INVESTIGATION OF DIFFERENT MATERIALS WITH POSITRON ANNIHILATION LIFETIME SPECTROSCOPY

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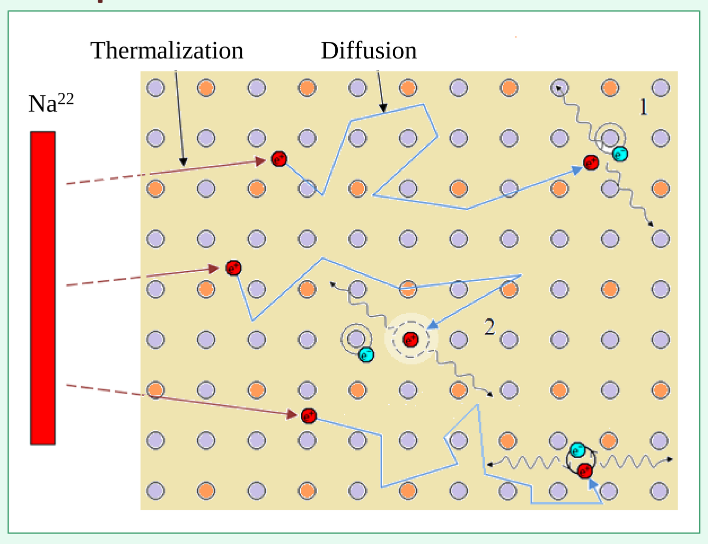
Methods of positron annihilation spectroscopy are sensitive to the materials electron structure, therefore this methods can be used to study such defects, as vacancies and porous. The method of measuring the positron lifetime (positron annihilation lifetime spectroscopy, PALS) is used in this work. The lifetime of positrons depends on the bulk electron density of the substance and concentration of defects - "traps" with a reduced electron density. Vacancy-type defects can be such "traps" for positrons. The lifetime of positrons in a defect-free substance varies for the different materials. In the vacancies positron lifetime increases in comparison with the bulk lifetime. The positron lifetime spectrum of materials containing defects is the sum of at least two exponential components: a short-lived and long-lived component. The lifetime of a long-lived component characterizes the type of defect. The concentration of defects can be determined from the trapping rate, which is related to the intensity of the long-lived component. Similar reasoning is also valid for the determination of pore sizes and concentration in porous materials where the positronium atoms are formed. PALS can be used also for the multiphase substances studying to determine the contribution of various phases, for example.
An important part of PALS is the simulation of experiments. Simulation is used for the correct evaluation of the source contribution to the experimental spectra, for the determination of positron implantation depth profile and for the selection of the optimal geometry of the experiments. Some results of Monte Carlo simulation of PALS experiment are discussed in presented work.

