Study of defect structure with new software for numerical analysis of PAL spectra

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Abstract. The positron trapping model is implemented into the code of LT 9-2 version of LT software. This allows to search directly for the positron trapping parameters of lifetime spectra relating to samples containing defects of vacancy type. The method of analysis, together with the possibility of simultaneous analysis of many lifetime spectra, enables one to reduce, in comparison with the conventional way of analysis, the number of free parameters used by the fitting procedure. LT 9-2 is employed to analyze artificial spectra simulated according to 2- and 3-state trapping model and the results are discussed with regard to the spectrum statistics and the way in which the calculation process is conducted.

1. Introduction
The LT program [1], and especially its newest version (LT 9), is one of the most popular software for positron lifetime spectra analysis. Usually, it is its simplest option, i.e. deconvolution of the lifetime spectrum into a few exponential components, which is chosen by most users. However, the program offers more options that can be used when dealing with some particular problems.

In the present paper we describe a new version (LT 9-2) of LT program which is especially useful for defect structure analysis by positron annihilation lifetime spectroscopy. To its code, the program has implemented the two- and three-state trapping models, which in connection with a possibility of simultaneous analysis of many lifetime spectra allows to reduce the effective number of free parameters used by the fitting procedure. This version is well tested for both artificial (simulated) lifetime spectra as well as the experimental ones.

The aim of this paper is to show the advantages of LT 9-2 and encourage the users to employ it in their investigations of defects in materials by PALS.

2. Defect analysis, theoretical models
The LT 9-2 program offers two theoretical models that can be used in analyses of positron lifetime spectra originated from samples containing defects of vacancy types:

1. The Conventional Model (CM) defined as a linear combination of exponential lifetime components

\[ S_{CM}(t) = \sum \frac{I}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right). \] (1)
2. The Simple Trapping Model (STM). LT 9-2 implements well-known [2,3] two- and three-state trapping models. As the two-state trapping model is a particular case of the three-state one it is the latter that will be discussed below. The model takes into account positron trapping (without the possibility of de-trapping) for two different kinds of defects. The trapping and positron annihilation processes (figure 1) are described by the system of differential equations

\[
\frac{dc_f}{dt} = (\lambda_f - \kappa_1 - \kappa_2) c_f \\
\frac{dc_1}{dt} = -\lambda_1 c_1 + \kappa_1 c_f \\
\frac{dc_2}{dt} = -\lambda_2 c_2 + \kappa_2 c_f
\]

with the initial conditions \( c_f(0) = 1 \) and \( c_{1,2}(0) = 0 \).

\( \kappa_1 \) and \( \kappa_2 \) are the trapping rates of the two types of defects, \( \lambda_f, \lambda_1, \lambda_2 \) are the annihilation rates (reciprocal of lifetimes \( \tau_f, \tau_1, \tau_2 \)) in the bulk and in the defects and \( c_f, c_1, c_2 \) denote the probabilities of finding the positron (at instant \( t \)) in the bulk, in the first or in the second type of defects. So the shape of the lifetime spectrum is

\[
S_{STM}^{STM}(t) = \lambda_f c_f + \lambda_1 c_1 + \lambda_2 c_2
\]

where, according to the solution of equations (2)

\[c_i = \frac{\kappa_i}{\lambda - \lambda_i} \left[ \exp(-\lambda t) - \exp(-\lambda_i t) \right], \quad i = 1, 2,
\]

and \( \lambda = \lambda_f + \kappa_1 + \kappa_2 \).

It can be easily noticed that the three-state trapping model can be transformed into a sum of three exponential components

\[
S_{STM}^{CM} = S_{CM} = I_0 \lambda \exp(-\lambda t) + \sum_{i=1}^2 I_i \lambda_i \exp(-\lambda_i t)
\]

where \( \lambda \) is given by equation (4),

\[I_i = \frac{\kappa_i}{\lambda - \lambda_i} \quad \text{and} \quad I_0 = 1 - I_1 - I_2,
\]

so formally there is no difference between the description of lifetime spectrum by STM or CM. The advantage of using the STM can be gained if one simultaneously analyzes more than one spectrum measured for the same material after its different treatment (more detailed explanation will be given in section 5).

3. Resolution
The experimental lifetime spectrum \( S_{ex}(t) \) is a convolution of the theoretical function \( S(t) \) (given by equation (1) or equation (3)) with the apparatus resolution function \( R(t) \)

\[
S_{ex}(t)=\int_0^\infty R(t-t_0)S(t_0)dt_0.
\]

The \( R \) function is approximated by a sum of a few Gaussians.
Each Gaussian is described by its intensity $I_i$, the width $(FWHM)_i = 2\sqrt{\ln 2\sigma_i}$ and the center position $t_{oi}$.

