Applications of positron annihilation spectroscopy in nuclear materials research

Janne Heikinheimo
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Abstract

In this work, positron annihilation spectroscopy was used in studying lattice point defects in some of the technologically relevant nuclear materials. In addition, the behaviour of the detectors were studied to deepen understanding of their influential properties in lifetime and Doppler broadening spectroscopy.

Detectors play a significant role in the performance of a measurement setup and in the quality of the obtained results, both in lifetime and Doppler broadening spectroscopy. Lifetime spectroscopy is very sensitive to the excess activity of studied samples, which limits its use in the study of nuclear materials. The only way of improving the tolerance of lifetime spectrometry is to add an extra coincidence detector to the setup. In Doppler broadening spectroscopy a detector energy resolution function directly affects the obtained results.

The sensitivity of two-detector lifetime spectroscopy to false coincidence events was studied by adding a cobalt-60 source next to the studied Si reference samples. The improvement of the radiation tolerance in a three-detector setup was estimated based on simple theoretical models. To study energy resolution function in Doppler broadening spectroscopy, a sodium-22 positron source was directly attached to the studied samples enabling simultaneous recordings of Doppler broadening and discrete photoabsorption spectrum. The impact of the source-detector geometry on the obtained results was studied and the reason behind the changing results is discussed based on systematic experiments supported by Monte Carlo simulations.

Microstructural defects play an important role in the properties of nuclear materials, such as corrosion and irradiation resistivity. Zircaloy-4 is currently the most used cladding alloy in nuclear power plants, but its oxidation in reactor conditions is a complex process including cyclic oxidation rates. In fusion power plants, materials close to the plasma are exposed to a very hostile environment including high temperatures and high particle irradiation fluxes. Tungsten is considered a promising candidate material for this purpose.

The fundamental oxidation properties of zirconium are discussed based on microstructural defect evolution in the studied Zircaloy-4 samples that were oxidized in pressurized water reactor-type conditions. Doppler broadening spectroscopy supported by theoretical modelling was harnessed to characterize lattice point defect behaviour in the sample oxide layers. Positron lifetime spectroscopy was applied in the study of mono-vacancies in pre-annealed proton-irradiated tungsten samples. Migration barriers for interstitial atoms and mono-vacancies were directly detected with a positron lifetime spectrometer connected to the cold temperature irradiation facility.

Keywords positron annihilation spectroscopy, high-purity germanium detector, Zircaloy-4, tungsten

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**Avainsanat** positroniannihilaatiospektroskoopia, germaniumilmaisin, Zircaloy-4, volframi

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Preface

The work presented in this thesis was conducted in the Antimatter and Nuclear Engineering group in Aalto University, Department of Applied Physics during the years 2012-2017.

First, I would like to express my gratitude to my supervising professor, Filip Tuomisto, for allowing me to work with the positron spectroscopy devices in his group and for the trust of giving me the possibility to do technical development tasks with them. I am especially grateful for his advice in research related questions. His recommendations were in a crucial role in achieving high-quality scientific results. I am also grateful for the financial support that was given from Filip’s projects.

My thanks go to the whole Antimatter and Nuclear Engineering group (former Positron and Defect Spectroscopy group) for supporting my work and for the good atmosphere. I enjoyed all the practical jokes, strange discussions, and nitrogen experiments. Special thanks go to Dr. Klaus Rytsölä, Dr. Floris Reurings and Dr. Esa Korhonen for giving me technical support and instructions related to the maintenance and development of positron spectroscopy devices. I would like to thank Dr. Rene Bes, Dr. Jarmo Ala-Heikkinen, Dr. Ilja Makkonen, Dr. Susan Ortner (NNL, UK) and Dr. Kenichiro Mizohata (University of Helsinki) for the good collaboration with the joint articles. I also want to thank Prof. Tuomisto, Dr. Bes, Dr. Makkonen, Ms. Vera Prozheeva, and Mrs. Nora Skeppar-Hosioja (my mother-in-law) for giving their valuable time in commenting my thesis.

I am very grateful to my parents, sisters and other close relatives for their support during my doctoral studies and before that. You encouraged me to educate myself and didn’t judge me for selecting a scientific career instead of an artistic one. You also tried to understand what I have been doing and, even though I probably wasn’t able to pass you a lot of information in understandable format, this was encouraging.

Finally, I am most grateful to my wife Annakaisa and children Elli and Ainomari for your love, patience and flexibility during my work. Regardless of wet diapers, high noise level, and long evening routines, you made the home that was a good place to come to after work. Thank you, Annakaisa, for your understanding and support. I couldn’t have done my work without you.
Preface

Espoo, December 21, 2017,

Janne Heikinheimo
This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution


The author performed the experiments and analyzed the experimental data. He was the main author of the paper.

Publication II: “Monte Carlo analysis of germanium detector performance in slow positron beam experiments”

The author did a part of the simulations and the data treatment. He was instructing the other parts of the work and was the main author of the paper.

Publication III: “Detector resolution in positron annihilation Doppler broadening experiments”

The author performed the experiments and the simulations, analyzed the data and was the main author of the paper.

Publication IV: “Positron annihilation analysis of the atomic scale changes in oxidized Zircaloy-4 samples”

The author did the positron experiments, analyzed the data and performed a part of the calculations. He was the main author of the paper.
Author’s Contribution

**Publication V: “Direct observation of mono-vacancy and self-interstitial recovery in tungsten”**

The author did the positron experiments and a part of the analysis. The author wrote the first draft of the manuscript.
Today's world is fighting against increasing carbon dioxide concentration in the air and water caused by burning of fossil fuels [1]. In the air, carbon dioxide is a known greenhouse gas and acts as a driver for the climate change. In the oceans, dissolving carbon dioxide causes a drop in the pH value. This affects biological systems in the oceans and finally the food chain. However, the consumption of fossil fuels is prone to rather increase than decrease as the world's population is growing and developing countries suffer from the lack of energy [2]. This situation requires immediate actions on one hand in applying and developing low-carbon or carbon-free ways of producing energy and on the other hand, reducing fossil fuel based energy production and economy.

Nuclear power is a carbon-free way of producing electricity. It is also one of the most efficient ways of generating electricity with respect of the plant's size and fuel consumption. However, uranium that is currently used as fuel in the nuclear reactors will end some day. At the 2014 level of uranium requirements, the identified resources are sufficient to run current global nuclear power fleet for over 135 years [3]. In the future fission reactors, alternative fuels are also considered, such as thorium and spent nuclear fuel. In the long run, fusion power may offer an economically reasonable way of producing electricity. Even though it is technologically challenging and expensive, fuel resources of deuterium-tritium based reactor using lithium as a breeder, would last over a million years [4].

The research related to nuclear materials aims at increasing understanding of the materials behaviour in current and future nuclear power plants, especially from two points of view: material behaviour in accident or non-conventional conditions and prolonged or more economical way of using materials in nuclear power plants. These goals demand world wide collaboration between research laboratories for achieving and implementing new knowledge.

The role of lattice point defects in nuclear materials is very important in determining their properties, such as radiation tolerance, diffusion of atoms in the material and mechanical endurance. Positron annihilation spectroscopies can be used to identify and characterize lattice point defects starting from very small quantities.
Introduction

However, the research of irradiated nuclear materials could be challenging with the positron spectroscopies, especially with the lifetime spectroscopy, where excess activity interferes obtained results. This thesis includes our study of applying a three-detector lifetime spectrometer in the research of high-activity materials, and quantitative measures for its operation from the detector point of view (Publication I).

This thesis also enlightens the features of high-purity germanium detectors in Doppler broadening spectroscopy; the optimized dimensions for the detection of positron annihilation radiation are demonstrated; studies of changing energy resolution and its implications to spectral analysis are included as well (Publications II and III). Experimental measurements and Monte Carlo simulations were applied in the analysis.

Zirconium alloys are used as fuel cladding materials in current fission power plants. In nuclear-grade zirconium alloys, the mass percentage of zirconium is more than 95% taking advantage of its low neutron absorption cross section and its corrosion resistance. Still, the oxidation of zirconium limits the lifespan of fuel elements and may cause different kinds of security concerns under accident conditions. The oxidation has complexities that have not been covered so far. This thesis presents a study of lattice point defects in a pressurized water reactor-type environment oxidized Zircaloy-4 (zirconium alloy) applying Doppler broadening spectroscopy. The interpretation of the results is supported by density functional theory calculations. The implications of the observed lattice point defects to oxidation rate, diffusion activation energy analysis, and oxide porosity are discussed (Publication IV).

Tungsten is nowadays considered the most suitable plasma facing material for future fusion test reactor ITER and a full size demonstration reactor DEMO. This thesis includes a low-temperature tungsten irradiation study applying positron lifetime spectroscopy for defect recovery detection. Self-interstitial atom and mono-vacancy recoveries are detected and analysed as a function of annealing temperature (Publication V).
2. Defects in nuclear materials

For nuclear materials one of the most important properties is their resistance to radiation damage. The ability of material to endure radiation goes back to its micro-structural self-healing through annihilation of lattice point defects [5]. Recently, a study of small defect sinks in Ni-based alloys showed that the radiation damage in an alloy can be decreased by 100 times compared to pure nickel [6].

In addition to irradiation, structural and functional materials in nuclear reactors (fission or fusion) are exposed to high temperatures which could accelerate, for example, defect clustering or chemical reactions with the surrounding elements. This would deteriorate designed properties of the materials.

