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A Model for Joint Processing of LT and CDB Spectra of Dielectric Nano-sized Powders

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Abstract. A model that allows interpretation of positron annihilation spectra (LT and CDB) in nanodispersed dielectric powders is developed. Model takes into account e^+ capture by vacancy-type defects, formation of e^+ surface-bound states, as well as the formation of quasi-free positronium (inside crystallites) which may escape into intergranular space where it becomes thermalized during elastic collisions. The process of annihilation of ortho-Ps is narrowed down to its conversion into the para-state as a result of collisions with oxygen molecules (O_2) adsorbed on the surface of crystallites. A computer program for lifetime spectra fitting that accounts on the parameters of the above model is developed (with ROOT framework). Combination of the program with our CDB software allows joint processing of the LT and CDB annihilation spectra of nanopowders.

INTRODUCTION

It is well known that a positronium atom (Ps) is not formed in conducting substances (including polycrystalline). This is because of the presence of a large number of quasifree electrons near the positron, none of which spend enough time close e^+ to talk about the formation of the Ps atom. In dielectric substances Ps formation is quite possible, which leads to the presence of a long-time component in the LT (lifetime) spectra. Below, we consider the most typical scenario of the formation and annihilation of various positron states in nanodispersed powders (particularly in Al_2O_3 powders). The proposed model is based on the work of Ch. Dauwe [1, 2] and will be used for fitting of the LT and CDB (Coincidence Doppler Broadening) spectra of various powders using the software that we are developing [3, 4].

FORMULATION OF THE MODEL

A scheme of formation of various states e^+ in Al_2O_3 nanopowders is shown in Fig. 1. During e^+ ionization slowing down, the positron creates many ion-electron pairs. Then it becomes thermalized and stays for a short time (about 50-100 ps) in a quasi-free state (qf-e^+). qf-e^+ can either annihilate with a rate of λ_b, or be captured by a vacancy-type defect (as a result vac-e^+ is formed). qf-e^+ can also reach a crystallite boundary and be localized there in the surface-bound state, surf-e^+. Moreover, qf-e^+ can interact with one of the secondary (track) electrons and form a quasi-free positronium atom, qf-Ps, which diffuses in the bulk of crystallite and may reach its boundary. After that qf-Ps flies into the space in between the crystallites, having excess kinetic energy (1-2 eV). It occurs due to the fact that qf-Ps is an electrically neutral particle and, unlike a positron, does not experience polarization attraction to the surface of the crystallite. So Ps atom does not form a surface-bound state. In the inter-crystallite space we must distinguish two different spin states of the Ps atom – ortho-Ps and para-Ps (o-Ps, p-Ps), since their annihilation rate significantly differs when they reside in-between the crystallites.

Below, we do not consider a short initial time interval (some tens of ps) during which thermalized e^+ may meet one of the track e^- and form qf-Ps. Subsequent evolution of the positron states, including qf-e^+ capture by vacancy-type defects, formation of surf-e^+ as well as o-Ps and p-Ps is described by the following equations:

$$n_b(t) = (1 - P_{Ps})e^{-(\lambda_b + \varkappa_v)t}, \tag{1}$$

$$n_v(t) = (1 - P_{Ps})\frac{\varkappa_v[e^{-\lambda_v t} - e^{-(\lambda_b + \varkappa_v + \varkappa_s)t}]}{\lambda_b + \varkappa_v + \varkappa_s - \lambda_v}, \tag{2}$$

$$n_s(t) = (1 - P_{Ps})\frac{\varkappa_s[e^{-\lambda_s t} - e^{-(\lambda_b + \varkappa_v + \varkappa_s)t}]}{\lambda_b + \varkappa_v + \varkappa_s - \lambda_s}, \tag{3}$$

$$\dot{n}_{Ps}(t) = -P_{Ps}J(t) - \lambda_{Ps}n_{Ps}, \qquad n_{Ps}(0) = P_{Ps}, \tag{4}$$

$$\dot{n}_o(t) = \frac{3P_{Ps}J(t)}{4} - \left(\lambda_{3\gamma} + \lambda_{po} + \frac{\lambda_{opc}(t)}{4}\right)n_o, \qquad n_o(0) = 0, \tag{5}$$