4. Analysis of series of spectra

LT 9-2, similarly to a few previous versions of this program, can process a series of lifetime spectra simultaneously. Usually, many spectra in a series are described by the same parameters (e.g. the parameters relating to the resolution curve, to the source contribution, etc.). Such parameters are defined as common while the parameters relating to a single spectrum are called local. The introduction of common parameters reduces the amount of possible degrees of freedom in the mathematical problem, which makes the solution more unequivocal and reliable.

5. Defect structure analysis: Conventional model or STM?

As it was mentioned above, the descriptions of a single spectrum by CM (equation (1)) or by STM (equation (3)) are equivalent so an analysis of a single spectrum can be performed with any of the models with identical effectiveness. However, STM is more effective when we simultaneously analyze a series of lifetime spectra originating from samples of the same material after a thermal or mechanical treatment if the treatment does not change the structure of the bulk. In such a case the lifetime $\tau_f$ relating to positron annihilation in the bulk can be defined as a common parameter. CM does not depend directly on the bulk lifetime as the first lifetime in CM (equation (5)) depends not only on the positron lifetime in bulk but also on the trapping rates of defects (equation (4)), therefore it cannot be chosen as a common parameter. This means that for a series consisting of $n$ spectra, STM requires by $n-1$ free parameters less than CM— that makes the analysis with STM advantageous.

6. Testing calculations for simulated spectra

Below we describe main features concerning the input data, typical program operation and the results.

6.1. 2-state-trapping model

The spectra used in the test were simulated according to the 2-state trapping model, (i.e. according to equations (3)-(4) at the assumption that $\kappa_2 = 0$). Each spectrum contained an additional component imitating a “source contribution” and was convoluted with a “resolution function” (equation (7)).

| parameter | $\tau_f$ | $\tau_1$ | $c_s$ | $t_{o1}$ | $(FWHM)_1$ | $l_2$ | $(FWHM)_2$ | $B$ |
|-----------|---------|---------|------|---------|-------------|------|-------------|-----|
| sample    | $\tau_f$ | $\tau_1$ | $c_s$ | $t_{o1}$ | $(FWHM)_1$ | $l_2$ | $(FWHM)_2$ | $B$ |
| source    | $\tau_f$ | $\tau_1$ | $c_s$ | $t_{o1}$ | $(FWHM)_1$ | $l_2$ | $(FWHM)_2$ | $B$ |
| resolution function | $\tau_f$ | $\tau_1$ | $c_s$ | $t_{o1}$ | $(FWHM)_1$ | $l_2$ | $(FWHM)_2$ | $B$ |
| background | $\tau_f$ | $\tau_1$ | $c_s$ | $t_{o1}$ | $(FWHM)_1$ | $l_2$ | $(FWHM)_2$ | $B$ |

Table 1. Values of the parameters used in simulations according to 2-state-trapping model and the respective values found by the fitting for both series of spectra of statistics $30 \times 10^6$ counts and $3 \times 10^6$ counts.

| sample | source | resolution function | background |
|--------|--------|---------------------|------------|
| (30M)  | 120.2  | 200.0               | 10.0       |
|        | 386    | 270                 | 40.0       |
|        | 350    | 600(30 \times 10^6) |
|        | 60     | (3 \times 10^6)      |
| (3M)   | 122.3  | 201.7               | 9.2        |
|        | 393    | 272                 | 37.4       |
|        | 342    | 599.8               |            |
|        | 59.9   |                      |            |

$s$ - bulk lifetime, $\tau_f$ – lifetime in defect, $c_s$ – source contribution, $l_{o1,2}$ – shifts of the centers of Gaussians, $(FWHM)_1,2$ – widths of the Gaussians, $l_2$ – contribution of the second Gaussian, $B$ – background level.
consisting of two shifted Gaussians. The spectra contained 2000 channels of width of 28 ps. Each spectrum was multiplied by 30 million (first series) or 3 million (second series) and a constant background (4% of total counts) was added. Eventually, the points in the smooth spectra were scattered by a Poisson noise. The values of the model parameters taken to simulations were common for all the spectra in a series except for the trapping rate ($\kappa_1$) which changed from spectrum to spectrum. The assumed values of the common parameters are listed in table 1, whereas figure 2 shows the various values of $\kappa_1$. The analysis of the simulated spectra was carried out in the following steps: At the beginning only the first spectrum of the series was fitted with initial values of $\tau_f = 100$ ps, $\tau_1 = 180$ ps, $\kappa_1 = 1$ ns$^{-1}$, $c_s = 9\%$ and $\tau_s = 380$ ps. The values of other parameters (relating to background and the resolution function) were estimated by the program automatically. After the fitting the program displayed preliminary values of the searched parameters (figure 3). These values were used as the initial values in the common analysis of the whole series of spectra.

