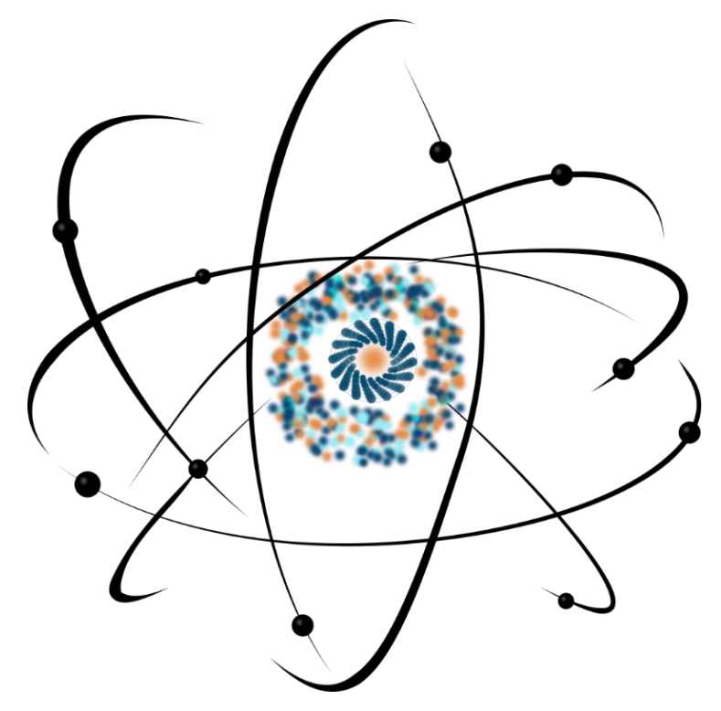

PALS models to estimate of free volume in ceramic materials with advanced nanoporosity