In a fission power plant, the material endurance at high temperatures is important for accident tolerance. Starting from the Fukushima accident in 2011 there has been an intensive effort in improving the properties of the fuel cladding materials in accident conditions related to the accelerated oxidation of zirconium [7–9]. In the future, Generation IV reactors are also designed to operate at much higher temperatures than current Generation III reactors. For the next generation, the design has to focus on the irradiation properties of materials at elevated temperatures [10].

In a fusion power plant, the plasma facing material also experience an extremely hostile environment in the form of high particle flux and high heat loads. In addition to radiation tolerance, the material should have high thermal conductivity for efficient heat transport and low atomic number to minimize plasma cooling [11,12].

This chapter describes the concepts and experimental methods related to lattice point defects, and presents some examples of their relevance to the research of nuclear materials.

2.1 Defects in the lattice

A crystalline lattice has a periodic structure of atoms defined by its unit cell parameters. However, in the real world, the structure of a material is rarely
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perfect but is interrupted by discontinuities called crystallographic defects. Even if the material was perfect, defects are created due to thermal energy. Migration barriers for defects prevent them from rearranging back to a perfect lattice configuration where the total energy is minimized.

The smallest possible defects in the lattice are called lattice point defects, where a defect occurs around a single lattice point and is not extended in any direction. Lattice point defects are mainly classified as follows: vacancy-type defect (a missing atom or atom cluster in a lattice), interstitial defect (an atom in an additional lattice site), Frenkel pair (nearby pair of a vacancy and an interstitial atom), antisite defect (in compounds different types of atoms with exchanged positions) and substitutional atom (an alien atom has replaced the original one).

Extended defects are classified according to their dimensions: linear and planar defects. Dislocations are linear defects, in which some atoms along a 1D line in a perfect lattice are misaligned. Planar defects are grain boundaries in a lattice where the structural sequence is interfered. For example, in stacking faults, a local deviation occurs in the lattice layer sequence.

2.2 Experimental methods

Lattice point defects can be probed with many methods based on the measurement of different material properties. This is an indirect way of detecting lattice point defects. If the defects have an influence on the electrical properties of the material, they can be characterized with electrical measurements, such as conductivity or Hall effect measurements. Optical properties can be measured for example with absorption and emission spectroscopies. In addition, optical photon spectroscopies can be applied to phonon mode (Raman spectroscopy) and spin resonance (Electron paramagnetic resonance, EPR) detection.

Direct detection of lattice point defects is also possible with state of the art microscopy methods applying mainly electrons. As an example, one of the most commonly used microscopy technique in nuclear material research is transmission electron microscopy (TEM), where a sample is cut to a 100 nm slice and a focused electron beam is guided through the sample to a fluorescent screen or CCD camera. Even though the accuracy of imaging can be of the order of atom size, the method is more suitable for the detection of extended defects rather than single missing atoms in the lattice [13].

Lattice point defects may also have an impact on the lattice structure, for example by changing the lattice constant. This kind of changes can be measured with X-ray diffraction (XRD) spectroscopy.

Yet another powerful characterization family is the particle beam methods, such as Secondary ion mass spectrometry (SIMS), Ion beam analysis techniques (IBA), electron beams and positron annihilation spectroscopies (PAS). It should be noted that usually a single method is not sufficient for getting the whole
Defects in nuclear materials

In this thesis I have used positron annihilation spectroscopies for vacancy-type defect characterization in nuclear materials.

2.3 Irradiation damage

Each defect formation in a lattice requires certain amount of energy. This is called (defect) formation energy. In particle irradiation an incoming particle collide with atoms in the material passing its kinetic energy in the collisions. When the passed energy for atoms is larger than the material characteristic threshold displacement energy, lattice point defects, such as vacancies and interstitial atoms, can be created due to irradiation.

An atom in the lattice struck by an irradiation particle is called primary knock-on atom (PKA). After the struck, the PKA is propagating in the lattice with an energy given in the struck minus the displacement energy. If the transferred energy is sufficiently high, the atom can also displace other atoms in the lattice forming a collision cascade. Finally, when the excited knock-on atoms have lost their energy, they are terminated as interstitial atoms in the lattice [15].

If the lattice contains a lot of mono-vacancies homogeneously or heterogeneously, they start to cluster forming dislocation loops [16, 17], voids [18] and stacking faults [19, 20] (cf. section 2.1). Increasingly, these lead to macroscopic effects such as swelling, hardening, embrittlement and direct failure.

In the case of especially proton, neutron or alpha particle irradiation, in addition to radiation damage, the target material may form radioactive isotopes via nuclide reactions. As a consequence, materials close to the core of a fission or fusion reactor are activated and need to be handled as a radioactive waste after decommissioning.

2.4 Corrosion

Corrosion is a chemical process where oxygen or some other oxidizer is transferred to a compound to form an energetically more favorable configuration. An every day example of corrosion is rust forming on metal surface, where oxygen is transferred from air to the metal forming metal-oxide compounds.

Corrosion is generally a diffusion controlled process, where electrons from the metal surface diffuse to the oxide surface and \( \text{O}^{2-} \) ions are formed. There are in principle two ways, how the reactants (oxygen and metal ions) are brought together: either the oxygen-anions are diffused through the oxide layer to the metal surface or the cations are diffused to the oxide surface. When diffusion through the oxide layer is the rate-controlling process, the reaction speed follows the so called parabolic law: the oxidation speed decreases as the oxide layer grows thicker [21]. However, the oxidation process can be much more
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complicated when defects, cracks or impurities appear in the oxide layer.

In most of the commercial nuclear reactors, the fuel rods are placed in a corrosive environment. Corrosion is one of the factors that limits the life-span of a nuclear fuel rod. Corrosion can also be critical for nuclear safety in a case of, for example, loss of coolant accident (LOCA). During LOCA the fuel cladding temperature is increased due to coolant failure leading to an accelerated cladding corrosion rate. Increasing fragile corrosion layer decreases the thickness of ductile metallic cladding wall, which is then more prone to mechanical failure, such as ballooning and rupture. Also hydrogen is released during the oxidation in water cooled reactors and it can cause an explosion risk inside the reactor cover [22].
3. Positron annihilation spectroscopy

Positrons offer unique information about the studied material based on their inherent properties: positrons are light particles, they are positively charged and they annihilate with electrons. A positron has a mass of an electron allowing it to penetrate deeper and cause less damage in the studied samples in comparison to heavier particles. It has a positive elementary charge $+e$ and therefore it is repelled by the positive atom cores in the material. In crystalline matter in the case of a missing atom, the electrical potential energy of a positron is locally decreased. The positron feels this attractive, and may get trapped in the defect. As an anti-particle of an electron positron annihilates with an electron in a short time frame of the order of 100–400 ps. In the annihilation process the mass of the electron-positron pair transforms into two or three $\gamma$ photons. The energy and the momentum of the annihilation pair are conserved.

3.1 Theory of positrons in a lattice

3.1.1 Positron states

When a positron enters the material, its kinetic energy decreases rapidly (of the order of 1 ps) mainly due to electronic excitations, ionizations and phonon scatterings after which a positron has only thermal energy and is in a Bloch-like delocalized state in the periodic lattice. At this state the transport of a positron can be described with the diffusion theory [23]. A characteristic diffusion length of a positron during its lifetime $\tau$ is $L_+ = \sqrt{D_+ \tau} = 100–200$ nm, where $D_+$ is material dependent positron diffusion coefficient. Diffusion of the positrons in solids is discussed more deeply in Ref. [24].

The wave function of a positron can be described with a single particle Schrödinger equation

$$-\frac{1}{2m^*} \nabla^2 \psi_+(r) + V(r) \psi_+(r) = E_+ \psi_+(r), \quad (3.1)$$

where $m^*$ is the effective mass of a positron, $\psi_+(r)$ single particle positron
Positron annihilation spectroscopy

Figure 3.1. Illustration of a positron traveling path. A positron may get trapped in the crystal lattice into a point defect, where it experiences defect specific environment that produces characteristic annihilation parameters, such as lifetime or Doppler broadening.

wave function, $E_+$ positron eigenenergy, and $V(r)$ the positron potential energy containing Coulomb potential and electron-positron correlation effects. A positron may get trapped into a lattice point defect due to decreased Coulomb repulsion caused by e.g. a missing atom in the lattice. In the case of trapping, positron wave function is localized. Generally speaking the electron density in the positron traps is reduced compared to the bulk lattice and this lengthens the positron lifetime. The electron momentum environment changes as well in the traps, which affects the momentum distribution of annihilation $\gamma$ photons. Figure 3.1 illustrates a possible positron path in the crystalline sample.

The positron lifetime and Doppler broadening parameters can be calculated when the corresponding electronic structure is known. The positron annihilation rate $\lambda$ is the inverse of positron lifetime $\tau$ and proportional to the overlap of electron and positron densities [25]

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

where $r_e$ is the classical electron radius, $c$ the speed of light, $n_-(r)$ the electron density and $\gamma(n_-(r))$ the enhancement factor of the electron density at the positron (as a positively charged particle positron draws negatively charged electrons closer and vice versa). Doppler broadening spectrum results from the momentum distribution of annihilating electron-positron pairs, which requires knowledge of the electron wave functions $\psi_i$. It can be written as

$$\rho(p) = \pi r_e^2 c \sum_i \left| \int e^{-ip \cdot r} \psi_+(r) \psi_i(r) dr \right|^2,$$
where index \( i \) runs over all occupied electronic states, and \( \gamma_i \) is the electron-state-dependent enhancement factor [26–28].