Note: The best practice, which allows to avoid unnecessary arbitrariness in the analysis of positron lifetime data is to determine the instrument resolution function by a measurement of a reference sample with known lifetime(s) and kept it fixed in the subsequent analysis of lifetime spectra. It seems, however, that for a long series of spectra, measured in identical conditions, there is an alternative way of determining of the resolution function. It consists in choosing the parameters of the resolution function as common for the all analyzed spectra. One of the aims of the test described was to determine whether such a procedure proves itself successful in obtaining good results.

Before the common analysis started the status of each of the listed parameters was defined. All of the parameters were chosen as common except $\kappa_1$, $t_{01}$ and $B$ (figure 3) which were defined as local.

Table 1 contains the final values of common parameters obtained from the fitting and the assumed values of these parameters. The found values are very close to the assumed ones both for the series with $30 \times 10^6$ counts as well as for the series with $3 \times 10^6$ counts in a spectrum.

| Parameter                        | Value  | Fixed | Global |
|----------------------------------|--------|-------|--------|
| LIFETIME of sample comp. no. 1   | 0.205/80 | yes   |        |
| SOURCE CONTRIBUTION              | 9.000/00 | yes   |        |
| LIFETIME of SOURCE comp. no. 1   | 0.380/00 | yes   |        |
| Trapping const. KAPPA 1          | 1.015/02 | yes   |        |
| FREE positron LIFETIME           | 0.126/40 | yes   |        |
| FWHM                             | 0.267/40 | yes   |        |
| FWHM no. 2                       | 0.348/19 | yes   |        |
| SHIFT of ESG no. 2               | 4.693/76 | yes   |        |
| FRACTION of ESG no. 2            | 41.142/94 | yes  |        |
| Shift of “ZERO”                  | 0.000/00 | no    |        |
| BACKGROUND                       | 602.313/81 | yes  |        |

Figure 2. Left axis: The assumed (lines) and determined values (points) of $\kappa_1$ for the spectra of statistics $30 \times 10^6$ and $3 \times 10^6$ counts (denoted by 30M and 3M), simulated according to the 2-state-trapping model. Triangles represent results obtained with STM and circles – with CM. Right axis: The assumed values of $\tau_f$ (line) and the values determined with CM.
The found and assumed values of \( \kappa_1 \) are compared in figure 2. Some discrepancies between them are seen for \( \kappa_1 > 80 \text{ ns}^{-1} \). As expected, the discrepancies are much higher for spectra of lower statistics.

### 6.2. Conventional model

For comparison the same series of spectra (which were generated according to 2-state-trapping model) were analyzed with the help of CM. In this case the *local* parameters were \( \tau = \lambda^{-1} \) (where \( \lambda \) is defined by equation (4)), \( I_0 \) and \( I_1 \) (equation (6)). The status of *common* had \( \tau_i = \lambda_i^{-1} \) as well as the source and resolution parameters. The found values of \( \tau, \tau_1, I_0 \) and \( I_1 \) were recalculated into \( \tau_f \) and \( \kappa_1 \) on the basis of formulas which result from equations (4) and (6)

\[
\tau_f = \frac{\tau \tau_1}{I_0 \tau_1 + I_1 \tau}
\]

and

\[
\kappa_1 = \frac{I_1}{I_0} \left( \tau_f^{-1} - \tau_1^{-1} \right)
\]

The calculated values of \( \tau_f \) are shown in figure 2 (right axis). Only a few initial values of \( \tau_f \) (relating to the spectra with low trapping parameters) are close to their correct values. When \( \kappa_1 \) is higher than 10 the discrepancies between the found and correct values of \( \tau_f \) are large. Therefore in calculations of \( \kappa_1 \) from equation (10) the best value of \( \tau_f \), i.e. the first one, was used. Such determined values of \( \kappa_1 \) are shown also in figure 2 (left axis). They are much lower than the respective correct values when \( \kappa_1 \) exceeds ~10 ns\(^{-1} \). The comparison of the resulting values of \( \kappa_1 \) presented in figure 2 depicts evidently the advantage of direct using the STM in analysis of lifetime spectra.