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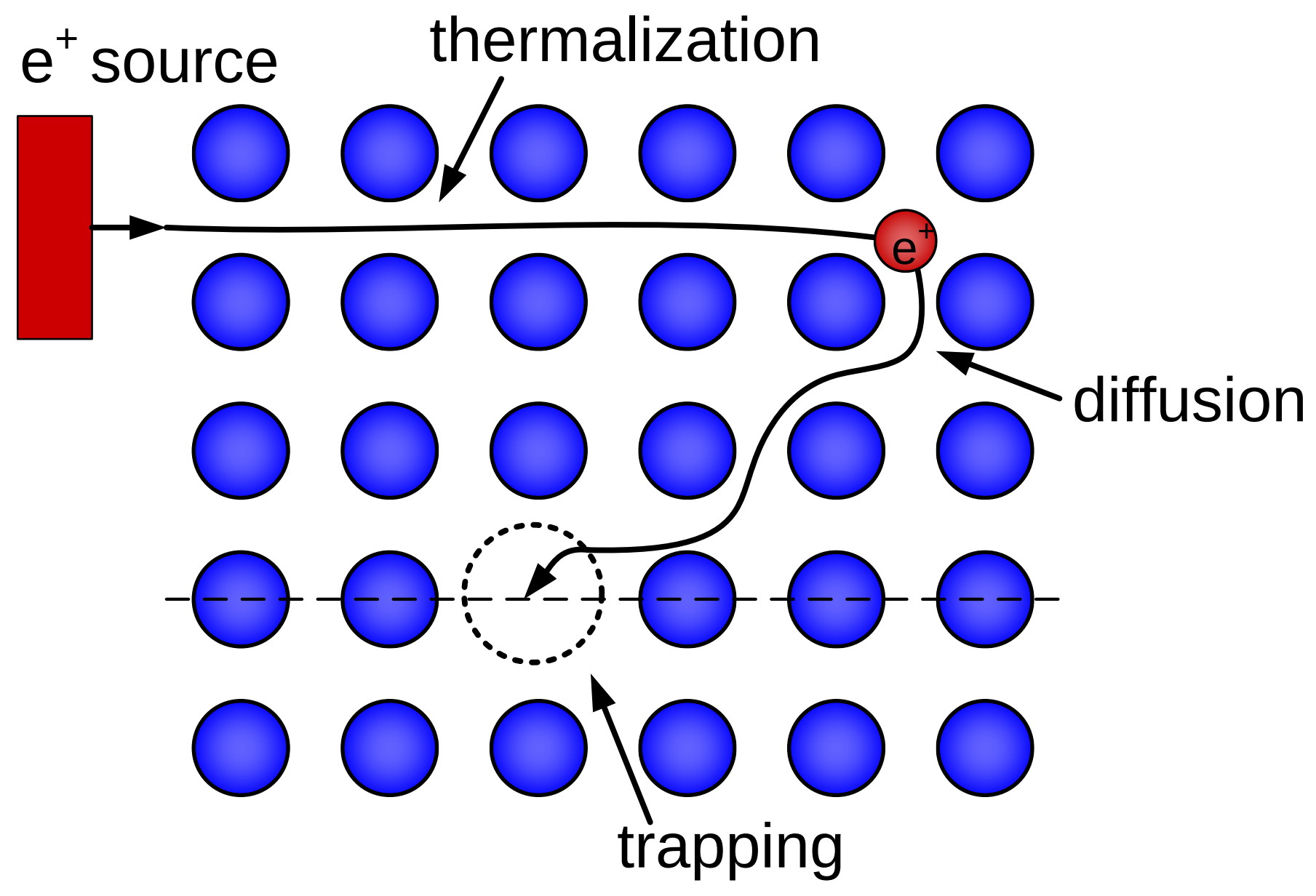
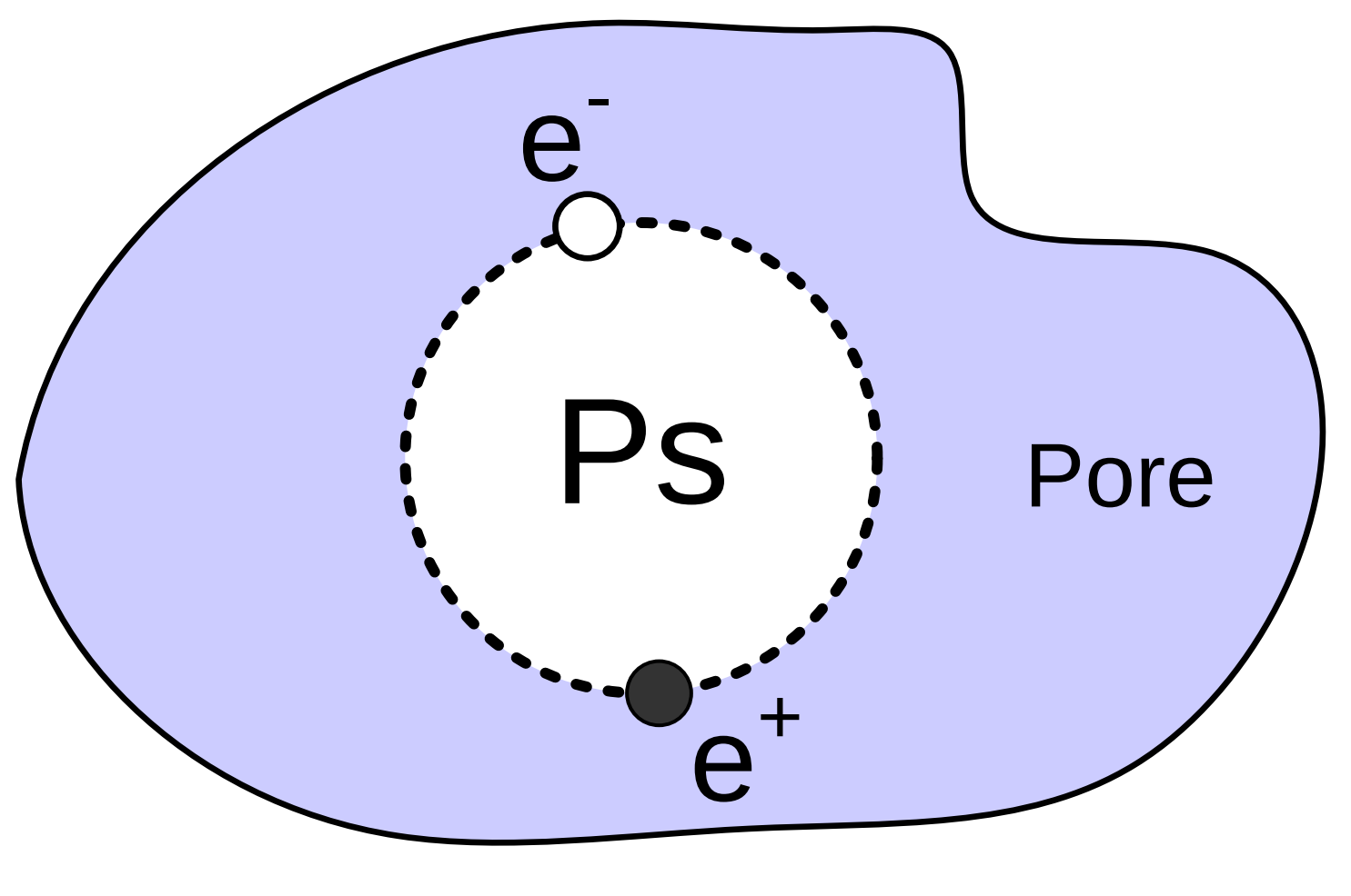
Herein we demonstrate the specifics of using positron annihilation lifetime spectroscopy (PALS) method for the study of free volume changes in functional ceramic materials. Choosing technological modification of $MgAl_2O_4$ spinel as an example, we show that for ceramics with well-developed porosity, free-volume defects facilitated positron trapping channels are enabled and ortho-positronium atoms decay may occur. Trapping in channels is described by two components and decay process by single or multiple components, depending on how well porosity is developed and on the experimental configuration. When using universal positron annihilation lifetime spectroscopy analysis, three components are the most suitable fit in case of $MgAl_2O_4$ ceramics. In the analysis of the second component, it is shown that technological modification (increasing sintering temperature) leads to volume shrinking and decreases the number of extended positron trapping defects near grain boundaries. This process is also accompanied by the decrease of the size of nanopores or nanovoids (described by the third component), while the overall number of nanopores is not affected. The universal approach to the analysis of positron annihilation lifetime spectra presented here can be applied to a wide range of functional materials with pronounced porosity.

