Applications of Positron Annihilation Spectroscopy

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Abstract. Positron annihilation spectroscopy techniques are well established nuclear techniques with applications which nowadays range from structural investigations of materials to investigations of biological samples and medical imaging. They have extensively been used more than thirty years, but with constant improvements in measuring methods and with new applications, especially in investigations of technologically important materials. In standard positron annihilation spectroscopy suitable positron source is used, and techniques include positron lifetime measurements, Doppler broadening spectroscopy and angular correlation measurements. In the recent times slow positron beams combined with these techniques are applied as well, providing depth-profiling of the samples.
We are going to present digitized positron lifetime system and a novel system for simultaneous positron lifetime and Doppler broadening spectroscopy developed at the Department of Physics in Zagreb and measurements with these systems using ^{22}Na as positron source. Their advantages compared to conventional systems and further development of the positron annihilation spectroscopy techniques by employing signal digitizers in multi-detector systems and possible applications will be described.

1. Introduction

Researchers in many scientific areas and applications are focusing on ever smaller and smaller dimensions and therefore searching appropriate investigative methods. Nuclear methods have proved themselves as especially useful, and among them positron annihilation spectroscopy (PAS) has been playing eminent role since the beginning of its exploitation several decades ago, and still presents very vigorous field of research [1]. PAS is based on the detection of gamma radiation after annihilation of positron with an electron in the studied sample, using either positron lifetime or annihilation gamma ray information, such as energies or angles of detected gamma rays, to extract basic structural features of studied samples.
Positron as electron anti-particle was predicted by P. Dirac in 1928 [2], and as a first antiparticle was discovered by C. Anderson in cosmic rays in 1932 [3]. Analogous to proton and electron which are bound in hydrogen atom, S. Mohorovičić has predicted that positron and electron can form bound state [4], later called positronium, and which was discovered by M. Deutsch in 1951 [5].
Beside the fundamental research with positrons in investigations of quantum electrodynamics laws, e.g. [6], already at the end of forties it was realized that information carried by gamma rays after annihilation of positrons can be used to study structural properties of various samples, and since then various techniques of PAS have been successfully employing in various fields of research and applications. Initial investigations which have used radioactive positron sources have been recently complemented with slow positron beams as well, available also as table-top beam systems. One of the most useful and productive applications of PAS has been in material properties research, for some general reviews of applications and techniques see e.g. [7].

The other outstanding field of application of positron annihilation detection is medical imaging e.g. [8]. Positron annihilation is used in various imaging systems such as gamma camera, sPECT, PET, CT-PET, etc.
Investigations of semiconductors was one of the most active fields of research in material research, and they have been followed the initial investigations of metals and alloys. When positrons diffuse through some crystal, they can be captured in trapping sites produced by crystal imperfections e.g. vacancies and dislocations. This changes positron lifetime in the crystal, and the measured positron lifetimes can be correlated with structural imperfections and their concentrations.
Investigations of various porous materials is another very active and import filed of research, see e.g. [9]. In porous materials beside direct positron annihilation, if available space permits, a formation of positronium can be possible. Positronium formation and their lifetimes in voids can give information about the sizes and distributions of the voids in the investigated samples. Particularly interesting are investigations of new structural types of zeolites, zeotypes and mesoporous materials, with wide range of applications from petrochemistry to the air separation, water desalination and purification, and nuclear waste management. And there are also possible medical and biological applications such as e.g. for regeneration of artificial dialysis solution, in administration of contrast agents in magnetic resonance diagnosis, for protein binder and carrier, as well as carrier for vitamins, minerals or toxic compounds, etc. Of course, also many other fields of research have been very successfully exploited these techniques, e.g. [1].
Although PAS has reached this stage of maturity, the need to reach even better precision or supplemental information is constantly triggering new developments of the methods and techniques in PAS. One of the best examples is recent progress and standing development in the usage of slow positron beams in the achieving depth-sensitivity, targeting surface and near-surface regions, e.g. [7,10], and development of table-top positron beam systems. The principle is that the positrons from e.g. radioactive positron source are slowed down to eV energies and then accelerated to the desired energies. This technique is of great importance for nano-scale investigations of some technology important materials like e.g. metallic layers, thin films, layered semiconductors, porous materials etc. providing information on native or induced defects and surface structural imperfections.
Also new detection methods based on the novel detectors and electronics are opening new possibilities through combination of various PAS techniques in unified measuring systems, which can provide correlations of, previously also accessible, but uncorrelated, data.
In section 2 we will present some basic PAS techniques, in section 3 digitized positron lifetime system developed at the Department of Physics in Zagreb will be described, and in section 4 the extension of this system by inclusion of Doppler broadening spectroscopy and the unified PALS and Doppler broadening system will be presented.

