Modification of free volume in the nanostructured $MgAl_2O_4$ ceramics caused by water molecules

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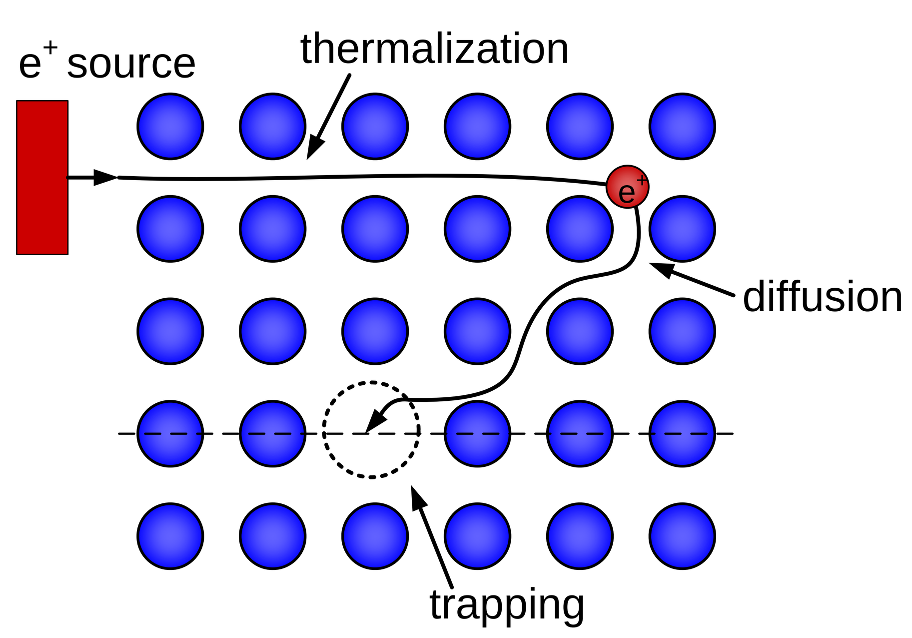
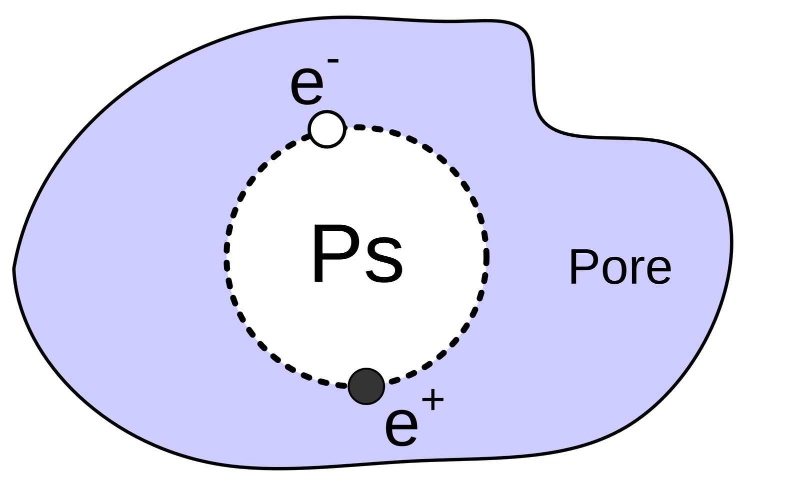
The o-Ps-related modes are used for study of free-volume entities in nanostructured spinel $MgO\text{-}Al_2O_3$ ceramics after drying and water-immersion treatment. It is established that water-sorption processes in magnesium aluminate ceramics lead to corresponding increase in the positron trapping rates of extended free-volume defects located as extractions of addition phases near grain boundaries. These phases and free-volume entities in ceramic structure serve as specific trapping centers for positrons penetrating ceramics. It is demonstrated that Tao-Eldrup model can be adequately used for free volume calculations (or nanopores size) in $MgO\text{-}Al_2O_3$ ceramics using o-Ps lifetimes defined from third and fourth components spectra.

