum determination for electron interaction with its antiparticle, positron. This phenomenon realized as positron annihilation lifetime (PAL) spectroscopy, can be applied to study free-volume imperfections (such as vacancies, vacancy-like clusters, voids, pores, void agglomerates, and even macroscopic cracks) in crystals, glasses, coarse-grained or fine-milled powders, ceramics, bulk alloys, etc.
This work is aimed to analyze possibilities of positronics in application to free-volume defects caused by nanostructurization in nanoparticle (NP) embedded solids, where guest NPs can affect both positron-trapping and Ps-decaying channels in an overall balance of annihilation events in host matrix. Nanostructurization is considered as modified trapping, which involves three elementary components, these being positron/Ps trapping reduction/enhancement and Ps-to-positron trapping conversion.

2. Model

2.1. Methodological background.

In nanomaterials, the PAL spectra typically yield three distinct lifetimes $\tau_{1,2,3}$ with $I_{1,2,3}$ intensities reflecting competitive input from mixed positron-Ps trapping channels under normalization [3,6]:

$$I_1 + I_2 + I_3 = 1. \quad (1)$$

The longest PAL component ($\tau_{2,3}$) originates from decaying of spin-triplet ortho-positronium o-Ps states in free-volume holes. This process stretched intrinsically in a vacuum ending by emitting two $\gamma$-rays, the process known as pick-off annihilation [3-5].

The intermediate PAL component ($\tau_{1,2}$) results from positron annihilation from free-volume defect sites such as atomic and sub-atomic voids (vacancies, vacancy-like clusters, etc.). Being trapped by such defect, the positron annihilate with lifetimes $\tau = \tau_{o}$ ranging from 0.2-0.3 to 0.5 ns [3,5].

In case of three-component fitting of the detected PAL spectra, the resolution of all inputs is essentially disturbed by additional contribution in the first shortest component ($\tau_{1,2}$) arising from spin-singlet para-positronium p-Ps states, giving $\tau_{p}=0.125$ ns with relative population of $I_p=I_{2/3}$ for a vacuum. Thus, the annihilation from defect-free bulk states are currently admixed to p-Ps decaying, thus complicated the physical meaning of this component. So direct correlations are not allowed for this ($\tau_{1,2}$) component and material-related parameters of a medium.

2.2. Methodology of Ps-to-positron trapping conversion within x3-x2-CDA.

In our model, we distinguish all inputs in the first PAL component to extract the “pure” feedback caused by NP-related free-volume positron traps themselves. Assuming an additive two-state positron trapping model for these defects, we obtain a possibility of their quantitative parameterization. Like [7,8], we use the generalization procedure allowing transformation of the measured PAL spectra from x3-term to x2-term (most generalized) decomposition forms.

Firstly, this analysis is applied to host matrix without embedded guest NPs having ($\tau_{1,2,3}$, $I_{1,2,3}$) inputs in three-term decomposed row PAL spectrum ($I_{1,2,3}$ = 1). This model can be easily transferred to the known x2-component trapping model by removing $I_p=I_{2/3}$ input of p-Ps annihilation with $\tau_{p}=0.125$ ns lifetime from the first channel and ($\tau_{1,2,3}$) input from the third channel to the generalized trapping channel (within the generalized x2-term approach). Thus, we can estimate the contribution ($\tau_{a,L_a}$) to the first channel other than p-Ps:

$$\tau_a = \tau_{a,L_a} = \tau_{a,L_a} - \tau_{p,L_p}; \quad (2)$$

$$L_a = I_{a,L_a} - I_p. \quad (3)$$

Then, returning to NP-embedded substance having ($\tau_{1,2,3}$, $\tau_{1,2,3}^*$) and ($\tau_{1,2,3}$, $\tau_{1,2,3}^*$) inputs in the x3-term decomposed PAL spectrum ($I_{1,2,3}^* + I_{1,2,3}^* + I_{1,2,3}^* = 1$), we find input from additional channel ($\tau_{int,L_{int}}$) assuming its relation to int-sites and remainder of o-Ps-sites taken like in host matrix:

$$I_{1,2,3}^* = I_{int} + I_{a,L_{a}}^{(int,L_{int})}; \quad (4)$$

$$\tau_{1,2,3}^* = \tau_{int,L_{int}} + \tau_{a,L_a}^{(int,L_{int})} \cdot I_{2,3}^* - I_{int}. \quad (5)$$

Under this condition, it seems reasonably to equilibrate ($\tau_{a,L_a}$) input in ($\tau_{1,2,3}^*$) component (i.e. without p-Ps) with the same as ($\tau_{int,L_{int}}$) input in ($\tau_{1,2,3}^*$) component (the full inter-channel balance):

$$\tau_{a,L_a} \cdot I_{a,L_a} = \tau_{int,L_{int}} \cdot I_{2,3}^* - I_{int}. \quad (6)$$