Positron annihilation lifetime spectroscopy

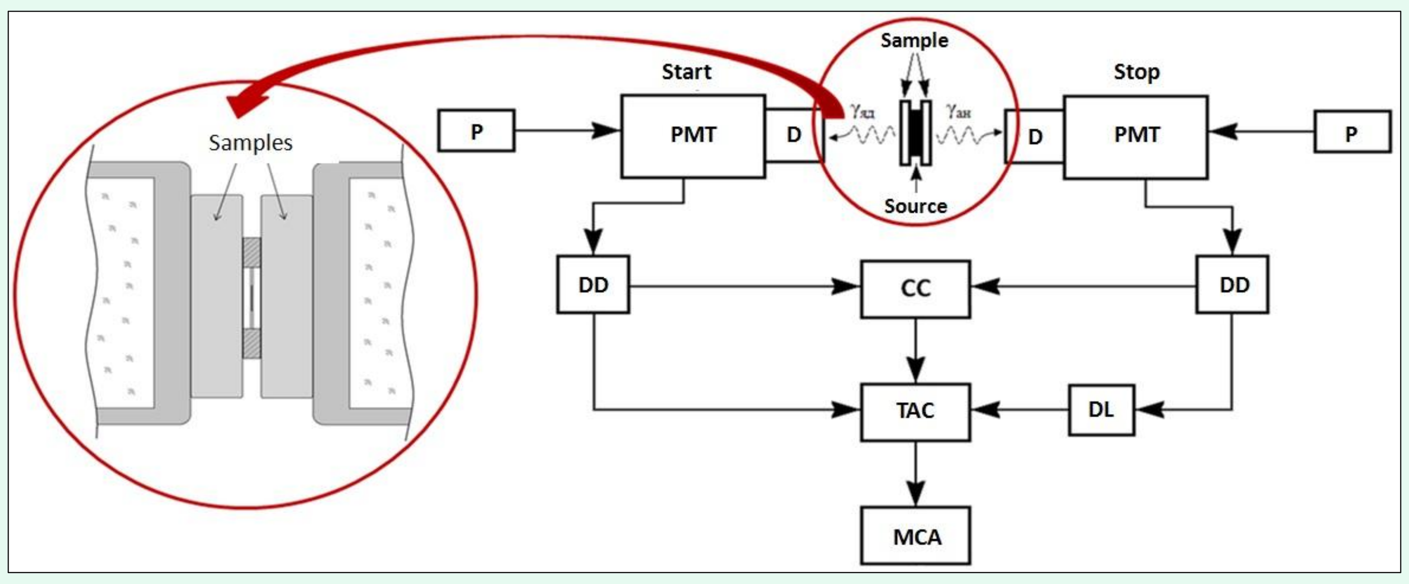
The study of the defect structure of matter using the positron annihilation is based on measuring the positron lifetimes in matter, changes in the energy of annihilation gamma quanta, or in the direction of their emission. The subjects of the study usually are the electron density of the material, the type and concentration of defects, the chemical environment of the positron annihilation point, the changing of these parameters under various external influences.



In the sample fast positrons are slowing down to thermal energies in a time less than 1 picosecond. Then they annihilate either in free collisions with the electrons of the substance or from the localized state at the trapping centers. Such trapping centers include, first of all, vacancies and vacancy complexes. When positively charged ion is removed from the crystal lattice a vacancy is formed, and it will be locally negatively charged, due to the overflowing of the surrounding electron density into the vacancy volume. This effect causes the attraction of the positron to the vacancy.

The positron lifetime is inversely proportional to the electron density in defect. Since the electron density in different types of defects differs, the positron lifetime is an individual characteristic of each type of defects. By decomposing the lifetime spectrum into exponential components, it is possible to determine the types of defects in the sample. The intensity of each component of lifetime spectrum is proportional to the concentration of a given type of defect in the sample.

Positron annihilation lifetime spectrometer and measuring geometry for solid-state samples



The positron lifetime is measured as the time interval between the signal from the nuclear gamma quantum accompanying positron production in the beta decay of ^{44}Sc, and the signal from the annihilation gamma quantum: $e^+ + e^- \rightarrow 2\gamma$.

Determination of vacancies concentration with using the trapping model

When the lifetime spectrum is decomposed into only two components, one of which corresponds to annihilation from the free state τ_B and the other from the trapped state in vacancies τ_V, the intensity of these components can be used to calculate the concentration of vacancies:

$$C_V = \frac{1}{\mu_V}\frac{I_V}{I_B}\left(\frac{1}{\tau_B}-\frac{1}{\tau_V}\right),$$