$$\dot{n}_p(t) = \frac{P_{Ps}J(t)}{4} + \frac{\lambda_{opc}(t)}{4}n_o - (\lambda_{2\gamma} + \lambda_{po})n_p, \qquad n_p(0) = 0. \tag{6}$$

surface-e$^+$ 0.5-0.7 ns

e$^+$ in Al-vac ~0.3 ns

qf-e$^+$; 0.18 ns

e$^+$*

qf-Ps; 0.2 ns
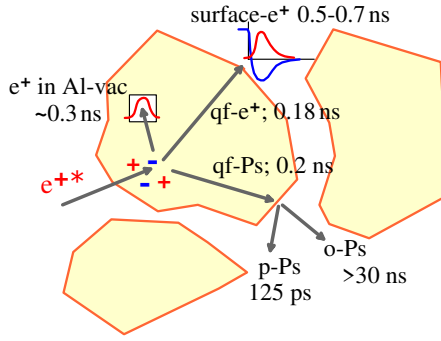
p-Ps 125 ps

o-Ps >30 ns

FIGURE 1. Formation of different positron states in Al$_2$O$_3$ nanopowders.

Here $n_b(t)$, $n_v(t)$, $n_s(t)$ and $n_{Ps}(t)$ are the probabilities to observe qf-e^+, vac-e^+, surf-e^+ and qf-Ps at a time t; λ_b, λ_v, λ_s and λ_{Ps} are the annihilation rates of e^+ in these states. P_{Ps} is the qf-Ps formation probability, $\varkappa_v$ is the qf-e^+ trapping rate by vacancy-type defects (here they are Al monovacancies), $\varkappa_s$ is the rate of reaching the cristallite boundary by qf-e^+ (as a result qf-e^+ transformes into surf-e^+). Actually the first three equations describe behaviour of positrons, escaping formation of qf-Ps. $n_o(t)$ and $n_p(t)$ are probabilities to find o-Ps and p-Ps in inter-crystallite space. $\lambda_{3\gamma} \approx 0.007$ ns^{-1} and $\lambda_{2\gamma} \approx 8$ ns^{-1} are the o-Ps 3γ-annihilation rate and p-Ps 2γ-annihilation rate in vacuum. λ_{po} is the pick-off annihilation rate of Ps, related with its short stayings in a crystallite near-surface layer, where e^+ wave-function overlaps with the wave function of e^- of the Al$_2$O$_3$ molecules of the top-surface layer of the crystallites. $\lambda_{opc}(t)$ is the ortho-to-para-Ps conversion rate. This process of Ps spin-conversion is due to the presence of the paramagnetic centers on the crystallite surface (adsorbed O$_2$ molecules). $J(t)$ is the diffusion flux of qf-Ps to the crystallite boundary (it determines o-Ps and p-Ps formation probabilities in the intercrystallite space).

Now let us estimate λ_{po} rate and demonstrate that one may neglect it below. Actually, according to the Tao-Eldrup model $\lambda_{po} \approx 2$ ns$^{-1} \cdot 2\delta_{TE}/\ell$, where $\delta_{TE} = 1.66$ Å and ℓ is the characteristic distance between the crystallites (comparable with the size of crystallites). Assuming that $\ell \simeq 100$-200 nm, we obtain $\lambda_{po} \approx 0.003$-$0.006$ ns^{-1}. So it leads to $\lambda_{po} < \lambda_{3\gamma} \approx 0.007$ ns^{-1}. In more coarse powders, it will be even less. Note, that λ_{po} does not depend on o-Ps velocity (when Ps velocity decreases, both the Ps time-of-flight between the crystallites and the Ps residence time in the crystallite near-surface electron layer increase proportionally). On the contrary, the ortho-para conversion rate, λ_{opc}, essentially depends on the Ps velocity. It is proportional to the frequency of Ps collisions with paramagnetic centers. In such collisions, the spin coupling between e^+ and e^- is broken and then restores again similar to how it occurs at Ps formation. So each act of ortho-para-conversion decreases $n_o(t)$ by a factor 3/4 in accordance with the spin statistics: $n_o \to 3n_o/4$. We do not take into account the inverse process of converting para-Ps to ortho-Ps state because of the very fast 2γ self-annihilation of p-Ps.