EXPERIMENTAL: Positron Annihilation Lifetime (PAL) Spectroscopy

Positron trapping in defects



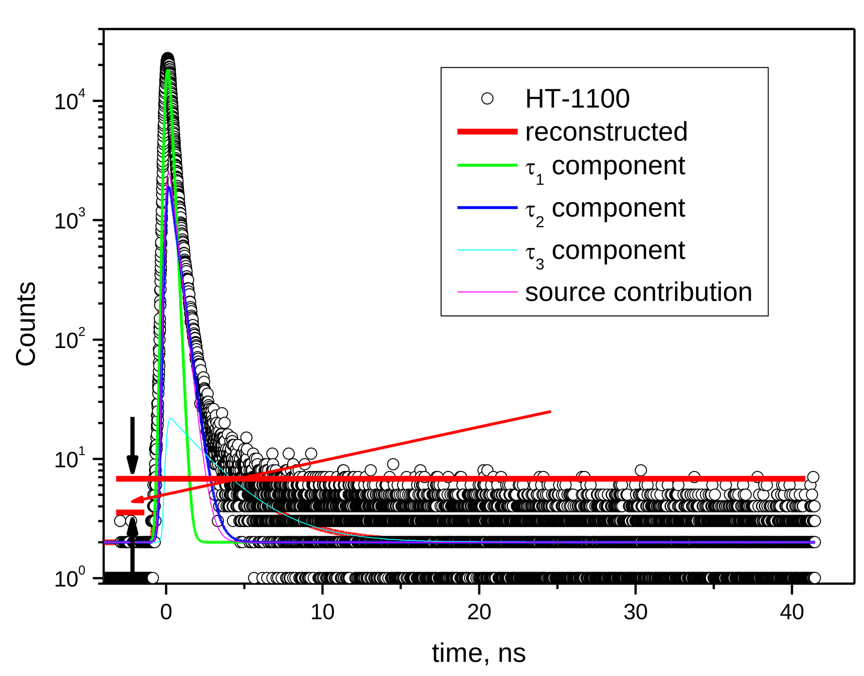
Localized in pore positronium Ps

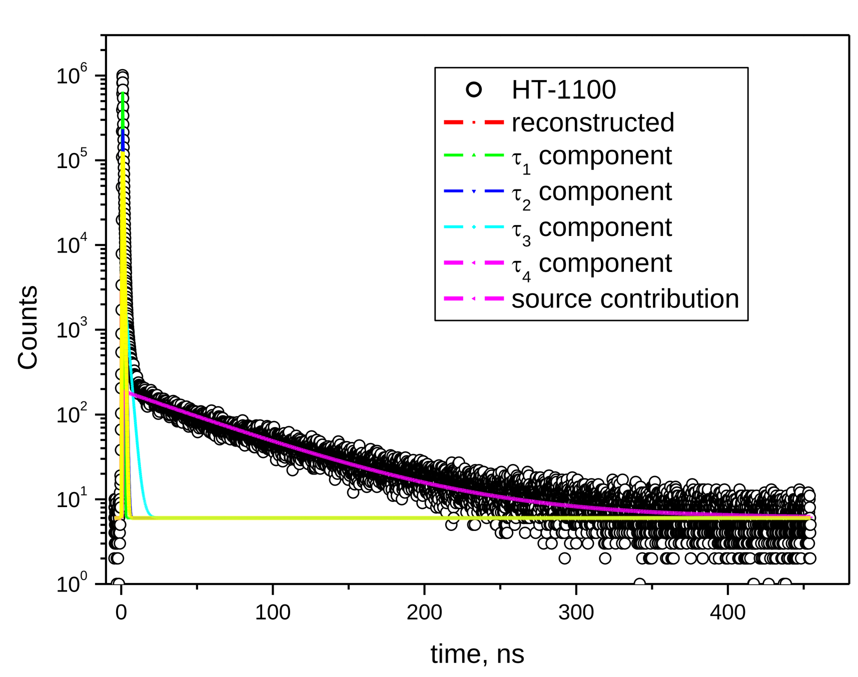


75 % o-Ps
25 % p-Ps

The PAL spectra were recorded with conventional fast-fast coincidence system (ORTEC) of 230 ps resolution (determined by ^{60}Co isotope measuring) at the temperature T = 22 °C and relative humidity RH = 35 %, provided by special climatic installation. The obtained results agreed well with each other within experimental uncertainties, being no more than ±0.005 ns in lifetimes and ±0.01 in component intensities. Each spectrum was measured with a channel width of 6.15 ps (the total number of channels was 8000) and contained at least ~10^6 coincidences in a total, which can be considered as conditions of normal PAL measurement statistics.