### 6.3. 3-state trapping model

This time a series of lifetime spectra was simulated according to the 3-state-trapping model (equations (3)-(4)). The simulation procedure was similar to those described in the previous example. Each spectrum statistics was \( 30 \times 10^6 \text{ counts} \) (first series) or \( 3 \times 10^6 \text{ counts} \) (second series). The source, resolution and background parameters were identical with those chosen in the previous case. The common parameters used in simulations are shown in table 2 and values of the trapping rates (\( \kappa_1 \) and \( \kappa_2 \)) in figure 4.

We attempted fitting the data in several ways. It turned out that satisfactory results can be obtained

| sample | source | resolution function | background |
|--------|--------|---------------------|------------|
| parameter | \( \tau \) | \( \tau_1 \) | \( \tau_2 \) | \( c_s \) [%] | \( (\text{FWHM})_1 \) | \( l_2 \) [%] | \( l_{01} \) | \( (\text{FWHM})_2 \) | \( B \) |
| assumed values | 120.0 | 200.0 | 300.0 | 10.0 | 270 | 40.0 | 5.00 | 350 | 600 (30 \times 10^6) |
| found values | 120.8 | 200.6 | 304.3 | 10.0 | 270 | 40.2 | 4.95 | 350.8 | 599.8 |
| (3M) | 120.2 | 200.1 | 300.4 | 10.0 | 269.4 | 41.0 | 4.89 | 352.4 | 60.1 |

| \( \sigma \) - bulk lifetime, \( \tau \) – lifetime in first type of defects, \( \tau_1 \) – lifetime in second type of defects \( c_s \) – source contribution, \( l_{01}, l_2 \) – shifts of the centers of Gaussians, \( (\text{FWHM})_1, (\text{FWHM})_2 \) – widths of the Gaussians, \( I_2 \) – contribution of the second Gaussian, \( B \) – background level. |

when the initial values of the model parameters are not too far from their right values and when the fitting procedure consists of several stages. The starting values of *source contribution* and *source lifetimes* are also crucial. Below we described a successful attempt:
Stage 1. First spectrum (described by low trapping rates) is fitted with starting parameters \( \tau_f = 100 \text{ ps}, \kappa_1 = \kappa_2 = 0.1 \text{ ns}^{-1} \) (free parameters), \( \tau_1 = 190 \text{ ps}, \tau_2 = 320 \text{ ps}, c_s = 12\% \) and the correct value of \( \tau_s = 386 \text{ ps} \) (a fixed parameter). Starting values of the resolution and background parameters are estimated automatically by the program and treated as free ones.

Stage 2. The whole series is included into common fitting with the previously obtained values of parameters as the starting values. The parameters \( \tau_f, \tau_1, \tau_2, c_s \) and the resolution and background parameters have the common status, \( \kappa_1 \) and \( \kappa_2 \) are local while \( \tau_s \) is still fixed at its correct value.

Stage 3. The last spectrum of the series (described by the highest trapping rates) is analyzed separately. The fitting procedure starts from the current values of parameters obtained on stage 2. Only \( \tau_1, \tau_2, \kappa_1, \kappa_2 \) are free. All of the other parameters are fixed.

Stage 4. The series is analyzed from the last spectrum to the first one with previously determined values of parameters. The statuses of parameters are chosen like in the stage 2.

Table 2 contains the final values of common parameters whereas the determined values of \( \kappa_1 \) and \( \kappa_2 \) (points) for the first series of spectra (3\( \times \)10\(^6\) counts – solid symbols) and the second series of spectra (3\( \times \)10\(^6\) counts – opened symbols) simulated according to the 3-state-trapping model.

![Figure 4](image.png)

Figure 4. The assumed (lines) and determined values of \( \kappa_1 \) and \( \kappa_2 \) (points) for the first series of spectra (30\( \times \)10\(^6\) counts – solid symbols) and the second series of spectra (3\( \times \)10\(^6\) counts – opened symbols) simulated according to the 3-state-trapping model.

7. Conclusions
The testing calculations with the help of simulated spectra show that direct applying of the trapping model to the lifetime spectra analysis allows to obtain much better values of parameters characterizing the positron trapping process than in the case when the spectra are decomposed in the conventional way.

For the 3-state-trapping model the convergence of the fitting procedure is slow and its success strongly depends on the choice of values of initial parameters as well as on the details of the fitting process. Usually, the satisfactory results are achieved after many attempts.

Acknowledgement
Partial financial support of the Ministry of Science and Higher Education of Poland under the grant number 581/T/2006 is acknowledged.

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