The diffusion flux $J(t)$ of qf-Ps on the grain boundary entered Eq. (4), as well as Eq. (4) itself, may be obtained by solution of the diffusion equation on the concentration of qf-Ps for the spherical grain (crystallite) having the radius L (D_{Ps} is the qf-Ps diffusion coefficient, λ_{Ps} is its annihilation rate):

$$J(t, \lambda_{Ps}, \lambda_J) = \frac{6\lambda_J e^{-\lambda_{Ps}t}}{\pi^2}\sum_{m=1}^{\infty} e^{-\lambda_J m^2 t}, \quad \text{where} \quad \lambda_J = \frac{\pi^2 D_{Ps}}{L^2}. \tag{7}$$

Kinetics of qf-Ps annihilation can be expressed as follows:

$$n_{Ps}(t) = P_{Ps}e^{-\lambda_{Ps}t}\left[1 - \int_0^t J(\tau)e^{\lambda_{Ps}\tau}d\tau\right], \tag{8}$$

$$\int_0^t J(\tau)e^{\lambda_{\mathrm{Ps}}\tau}d\tau = \frac{6}{\pi^2}\sum_{m=1}^{\infty}\lambda_J\int_0^t e^{-\lambda_J m^2\tau}d\tau = \frac{6}{\pi^2}\sum_{m=1}^{\infty}\frac{1-e^{-m^2\lambda_J t}}{m^2} = 1 - \frac{6}{\pi^2}\sum_{m=1}^{\infty}\frac{e^{-m^2\lambda_J t}}{m^2}.$$

For this sum, it is possible to suggest rather accurate analytical approximation, which simplifies carrying out numerical calculations when processing the spectra:

$$n_{\mathrm{Ps}}(t) = P_{\mathrm{Ps}}e^{-\lambda_{\mathrm{Ps}}t}\frac{6}{\pi^2}\sum_{m=1}^{\infty}\frac{e^{-m^2\lambda_J t}}{m^2} \approx P_{\mathrm{Ps}}e^{-\lambda_{\mathrm{Ps}}t}(0.39e^{-3.27\sqrt{\lambda_J t}} + 0.61e^{-\lambda_J t}). \tag{9}$$

Before discussing expressions for o-Ps and p-Ps, we make one simplification. In fact, the entire picture of the e^+ annihilation in nanopowders may be divided into two stages. The first stage is the annihilation of qf-e^+, vac-e^+, surf-e^+ and qf-Ps. The second stage is the thermalization and annihilation of Ps atoms in intergranular space. The duration of the first stage is about several nanoseconds. The second stage lasts much longer. Therefore, when all qf-Ps escape the intergranular space, the following equations can be used:

$$\dot{n}_o(t) = -\left(\lambda_{3\gamma} + \lambda_{po} + \frac{\lambda_{opc}(t)}{4}\right)n_o, \qquad n_o(0) = \frac{3P_{\mathrm{Ps}}}{4}\int_0^{\infty}J(t)dt, \tag{10}$$

This integral from $J(t)$ (it is the qf-Ps escape from the crystallite bulk) can be calculated exactly [5]:

$$\int_0^{\infty}J(\tau)d\tau = \frac{6}{\pi^2}\lambda_J\sum_{m=1}^{\infty}\int_0^{\infty}e^{-m^2\lambda_J\tau - \lambda_{\mathrm{Ps}}\tau}d\tau = \frac{6}{\pi^2}\sum_{m=1}^{\infty}\frac{1}{\lambda_{\mathrm{Ps}}/\lambda_J + m^2} =$$

$$= \frac{3}{\pi^2}\sqrt{\frac{\lambda_J}{\lambda_{\mathrm{Ps}}}}\left(\pi\coth\pi\sqrt{\frac{\lambda_{\mathrm{Ps}}}{\lambda_J}} - \sqrt{\frac{\lambda_J}{\lambda_{\mathrm{Ps}}}}\right), \qquad \int_0^{\infty}J(\tau)d\tau\bigg|_{\lambda_{\mathrm{Ps}}/\lambda_J\to 0} = 1. \tag{11}$$