### 3.1.2 Positron trapping

Typically a positron trap is so deep (binding energy a couple of electron volts) that thermal escape of a positron is not possible. This applies, for example, to vacancy-type defects. However, there are also shallow positron traps in the materials, from which positrons may get thermally excited: in metals dislocation lines and in semiconductors Rydberg states around negative ions.

Positron trapping rate \( \kappa \) is proportional to the defect concentration \( c \) as

\[
\kappa = \mu c,
\]  

(3.4)

where \( \mu \) is the material-specific positron trapping coefficient. \( \mu \) generally has a value close to \( 10^{15} \) s\(^{-1} \) [29]. \( \kappa \) may be dependent on the temperature based on the type of trapping defect and the material. In the most frequent case in semiconductors, where positrons are trapping to a defect with the negative charge state, \( \kappa \propto T^{-1/2} \). In metals, vacancy-type defects are by default charge neutral, and the positron trapping rate is less dependent on the temperature.

Positron trapping into defects can be described with so called kinetic equations [30]. In the case of a single-type open volume defect \( d \), the equations are (detrapping is negligible)

\[
\frac{dn_b(t)}{dt} = -(\lambda_b + \kappa_d)n_b(t) \quad \text{and} \quad \frac{dn_d(t)}{dt} = -\lambda_d n_d(t) + \kappa_d n_b(t),
\]  

(3.5)

(3.6)

where \( n_b \) is the normalized positron density in the bulk, \( \lambda_b \) annihilation rate in the bulk, \( \kappa_d \) trapping rate to the defect \( d \), \( n_d \) normalized positron density in the defect \( d \), and \( \lambda_d \) annihilation rate in the defect \( d \). The solution for the positron probability of being alive \( n(t) = n_b(t) + n_d(t) \) with the boundary conditions \( n_b(0) = 1 \) and \( n_d(0) = 0 \) is

\[
n(t) = \frac{\lambda_b - \lambda_d}{\lambda_b - \lambda_d + \kappa_d} \exp[-(\lambda_b + \kappa_d)t] + \frac{\kappa_d}{\lambda_b - \lambda_d + \kappa_d} \exp[-\lambda_d t].
\]  

(3.7)

As the annihilation rate is the time derivative of the number of positrons (or positron density) in the material, the experimental positron lifetime distribution \((-dN(t)/dt)\) consists of exponentially decaying components.

The fraction of positrons annihilating in the state \( i \) can be calculated with

\[
\eta_i = \kappa_i \left( \lambda_b + \sum_i \kappa_i \right)^{-1}.
\]  

(3.8)
3.2 Lifetime experiments

The positron lifetime spectroscopy is based on a reliable fast detection and separation of positron birth and annihilation events. This requires fast electronics to obtain the positron lifetime accurately enough. Nowadays the development of fast digitizers has reached the level where the digitizing frequency and accuracy are sufficient for direct digitization of the detector pulses without analog converters [32]. I have applied in the measurements of this thesis a fast digital oscilloscope for positron lifetime recordings [33].

The conventional positron lifetime spectrometer consists of two fast detectors (producing timely accurate pulses) in coincidence and a positron source placed between two samples that are supported by a sample holder. The source-sample package is placed between the two detectors.

Positron lifetimes are collected to the positron lifetime histogram that is a sum of exponentially decaying components

$$-\frac{dN(t)}{dt} = \sum_{i=1}^{k} I_i \lambda_i \exp(-\lambda_i t), \quad (3.9)$$

where $\lambda_i = 1/\tau_i$ is the experimental decay component of the positrons annihilating in the state $i$ and $I_i$ is the corresponding intensity of the component (c.f. equation (3.7)). However, the time resolution of the spectrometer is always
Positron annihilation spectroscopy

present in the measured spectra. The obtained experimental spectrum is in fact a convolution of the spectrometer’s time resolution function and the equation (3.9). The time resolution of the spectrometer can be approximated with a Gaussian function. A typical value for the full width at half maximum (FWHM) for the function is 250 ps. Because of the time resolution, only two or three components can be resolved from the measured spectrum [31, 34]. Figure 3.2 shows an example of the lifetime spectra with a single component and two distinguishable components obtained from Si and diamond samples, respectively.

Even though the error margins may vary a lot in the fitting of individual components, the average lifetime $\tau_{ave}$ is statistically very accurate. It can be written as

$$\tau_{ave} = \sum_i I_i \tau_i \text{ or } \tau_{ave} = \eta_b \tau_b + \sum_j \eta_j \tau_j,$$

(3.10)

where the first version applies for experimentally obtained components and in the second one, $\eta$ is the fraction of positrons annihilating in the corresponding defect (or state). In the lifetime spectrum of $10^6$ events, the error margin of the average positron lifetime is less than 1 ps.

The positron source applied in the experiments is typically radioactive $^{22}$Na isotope in a NaCl compound wrapped in thin (1 μm) metal foil. The decay of $^{22}$Na produces a positron and neutrino, where the positron has a kinetic energy between 0 and 540 keV resulting approximately exponential stopping profile in the studied samples [35]. After the decay the daughter nuclide $^{22}$Ne is left in the excited state that recombines fast (less than 1 ps) resulting a 1.27 MeV $\gamma$ photon. The photon is detected and interpreted as a START signal of positron life. Subsequently, the positron annihilates with an electron, and two 511 keV $\gamma$ photons propagating in the opposite directions are created. These are interpreted as STOP signals. The distinction between the START and STOP events is done based on the different energies of the detector pulses.

In the conventional way of doing lifetime experiments, the measured spectrum is not only affected by the annihilation events from the sample material, but also the salt mixture, wrapping material and surfaces cause additional input that should be removed before the actual analysis of the sample lifetime components. Annihilation events in the wrapping can be approximated with the semi-empirical Bertolaccini-Zappa formula that is dependent on the sample $Z$ value, the foil thickness and density [36]. The annihilations in the free volume, such as in the source edges, can be reduced by fitting a long lifetime component to the spectrum. In our analysis, we have used a 1500 ps component for approximating the amount of positrons annihilating in the free space (and forming positronium). Finally, if the sample has a single lifetime component or components having clearly shorter lifetime than 400 ps, the reduction estimation of the source-sample surfaces and salt components can be done with the fitting of the 400 ps component to the spectral data.
Figure 3.3. Example of a Doppler broadening spectrum after background reduction with the selected $S$ and $W$ regions. The spectrum is measured in Si sample.

3.3 Doppler experiments

The momentum of a thermalized positron is a lot smaller than the momentum of electrons in a crystalline lattice. Therefore, the momentum seen in the Doppler broadening of the annihilation photons is that of an electron at the annihilation location.

When a positron annihilates with an electron, two $\gamma$ photons are created with the energies of $E = 511$ keV $\pm \Delta E$, where $\Delta E$ corresponds to the Doppler shift caused by the momentum of the annihilating electron-positron pair. These shifts are recorded experimentally with a high-purity germanium detector of a high energy resolution, and the shifts cause the characteristic broadening of 511 keV annihilation peak based on the chemical environment of annihilating positrons.

The recorded Doppler shifts are $\Delta E = cp_L/2$, where $c$ is the speed of light and $p_L$ is the one-dimensional longitudinal momentum component, and the Doppler broadening is

$$\rho(p_L) = \int \int dp_x dp_y \rho(p).$$

(3.11)

In Doppler broadening experiments, a measurement with mono-energetic positrons is easy to realize (much easier than in lifetime measurements). Therefore, the Doppler broadening measurements are conventionally performed applying mono-energetic slow positrons to obtain depth profiling of the studied samples. Stopping profiles for mono-energetic positrons with various energies is illustrated in figure 3.4. The stopping of positrons follows the so called Makhovian profile that can be described with

$$P(x) = -\frac{d}{dx} \exp(-x/x_0^2),$$

(3.12)
where $x_0$ depends on the mass density of a sample and the positron energy.

The shape of the Doppler-broadened 511 keV annihilation line is generally characterized by dividing it into two types of regions as in figure 3.3. The central region describes the count rate of the low momentum electrons, and the wing regions, taken from the peak edges, describe the count rate of the high momentum electrons (equation (3.11)). The peak shape is conveniently described by using the $S$ and $W$ parameters. The $S$ parameter is defined as the counts in the central region divided by the total number of counts in the annihilation peak and the $W$ parameter is defined accordingly as counts in the wing regions divided by the total number of counts in the annihilation peak.

The $S$ and $W$ parameters are very sensitive to changes in the electron momentum distribution at the annihilation site. If saturation trapping at a certain type of defect (e.g., a vacancy) produces parameters $S_V$ and $W_V$ and bulk type reference sample $S_B$ and $W_B$, the measurement for the sample with this one type of defect will give

$$S = \eta_B S_B + \eta_V S_V \quad \text{and} \quad W = \eta_B W_B + \eta_V W_V,$$

where $\eta_B$ and $\eta_V$ are the annihilation fractions in the bulk and in the vacancy respectively, and $\eta_B + \eta_V = 1$. For a single kind of a defect, the $W$ parameter depends linearly on the $S$ parameter. Therefore the $S$ and $W$ results are conveniently presented in a $SW$ plot, where $W$ values are plotted as a function of $S$. Based on the equation (3.13), different kinds of defects could introduce separable characteristic slopes $R = (S_V - S_B)(W_V - W_B)$ in the $SW$ plot. If the bulk lifetime ($\tau_B = 1/\lambda_B$) of the sample is known, the defect concentration in the

![Figure 3.4. Makhovian stopping profiles for mono-energetic positrons with various energies (PIV).](image-url)
samples can be estimated with
\[
c_V = N_{\text{at}} \frac{\lambda_B}{\mu_V} \frac{S - S_B}{S_V - S},
\]
where \(N_{\text{at}}\) is the atom density in the sample, \(\mu_V\) the trapping coefficient of the defect.

