INTERPRETATION OF POSITRON LIFETIME SPECTRA VIA LEAST SQUARES PRONY METHOD

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A method of numerical analysis of positron annihilation lifetime spectra has been devised. A new approach to determine the number of components in a spectrum was proposed and regularization procedure to solve the inverse problem concerning the estimation of useful components characteristics was formulated. The results obtained for model spectra demonstrate high resolution capability of proposed method.

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1. INTRODUCTION

One of the key problem in the modern nuclear power industry is the insufficient radiation resistance of the main structural materials of operating nuclear plants – of different classes stainless steels and of zirconium alloys. In particular, austenitic steels are characterized by a strong radiation swelling, which is related to formation during irradiation of vacancy clusters – microvoids and vacancy loops [1]. Positron beam presents a unique probe for vacancy-type defects.

The positron is an antiparticle of the electron, which has the same mass (0.511 MeV/c^2), but a positive charge. After implantation into solid energetic positron quickly loses its energy and thermalizes (for $\sim$ 3 ps). Thermalization time is much less than its mean lifetime.

After reaching thermal equilibrium with the host positron is scattered by phonons and walks randomly. The random walk lasts much longer than the thermalization process, i.e. between 100 and 500 ps. Due to the repulsion of positively charged ion cores and the attraction to the conduction electrons positron localizes mainly in the interstitial space and its positive charge causes that it annihilates mainly with the valence or conduction electron. The probability of the annihilation with the core electrons is much lower. In perfect crystal all positrons annihilate with the same rate λ_b which is the characteristic of material under study.

In the crystal with structural defects positron may be attracted to the local formations which are characterized either by excess negative charge, or by increased affinity to the positron. Such defects can be defined as positron-sensitive. Vacancies, vacancy clusters, as well as other local free volumes present defects of the first type.

Each element has a unique positron affinity and the latter may localizes within particular precipitates of high affinity, which form the positron-sensitive defects of the second type. Elements important in the reactor material science, have the following values of this characteristic [2]: Fe, -3.84 eV; Cu, -4.81 eV; Ni, and Mn, -3.72 eV.

Positron annihilation spectroscopy (PAS) involves mainly three methods of analysis:

- the temporal distribution of annihilation photons;
- the angular distribution of annihilation photons;
- the Doppler broadening of the annihilation line with the energy of 0.511 MeV.

The first of these techniques gives information on the electron density of the material at the place of annihilation, and two others – information on the momentum distribution of the electron-positron annihilation pair and consequently information of the chemical environment of the annihilation site.

Positron lifetime τ is determined by the overlap of the electron density $n_-(\mathbf{r})$ and the positron density $n_+(\mathbf{r}) = |\psi_+(\mathbf{r})|^2$ at the annihilation site

$$\lambda = \frac{1}{\tau} = \pi r_0 c^2 \int |\psi_+(\mathbf{r})|^2 n_-(\mathbf{r}) \gamma d\mathbf{r}, \qquad (1)$$

where $\gamma = \gamma[n_-(\mathbf{r})] = 1 + \Delta n_-/n_-$ – the correlation function, which describes the increase Δn_- in electron density due to the Coulomb attraction between a positron and an electron, r_0 is the classical electron radius.

Since an open-volume defect has reduced local electron density, the positron lifetime in such defect increases with respect to the defect-free sample. Thus, in experimental spectrum component with longer lifetime, which is a measure of the defect size, appears.

To measure the positron annihilation lifetime spectrum most common source by far has been ^{22}Na

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which has long half life (2.6 y) coupled with reasonable price. The method consists in measuring the counting rate of delayed coincidences between nuclear γ-ray with energy 1.28 MeV generated simultaneously with the birth of positron in e^+-decay $^{22}Na \rightarrow {}^{22}Ne + e^+ + \gamma(1.28\text{ MeV})$ and one of annihilation γ-quanta of an energy of of 0.511 MeV.

The time difference between these two signals determines the positron lifetime for a single event. The lifetime is a random quantity and like any random variable must be described by its probability distribution function or equivalently by the set of all its moments.

In a sample containing k various positron-sensitive defects the positron lifetime spectrum has the form

$$s(t) = \sum_{j=1}^{k+1} \frac{I_j}{\tau_j} exp\left(-\frac{t}{\tau_j}\right), \qquad (2)$$

i.e. is the weighted sum of $(k+1)$ identical distributions, each of which can be completely described by a single moment – mean value τ_j or mean positron lifetime for the state j. The aim of the spectrum analysis is the extraction from the experimental signal the set of these parameters $\{I_j, \tau_j\}$ for $j = 1, \ldots, k+1$.