Then

$$n_o(t) = n_o(0)\exp\left(-\lambda_{3\gamma}t - \lambda_{po}t - \int_0^t\frac{\lambda_{opc}(\tau)}{4}d\tau\right). \tag{12}$$

To find the p-Ps annihilation kinetics, one may use that p-Ps 2γ-annihilation rate is substantially greater than all other annihilation rates. So we can assume that all p-Ps which were formed during the time interval $t...t+dt$ annihilate during the same time interval (i.e. $\dot{n}_p(t) \approx 0$). Then

$$n_p(t) \approx \frac{1}{\lambda_{2\gamma} + \lambda_{po}}\left[\frac{P_{\mathrm{Ps}}}{4}J(t) + \frac{\lambda_{opc}(t)}{4}n_o(t)\right]. \tag{13}$$

For the sum entering expression for $J(t)$ in Eq. (7), we also obtained the analytical approximation. Then the first term in (13) takes the form:

$$\frac{P_{\mathrm{Ps}}}{4(\lambda_{2\gamma} + \lambda_{po})}J(t) \approx \frac{P_{\mathrm{Ps}}}{4(\lambda_{2\gamma} + \lambda_{po})}\cdot\frac{6\lambda_J e^{-\lambda_{\mathrm{Ps}}t}}{\pi^2}\left[\sqrt{\frac{\pi}{2\lambda_J t}}\cdot e^{-\sqrt{33\lambda_J t}} + e^{-\lambda_J t} + e^{-4\lambda_J t}\right].$$

Thermalization kinetics of Ps atoms ejected into intercrystalline space requires separate consideration. These Ps atoms lose their kinetic energy in collisions with the surface of the crystallites. Since the energy loss rate of the Ps atoms is small due to the large mass difference of Ps and colliding object, the thermalization kinetics is rather slow [1]. Assuming the ortho-para conversion rate is proportional to the frequency of Ps collisions with O_2 molecules, one obtains the following expression for $\lambda_{opc}(t)$:

$$\lambda_{opc}(t) = \frac{\mu v(t)}{\ell} = \frac{\mu v_{th}}{\ell}\cdot\frac{1 + \nu e^{-\alpha t}}{1 - \nu e^{-\alpha t}}, \qquad \nu = \frac{v_0 - v_{th}}{v_0 + v_{th}}, \qquad \alpha = \frac{2mv_{th}}{M\ell}. \tag{14}$$

Here m is the mass of Ps, and M is the mass of the object with which it collides (for example, when Ps collides with a single Al_2O_3 molecule, $m/M = 10^{-5}$), the recoil energy will be less, if Ps collides with a heavier object. v_0 is the initial Ps velocity at the moment when Ps escapes outside the crystallite (if Ps escapes having kinetic energy of 1 eV,

then $v_0 \approx 4.2 \cdot 10^7$ cm/s. $v_{th} \approx 8 \cdot 10^6$ cm/s is the thermal velocity of Ps at room temperature. It is clear that the ratio $\nu = \frac{v_0 - v_{th}}{v_0 + v_{th}}$ is very close to 1. With increase of time, the rate λ_{opc} decreases from $\mu v_0 / \ell$ down to $\mu v_{th} / \ell$.

The intergal vs. $\lambda_{opc}(t)$ over t, entering Eq. (12), is calculated analytically:

$$\int_0^t \frac{\lambda_{opc}(\tau)}{4} d\tau = \frac{\mu v_{th} t}{4\ell} + \frac{\mu M}{4m} \ln \frac{1 - \nu e^{-\alpha t}}{1 - \nu}. \tag{15}$$

If we assume that $\ell \simeq 100$ nm and the typical time of λ_{opc} variation is 10 ns (it means that $\alpha = \frac{2mv_{th}}{M\ell} \simeq 0.1$ ns^{-1}), we can estimate m/M ratio: $m/M \simeq 10^{-6}$. It means that when Ps collides with the surface of crystallites, approximately 10 Al$_2$O$_3$ molecules take on the recoil energy of the Ps atom.