### 3.4 Modelling of positron states and annihilation using first-principles calculations

Density-functional theory (DFT) within the Kohn-Sham method is one of the main tools applied for first-principles material modelling [37, 38]. We have used in the context of this thesis two-component formulation of DFT [25], where the fundamental quantities are electron and positron densities. In the calculations, the energy functional of the system has been minimized assuming that the positron density does not affect the average electron density. The studied lattice has been modelled with a supercell that is a multiple of the repeating unit cell of the lattice. First, it has been relaxed taking into account the repulsive forces due to the localized positron on the ions in the lattice.

In modelling of the electron system, we have used DFT with local-density approximation (LDA) [39] and the projector augmented-wave method (PAW) [40, 41] in the Vienna Ab initio Simulation Package (VASP) [41–43]. After obtaining the electron densities, positron trapping states were modelled with the two-component DFT using the LDA and zero-positron-density limit of functionals [25]. Finally, the momentum distributions have been obtained using the state-dependent model (cf. equation (3.3)) [28] and reconstructed PAW [44, 45]. To compare measured and simulated results, the momentum distributions were convoluted with the experimental Gaussian resolution function.

### 3.5 Detector modelling with the Monte Carlo method

Monte Carlo simulations are a good way of studying small details in the detector photo-absorptions that are otherwise difficult or impossible to detect in an experimental setup [46]. In this thesis we have used the Monte Carlo N-particle transport (MCNP) code for detector simulations [47].

The physical treatment of photons in the MCNP code includes the photoelectric effect, pair production, incoherent (Compton) scattering, coherent (Thompson) scattering, and fluorescent photons after photoelectric absorption. Electrons are treated in the simulations according to the thick-target bremsstrahlung (TTB) modelling, where electrons travel in the direction of the incident photon and are immediately stopped.

In the photoelectric effect, a photon is absorbed completely giving its energy to release one electron in an atom and to the kinetic energy of the electron.
Recombination effects in the excited atom are also taken into account. These effects could result in fluorescent photons and/or Auger electron.

In pair production, the energy of the photon goes to the creation of an electron-positron pair and to their kinetic energies. Positrons are treated according to the TTB modelling, as the electrons. When the positron energy is below the defined energy cut-off, it is considered to be annihilated with an electron producing two photons going in the opposite directions with an energy of $mc^2 = 511\text{keV}$.

In Compton scattering, a photon is scattered from a free electron. In this event, the objective is to determine the energy of the scattered photon $E'$ and the deflection from the line of flight $\mu = \cos(\theta)$. The differential cross section for the process is given by the Klein-Nishina formula [48]

$$
\sigma_{\text{KN}}(\alpha, \mu)d\mu = \pi r_e^2 \left( \frac{\alpha'}{\alpha} \right)^2 \left[ \frac{\alpha'}{\alpha} + \frac{\alpha}{\alpha'} + \mu^2 - 1 \right] d\mu,
$$

where $r_e$ is the classical electron radius and $\alpha$ and $\alpha'$ are the incident and final photon energies ($\alpha = E/mc^2$ and $\alpha' = \alpha/(1 + \alpha(1 - \mu))$). The MCNP code uses modified Klein-Nishina formula, which includes corrections for incoherent Compton scattering [47]

$$
\sigma_1(Z, \alpha, \mu)d\mu = I(Z, \nu)\sigma_{\text{KN}}(\alpha, \mu)d\mu,
$$

where $I(Z, \nu)$ is an appropriate scattering factor and $\nu = \sin(\theta/2)/\lambda$.

Thompson scattering does not involve energy losses, and it is only a photon process which does not produce electrons. The differential cross section for Thompson scattering is

$$
\sigma_2(Z, \alpha, \mu)d\mu = C^2(Z, \nu)T(\mu)d\mu,
$$

where $C^2(Z, \nu)$ is a form factor and $T(\mu) = \pi r_e^2(1 + \mu^2)d\mu$ is the energy-independent Thompson cross section.
Positron annihilation spectroscopy
4. Detectors in positron annihilation spectroscopies - Threat or opportunity?

There exist several different kinds of positron annihilation spectroscopy techniques, which differ in the way of treating positrons, and in the way of measuring their annihilation. Two most common material characterization techniques utilizing positron annihilation are lifetime and Doppler broadening spectroscopy, where in the former accurate timing (fast charge and light collection of the detector) and in the latter accurate energy distinction (a good energy resolution of the detector) is in the key role. We have studied the measurement situations in lifetime and Doppler broadening spectroscopy, which tend to change the obtained results based on the detector properties.

We have initiated a digital lifetime spectroscopy device for measuring lattice point defects in highly radioactive nuclear materials applying a third detector in the conventional digital two-detector measurement setup in Publication I. The problems arising from the excess activity in the two-detector setup, and the potential improvement of adding a third coincidence detector in the setup are discussed.

In Doppler broadening spectroscopy, the optimal dimensions of a germanium detector, the energy dependency of steel absorption coefficient, and incident radiation geometry are discussed based on Publications II and III.

4.1 Three-detector positron lifetime spectroscopy

When the activity of studied samples increases, not only do the spectroscopy limits of the conventional setups become an obstacle but also the radioactive contamination of the setup related devices and the radiation dose exposed to a user. In conventional positron lifetime spectroscopy, the samples do not require any processing prior to measurements as, for example, in TEM. In a positron lifetime setup, one needs only to consider how to mount and support the samples on both side of the positron source and how to get that package between the two detectors. In principle, the sample-source package could be prepared and measured inside a glove box to control the radiation exposure of users and materials. However, the excess activity in the sample-source package may cause...
Figure 4.1. Configurations for two- and three-detector setups for positron lifetime measurements. In (a) a false lifetime event is detected due to radiation background producing a wrong stop pulse, and in (b) the false stop pulse is discriminated due to extra coincidence condition (PI).

Adding a third coincidence detector to a conventional two-detector lifetime setup is possible as positron events produce three γ photons altogether: a 1.27 MeV birth and two 511 keV annihilation photons propagating to the opposite directions. Three-detector positron lifetime setups have been developed in order to enable the study of structural steels containing 60Co radioactive isotope emitting two coincident γ photons per decaying atom [49, 50]. The setup can also be feasible for reducing excess acquired random γ radiation. Figure 4.1 illustrates possible configurations for two- and three-detector setups.

In the conventional lifetime spectrometer, the activity $A$ of a positron source (or an other coincidence source producing two or more γ photons) can be estimated from the peak-to-background ratio. Assume that the two detectors have efficiencies $\varepsilon_1$ and $\varepsilon_2$, and count rates $C_1$ and $C_2$, producing coincidence count rate (peak count rate) $R_c = \varepsilon_1 \varepsilon_2 A$. On the other hand, random count rate (background count rate) can be estimated with the help of Poisson statistics as $R_r = (1 - \exp(-C_2 \Delta t))C_1 \approx C_1 C_2 \Delta t = \varepsilon_1 \varepsilon_2 A^2 \Delta t$, where $\Delta t$ is the time window of a spectrometer. The similar kind of interpretation can also be applied to a three detector setup leading to the relation of source activity and peak-to-background ratio:

Two detectors:  \[ \frac{R_c}{R_r} = \frac{1}{A \Delta t} \]  \tag{4.1} 

Three detectors:  \[ \frac{R_c}{R_r} = \left( \frac{1}{A \Delta t} \right)^2 \]  \tag{4.2} 

Assuming that the time window of a spectrometer is $\Delta t = 10$ ns, and the source activity in two-detector setup is 1 MBq, the source activity could be 10 times higher in the three-detector setup without increasing the spectral background.
Figure 4.2. The effect of excess fast coincidences to the lifetime spectra from Si-samples. On the left hand side, spectra without background reduction and source corrections are shown. On the right hand side, normalization, background reduction and source corrections for $^{22}$Na were applied (PI).

The tolerance for random counts in the three-detector setup increases as well. If similar kind of detectors are used in the two- and three-detector setups, the random activity (non-coincidence activity of the samples) can be approximately 50 times higher in the three-detector setup. However, the total count rate in a three-detector setup is significantly smaller.

Random non-coincidence activity of the studied samples in two- and three-detector setups increases the spectral background. It is, however, much more challenging to predict the implications of excess coincidence activity in the samples (for example in irradiated structural steels). Ideally, a three-detector setup would discriminate all two-coincidence events originating for example from $^{60}$Co decays. As a preliminary step, we have studied quantitatively how excess coincidence activity of the samples alters acquired lifetime spectra in a fully digital two-detector setup that can be transformed into a three-detector setup in Publication I.

In the spectrometer utilizing two scintillator detectors, additional activity was introduced by inserting a 500 kBq $^{60}$Co source next to the regular sample-source package. In its decay, $^{60}$Co emits 1.17 and 1.33 MeV $\gamma$ photons simultaneously producing false coincidence events. For a real positron lifetime spectrum, we used single crystal silicon samples in the both sides of a conventional aluminium wrapped positron source. In the experiments, the time resolution of the setup was 270 ps (FWHM). The ratio between $^{60}$Co and $^{22}$Na was tuned by reducing sodium in the lifetime source. Resulting spectra and associated average decay components are presented in figure 4.2 and table 4.1.