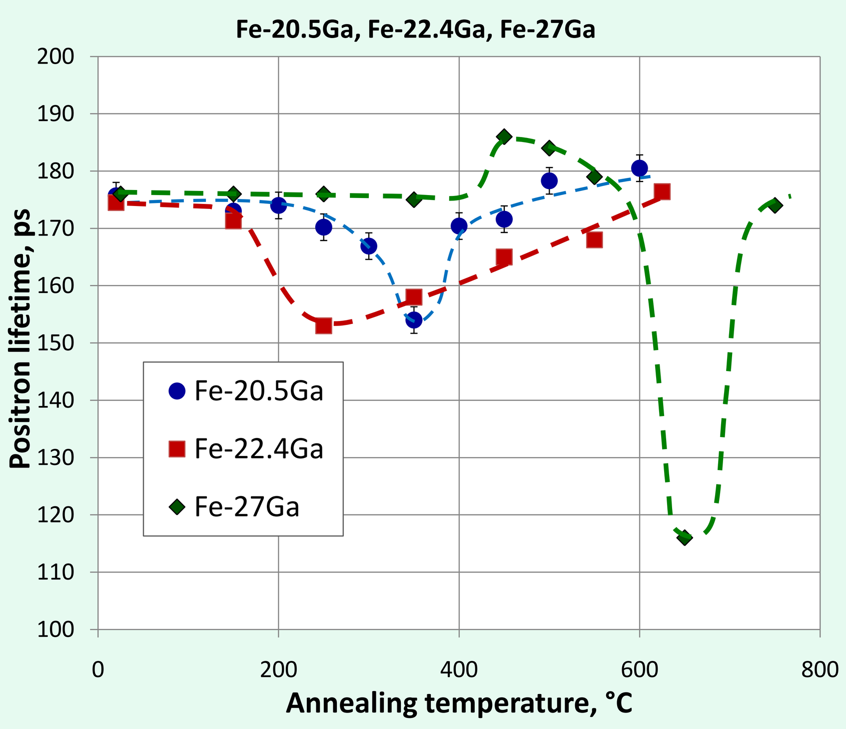
where the trapping rate:
$\mu_V \approx 10^{15}$ at. s^{-1}

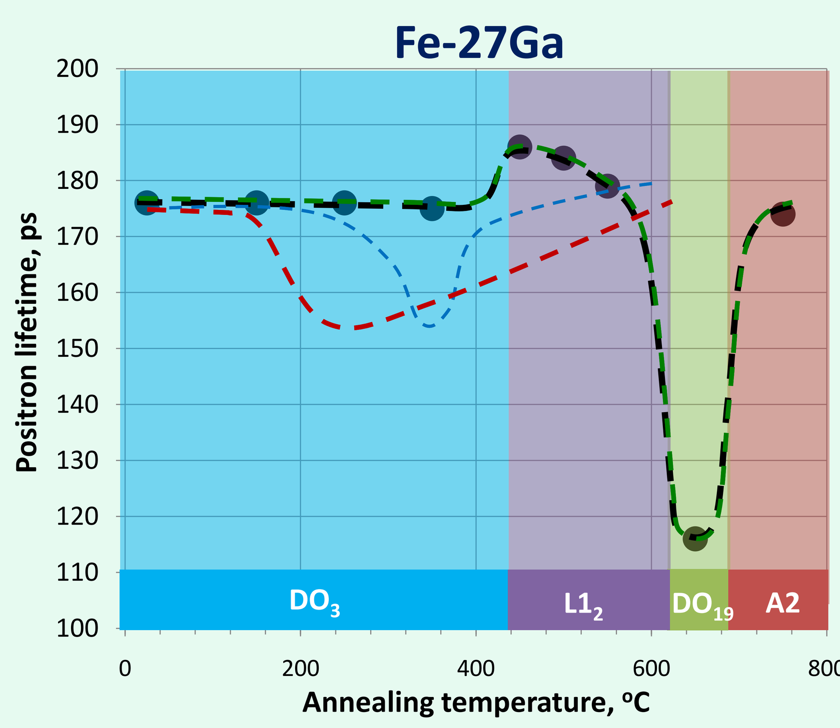
The dynamic range of the spectrometer in measurements of the vacancies concentration is:

Maximum concentration: $C_V^{max} = 10^{-4} at.^{-1}$

Minimum concentration : $C_V^{min} = 10^{-7} at.^{-1}$

The results of Fe-Ga alloys investigation





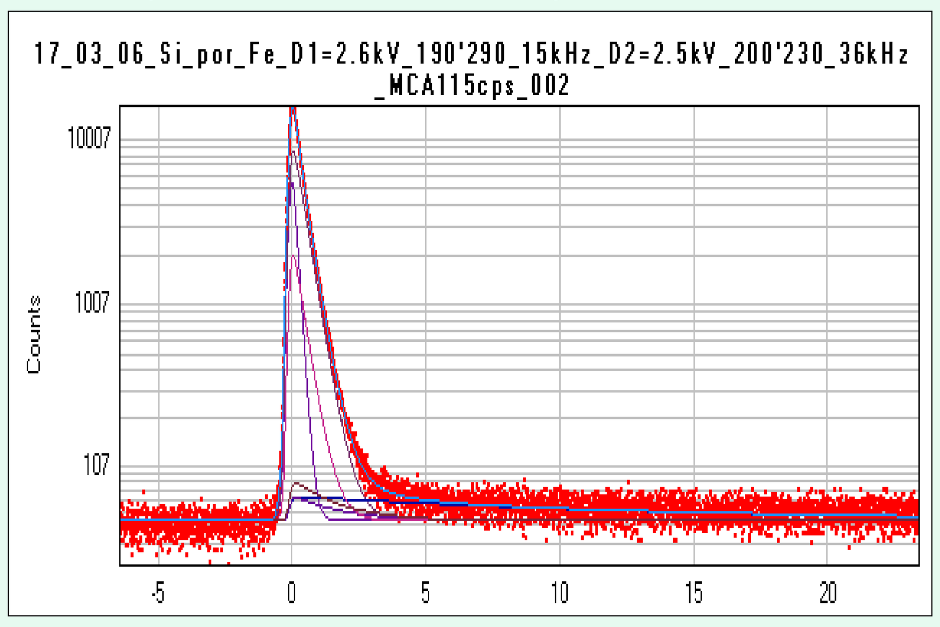
In Fe-20.5Ga, the average positron lifetime begins to change after annealing above 200° C, when the alloy partially transform into the metastable $D0_3$ phase. Annealing at 350° C leads to the maximum $D0_3$ fraction and a minimum value of the average positron lifetime (155 ps) is achieved. The decrease in the lifetime is apparently due to an increase of the fraction of positrons annihilating in $D0_3$ phase with a low vacancy concentration. A similar effect is well known for Fe_3Al, where the $D0_3$ phase also has a low positron lifetime close to the bulk lifetime (τ_B).
The maximum intensity of the component corresponding to the defect-free $D0_3$ structure is about 25% at a temperature of 350° C. Further annealing above 400° C leads to a sharp increase of the average lifetime of positrons due to the formation of $L1_2$ phase, with a high content of monovacancies.
In Fe-22.4Ga sample, the formation of D03 occurs faster due to the greater closeness of its composition to the stoichiometric composition. The formation of $L1_2$ also begins earlier, which is also associated with slow cooling in the furnace.
Although the results of structural analysis show a high volume fraction of $D0_3$ in Fe-27Ga before the formation of the $L1_2$ phase, this does not lead to a decrease in positron lifetime. This means that the concentration of vacancies in $D0_3$ phase in Fe-27Ga sample is more than $2*10^{-4}$ at^{-1}, in contrast to alloys with a lower Ga content. Fe vacancies could form to compensate the deviation of the composition of Fe-27Ga from the stoichiometric composition of completely ordered $D0_3$ phase.