Parameter μ characterizes efficiency of ortho-para conversion at each collision. Fitting the spectra we have found that $\mu \simeq 10^{-5}$-10^{-4}, so that the fraction of collisions in which Ps interacts with O$_2$ molecules adsorbed on the surface is small.

Shape of the LT spectrum is calculated in a conventional way. According to (1-6), the number of annihilations in the k channel of the time analyzer is:

$$C_{th}\left(t = \frac{t_k + t_{k+1}}{2}\right) \propto \left[\lambda_b n_b + \lambda_v n_v + \lambda_s n_s + \lambda_{Ps} n_{Ps} + (\lambda_{3\gamma} + \lambda_{po})n_o + (\lambda_{2\gamma} + \lambda_{po})n_p\right] \Delta t =$$

$$= \left[\lambda_b n_b + \lambda_v n_v + \lambda_s n_s + \lambda_{Ps} n_{Ps} + \left(\lambda_{3\gamma} + \lambda_{po} + \frac{\lambda_{opc}(t)}{4}\right)n_o + \frac{P_{Ps}}{4}J(t)\right]\Delta t. \tag{16}$$

To compare this expression with the experimental data, we must convolute it with the resolution function of the spectrometer and add the random coincidences background. If the experiments are done in air, the o-Ps quenching rate by air $\lambda_{air} \approx 0.004$ ns^{-1} [6] should be added to $\lambda_{3\gamma}$ (mostly oxygen is involved in this process).

This model also allows to calculate the intensity of the para-positronium ("narrow") component observed in CDB experiments:

$$Y_p = \int_0^\infty \lambda_{2\gamma} n_p(t)dt \approx \frac{\lambda_{2\gamma}}{4(\lambda_{2\gamma} + \lambda_{po})}\left[P_{Ps}\int_0^\infty J(t)dt + \int_0^\infty \lambda_{opc}(t)n_o(t)dt\right]. \tag{17}$$

In case of $\lambda_{3\gamma} + \lambda_{po} \ll \lambda_{opc}(t)$ and taking into account Eq. (15), the last term is reduced to:

$$n_o(0)\int_0^\infty \frac{\lambda_{opc}(t)}{4}\exp\left(-\int_0^\infty \frac{\lambda_{opc}(\tau)}{4}d\tau\right)dt = n_o(0)\left[1 - \exp\left(-\int_0^\infty \frac{\lambda_{opc}(t)}{4}dt\right)\right] = n_o(0). \tag{18}$$

Thus, taking into account Eqs. (10) and (11), we arrive to ($\lambda_{2\gamma} \gg \lambda_{po}$):

$$Y_p \approx P_{Ps}\int_0^\infty J(t)dt = \frac{3P_{Ps}}{\pi^2}\sqrt{\frac{\lambda_J}{\lambda_{Ps}}}\left(\pi \coth \pi \sqrt{\frac{\lambda_{Ps}}{\lambda_J}} - \sqrt{\frac{\lambda_J}{\lambda_{Ps}}}\right). \tag{19}$$

This expression has simple physical meaning. In this model the o-Ps atoms, which fly in the space in-between crystallites, do not annihilate by themselves ($\lambda_{3\gamma} \to 0$). Colliding with O$_2$, these o-Ps atoms convert to p-Ps atoms, which then decay into two 511 keV photons. Therefore, in this particular case all Ps atoms, which escape the crystallites and annihilate there, contributes to the narrow component of the CDB spectrum.

The developed model contains the following adjustable parameters: λ_b, λ_v, λ_s, P_{Ps}, $\varkappa_v$, $\varkappa_s$, as well as μ and m/M. However, one may take into account that the annihilation rates of qf-e$^+$ and qf-Ps must be close to each other $\lambda_{Ps} \approx \lambda_b$. Eq. (19) also imposes additional relation on the parameters. Parameter λ_b is determined (and fixed) from the fit of the coarse-grain defect-free powder. Also, if we assume that $D_{Ps} \approx 1$ cm^2/c, then $\lambda_J = \frac{\pi^2 D_{Ps}}{L^2}$ also becomes fixed. An example of application of this model for processing of the spectra of Al$_2$O$_3$ nanopowders is given in our 2-d paper of this issue [4].

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