Transferring x3-term PAL spectrum into x2-term one with ($\tau_{a,L_a}$) and ($\tau_{1,2,3}^*$) components like in host matrix, we find compensating ($\tau_{a,L_a}$) input arising from this additional trapping channel ($\tau_{int,L_{int}}$).
Parameterization of NP-sites can be performed accepting \((\tau_n, I_n)\) and \((\tau_{int}, I_{int})\) as components of the generalized \(x^2\)-term PAL spectrum of nanostructurized substance. The second component with \(\tau_{int}\) lifetime reflects positron trapping sites appeared due to embedded NP. Under accepted prerequisites, these extended free-volume defects can be associated with pseudogap holes at the interface between the outer surface layer of agglomerated NPs and innermost layer of surrounding host matrix [2,7,8]. The bulk lifetime recalculated respectively to these components in according to eq. (4) can be accepted as bulk positron lifetime related to NPs. For monolith NPs, this value tends to bulk lifetime of corresponding substance, while in looser media it is higher. The positron trapping rate of NP-related traps \(\kappa_d\) can be also estimated within this scheme in terms of two-state trapping model [3,6].

Thus, this approach allows description of nanostructuralization in substances in terms of \(Ps\)-to-positron trapping conversion within the same \(host\) matrix, i.e. the process occurring as transformation of \(o-Ps\)-sites in a \(host\) matrix to positron-trapping sites in the NP-embedded \(host-guest\) matrix. In contrast to conventional \(x^3\)-term decomposition, describing PAL spectra in terms of mixed positron-\(Ps\) trapping, this approach can be defined as \(x^3-x^2\)-coupling decomposition algorithm (\(x^3-x^2\)-CDA). It becomes meaningless, provided nanostructurization concerns defect-free annihilation channel, thus changing PAL parameters of annihilation from delocalized Bloch states in a \(host\) matrix. Therefore, this algorithm can be considered as test-indicator for nanostructurization, separating the processes of host-matrix modification from “pure” interplay between positron- and \(Ps\)-trapping.

3. Mathematical modelling and PAL-data interpretation algorithm

As an example, let’s consider the experimental results of S. Chakraverty et al. [7] on PAL response produced by guest NiFe\(_2\)O\(_4\) nanocrystals grown in \(host\) SiO\(_2\) glassy matrix. The \(x^3\)-term decomposed PAL spectra of these NiFe\(_2\)O\(_4\)-SiO\(_2\) nanocomposites evidently demonstrate gradual decrease in the intensity of \(o-Ps\) lifetime component \(I_3\) under nanostructurization, this process being inter-balanced by essential increase in the second component intensity \(I_2\) and defect-related lifetime \(\tau_2\) (see Table 1).

| NiFe\(_2\)O\(_4\) grain size | Fitting parameters |
|----------------------------|--------------------|
|                            | \(\tau_1, \text{ns}\) | \(I_1, \text{a.u.}\) | \(\tau_2, \text{ns}\) | \(I_2, \text{a.u.}\) | \(\tau_3, \text{ns}\) | \(I_3, \text{a.u.}\) |
| Pure SiO\(_2\)             | 0.116              | 0.501               | 0.370               | 0.272               | 1.62               | 0.227               |
| 40.0 nm                    | 0.133              | 0.515               | 0.400               | 0.389               | 1.64               | 0.096               |
| 25.0 nm                    | 0.137              | 0.558               | 0.400               | 0.385               | 1.76               | 0.057               |
| 15.0 nm                    | 0.139              | 0.540               | 0.416               | 0.433               | 1.50               | 0.027               |
| 6.8 nm                     | 0.143              | 0.561               | 0.420               | 0.417               | 1.43               | 0.022               |
| 5.6 nm                     | 0.131              | 0.508               | 0.392               | 0.462               | 1.13               | 0.030               |
| 4.8 nm                     | 0.133              | 0.506               | 0.406               | 0.452               | 1.08               | 0.042               |
| 3.5 nm                     | 0.142              | 0.520               | 0.432               | 0.451               | 1.29               | 0.029               |

Using analogy with inert gas bubbles in a metal matrix, the authors [7] explain such behavior due to positron-trapping free volumes at the interfaces of agglomerated NPs appeared instead of \(Ps\)-sites. The PAL modes were calculated from a condition of balanced intensities (assuming that percentage contribution to \(I_1\) by intensity of positrons annihilating within NPs \(I_{in}\) is the same as that of \(I_{int}\) to \(I_2\)). This allows authors [7] to ascribe their \(\tau_n\) (close to 0.140 ns) to specific positron lifetime in NPs themselves, which seems somewhat underestimated as for typical non-defect spinels [9,10].

