Positronics in contemporary nanocomposites science and engineering: the case of multinanoparticulate substances

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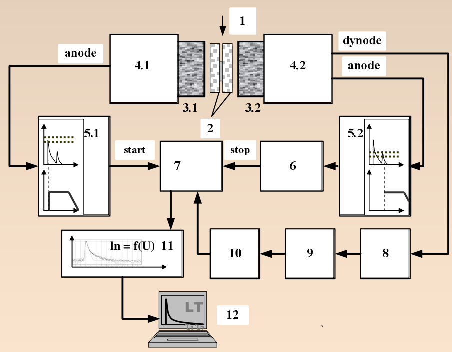
EXPERIMENTAL: Positron Annihilation Lifetime (PAL) Spectroscopy



Block-scheme of conventional sample-source "sandwich" arrangement for PAL measurements using the ORTEC apparatus:

1 – foil-covered ^{22}Na source,
2 – two identical samples,
3.1 and 3.2 – scintillators of γ-quanta,
4.1 and 4.2 – photomultipliers,
5.1 and 5.2 – constant fraction discriminators,
6 – delay line,
7 – time-pulse height converter,
8 – preamplifier,
9 – amplifier,
10 – single channel analyzer,
11 – multichannel analyzer,
12 – personal computer.

Mixed channels of positron trapping and o-Ps decaying in unconstrained x3-term decomposed PAL spectra

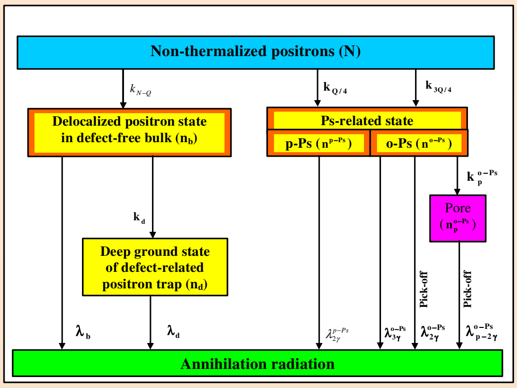
$n^{p\text{-}Ps}$ – number of p-Ps at time **t;**
$_{2\gamma}\lambda^{p\text{-}Ps}$ – 2γ-quanta annihilation rate of p-Ps;
$n^{o\text{-}Ps}$ – number of o-Ps at time **t**
$_{3\gamma}\lambda^{o\text{-}Ps}$ – 3γ-quanta annihilation rate of o-Ps;
$_{2\gamma}\lambda^{o\text{-}Ps}$ – annihilation rate of pick-off o-Ps;
$_{p}n^{o\text{-}Ps}$ – number of pores within o-Ps is formed;
$_{p\text{-}2\gamma}\lambda^{o\text{-}Ps}$ – o-Ps annihilation rate in pick-off process through pores;
$_{p}k^{o\text{-}Ps}$ – positron trapping rate of pore.

$$\tau_{av.}^{\Sigma} = \frac{\tau_1 I_1 + \tau_2 I_2 + \tau_3 I_3}{I_1 + I_2 + I_3}$$

$$\tau_3 = [1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin(\frac{2\pi R}{R+\Delta R})]^{-1}$$