2. Positron Annihilation Spectroscopy Techniques

In positron annihilation spectroscopy with positrons from radioactive source, positron source is introduced in investigated sample and outgoing gamma rays which follow positron annihilation with electron in the sample are detected and analyzed. Positrons from the sources have a range of energies and can penetrate up to some maximal depth into the sample. On the other hand, positrons from the positron beam can have definite energy and penetration depth, and can be used for depth-profiling of the sample. After stopping in the material positrons can be either directly annihilated with the surrounding electrons, or if available space permits, can

form positronium which eventually annihilates. The annihilation of positronium in material is mainly through so called pick-off process: annihilation of the positron in the positronium with one surrounding electron in the material.

There are three main techniques of positron annihilation spectroscopy and which can be used both with the positrons from sources and slow positron beams: 1) positron annihilation lifetime spectroscopy (PALS), 2) Doppler broadening spectroscopy and 3) angular correlations measurements.

The principles of these techniques are illustrated in Fig. 1. In the positron annihilation lifetime spectroscopy, when used with radioactive sources, ^{22}Na is usually used as positron source. In this case PALS is based on the measurements of the time difference between 1.274 MeV γ-ray, emitted from the daughter ^{22}Ne nucleus almost immediately after positron emission from the ^{22}Na, and one of the annihilated 0.511 MeV γ-rays emitted in positron annihilation. The collected time spectra contain various lifetime contributions and decomposition in individual time components and corresponding intensities can yield information about holes in the sample and their concentrations. This technique, when used with slow positron beam, should include some gating from the incoming positrons in beam, but with the definite positron energy, the exact penetration depth can be determined.

In Doppler broadening spectroscopy the precision measurement of energy shift of the annihilated 0.511 MeV γ-ray as a consequence of non-zero momentum of annihilated positron and electron pairs is used to extract information about electron distributions in the investigate sample. One can detect either only one annihilated gamma ray (single Doppler broadening spectroscopy) or, in order to reduce the background, coincidence between the two outgoing 0.511 MeV γ-rays can be used (coincidence Doppler broadening spectroscopy).

This non-zero momentum of annihilated positron-electron pairs causes also deviation from co-linearity of the two outgoing γ-rays, and these angular deviations can be registered in γ- γ coincidence measurements in one or two dimensions, and form basis of angular correlation measurements. But to achieve required angular resolution in these measurements gamma ray detectors should be several meters apart and require special laboratory arrangements.

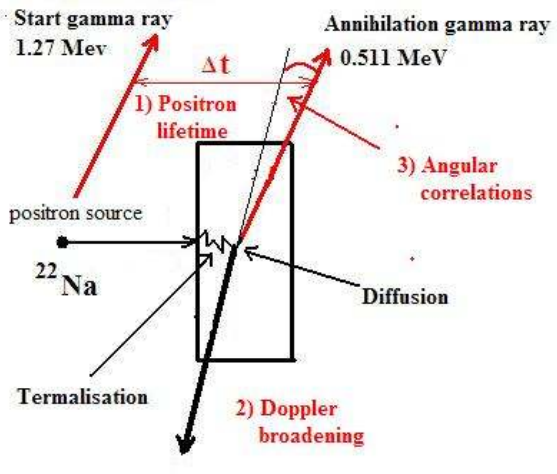

FIG. 1. Principles of three main techniques in positron annihilation spectroscopy (here presented with ^{22}Na positron source): 1) Positron annihilation lifetime spectroscopy, 2) Doppler broadening spectroscopy and 3) Angular correlations measurements.