The dedicated energy windows for $^{22}$Na START and STOP signals reduced clearly $^{60}$Co count rate. Still the effects of increasing relative Co-activity is visible when the $^{60}$Co / $^{22}$Na activity ratio is 6. Notably, when the activity of
Table 4.1. Average decay components of the lifetime spectra with additional fast-coincidence events in a two-detector setup. The spectral resolution was 270 ps (FWHM) (PI).

<table>
<thead>
<tr>
<th>$^{60}$Co / $^{22}$Na activity ratio</th>
<th>Fast coinc. count rate (%)</th>
<th>Average decay constant of a spectrum (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>222(1)</td>
</tr>
<tr>
<td>0.5</td>
<td>2.9</td>
<td>221(1)</td>
</tr>
<tr>
<td>6</td>
<td>101.5</td>
<td>147(1)</td>
</tr>
<tr>
<td>20</td>
<td>459.1</td>
<td>81(1)</td>
</tr>
</tbody>
</table>

$^{60}$Co is half of the $^{22}$Na activity, there is no visible effect of the excess coincidences in the Si spectrum. It should be noted that the activity of $^{22}$Na source cannot be increased a lot above 1 MBq in the conventional two-detector setup, because the increasing spectral background will decrease the accuracy of the lifetime component fitting.

A new spectrometer utilizing three-detector coincidence method is required for positron lifetime measurements when the activity or the coincidence activity of the studied samples increases. The new three-detector setup could be applied in studying irradiated nuclear materials, nuclear materials containing actinides or structural materials in reactor conditions.

4.2 Detector nuances in Doppler broadening spectroscopy

Doppler broadening spectroscopy offers detailed information of the chemical surroundings of open volume defects in crystalline materials. During the measurements, the Doppler broadening of the 511 keV annihilation peak is recorded which can be directly related to the electron momentum distribution of the annihilation site. In practice, a high-purity germanium (HPGe) detector is the only suitable choice for Doppler broadening measurements because of its stability and good energy resolution at 511 keV. However, it appears that the inherent properties of HPGe detectors may have a significant effect on the results and their interpretations.

As the computational approach has been improving in the last decade and is able to produce more accurate modelling of the positron annihilation characteristics, understanding the decisive properties of HPGe detectors in Doppler broadening measurements is increasingly important for obtaining high quality results. We have studied the nuances of HPGe detectors in Doppler broadening measurements and employed Monte Carlo simulations in Publication II and III.
Detectors in positron annihilation spectroscopies - Threat or opportunity?

Table 4.2. The optimization of detector crystal dimensions for a coaxial germanium detector with 511 keV $\gamma$ photons and the point source 2 cm from the end cap of the detector. The optimization is based on the Monte Carlo simulations (PII).

<table>
<thead>
<tr>
<th>Volume (cm$^3$)</th>
<th>Optimal dimensions</th>
<th>Peak efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diameter (cm)</td>
<td>Thickness (cm)</td>
</tr>
<tr>
<td>80</td>
<td>6.8</td>
<td>2.2</td>
</tr>
<tr>
<td>142</td>
<td>8.2</td>
<td>2.7</td>
</tr>
<tr>
<td>200</td>
<td>9.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

4.2.1 Detector dimensions

The manufacturing of high-purity germanium is an expensive procedure, and shows in the detector price tag. Optimization of the detector crystal dimensions is important also from the Doppler broadening measurement point of view because the larger crystal size generally increases the energy resolution of the detector. The optimization cannot be solely based on the efficiency declared by the manufacturer because the efficiency is dependent on the $\gamma$ photon energy and the source-detector geometry used in the measurements. A standard way of determining the detector efficiency (applied by the manufacturers) is to use $^{60}$Co calibration source located on the central axis 25 cm away from the end cap of the detector [51,52]. The efficiency is then the peak efficiency of the 1.33 MeV photopeak.

In the slow positron beam experiments applying an isotope positron source, the germanium detector is placed close to the samples into which positrons are implanted in order to maximize the detector count rate. From the calibration geometry and energy follow that the actual peak efficiency and the optimal dimensions of a germanium detection crystal for the 511 keV photopeak may be different from the ones declared by the manufacturer. Therefore, we have performed a Monte Carlo simulation study for coaxial HPGe detectors in which a 511 keV point source was placed 2 cm from the end cap of the detector (PII). The optimal dimensions for selected volume Ge crystals in a coaxial form are shown in table 4.2.

4.2.2 Energy dependency of the photoabsorption

In principle a photon mass-absorption coefficient of an element has quite a low gradient at the annihilation photon energies, especially in metals that are used in the slow positron beam setups for vacuum isolation [55]. Still, there is a possibility that steel between the annihilation event and the detector could change the intensity behaviour of the radiation as a function of energy so that the Doppler broadening parameters would change. This would make the Doppler broadening results dependent on the setup construction. To study the implications of the setup construction material on the Doppler broadening results, we used a mo-
Figure 4.3. Ratio curves for Ga vacancy in GaN. In the Monte Carlo simulations the source is at the central position 2 cm away from the detector end cap. The experimental and computational data is from [53,54] (PII).

momentum distribution obtained with the first-principles method for GaN bulk and Ga mono-vacancy in GaN as source distributions in the Monte Carlo simulations. We placed steel between the source and the counting germanium detector to record changes caused by absorptions in the steel (PII). Figure 4.3 illustrates the obtained ratio curve of the Doppler broadening results for Ga mono-vacancy in GaN. The first-principles results and the Monte Carlo distributions were convolved with the Gaussian resolution function of the detector.

To continue further, we placed steel plates between the source and the detector in the Monte Carlo simulations and observed whether the Doppler broadening parameters would change. The steel thickness in the simulations was up to 10 mm. We did not observe changes in the $S$ and $W$ parameters beyond the statistical limits nor in the behaviour of the ratio curves. We concluded that the change in the absorption rates as a function of energy caused by steel does not change the Doppler broadening results.

4.2.3 Changing energy resolution

Generally, the energy resolution of an HPGe detector is considered very stable but sensitive to external disturbances such as vibration. Also internal disturbances deteriorate the energy resolution. These may originate from bad electrical contacts and from leakage current on the surface of a germanium detector crystal. In normal operational conditions, previously mentioned facts will not disturb the Doppler broadening results.

p-type coaxial germanium detectors are mainly used in Doppler broadening experiments because of their good energy resolution. However, the vicinity of outer $n^+$ ohmic contact layer of the germanium detector crystal may show increasing hole trapping on the outer edges of the depletion zone causing local
Table 4.3. Resolution and skewing parameters for the 1274 keV photopeak with and without 6 mm steel plates, when the source distance from the detector end cap is altered. The statistical accuracy for the peak shape is less than 0.2%. The resolution enhancer of the spectrometer was applied in the measurement series (PIII).

<table>
<thead>
<tr>
<th>Distance (cm)</th>
<th>Steel</th>
<th>FWHM (keV)</th>
<th>$K_{0.1}$</th>
<th>$K_{0.02}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Resolution enhancer off</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>no</td>
<td>1.810</td>
<td>1.018</td>
<td>1.053</td>
</tr>
<tr>
<td>2</td>
<td>yes</td>
<td>1.741</td>
<td>1.022</td>
<td>1.076</td>
</tr>
<tr>
<td>4</td>
<td>no</td>
<td>1.722</td>
<td>1.014</td>
<td>1.066</td>
</tr>
<tr>
<td>4</td>
<td>yes</td>
<td>1.705</td>
<td>1.024</td>
<td>1.072</td>
</tr>
<tr>
<td>8</td>
<td>no</td>
<td>1.676</td>
<td>1.017</td>
<td>1.054</td>
</tr>
<tr>
<td>8</td>
<td>yes</td>
<td>1.673</td>
<td>1.015</td>
<td>1.044</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Resolution enhancer applied</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>no</td>
<td>1.667</td>
<td>1.012</td>
<td>1.040</td>
</tr>
<tr>
<td>2</td>
<td>yes</td>
<td>1.672</td>
<td>1.007</td>
<td>1.029</td>
</tr>
<tr>
<td>4</td>
<td>no</td>
<td>1.671</td>
<td>1.009</td>
<td>1.021</td>
</tr>
<tr>
<td>4</td>
<td>yes</td>
<td>1.669</td>
<td>1.005</td>
<td>1.029</td>
</tr>
<tr>
<td>8</td>
<td>no</td>
<td>1.671</td>
<td>1.005</td>
<td>1.021</td>
</tr>
<tr>
<td>8</td>
<td>yes</td>
<td>1.670</td>
<td>1.003</td>
<td>1.019</td>
</tr>
</tbody>
</table>

Degradation in the energy resolution [56, 57].

From the spatial dependency of the energy resolution follows that geometry of the incident radiation can change the Doppler broadening results (PIII). Moreover, the spatial dependency of the energy resolution causes non-Gaussian features in the resolution function. The Gaussian shape of the energy resolution function can be analysed using skewing factors for the peak shape determined in the IEEE Standard Test Procedures [51, 52]:

\[ K_{0.1} = \frac{FW.1M}{1.823 \text{ FWHM}} \text{ and } \]

\[ K_{0.02} = \frac{FW.02M}{2.376 \text{ FWHM}}, \]

where FWHM is the full width at half maximum, FW.1M full width at tenth maximum and FW.02M full width at fiftieth maximum of a photopeak. The values are calculated after background reduction applying linear interpolation between the data points. If the skewing factors $K_{0.1}$ and $K_{0.02}$ are larger than 1, then the photopeak is wider than it should be based on the FWHM value and assumed Gaussianity.