MATHEMATICAL TREATMENT of PAL DATA: LT computer program, 4-component fitting procedure





PAL RESULTS : Fitting parameters and positron trapping modes

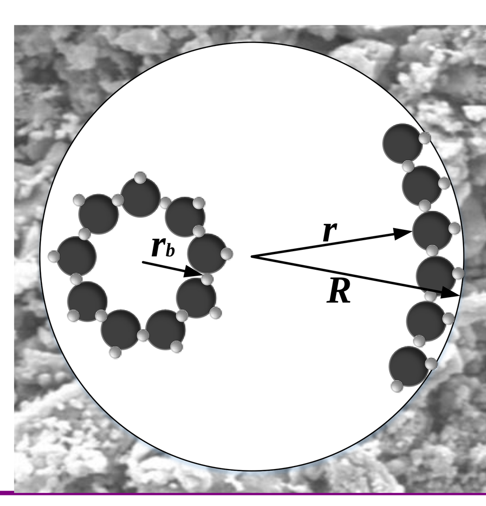
Sample pre-history	τ_1, ns	I_1, a.u.	τ_2, ns	I_2, a.u.	τ_3, ns	I_3, a.u.	τ_4, ns	I_4, a.u.
	Fitting parameters							
1300 °C								
drying	0.155	0.82	0.414	0.16	2.426	0.008	68.74	0.014
water vapour	0.161	0.76	0.400	0.21	2.619	0.018	58.33	0.007
drying	0.156	0.82	0.421	0.15	2.448	0.007	68.17	0.014

Sample pre-history	$\tau_{av.}$, ns	τ_b, ns	κ_d, ns^{-1}	R_3, Å	R_4, Å
	Positron trapping modes				
1300 °C					
drying	0.197	0.17	0.66	3.25	18.18
water vapour	0.213	0.19	0.80	3.40	16.30
drying	0.198	0.17	0.63	3.27	18.07

Tao-Eldrup Model:

$$\left(\frac{1}{\tau_{o-Ps}}\right)_{TE} = \lambda_{TE}(R) \cong \lambda_A\left[1-\frac{R}{R+\Delta R}+\frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]+0.00704$$

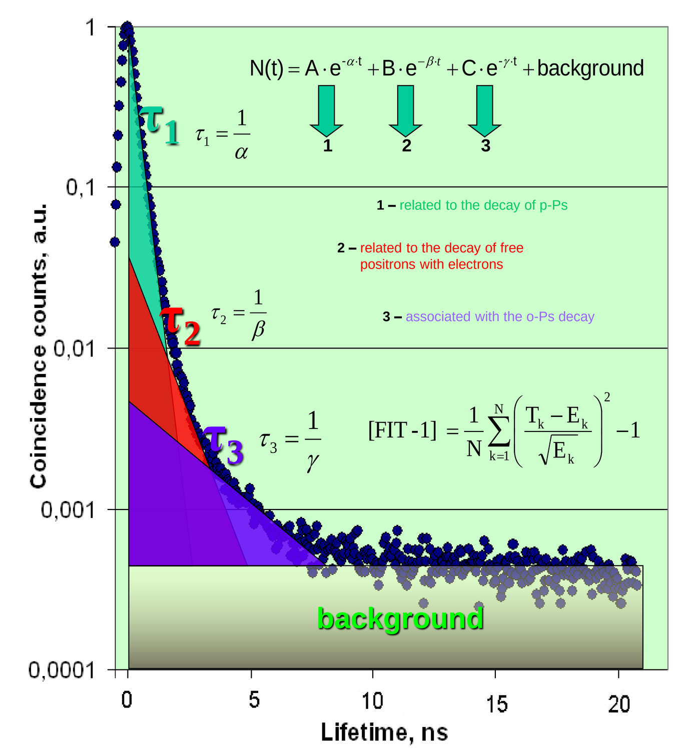
$$\tau_{av.} = \frac{\tau_1 I_1+\tau_2 I_2}{I_1+I_2} \qquad \tau_b = \frac{I_1+I_2}{\frac{I_1}{\tau_1}+\frac{I_2}{\tau_2}} \qquad \kappa_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b}-\frac{1}{\tau_2}\right)$$