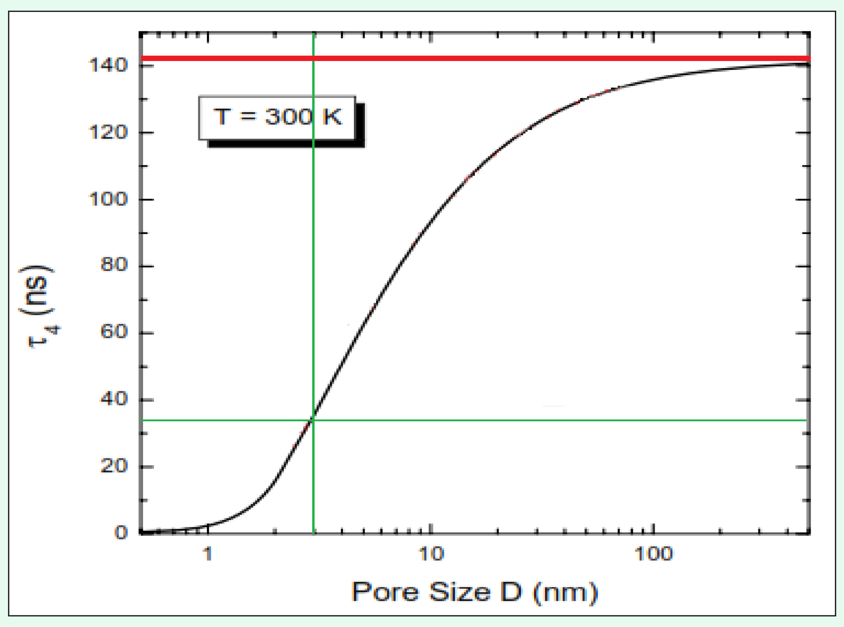
Simulation of positron lifetime spectrometer

The Monte Carlo simulation of positron lifetime spectrometer described here is based on GEANT4 used via the GATE simulation environment and the Matlab toolkit. It takes advantage of GEANT4's capabilities for modeling the setup as well as transport of beta particles and c-rays and their interactions with matter. It also takes advantage of the Matlab data structures for efficient processing of the GEANT's track data.
The simulated setup includes the positron source, samples, two cylindrical scintillators as detectors. The real construction and sizes of each geometry element is used in the model. All elements may be placed at different distances from the center of the spectrometer and from each other.
Typically for every arrangement of simulated setup 10 millions of source decays are generated. Nuclear photon and positron are generated for the each decay in the source, with their parameters, such as the time, the momentum and the energy. Then two annihilation photons are emitted as a result of the positron annihilation.
The model considers the photoelectric effect, the coherent and Compton scattering for photons and the multiple scattering, the ionization, the bremsstrahlung for positrons and electrons. The changes for the particle's energy and momentum are calculated for each interaction.
The simulation allows to estimate an influence of the measuring geometry on the spectrum distortion, including the source contribution, and to choose the most appropriate measuring geometry for each kind of samples.

The results of porous Si investigation

If the investigated material contains the pores with a size > 0.1 nm, the formation of a positronium atom in matter becomes possible. The positronium lifetime can be quite large (up to 140 ns in vacuum), so its formation in matter can be concluded from the presence in the measured lifetime spectrum of the component with a lifetime of about 1 ns. The lifetime and intensity of this component can be used to determine the concentration and size of the pores, similar to the trapping model for vacancies.
A significant limitation in the measurement of this long-lived component of the spectrum can be a high activity of the positron source, since random annihilation events (genetically not associated with the starting gamma quantum) can occur in a shorter time interval than the lifetime of positronium in the pore. Therefore, it is necessary to select a source activity that will allow to determine the true lifetime of positronium.





From the results of spectrum processing, it was found that the contribution of positronium to the spectrum is 5%. Of these, 4% falls on pores with a lifetime of 33.5 ns. According to the RTE model, this lifetime corresponds to a pore diameter of about 3 nm.

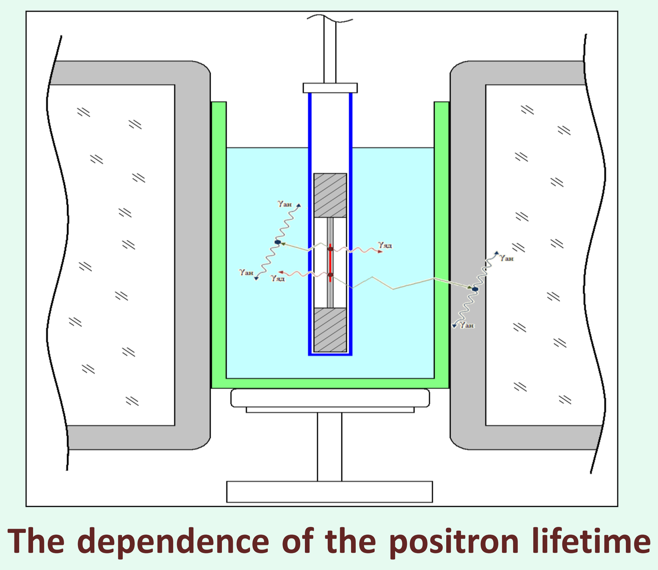
The results of polymer films investigation