For particular defect mean positron lifetime depends only on the type of defect, and corresponding strength of this component, i.e. its intensity, is directly related to the defect concentration. In principle, both items of information, i.e. the kind and relative abundance of the defect under investigation, can be obtained independently by a single measurement.

For the analysis of positron lifetime spectra various approaches have been used but up to now the most commonly used are approaches based on the Gauss-Newton non-linear least square fitting [3]. It is well known that it presents a time-consuming iterative scheme of multidimensional minimization.

In the paper the new approach to this problem is proposed. It is also based on a nonlinear least squares method, but it uses efficient (fast) algorithms. Within this approach we studied two problems.

The first one concerns estimation of the number of components which compose the experimental positron lifetime spectrum. The conventional solution is to start with one-component fit and add components as long as the variance of the fit decreases. The weakness of this solution is well known: the variance of the fit usually does not reach a minimum value but rather monotonically decreases with increasing of model order.

Another problem concerns the ill-posed nature of the inverse problem [4] under study. This means that the problem is inherently unstable and so for its solution one have to use some sort of regularization procedure.

2. COMPUTATIONAL PROCEDURE

In experiment a continuous signal (2) is necessarily discretized i.e. its sample values is measured in the nodes of some uniform grid. In this case, the discretized spectrum of positron lifetime is defined as a set of N data points $x[1]$, $x[2]$, ... , $x[N]$, corresponding to values of the function $s(t)$ at a points $t = 0, \Delta, ..., (N-1)\Delta$.

Real positron lifetime spectrum differs from this model in that it contains not only the useful signal but also a noise. Therefore let us try to estimate this spectrum with a general p-membered model of complex exponentials

$$\tilde{x}[n] = \sum_{j=1}^{p} A_j exp\left[(\alpha_j + i2\pi f_j)(n-1)\Delta + i\theta_j\right]. \qquad (3)$$

Here i is imaginary unit; $1 \le n \le N$; A_j, α_j, f_j and θ_j are the amplitude, damping coefficient, frequency and phase constant accordingly for j-th complex exponential. Note that we do not impose any restrictions on the values of all these parameters. As a consequence sum (3) may contains both pure decaying exponential, corresponding to the individual distribution in the spectrum (2) and high-frequency undamped sinusoid corresponding to the noise component in the experimental signal. Accordingly, the order of the model in general will be greater than the number of states in the positron lifetime spectrum.

In shorthand notation one can write down the function of discrete time (3) as

$$\tilde{x}[n] = \sum_{j=1}^{p} h_j z_j^{n-1}, \qquad (4)$$

where

$$h_j = A_j exp(i\theta_j), \qquad (5)$$

$$z_j = exp[(\alpha_j + i2\pi f_j)\Delta]. \qquad (6)$$

For N sampled values one have to minimize the sum

$$\rho = \sum_{n=1}^{N} |\varepsilon[n]|^2, \qquad (7)$$

$$\varepsilon[n] = x[n] - \tilde{x}[n] = x[n] - \sum_{j=1}^{p} h_j z_j^{n-1}, \qquad (8)$$

simultaneously over parameters h_j, z_j and the number of terms p. This is an extremely complicated nonlinear problem even for the case where the order p of the exponential model is known in advance.

The traditional way to resolve this problem implies the application of iterative algorithms of multidimensional minimization. This approach has the following shortcomings. These algorithms are tedious, the obtained solution is very sensitive to the choice of starting values of the independent variables and the solution may converge to a local but not to the global extremum in multidimensional space. However these methods as a rule are very flexible and can be applied to any non-linear approximation of sampled values and not necessarily to the exponential one.

On the other hand for the latter approximation there is a group of specially developed methods usually defined as the Prony method [5]. The Prony

method is not iterative and reduces the nonlinear aspects of the problem to finding roots of polynomials. It is worth noting that for the last task highly effective computational algorithms have been elaborated. That is why the Prony method was used as the basis for an effective scheme of interpretation of positron annihilation lifetime spectra.

3. ANALYSIS OF THE MODEL POSITRON ANNIHILATION LIFETIME SPECTRA

On the basis of the Prony method the computer code Q_fit was written for processing positron annihilation lifetime spectra. To test the performance of this code we used several series of simulated spectra. This approach is analogous to the one proposed in [6]. Moreover, in order to compare the results of processing of the spectrum with different codes we used the same set of input parameters as in [6].