$$V_f = \frac{4\pi R^3}{3}$$

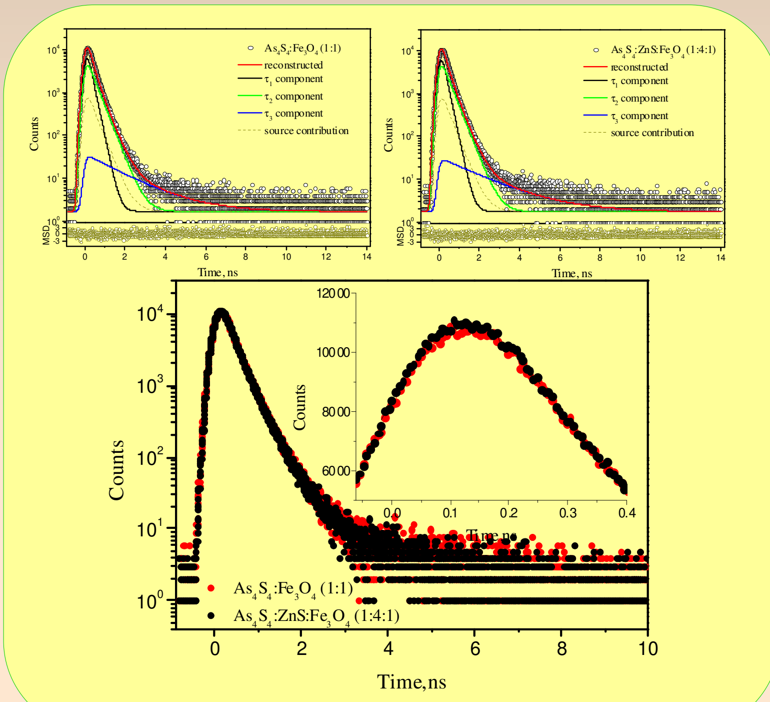
R – pore radius;
ΔR≈0.166nm – fitted empirical electron layer thickness; V_f – free volume size.



Conclusions:

Possibilities of positron annihilation lifetime (PAL) spectroscopy applied to characterize nanosization processes under high-energy mechanical milling are analyzed for multiparticulate arsenical-based systems, such as monoparticulate As_4S_4, biparticulate As_4S_4/Fe_3O_4 and triparticulate $As_4S_4/ZnS/Fe_3O_4$.
The algorithm to treat registered PAL spectra for such substances within three-state mixed trapping model evolving competitive channels of positron and positroniun Ps (bound electron-positron state) channels (x3-x2-CDA, coupling decomposition algorithm) is given.
It is shown that coexistence of nanocrystalline As_4S_4 phase and supplemented amorphous substance is crucial feature of these materials, the latter being generated owing to *reamorphization* of disordered phase initially existed in arsenic sulphide prepared by conventional synthesis from elemental precursors and direct milling-driven vitrification of nanocrystalline As_4S_4 phase.

Experimental PAL spectra



PAL spectra of multinanoparticulate arsenical-based systems reconstructed from unconstrained x3-fitting: biparticulate As_4S_4/Fe_3O_4 and triparticulate $As_4S_4/ZnS/Fe_3O_4$.