To investigate the thick samples, like polymer films, the measuring geometry with the substrate should be used. As an substrate it is necessary to use annealed materials with a known, one-component positron lifetime spectrum. The contribution of the substrate should be estimated using Monte Carlo simulation.
Three samples of polymer films were investigated – polyethylene (PE), polylactide (PLA) and polycaprolactone (PCL). The results are consistent with the theory.

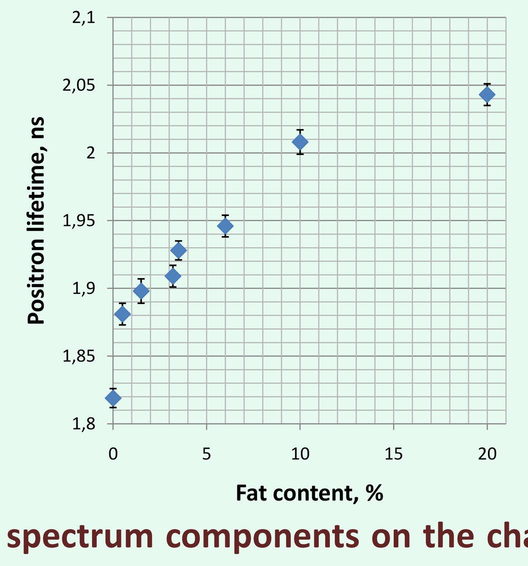
	τ_3, ns	R, Å
PE	2.23±0.03	3.19±0.16
PLA	1.97±0.02	2.82±0.02
PCL	2.24±0.01	3.060±0.008

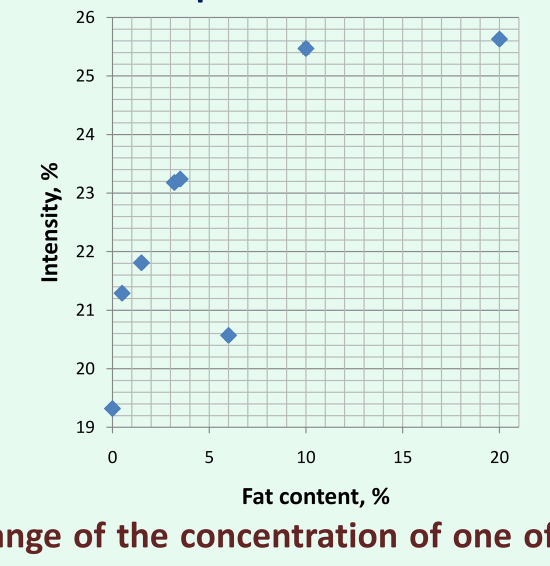
The results of two-phase liquid samples investigation

Measuring geometry for liquid-state samples



The dependence of the positron lifetime spectrum on the concentration of one of the phases





The dependence of the positron lifetime spectrum components on the change of the concentration of one of the phases in a two-phase system was studied on the example of milk cream. The change in the fat content was carried out by a stepwise dilution of the cream with water. The changes in the lifetime and intensity of the long-lived component with the fat content changing in the sample is observed.

Conclusion

Positron annihilation lifetime spectroscopy is a traditional method of non-destructive testing, allowing to study electronic structure of materials, mechanical and radiation-induced defects. It can be used for investigation of different materials, but each experiment had it's own features and limitations. The Monte Carlo simulation of the positron lifetime spectrometer should be used to choose the most appropriate measuring geometry for each kind of samples.
For solid-state samples this method can determine, for example, the size and concentration of vacancies or pores (the results for Fe-Ga alloys and porous Si are shown).
For multiphase system this method can determine the contribution of various state (the results for fat content in cream are shown).