We studied the implications of the resolution dependency by measuring spectra of Si single crystal samples attached to a aluminium wrapped $^{22}$Na positron source when the distance of the samples and the detector was altered and steel placed between the samples and the detector (PIII). To analyse the resolution
function of the detector, we studied the single energy $\gamma$ photons originating from the relaxation of the $^{22}$Na daughter nuclide $^{22}$Ne with the energy of 1273.73 keV. Table 4.3 lists the results of a measurement series in which we also applied the energy enhancement property of the spectrometer (specified later). The results show that the energy resolution of the detector (FWHM) deteriorates when the sample is closer to the detector. Steel between the sample and the detector improves the FWHM value but on the other hand the skewing factors increase. The geometrical effects on the energy resolution function diminished when the resolution enhancer of a spectrometer was applied. In the spectrometer applied in these experiments, the resolution enhancer corrected the fine gain for individual pulses based on their rising edge. The change in the detector pulse rising edge is mainly caused by charge carrier trapping at the detector crystal [58].

When we finally analysed the Doppler broadening data of the corresponding spectra, we observed a change in the $S$ parameter that can be associated with the change in the resolution function. The characteristic geometrical dependency of the Si sample $S$ parameter is shown in figure 4.4.

To study more closely how the absorption is changing in the detector crystal, we performed Monte Carlo simulations with similar configurations. We divided the crystal into 33 coaxial counting regions, and gathered the resulting count densities into 2D countmaps for comparison. Figure 4.5 shows the simulated absorption densities, where the error for the count density in a cell is less than 3%. We used a 511 keV point source in the simulations. The results illustrates that when the source is close to the detector, photo-absorptions are concentrated in the centre front end of the detector crystal. As the source distance is increased, absorptions are more evenly distributed in the crystal. When steel is placed
between the source and the detector, counts are reduced in the outer edge of the detector crystal.

The acquired results support the anticipated spatial dependency of the energy resolution in the detector crystal and its influence on the resolution function and the associated Doppler broadening parameters. These results highlight the importance of using well known reference samples regularly in the measurements.
and enlighten the underlying reason for detector and geometrical dependency of the Doppler broadening results.

4.2.4 Comparison of the results

There are mainly two reasons behind the difficulty of the comparison of Doppler broadening results: detector and spectrometer dependent channel width, and the resolution function of a spectroscopy setup (cf. section 4.2.3).

The finite channel width of the spectrometer causes several problems in the data analysis when the results measured with different spectrometers or spectrometer settings (that are dependent on the detector) are compared. The channel width and peak position determines the actual energy regions for the $S$ and $W$ parameters. The channel width of a specific detector spectrometer pair can be reduced with the data interpolation (such as linear interpolation). Even though the energy region determination can be overcome with the interpolation method, the interpolated spectrum can include shaping effects that differ from the original spectrum.

Generally the energy resolution of a germanium detector is close to Gaussian, and can be approximated with a reasonable accuracy with a Gaussian function. However, the real function may show non-Gaussian features as illustrated in section 4.2.3. The measured experimental Doppler broadening spectrum is a convolution of the 1D momentum distribution of the annihilating positron-electron pairs and the detector resolution function. If we assume that the resolution function of the spectroscopy setup is Gaussian enough and would like to make a comparison with results of another setup with different Gaussian resolution function, we can apply yet another convolution to the spectrum with a higher resolution with a Gaussian resolution function of

$$\text{FWHM}_{a} = \sqrt{\text{FWHM}_{s1}^2 - \text{FWHM}_{s2}^2},$$

where FWHM$_{s1}$ is larger than FWHM$_{s2}$.

If one cannot access the original spectra, one can compare the $S$ parameters measured with different kinds of setups as suggested in [59].

Understanding the origin and consequences of possibly different Doppler broadening results for the same sample is important for maintaining quality of the measurements.
5. Zirconium oxidation in reactor conditions

Zirconium alloys are commonly used as a cladding material for nuclear fuel. The research related to the oxidation of zirconium in nominal and accident conditions is nowadays concentrating on different coatings of zirconium and their properties [8]. However, the oxidation of zirconium is not yet completely understood, and the development of different zirconium alloys is continuing as well [7, 60–62]. The operation of the reactor core is estimated with the fuel performance codes. The codes are currently based on experimental knowledge and empirical relations instead of the first-principles methods [63, 64].

The oxidation of Zr is cyclic, including periods of diminishing growth rate changing abruptly to higher rates. The identification of the rate-controlling mechanism is difficult as many of the oxide properties change as the oxide grows thicker, such as the metal matrix composition, the second phase particle (SPP) composition, the SPP size distribution, the oxidation state of alloying elements in the oxide, the oxide phases and grain sizes, the stress state in the oxide and metal, dislocations in the metal, crack distributions in the oxide, and oxide conductivity [60–62, 65]. Also many atomistic studies have been performed in ZrO₂ to get insight in the oxidation properties [66–68].

We have performed positron studies to gain understanding of the role of lattice point defects in the growing ZrO₂ in PWR-type conditions in Publication IV. We considered also the implications of the defects in oxygen diffusion and oxidation rate.

5.1 Doppler broadening measurements

The samples examined were cut from recrystallization annealed Zircaloy-4 sheet. They were exposed to PWR-type water at 350 °C for various periods of time, as shown in table 5.1. The thicknesses were determined by weight gain using the standard conversion factor of 14.7 mg/dm². The samples exposed for 131 days or less were within the first cycle of oxidation (pretransition), the 249 day sample was within the second cycle and the 365 day sample was within the third cycle of oxidation.
We used Doppler broadening spectroscopy to observe differences in lattice point defects in oxidized Zr. The $S$ parameter as a function of positron implantation energy is presented in figure 5.1. The unoxidized Zircaloy-4 can be recognized with high positron implantation energies for samples with a thin oxide layer. The $S$ parameter stays around 0.51 for the sample with 0.46 μm oxide layer.

**Figure 5.1.** The $S$ parameter for Zircaloy-4 samples with oxide layers of various thicknesses (PIV).

**Table 5.1.** Zircaloy-4 sample exposure times in PWR-type conditions and the corresponding oxide thickness (PIV).

<table>
<thead>
<tr>
<th>Exposure time (days)</th>
<th>Oxide thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>0.46</td>
</tr>
<tr>
<td>20</td>
<td>1.13</td>
</tr>
<tr>
<td>64</td>
<td>1.76</td>
</tr>
<tr>
<td>106</td>
<td>2.09</td>
</tr>
<tr>
<td>131</td>
<td>2.11</td>
</tr>
<tr>
<td>249</td>
<td>3.50</td>
</tr>
<tr>
<td>365</td>
<td>4.47</td>
</tr>
</tbody>
</table>
Figure 5.2. Experimental $W$ presented as a function of $S$. Trends lines are shown between characteristic positron states labeled with A and A’ corresponding to vacancy-type complexes in a lattice with less oxygen vacancies, B corresponding to a metal-oxide interface with larger number of oxygen vacancies in the complexes, and C corresponding to a positron state in Zr metal (PIV).

when the positron implantation energy is above 23 keV. The oxide layer seems to have a flat section for the $S$ parameter around 5 keV. The $S$ parameter starts to evolve around 7–9 keV with the increasing implantation energy towards the value of Zircaloy-4 in all samples. The positron states at the sample surface are undefinable by default, and the experimental values are used only for the determination of positron diffusion lengths in the samples.

Based on the positron diffusion lengths (< 20 nm) and the implantation profiles (cf. equation (3.12) and figure 3.4) in the samples (PIV), we concluded that the change observed in the $S$ and $W$ parameters in the oxide layer is not caused by the positron diffusion from the metal-oxide interface to bulk oxide or vise versa, but the oxide layer has differently distributed positron states depending on the thickness in the oxide layer. Figure 5.2 shows observed positron states in the experiments as $SW$ values. According to the diffusion analysis, intermediate states occur between A and B or A’ and B sites. Starting from the surface, A and A’ present near-surface states in the oxide at around 100 nm depth, B metal-oxide interface and C metallic Zr.

The depth of the positron trapping site B, can be estimated with the help of the changing trend lines in figure 5.2. The estimation is based on the fact that at the lower implantation energies, positrons only see states located between
Zirconium oxidation in reactor conditions

Figure 5.3. Positron density isosurface in a ZrO$_2$ supercell containing 106 atoms, where two neighboring Zr atoms are missing forming a di-vacancy. Zr atoms have gray color and O atoms red.

Table 5.2. Oxide thickness evaluated from the positron data presented in figure 5.2 (PIV).