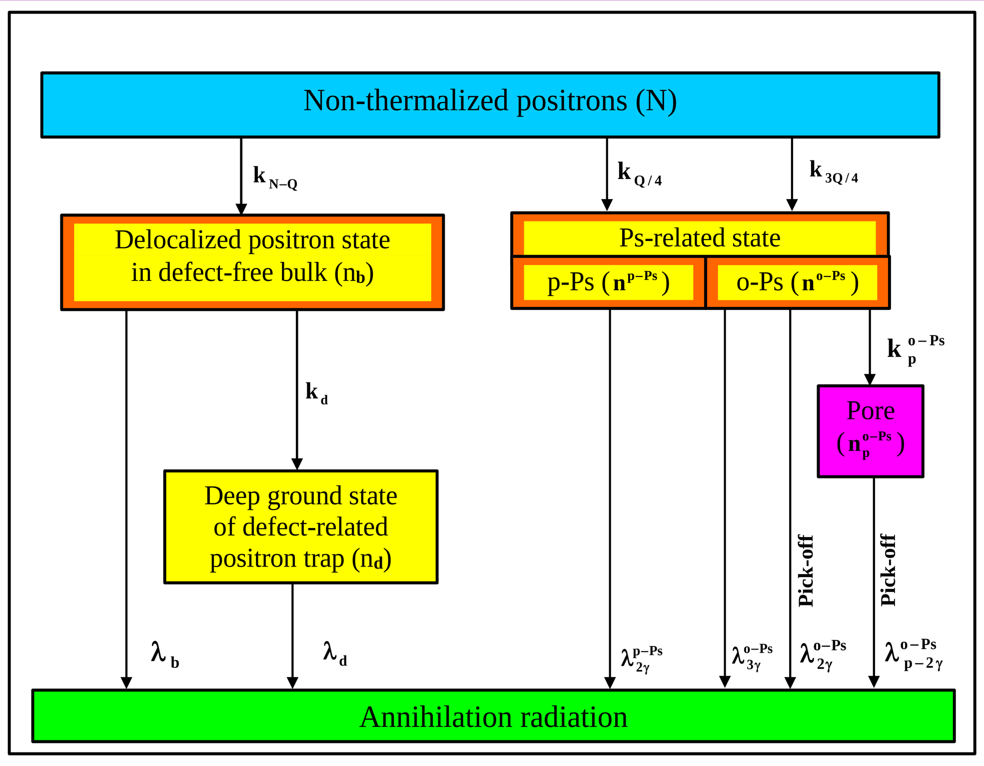


It is shown, he third and fourth longest components of lifetime spectra are due to "pick-off" annihilation of o-Ps atoms in nanopores. The Tao-Eldrup model can be applied in order to calculate free volume radii in ceramics.
In the case of water-immersed samples, physisorbed water practically not modify positron tapping defects near grain boundaries. O-Ps annihilates thought a "bubble" mechanism within liquid water.

Sample pre-history	τ_n, ns	I_n, a.u.	τ_{int}, ns	I_{int}, a.u.	κ_d, ns^{-1}
water-free (guest influence)	0.219	0.596	0.436	0.217	0.607

MATHEMATICAL TREATMENT of PAL DATA: LT computer program, 3-component fitting procedure





PAL RESULTS : ceramics sintered at 1300 °C Fitting parameters and positron trapping modes within 3-component fitting

Sample pre-history	τ_1, ns	I_1, a.u.	τ_2, ns	I_2, a.u.	τ_3, ns	I_3, a.u.
	Fitting parameters					
water-immersed host matrix	0.22	0.54	0.46	0.32	1.88	0.15
water-free (initial) host-guest matrix	0.22	0.72	0.44	0.26	2.19	0.02

Sample pre-history	$\tau_{av.}$, ns	τ_b, ns	κ_d, ns^{-1}	$\tau_2 - \tau_b$, ns	τ_2/τ_b
	Positron trapping modes				
water-immersed	0.31	0.27	0.9	0.19	1.7
water-free (initial)	0.27	0.25	0.6	0.19	1.7

PAL MODELS of nanostructurized "host-guest" chemistry x3-x2 algorithm