PAL spectra fitting within unconstrained x3-decomposition

Sample	Fitting parameters: [fit-1] -	τ_1, ns	I_1, a.u.	τ_2, ns	I_2, a.u.	τ_3, ns	I_3, a.u.	Component input: $\tau_{av.}^1$, ns	$\tau_{av.}^2$, ns	$\tau_{av.}^3$, ns	$\tau_{av.}^{\Sigma}$, ns	Traping modes: $\tau_{av.}$, ns	τ_b, ns	κ_d, ns^{-1}	$\tau_2-\tau_b$, ns	τ_2/τ_b	Volume: R_3 nm	f_3 %
As_4S_4:Fe_3O_4 1:1	0.07	0.215	0.695	0.406	0.297	1.995	0.008	0.149	0.121	0.017	0.287	0.272	0.250	0.66	0.16	1.62	0.288	0.15
	0.07	0.222	0.732	0.419	0.260	2.278	0.007	0.162	0.109	0.017	0.288	0.273	0.253	0.56	0.17	1.66	0.313	0.17
As_4S_4:ZnS 1:4	0.02	0.239	0.749	0.434	0.234	2.145	0.016	0.179	0.102	0.035	0.316	0.285	0.267	0.45	0.17	1.62	0.301	0.34
	0.03	0.238	0.753	0.440	0.231	2.207	0.015	0.179	0.102	0.034	0.315	0.285	0.267	0.45	0.17	1.65	0.307	0.34
As_4S_4 : ZnS : Fe_3O_4 1:4:1	0.01	0.219	0.689	0.410	0.302	2.242	0.009	0.151	0.124	0.020	0.294	0.277	0.255	0.65	0.15	1.61	0.309	0.20
	0.03	0.221	0.709	0.419	0.282	2.610	0.008	0.157	0.118	0.021	0.296	0.278	0.256	0.61	0.16	1.64	0.339	0.24
FIX τ_1																		
As_4S_4:Fe_3O_4 1:1	0.05	0.191	0.486	0.374	0.506	2.071	0.009	0.093	0.189	0.018	0.300	0.284	0.254	1.31	0.12	1.47	0.294	0.17
	0.06	0.193	0.485	0.372	0.507	2.191	0.008	0.094	0.188	0.018	0.301	0.284	0.256	1.27	0.12	1.45	0.305	0.18
As_4S_4 : ZnS : Fe_3O_4 1:4:1	0.01	0.191	0.454	0.370	0.536	1.929	0.010	0.087	0.198	0.020	0.305	0.288	0.259	1.37	0.11	1.43	0.281	0.17
	0.01	0.193	0.463	0.372	0.527	1.948	0.010	0.089	0.196	0.020	0.305	0.288	0.259	1.33	0.11	1.43	0.283	0.17
	0.01	0.200	0.498	0.380	0.492	2.027	0.010	0.100	0.187	0.020	0.306	0.289	0.261	1.17	0.12	1.45	0.291	0.18
	0.02	0.200	0.504	0.381	0.488	2.285	0.009	0.101	0.186	0.020	0.307	0.289	0.261	1.17	0.12	1.46	0.314	0.21
As_4S_4:ZnS 1:4	0.04	0.190	0.360	0.353	0.620	1.816	0.020	0.068	0.219	0.036	0.324	0.293	0.268	1.54	0.08	1.32	0.271	0.30
	0.04	0.194	0.378	0.356	0.602	1.835	0.020	0.073	0.214	0.036	0.324	0.294	0.269	1.44	0.09	1.32	0.272	0.30
	0.04	0.200	0.408	0.361	0.573	1.867	0.019	0.082	0.207	0.036	0.324	0.294	0.271	1.30	0.09	1.34	0.276	0.30
	0.05	0.200	0.428	0.369	0.555	2.234	0.017	0.086	0.205	0.038	0.329	0.295	0.270	1.29	0.10	1.37	0.308	0.38

PAL spectra fitting within x3-x2-CDA

Effect of ZnS: **AZF-141 = As_4S_4 : ZnS : Fe_3O_4 (1:4:1)** *irt* **AF-11 = As_4S_4 : Fe_3O_4 (1:1)**
Effect of Fe3O4: **AZF-141 = As_4S_4 : ZnS : Fe_3O_4 (1:4:1)** *irt* **AZ-14 = As_4S_4:ZnS (1:4)**

Samples	τ_n [ns]	I_n [a.u.]	τ_{int} [ns]	I_{int} [a.u.]	t_{av1} [ns]	t_{av2} [ns]	τ_{av}^{Σ} [ns]	τ_b [ns]	κ_d [ns^{-1}]	$\tau_2-\tau_b$ [ns]	τ_2/τ_b
Effect of ZnS:											
AZF-141 irt AF-11	0.190	-0.027	0.456	-0.026	-0.005	-0.012	0.320	0.266	1.500≅1.50	0.190	1.713≅1.7
AF-11 irt AZF-141	0.190	0.028	0.456	0.024	0.005	0.011	0.312	0.260	1.412≅1.41	0.196	1.754≅1.7
Effect of Fe3O4:											
AZF-141 irt AZ-14	0.189	0.265	0.364	0.316	0.050	0.115	0.285	0.256	1.380≅1.38	0.108	1.421≅1.4