<table>
<thead>
<tr>
<th>Weight gains (μm)</th>
<th>SW plots (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.46</td>
<td>0.42</td>
</tr>
<tr>
<td>1.13</td>
<td>1.04</td>
</tr>
<tr>
<td>1.76</td>
<td>1.36</td>
</tr>
<tr>
<td>2.09</td>
<td>1.74</td>
</tr>
<tr>
<td>2.11</td>
<td>1.87</td>
</tr>
</tbody>
</table>

the AB or A'B trend lines. The curvature changes, when positrons also start annihilating in the unoxidized Zircaloy-4. Taking into account the Makhovian implantation profiles for mono-energetic positrons (cf. figure 3.4), the changing effect of the site C starts approximately at the depth of $2\bar{z}_b$, where $\bar{z}_b$ is the mean implantation depth at B. Based on the previous estimation, the depth of the trapping site B is compared to the oxide thickness obtained with the weight gains in table 5.2. This comparison shows that the trapping site B is close to the metal-oxide interface; in accordance with the predictions.

5.2 Density functional theory calculations

We also modelled the positron states and annihilation at different kinds of defects in the ZrO$_2$ lattice applying two-component DFT. We observed that the positron density in the lattice is well localized producing reliable model parameters. Localized positron density in the case of Zr divacancy in ZrO$_2$ lattice is illustrated
in figure 5.3 and obtained $S$ and $W$ results are shown in figure 5.4. In figure 5.3, the positron density is coupled strongly for the adjacent Zr-vacancies, indicating that divacancies can have different annihilation parameters than separated Zr mono-vacancies. According to the calculations, single oxygen site vacancies do not trap positrons, but the amount of oxygen site vacancies can be recognized in $m\text{V}_{\text{Zr}} - n\text{V}_\text{O}$ vacancy clusters.

When we compared the measured results to the calculated ones (figure 5.4), we noticed that the oxide close to the metal-oxide interface has increased number of oxygen site vacancies (observed in the cation vacancy complexes). At the near-surface states (A and A’ at 50-100 nm from the surface) the amount of oxygen site vacancies has reduced. As the oxide ages, the near-surface states start shifting towards another state, from A to A’. It is not clear whether the new state A’ presents Zr di-vacancy complexes or another kind of change in the lattice, but still the calculations suggest that the changing state is caused by increasing oxygen around a vacancy-type positron trap. An overview of the positron results and their interpretation is presented in figure 5.5. They are in accordance with the previous results [69].

5.3 Interpretation of the oxidation mechanism based on the structural analysis

The oxidation process may be described by the expressions:
Figure 5.5. Characterization of the number of oxygen vacancies in zirconium oxide (in Zr-vacancy complexes) based on the Doppler broadening results and DFT calculations (PIV).

at the metal-oxide interface:

\[ \text{Zr}_m \rightarrow \text{Zr}_{Zr} + 2V^{2+}_O + 4e^- \]

at the oxide surface:

\[ 2V^{2+}_O + 2\text{H}_2\text{O} + 4e^- \rightarrow 2\text{O}_2 + 4\text{H} \]

where \( \text{Zr}_m \) is the zirconium metal, \( \text{Zr}_{Zr} \) is a zirconium cation in the oxide, \( V^{2+}_O \) is an uncharged oxygen-site vacancy in the oxide, \( \text{O}_O \) is oxygen anion in the oxide, \( \text{H} \) is hydrogen which may be released into the water or dissolve into the oxide and \( e^- \) is an electron.

An imbalance between the movement of the metal-oxide interface (defined by the oxidation of Zr) and the transport of oxygen anions across the oxide would produce an excess of oxygen site vacancies. More importantly, the dissolution of oxygen from the oxide into the metal is occurring at the same time as oxidation, and can also produce oxygen site vacancies in the oxide:

\[ \text{Zr}_m + \text{O}_O \rightarrow \text{Zr}(\text{O}) + V_O \]

where \( \text{Zr}(\text{O}) \) represents O in solution in metallic Zr. Positron results support the theory of dissolution of oxygen from \( \text{ZrO}_2 \) into the metallic Zr, since the oxide is developing over time towards its chemical equilibrium that appears
to be the surface state of the oxide, and on the other hand the oxide shows excessive amount of oxygen vacancies in the oxide close to the metal-oxide interface. Oxygen dissolution from the oxide into the metal offers an explanation to a number of observations in the literature: the time dependent oxidation between transitions, the activation energy for oxidation, the development of fine-scale pores in the oxide.

The transition to the higher oxidation rate happens approximately after every 2 μm oxide growth and each cycle is associated with a layer of oxide with little or no cracking and a similar thickness layer with a large number of micro-scale lateral cracks. These cracks could act as sinks for the vacancy excess which accelerates the oxygen transport from the oxide to the metal.

The activation energy for pre-transition oxidation for most gaseous / steam environments is in the range 1.0–2.1 eV, with a modal value around 1.5 eV [70–77]. For most aqueous exposures, and some lower-temperature steam or gaseous exposures, the measured activation energies fall around 0.6±0.3 eV [78–82].

When the activation energy for the diffusion of oxygen in ZrO₂ is measured by means which do not involve the oxidation of Zr, then the values for lattice diffusion fall in the range 2.3–2.5 eV [83,84], the values for grain boundary diffusion in 1.2–2.0 eV [81,85], and effective diffusion coefficients in 1.0–2.0 eV [81,86–88]. Comparing these values with the activation energies for oxidation suggests that the rate-controlling process for pre- or inter-transition oxidation is grain boundary diffusion at intermediate temperatures. In aqueous environments, the activation energy is too low for solid state oxygen diffusion to be the rate-controlling process.

The activation energy for diffusion is the sum of the energies required to form a vacancy and to allow it to migrate. If vacancy formation is a by-product of oxygen dissolution into the metal, then thermal activation is required only for vacancy migration. There have been several ab initio calculations of the formation energy of an oxygen site vacancy in O-poor ZrO₂ (as would be the case near the metal-oxide interface). These are in the range 0.8-1.1 eV [67,84]. The difference between this value and the activation energy for diffusion (1-2 eV) is sufficiently close to the activation energy for aqueous oxidation for vacancy migration from sub-oxide to free surfaces to be the rate-controlling process for most aqueous and in-reactor oxidations.

As the oxide ages, very small equiaxed, closed pores, around 2 nm diameter, are found during TEM examinations of zirconium alloy oxides [89,90]. It has been suggested that such fine-scale porosity can result from localised corrosion or in response to local tetragonal to monoclinic oxide transformation stresses. However, pores are not connected to the surface and the stress-induced features would produce elongated defects. It is likely that high vacancy concentration evolves to larger vacancy-type clusters that are visible with TEM.

In this chapter, nanometer size defects in oxide-Zircaloy-4 have been characterized as the oxide grows thicker. As a result, the number of O-site vacancies close to the metal (in the cation vacancy clusters) increases greater than what could
be expected by thermal equilibrium. The excess amount of O-site vacancies at the metal-oxide interface can explain many previously observed features of zirconium oxidation. The presented vacancy characterization may help in finding the most important oxidation rate control mechanism in zirconium based alloys in reactor conditions and applying it to nuclear performance codes.
6. **Micro-structural defects in tungsten**

In a fusion power plant, plasma facing material is exposed to extremely hostile environment consisting of high temperature and high neutron irradiation fluxes. Tungsten (W) is currently considered the most suitable candidate for plasma facing material in the fusion test reactor ITER and the full size demonstration reactor called DEMO [91]. Therefore a lot of effort has lately been used to study tungsten properties in irradiation conditions [92–95]. Mono-vacancies and self-interstitial atoms (SIAs) have the key role in particle irradiation durability, and they have been experimentally studied in tungsten e.g. with high-voltage electron microscopy and TEM [96–98]. In these experimental methods, the estimation of mono-vacancy densities in the studied material is based on the detection of extended defects rather than individual mono-vacancies [14], from which follows that the anticipated migration or annihilation of mono-vacancies is that of an extended defect. Positron annihilation spectroscopy has earlier been applied to study irradiation damage phenomena in tungsten under helium and hydrogen irradiations at high temperatures [92, 99–101]. There is still a need to directly observe mono-vacancy formation and annihilation events in low-temperature irradiated tungsten.

We have studied polycrystalline tungsten irradiated with 10 MeV protons in the unique positron lifetime measurement setup at Helsinki University particle accelerator laboratory that allows *in situ* particle irradiation and lifetime experiments at low temperatures [102] in Publication V. To create evenly distributed vacancy density in the samples, the sample-source package must not be too thick, i.e. less than 170 μm to avoid end-of-range effects. On the other hand, the samples must be thick enough to ensure that positrons are annihilated in the samples. The characteristic penetration depth for positrons in tungsten is 14 μm. We selected for the irradiation experiment polycrystalline tungsten foil (99.95%, Goodfellow) of the thickness 50 μm. The samples were annealed at 1700 °C in vacuum conditions before the experiments to remove all existing vacancies.
Figure 6.1. Average positron lifetime as a function of annealing temperature in proton-irradiated tungsten. Measurements were performed in low temperature conditions. Two separated lifetime components are shown in the upper panels along with the intensity of the second lifetime component (PV).

6.1 Positron lifetime experiments

We irradiated the tungsten samples at 35 K and measured a series of lifetimes at the same temperature after annealing. The annealing time was approximately 3600 s, and the increment in the annealing temperature was 10 K covering the range 35–300 K. When we compared the lifetime results against the irradiation
dose in figure 6.1, we observed significant changes in the average lifetime ($\tau_{ave}$) only after the $1 \times 10^{16}$ cm$^{-2}$ irradiation, which is higher than could be expected (PV). This suggests that the migration barrier for SIAs in tungsten is less than 0.1 eV, which is in agreement with the literature [96]. SIAs may also get trapped with a structural defect or an impurity atom. In this case SIAs have greater migration barriers [103]. This can explain the recovery observed between 50 and 150 K.