EXPERIMENTAL:
Positron Annihilation Lifetime (PAL) Spectroscopy

Positron trapping in defects



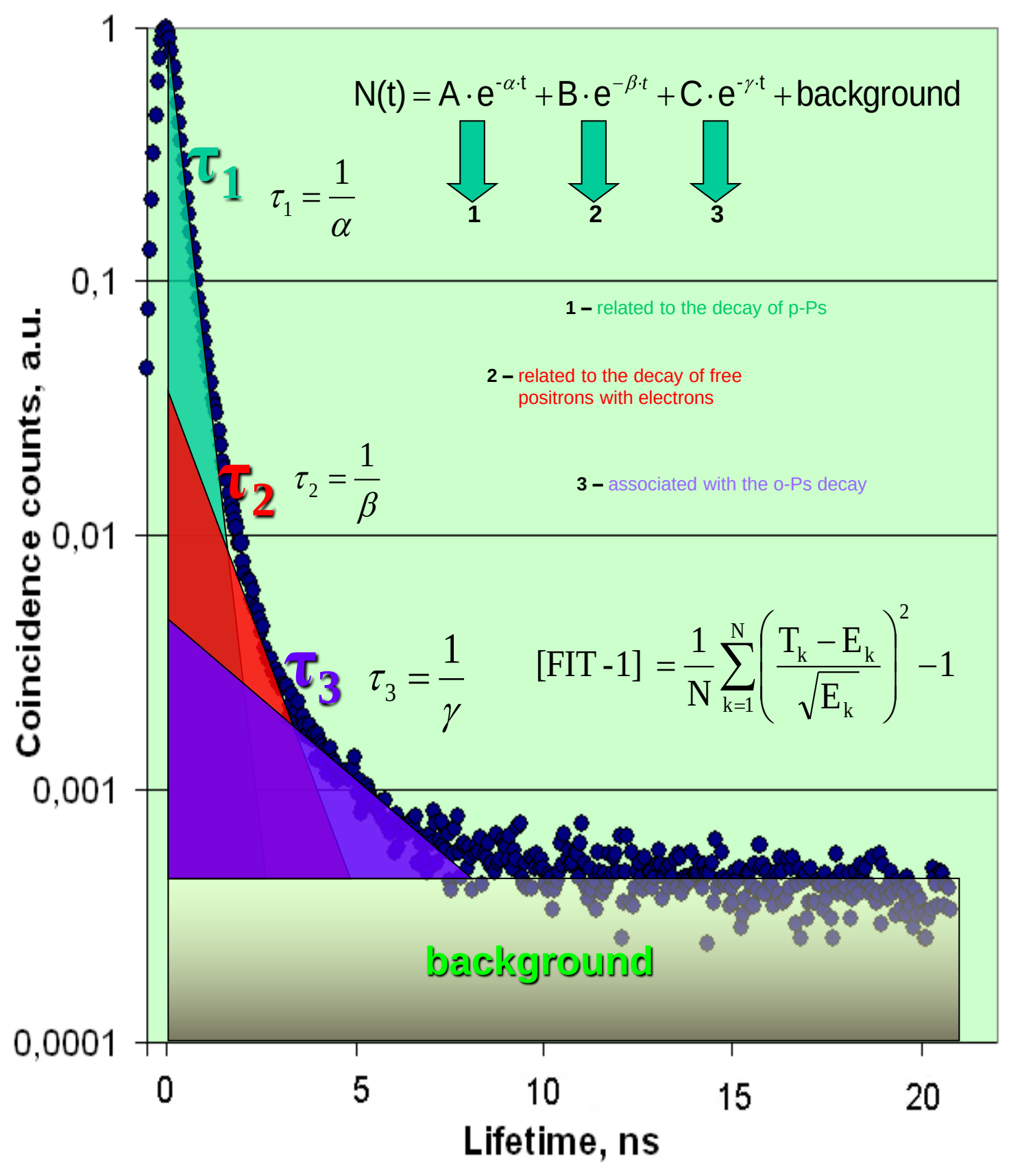
Localized in pore positronium Ps



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.