For a given set of lifetime values and relative intensities a number of different spectra were simulated which formed the series. Each spectrum in the series consists of a given number of counts. For each count we first selected particular state in (2) in which the positron annihilates and then for this state generated one deviate with an exponential distribution function. In both cases the inverse function method was used to transform the random deviate with a uniform probability distribution.

Each spectrum then has been convoluted with a spectrometer time resolution function which as in [6] was taken in the form of the single Gaussian with FWHM = 270 ps. For convolution we used a FFT-algorithm after prior setting up of buffer zone of zero-padded values at the end of a spectrum and bounding the Fourier transform of spectrometer resolution function. Similar algorithms were used for the inverse operation of deconvolution.

Series A. [2 components: 150 ps (50%) , 250 ps (50%); number of channels: 128; time calibration: 33 ps/channel; counts per spectrum: 2×10^6 ; number of spectra in a series: 5].

Let us use this simplest two-component spectrum with well separated and equally intensive components to illustrate the procedure of determining the number of states in (2). First of all we applied the program Q_fit to the pure noise-free spectrum when the sampled values were obtained by exact integration of the useful signal (2) over the channels of MCA. For a successively increasing order of exponential model (3) we obtained:

1) $p = 1$: pure decreasing real exponential (that is both frequency and phase constant are zero within computational accuracy) and average lifetime $\tau \approx 195$ ps.

2) $p = 2$: the single exponential splits into two pure decreasing real exponentials whose parameters are exactly equal to the input ones.

3) $p = 3, 4, 5$: all terms of the exponential model can be subdivided into two subsets The first subset is comprised of two real exponentials, the same as in 2). The second subset includes the remaining exponentials of the model and all of them within the computational accuracy have zero intensity.

4) $p = 6$: interruption in the subroutine for the fast solution of the covariance equations of linear prediction because in the iterative process the variance of forward prediction became negative.

In Fig.1,a mean lifetime values of real exponentials versus the order of exponential model are shown. From this figure it is clear that the spectrum has two components.

The same conclusion can be drawn from the variance of linear prediction versus the order of exponential model dependency (Fig.1,b). Indeed, the value for $p = 2$ divides into two regions with sharply different diminishing rate of variance of both the forward and backward prediction. That is although for $p = 2$ the variance, strictly speaking, does not reach a minimum we nevertheless are able to figure out when further addition of exponential terms does not lead to any practically sufficient improvement of the approximation.

Unfortunately, for simulated spectra the situation is quite different. In this case the number of counts on each grid point is subjected to the statistical fluctuation, and the spectrum as a whole consists of the useful signal and a noise. For such spectrum the variance of both forward and backward prediction monotonically decrease as the order of the exponential model increases. Therefore in this case one have to use a different approach to determine the number of states in a spectrum.

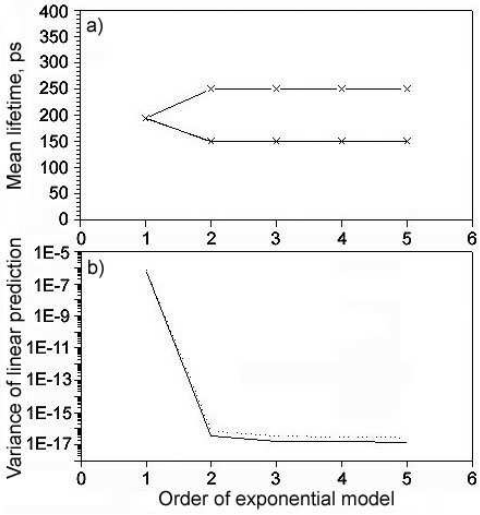

Fig.1. *Application of the program Q_fit to the noise-free spectrum of series A: (a) mean lifetime of pure decreasing real exponentials with nonvanishing energy; (b) variance of forward (solid line) and backward (dotted line) prediction*

Fig.1,a contains a hint of this approach. We already noted that the processing of positron lifetime spectrum belongs to the so called ill-posed inverse problem. Let us recall briefly the basic ideas that are used in inverse problem theory.

As a rule we can define two positive functionals A and B. The first of them measures the agreement of a model to the data while the second one measures something like the "smoothness" of the desired solution.