We were able to extract two components in the lifetime fitting (figure 6.1), where larger component was $180 \pm 15$ ps. According to previous studies, the lifetime for a mono-vacancy in tungsten should be in the range of 160–200 ps [99, 104]. However, the first lifetime component ($\tau_1$) was slightly higher than the bulk lifetime 110–112 ps measured for several single crystal tungsten samples. The clear drop in the average lifetime for $1 \times 10^{16}$ cm$^{-2}$ irradiated samples happens with the 50–150 K annealing temperatures. From the decomposition, it is clear that the reduction is caused by the drop in the intensity of the second lifetime component.

The fact that $\tau_1$ is greater than the bulk lifetime $\tau_B$ together with the $T^{-1.5}$ behaviour of the average lifetime in (PV) lead to the conclusion that there is an additional defect $D1$ close to the bulk lifetime that cannot be separated from the lifetime spectrum. This defect also caused the temperature dependence of the average lifetime. As the lifetime of the defect is close to the bulk value, the component can be addressed to structural defects such as lattice dislocations or grain boundaries. In Publication V we obtained for the positron trapping rate to $D1$ at 35 K a value of $\kappa_{D1} = 3\lambda_B$, and that the trapping rate at room temperature is negligible.

## 6.2 Positron trapping rate to mono-vacancies

According to the equation (3.4), we can directly estimate the mono-vacancy concentration in tungsten with $\kappa_{D2} = \mu_{D2} c_{D2}$, where the positron trapping coefficient $\mu_{D2}$ can be estimated to $1.6 \times 10^{-8}$ cm$^3$s$^{-1}$ [105]. With the approximation for $\kappa_{D1}$, we can estimate the positron trapping rate to mono-vacancies ($\kappa_{D2}$) using a three component model of equation (3.8) and (3.10) as

$$\tau_{ave} = \frac{\lambda_B \tau_B + \kappa_{D1} \tau_{D1} + \kappa_{D2} \tau_{D2}}{\lambda_B + \kappa_{D1} + \kappa_{D2}},$$

$$\implies \kappa_{D2} = \frac{\tau_{ave} - \tau_B}{\tau_{D2} - \tau_{ave}} \frac{\lambda_B}{\tau_{D1} - \tau_{ave}} \kappa_{D1} (T = 35\text{ K}).$$

When the effective trapping rate $\kappa_{D2}^* = 0.3\lambda_B$ for the as-received samples has been reduced from $\kappa_{D2}$, we obtained the trapping rate to mono-vacancies presented in figure 6.2. We also performed a high-temperature annealing experiment (annealing temperatures 410–700 K) to observe the disappearance of mono-vacancies through migration. $\kappa_{D2}$ for high temperature annealing series is shown in the figure as well.
Micro-structural defects in tungsten

Figure 6.2. Positron trapping rate to mono-vacancies in tungsten. The curves are fitted based on the isochronal annealing model (PV).

6.3 Vacancy annealing model

Activation energies $E_A$ for different annealing stages can be described with the help of the point defect annealing model. The defect concentration can be described for a single step as

$$N_{i+1}(T) = N_{\infty} + (N_i - N_{\infty}) \exp(-\nu t \cdot \exp(-E_A/(kT)))$$

where the subscript $i$ denotes the annealing step, $t = 3200$ s is the annealing time, and $\nu = 10^{13}$ s$^{-1}$ is an estimated frequency factor [106].

Fitting a linear model $E_A = E_0 + \alpha(T - T_1)$ for the activation energy for the low-temperature data gives values from 0.12 to 0.42 eV, when the temperature is between 50 and 150 K. At higher temperatures the activation energy is according to the fitting $1.85 \pm 0.05$ eV. Previous experimental work states that the migration barrier for self-interstitials is less than 0.46 eV [97], and for mono-vacancies the migration barrier was determined as $1.78 \pm 0.1$ eV [98]. The DFT calculations give migration barrier for SIA of 0.0026 [107], 0.005 [103], 0.006 [108] and 0.05 eV [109]. According to calculations, SIAs trap hydrogen and their dissociation energy would be 0.43 [103]. For mono-vacancies, calculated migration barriers are 1.45 [108], 1.71 [103] and 1.78 eV [109].

The study of low-temperature defects with positrons offer direct experimental information of the lattice point defect behaviour in tungsten that is hard or impossible to obtain another way. Therefore, it is an important step in modelling and improving the properties of tungsten based solutions for the future fusion power plants.
7. Summary

In this thesis, positron annihilation spectroscopies were developed and studied from the detector point of view. Positron annihilation spectroscopies were also used for lattice point defect characterization in oxide Zircaloy-4 samples, and in low-temperature irradiated polycrystalline tungsten.

The results obtained with the conventional two-detector positron lifetime spectrometer get spurious if the activity of the studied samples is more than 0.5 MBq. Increment of the positron source activity could increase the activity tolerance of the spectrometer, but still, it increases the spectral background and reduces the sensitivity of the spectrometer. Preliminary features of a digital three-detector coincidence spectrometer have been considered in this thesis. The study indicates that the sample radiation tolerance can be 50 times higher in a three-detector spectrometer compared to the one applying only two detectors. Also the unwanted double coincidences should be removed from the spectrum. However, the count rate is expected to drop significantly. This can be compensated with the more active positron source, because the background level is lower in a three-detector spectrometer. Combined with a glove box, a three-detector setup could be used in the research related to e.g. irradiated structural nuclear materials.

In this thesis, the optimal dimensions of high-purity germanium detectors have been considered for Doppler broadening spectroscopy. This thesis includes also a study where possible reasons for geometrical dependency of the Doppler broadening spectroscopy are considered. As a conclusion, different energy resolution of the detector crystal edges seems to cause the geometrical dependency of the results. Implications of the specific output obtained with a detector-spectrometer pair have been considered for the comparison of the results, as well. Understanding the operation and features of the detector in Doppler broadening spectroscopy increases the quality and reliability of the obtained results. This thesis highlights the importance of regular calibration measurements as small changes in the setup can change the output significantly.

In this thesis, lattice point defects in PWR-type environment oxidized Zircaloy-4 samples have been studied applying Doppler broadening spectroscopy and DFT calculations. The spectroscopy method is not sensitive to individual O-
site vacancies, but they were characterized in cation vacancy complexes. In these, the Doppler broadening spectroscopy is sensitive to the number of oxygen vacancies. All samples with different oxide thickness had clusters with several oxygen site vacancies close to the metal-oxide interface. Close to the surface, the number of oxygen site vacancies in the complexes was reduced. In addition, two characteristic oxide states were recognized as the oxide aged. The characteristic behavior of oxygen vacancies in the vacancy clusters support the anticipated cyclic oxidation rate, oxygen dissolution into the sub-oxide and metal, and nm-scale closed voids within the oxide as it ages.

Migration barriers were studied for self-interstitial atoms and mono-vacancies in low-temperature proton-irradiated tungsten. The \textit{in situ} low- and high-temperature measurements were performed with positron lifetime spectroscopy. It was observed that the self-interstitial atoms started moving already below 35 K, which was used as the lowest reference temperature. After that the self-interstitial atoms stated moving between 50–150 K annealing temperatures, and the migration barriers were determined with the positron trapping rate and vacancy annealing model to 0.12–0.42 eV. The migration barriers were addressed to self-interstitial atoms bound to impurities or structural defects. Mono-vacancies started to move around 550 K, and the migration barrier was determined as 1.85±0.05 eV.

The studies of Zircaloy-4 oxidation and low-temperature irradiated tungsten presented in this thesis bring additional experimental information of the material nanometer scale changes as a function of oxide thickness or temperature, respectively. The results increase the physical understanding of the zirconium oxidation and tungsten irradiation properties, which can help in improving nuclear performance codes. In the future, understanding of the physical properties of the materials will be increasingly important for the development of current and new nuclear reactors, as the lifetime of the reactors should be prolonged and simultaneously the reactors have to be more secure.
References


References


References


Errata

Publication I

• In page 4, the round value of the energy of a photon emitted by a relaxed Ne-22 atom is incorrectly 1.28 MeV. The correct value is 1.27 MeV.

Publication II

• In equation (1) the index $i$ has been incorrectly placed as a subscript for variable $t$. Instead, it should be the subscript of $\lambda$.

Publication III

• Fig. 6. Physical dimensions of the simulated detectors: instead of mm, the unit of the dimensions should be arbitrary units. The real dimensions are presented in Fig. 5.

• Reference [13] misses the journal. The correct journal is Radiation Research.

• Reference [14] misses the proceedings and the pages: The proceedings is 2001 IEEE Nuclear Science Symposium Conference Record, and the pages are 2420–2423.
Currently, the world’s energy production relies heavily on burning of fossil fuels that cause greenhouse gas emissions in the air and water. Controlling the ongoing climate change caused by greenhouse gases, especially carbon dioxide, requires dramatic reduction in the emissions. Low-carbon power technologies play a key role in the required change.

Nuclear power produced via fission reactions and, maybe in the future, via fusion reactions is a carbon-free way of producing energy. This thesis concentrates on the research of reactor material properties applied in the fission or fusion power plants. The study with positrons brings additional experimental information for some of the important materials showing the nanometer size defect evolutions. This thesis also takes a deep look into the main positron annihilation spectroscopy techniques from the detector point of view. This can help in maintaining the quality of the obtained results.