Within \(x^3-x^2\)-CDA, we assume that full conversion between positron-trapping and \(Ps\)-decaying channels is alone process under nanostructurization in NiFe\(_2\)O\(_4\)-SiO\(_2\) composites, so that no intensities, but rather component inputs are inter-balanced in respect to eq. (9). So, we accept \((\tau_n, I_n)\) and \((\tau_{int}, I_{int})\) as first and second components of the \(x^2\)-term PAL spectrum ascribed to hypothetical medium formed
under nanostructurization. The defect-free bulk lifetime $\tau_{bNP}$ within 0.195±0.203 ns domain (Table 2) recalculated in respect to formalism of the x2-component trapping model given by eq. (4) [5-9], can be treated as specific lifetime in NPs themselves, i.e. in NiFe$_2$O$_4$ spinel. The defect-specific lifetime $\tau_{int}$ is a signature of positron-trapping volumes related to embedded NPs. In general, this value shows growing tendency with decrease in NiFe$_2$O$_4$ grain size towards 3.5 nm as it follows from Table 2. The same is character for positron trapping rate in these defects at the interfaces of NPs $\kappa_d$, which is a result of NP-related positron-trapping input in the PAL spectrum. Slight deviations in $(\tau_{int}-\tau_{bNP})$ and $\tau_{int}/\tau_{bNP}$ values, which can be accepted in x2-component model as signatures of defect size and type [2-6], testify in a favor of rather unchanged nature of these defects irrespectively to NiFe$_2$O$_4$ grain size.

**Table 2.** PAL trapping modes describing nanostructurization in NiFe$_2$O$_4$-SiO$_2$ nanocomposites [7] for guest NiFe$_2$O$_4$ nanocrystals in respect to host pure SiO$_2$ within x3-x2-CDA

| NiFe$_2$O$_4$ grain size | $\tau_{in}$, ns | $I_{in}$, a.u. | $\tau_{int}$, ns | $I_{int}$, a.u. | $\tau_{bNP}$, ns | $\kappa_d$, ns$^{-1}$ | $(\tau_{int}-\tau_{bNP})$, ns | $\tau_{int}/\tau_{bNP}$, a.u. |
|--------------------------|-----------------|-------------|-----------------|-------------|-----------------|-----------------|-----------------------------|-----------------------------|
| 3.5 nm                   | 0.145           | 0.468       | 0.437           | 0.416       | 0.211           | 2.17            | 0.226                       | 2.07                        |
| 4.8 nm                   | 0.136           | 0.434       | 0.411           | 0.402       | 0.200           | 2.37            | 0.210                       | 2.05                        |
| 5.6 nm                   | 0.133           | 0.456       | 0.394           | 0.426       | 0.195           | 2.42            | 0.199                       | 2.02                        |
| 6.8 nm                   | 0.145           | 0.515       | 0.423           | 0.391       | 0.203           | 1.95            | 0.221                       | 2.09                        |
| 15.0 nm                  | 0.141           | 0.488       | 0.420           | 0.401       | 0.202           | 2.11            | 0.218                       | 2.08                        |
| 25.0 nm                  | 0.143           | 0.433       | 0.406           | 0.317       | 0.197           | 1.91            | 0.209                       | 2.06                        |
| 40.0 nm                  | 0.143           | 0.329       | 0.413           | 0.274       | 0.203           | 2.09            | 0.210                       | 2.03                        |

Principally, the reverse process, tending the positron trapping towards Ps-decaying, can be also well described within this approach due to simultaneous negative values of $I_{in}$ and $I_{int}$ intensities, which was demonstrated previously at the example of other nanostructurized substances [2,11].

4. Conclusions

Nanostructurization in host matrix substances due to embedded guest nanoparticles is considered as a modified process in PAL spectroscopy, which involves conversion between Ps-decaying and positron-trapping channels. The developed algorithm allows estimation free volumes of interfacial voids responsible for positron trapping and bulk lifetimes in nanoparticle-embedded substances.

5. References

[1] Vollath D 2013 Nanomaterials: An Introduction to Synthesis, Properties and Applications. Second Edition (Weinheim: Wiley-VCH Verlag GmbH)
[2] Shpotyuk O, Filipecki J, Ingram A, Golovchak R, Vakiv M, Klym H, Balitska V, Shpotyuk M and Kozdras A 2015 Nanoscale Res. Lett. 10 77-1
[3] Krause-Rehberg R and Leipner H 1999 Positron annihilation in semiconductors: defect studies (Heidelberg: Springer)
[4] Jean Y C, Mallon P E and Schrader D M 2003 Principles and application of positron and positronium chemistry (New Jersey-London-Singapore-Hong Kong: World Sci. Publ.)
[5] Shpotyuk O and Filipecki J 2003 Free volume in vitreous chalcogenide semiconductors: possibilities of positron annihilation lifetime study (Czestochowa: Ed. WSP)
[6] Tuomisto F and Makkonen I 2013 Rev. Mod. Phys. 85 1583
[7] Chakraverty S, Mitra S, Mandal K, Nambissan P M G and Chattopadhyay S 2005 Phys. Rev. B 71 024115-1
[8] Mitra S, Mandal K, Sinha S, Nambissan P M G and Kumar S 2006 J. Phys. D 39 4228
[9] Jensen K O and Nieminen R M 1987 Phys. Rev. B 35 2087
[10] Nambissan P M G, Mondal O, Chakrabarty S and Pal M 2013 Mater. Sci. Forum 733 219.
[11] Shpotyuk O, Ingram A, Shpotyuk Ya, Buňáková Z, Baláž P 2017 Polym. Eng. Sci. 57 502.