When A by itself is minimized the agreement becomes very good, but the solution becomes unstable. In another extreme case, minimizing B by itself gives smooth solution that has nothing at all to do with the measured data. So, the central idea in inverse theory is to minimize the weighted sum of these two functionals.

Increasing of exponential model order leads to the improvement of the agreement between the solution and the underlying spectrum, that this solution becomes closer and closer to the nonsmooth initial signal. But the solution sought must look like the useful signal (2). So we have to smooth the derived solution. One way to do this is to maintain in decomposition (3) only a few most energetic pure decreasing exponentials.

From a standpoint of signal processing the energy E of a discrete sequence $x[i]$ $(i = 1, 2, ..., N)$ is defined as

$$E = \sum_{n=1}^{N} |x[i]|^2. \tag{9}$$

Therefore all terms of the exponential approximation can be divided into two subsets. The first one will be comprised by pure decreasing real exponentials, that is by terms j in (3) satisfying following conditions

$$\alpha_j < 0, \quad |f_j| < \varepsilon, \quad |\theta_j| < \varepsilon \tag{10}$$

where ε is the machine-dependent precision parameter which in our calculation was taken as 10^{-5}. Another subset will contain the remaining exponentials of the model, that is terms for which any of the conditions (10) has broken down.

Let us restrict our consideration to the spectra (most important for applications) which do not contain very weak components. In this case we can proceed further with a classification of exponential terms in approximation (3). For any spectrum we can calculate its energy E_s (9) and then leave in the first group only those exponentials whose energy exceed some prescribed fraction (say, 0.005) of E_s.

Thus far we have classified only individual terms of the exponential model. But there is also a restriction which should be imposed on the first subset of exponentials as a whole. Indeed, these exponentials will form the useful signal (2) and this signal as any probability distribution function should be normalized. Therefore useful components in the approximation (4), must satisfy the following master conditions:

1) each of them is real and decreasing, i.e. satisfies (10);

2) its energy is not negligible compared to the energy of the whole spectrum;

3) for a given order p these components as a whole form a normalized probability distribution function.

And as a last step we can define the optimal range of the exponential model as a range of p where the number of its terms satisfying master conditions and their mean values are virtually constant. The analysis showed that for series A the optimal range is defined by the following inequality $10 \leq p \leq 63$. Thus, we get the conclusion that a particular spectrum from this series consists of two components and these two components form the smoothed desired solution.

What we have just described can be viewed as a way to determine the number of states in a positron-lifetime spectrum and at the same time as a regularization procedure applied to the inverse problem under study.

Note that the algorithms used in code Q_fit and applied to the highest possible value p_{max}, gives at the same time solutions for all orders $p \leq p_{max}$ without any additional expenditure. Therefore the treatment of the entire series of spectra are naturally divided into two successive stages.

At the first one for a particular spectrum of the series the procedure described above is applied. The result is the estimations of number of states in the spectrum and of optimal range of the exponential model. At the second stage, these estimations are used in the computational procedure as input parameters. The code Q_fit for one particular value of p from optimal range determines the parameters of all components in the exponential approximation (3) and divides them into two subsets. Then first subset (forming the regular part of solution) is verified relative to the master conditions. If both of the master conditions are satisfied and at the same time the number of states in the regularized solution coincides with that defined in the first stage, then the found solution is accepted. Otherwise, the next value of p from the optimal range is selected.

To test and compare the performance of different codes we defined artificial and very complex four-component spectrum [6].

Series B. [4 components: 100 ps (25%), 250 ps (25%), 600 ps (25%), 1000 ps (25%); number of channels: 128; time calibration: 58 ps/channel; counts per spectrum: 2×10^6 ; number of spectra in a series: 10].

The results obtained by applying to this spectra of different codes are presented in Table. All codes were able to resolve four components in spectra, but the $MELT$ results show a correlation between two longest components. In this respect both $Posgauss$ and Q_fit performs better.As a whole Q_fit gives estimators with the smallest bias but with significantly larger errors. The scatter in the results of Q_fit may be due to the high resolution capability of the proposed method.

In Fig.2 for a particular data set from series B the mean lifetime for all exponentials satisfying the master conditions is shown. It can be seen that the whole range of the exponential model order in Fig.2 can be subdivided into three intervals: (1) $8 \leq p \leq 15$; (2) $32 \leq p \leq 35$; (3) $42 \leq p \leq 57$ where the parameters of pure decreasing exponentials remain virtually constant. These intervals are separated by transition ranges.