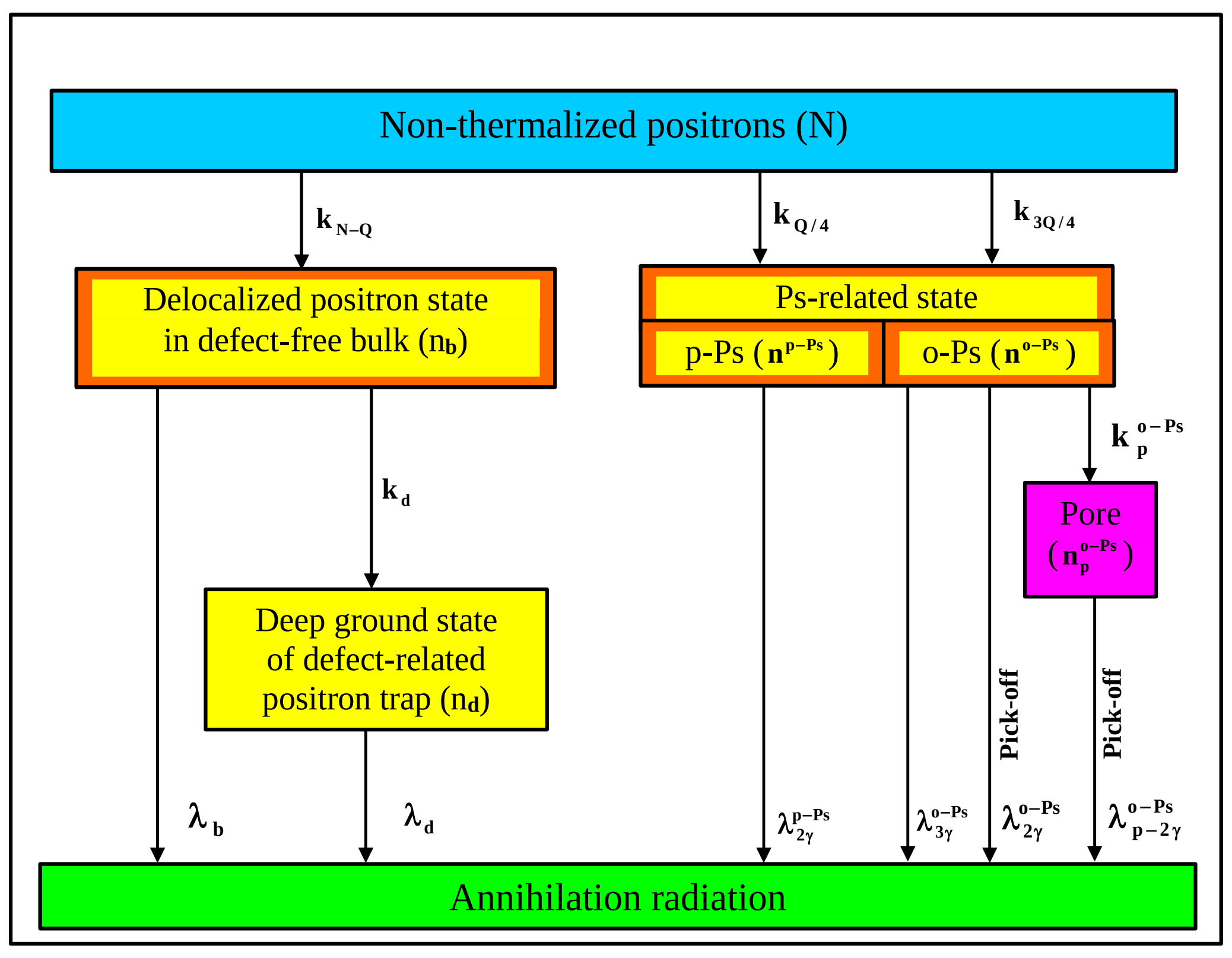
MATHEMATICAL TREATMENT of PAL DATA:
LT computer program, 3-component fitting procedure



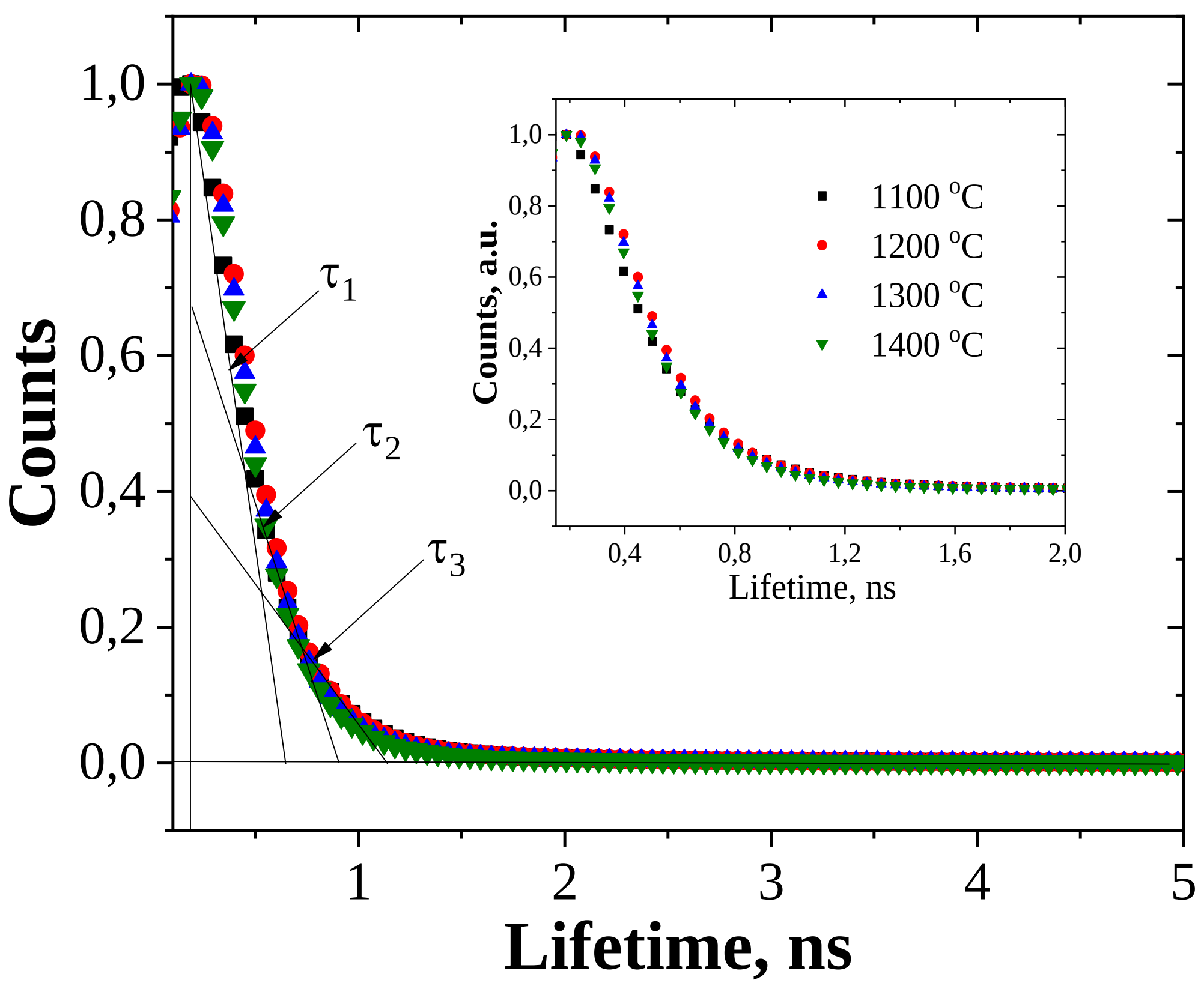
$$N(t) = A \cdot e^{-\alpha \cdot t} + B \cdot e^{-\beta \cdot t} + C \cdot e^{-\gamma \cdot t} + \text{background}$$

$$\tau_1 = \frac{1}{\alpha} \qquad \tau_2 = \frac{1}{\beta} \qquad \tau_3 = \frac{1}{\gamma}$$

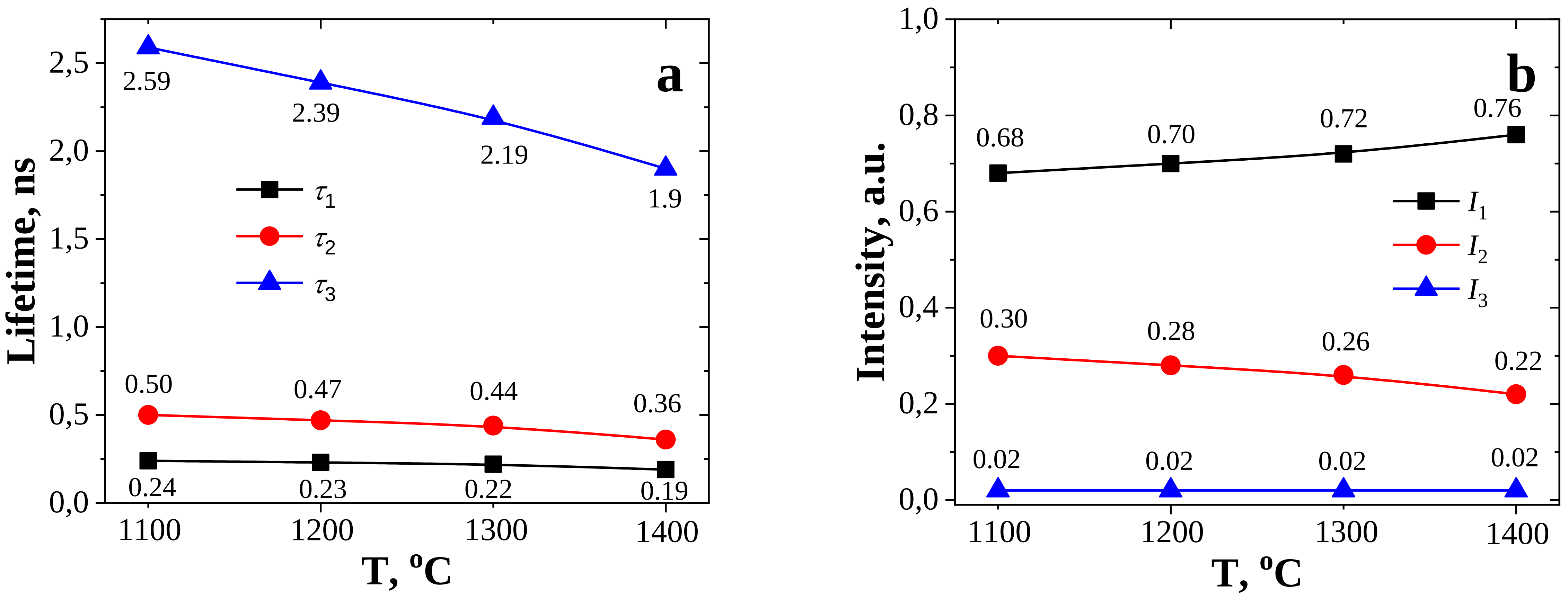
$$[\text{FIT-1}] = \frac{1}{N}\sum_{k=1}^{N}\left(\frac{T_k - E_k}{\sqrt{E_k}}\right)^2 - 1$$