Mean values for lifetimes τ_i and weights I_i, $i = (1, ..., 4)$ found by $MELT$, Posgauss [6] and Q_fit for simulated spectra, from the series B . The errors represent the standard deviations from the mean values.

Analysis method	$t_1(dt_1)$,ps $I_1(dI_1), \%$	$t_2(dt_2)$,ps $I_2(dI_2), \%$	$t_3(dt_3)$,ps $I_3(dI_3), \%$	$t_4(dt_4)$,ps $I_4(dI_4), \%$
Simulation	100 25	250 25	600 25	1000 25
$MELT$ [6]	103.1 (0.6) 25.27 (0.35)	254.9 (4.3) 23.94 (0.36)	559.3 (14.1) 20.92 (0.80)	947.8 (6.4) 29.87 (0.94)
$Posgauss$ [6]	100.6 (0.7) 25.31 (0.40)	254.9 (4.8) 25.34 (0.27)	618.4 (13.7) 25.89 (0.57)	1012.1 (8.1) 23.47 (1.02)
Q_fit	100.2 (1.7) 24.81 (1.32)	245.9 (14.2) 24.59 (0.78)	592.0 (28.0) 25.34 (0.93)	998.9 (12.9) 25.24 (1.78)

The first of them corresponds to a three component model, the second to the four components with biased estimations and the third to the four component model with unbiased estimations. So, the more exactly the noise in the spectrum is described the more reliable is the spectrum decomposition.

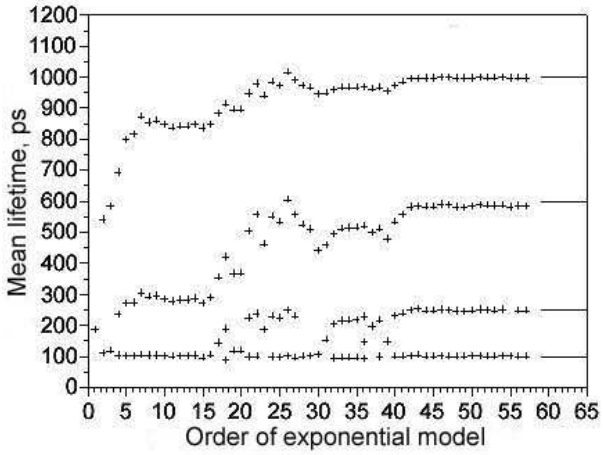

Fig.2. *Mean lifetime of the exponential model terms satisfying the master conditions for one particular data set from series B*

4. CONCLUSION

A new approach to analyze the positron lifetime spectra was proposed. This approach is based on a non-linear least square method but differs from the existing ones in that it uses fast algorithms and a more flexible basic set. This allows to use a model function with a large number of components and thus to describe readily and with reasonable accuracy both useful and noise parts of the spectrum.

These parts can further be separated and this separation is equivalent to some regularization procedure. It should be stressed that in contrast to the common practice we did not use any low pass filter. Therefore, our method is free from the undesired consequences of such filtering. As a result a regularized smooth solution gives unbiased estimations of parameters of the useful signal with a high resolution capability.

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ИНТЕРПРЕТАЦИЯ СПЕКТРА ВРЕМЕНИ ЖИЗНИ ПОЗИТРОНОВ НА ОСНОВЕ МЕТОДА НАИМЕНЬШИХ КВАДРАТОВ ПРОНИ

А.И. Кульментьев

Разработан метод численного анализа спектров времени жизни позитронов. Предложен новый подход определения числа компонент в спектре и сформулирована регуляризационная процедура решения обратной задачи оценки характеристик полезных компонент. Результаты, полученные на модельных спектрах, демонстрируют высокую разрешающую способность предложенного метода.

ІНТЕРПРЕТАЦІЯ СПЕКТРІВ ЧАСУ ЖИТТЯ ПОЗИТРОНІВ НА ОСНОВІ МЕТОДУ НАЙМЕНШИХ КВАДРАТІВ ПРОНІ

О.І. Кульментьєв

Розроблено метод чисельного аналізу спектрів часу життя позитронів. Запропоновано новий підхід до визначення числа компонент у спектрі і сформульована регуляризаційна процедура вирішення зворотної задачі оцінки характеристик корисних компонент. Результати, які отриманні на модельних спектрах, демонструють високу роздільну здатність запропонованого методу.