PAL RESULTS:
Fitting parameters and positron trapping modes within 3-component fitting



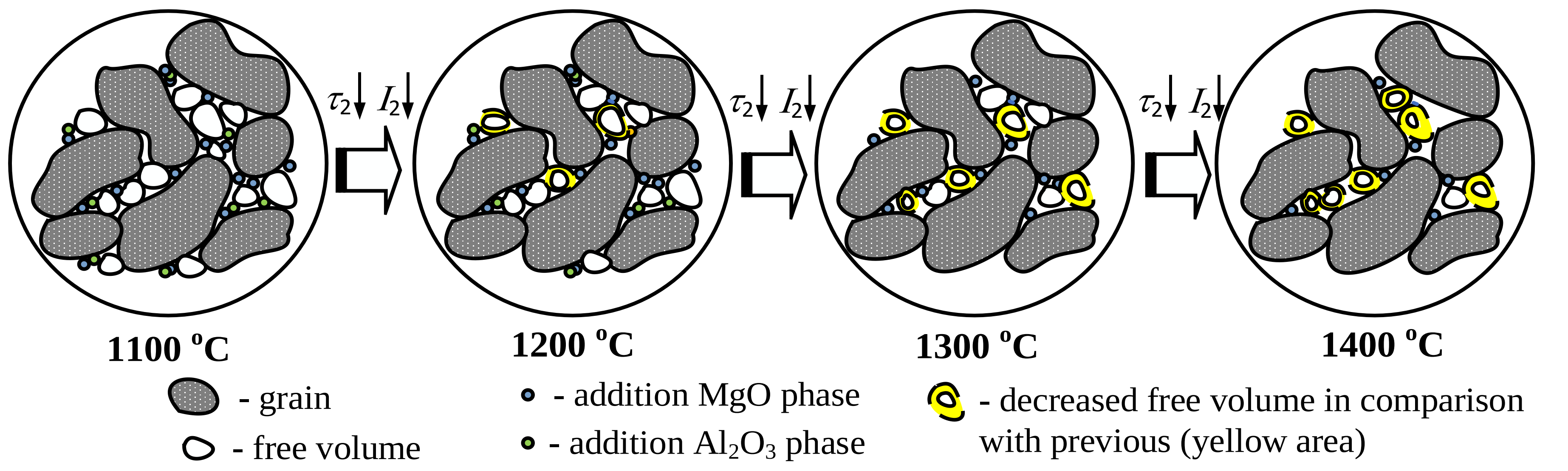
Normalized positron lifetime spectra for $MgAl_2O_4$ ceramics sintered at 1100–1400 °C during 2 hours with schematic illustration of tangents on each region at decomposition spectrum into three components.



Dependencies of lifetimes (*a*) and intensities (*b*) of PALS spectrum on the ceramics sintering temperature

For functional ceramic materials two PALS channels are enabled: positron trapping by extended free-volume defects (positron trapping sites) with short and average positron lifetimes (τ_1 and τ_2, respectively) and the channel related to the decay of o-Ps atoms (including the "pick-off" process) with long lifetime τ_3. In the frame of the proposed model [44], in $MgAl_2O_4$ ceramics the short positron lifetime (lifetime τ_1 and intensity I_1) reflects main microstructural features of the spinel with octahedral and tetrahedral vacancies, which are potential locations for positron trapping. Knowing lifetimes of this component one can estimate the sizes of voids formed by the principal phase in the material.

For $MgAl_2O_4$ ceramics obtained at 1100–1400 °C during 2 h, lifetime τ_1 of the first short component decrease slightly with increasing T_s, whereas intensity I_1 is increasing. Such changes speak in favor of ceramics quality increasing towards higher perfection level when using higher sintering temperatures. Lifetime of the second component τ_2 is related to the positron trapping in defect-related sites. As known from X-ray diffraction, $MgAl_2O_4$ ceramics contains different amounts of MgO/Al_2O_3 phases. These amounts decrease with increasing T_s. As confirmed by scanning electron microscopy studies, additional phases are irregularly distributed across the ceramics volume and are mainly localized near grain boundaries. Separated MgO and Al_2O_3 phases play a role of specific positron trapping centers in the ceramics free volume. Since ceramics obtained at lower temperatures include larger amounts of additional phases, positron trapping in such samples should be more pronounced. The third long component of PALS spectrum (the second channel of positron annihilation with lifetime τ_3 and intensity I_3) is connected to the decay of o-Ps atoms in nanopores and also to the "pick-off" annihilation process



Schematic depiction of the evolution of internal free volume defects at grain boundaries in $MgAl_2O_4$ ceramics

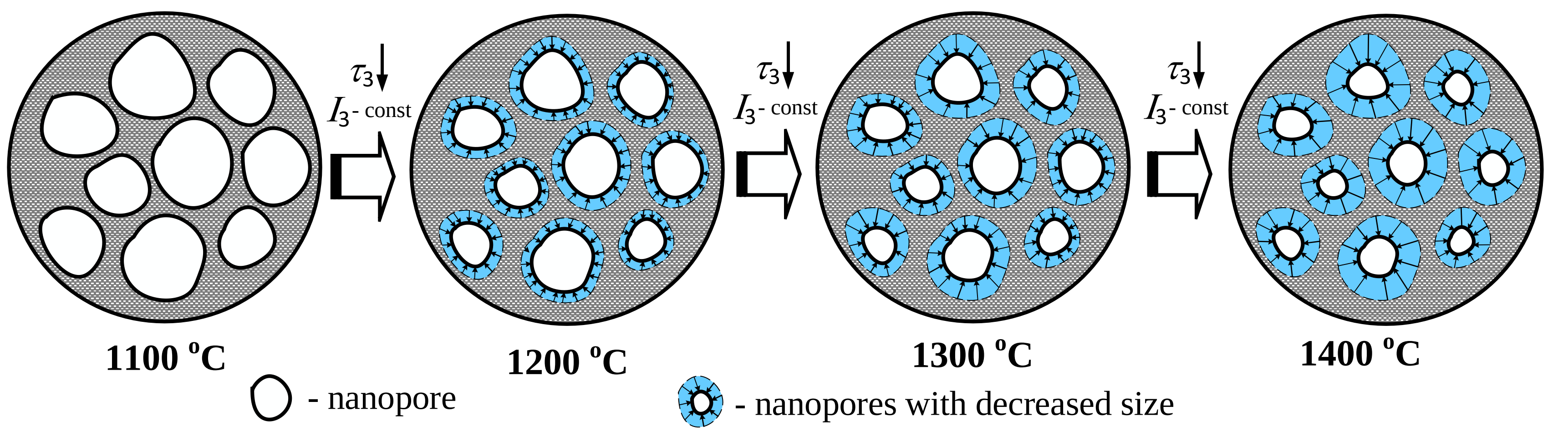


Diagram explaining the evolution of nanovoids in the internal structure of $MgAl_2O_4$ ceramics sintered at 1100-1400 °C during 2 hours.