3. Digitized Positron Annihilation Lifetime Spectrometer

Conventional positron annihilation lifetime spectrometer comprises analog electronics with scintillation detectors, differential constant fraction discriminators (CFDD) and time-to-amplitude converter (TAC) for recording time spectra [7]. Using one differential discriminator the 1.274 MeV gamma ray is selected (photo-peak) and used as a start signal, the other differential discriminator selects one 0.511 MeV annihilation gamma ray (photo-peak) and gives stop signal. The time difference between these two signals is converted by the TAC, saved and analyzed with MCA. Crucial thing in lifetime measurements is good time resolution of the setup and, beside of the quality of the scinitillation detectors and CFDDs, the achieved time resolution depends on the right settings of CFDDs. Standard PALS systems used in various investigations achieve time resolutions 200-250 ps, and some of the best achieve resolutions below 150 ps [11]. To achieve even better resolutions recently investigations using fast oscilloscope [12] or fast digitizers [13] have been undertaken and some, slight, improvements have been achieved [14], but also introduced complexity in off-line analysis. But, on the other hand, early digitalization of the detector signal can provide access to additional information, such as energies of the gamma rays and their correlation with the timing signal, which can be used in data analysis and interpretation, and offer additional flexibility in the measurements. Also, this approach opens possibilities for unification of various PAS systems in one measuring system and correlation of the data obtained in otherwise independent measurements, and therefore extraction of new information about the investigate samples (e.g. PALS and Doppler broadening spectroscopy measurements have been performed earlier also simultaneously, but the variables measured in the two spectroscopy systems could not be correlated).

At the Department of Physics, Zagreb, we have developed digitized positron annihilation lifetime system with full event storage capability for the simultaneous recording of time and energy of the γ-rays, which is improved version of setup presented in Fig. 1 in [15].

The system is comprising cylindrical BaF_2 scintillators (Ø 25 x 25 mm^2) coupled to XP2020 URQ photomultiplier tubes, analog CFDDs (Ortec 583B and FastComTec 7029) and digital data acquisition chain with CAMAC TDC (CAEN C414) and ADC (CAEN C205A) units. The achieved time resolution in full operating mode, with time and energy registration, is 203 ps, and 184 ps in only time recording mode. The achieved resolution has been improved against the one measured with system described in [15], mainly by using faster PMTs XP2020URQ instead of XP2020Q. But, recorded time and energy information for each event also provide possibilities for additional improvements of time resolution and background reduction by off-line filtering of coincidence events and by imposing appropriate cuts, Fig. 2. The advantage of the system is also flexibility in off-line analysis, in particular in estimation of three-gamma contribution and positronium formation. Estimation of positronium contribution can be of particular interests in investigation of porous materials and different zeolites, a program recently started with this setup [16]. These investigations of positronium formation are possible with the conventional setups as well and have been performed for different samples, but different choices of accepted gamma ray energies require different settings of the stop gamma ray CFDD, and new measurement for each setting. Our setup provides opportunity for off-line variation of the cut on the annihilation gamma ray energies, and only one measurement with suitable chosen hardware threshold is sufficient (in order to reduce the recorded data set we also put the upper threshold on the CFDDs, although in principle only appropriate lower threshold, to select start and stop signal, is sufficient, and all other cuts can be done off-line).

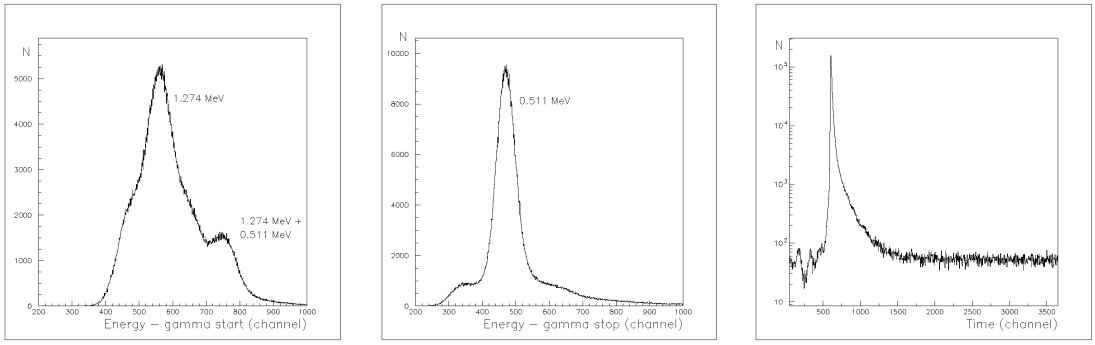

FIG. 2.: Energies of recorded start and stop gamma rays with the imposed hardware thresholds on the CFDDs and selecting 1.274 MeV and 0.511 MeV fotopeaks, left and middle, respectively, and recorded time distribution for one of the investigated zeolite samples, right.

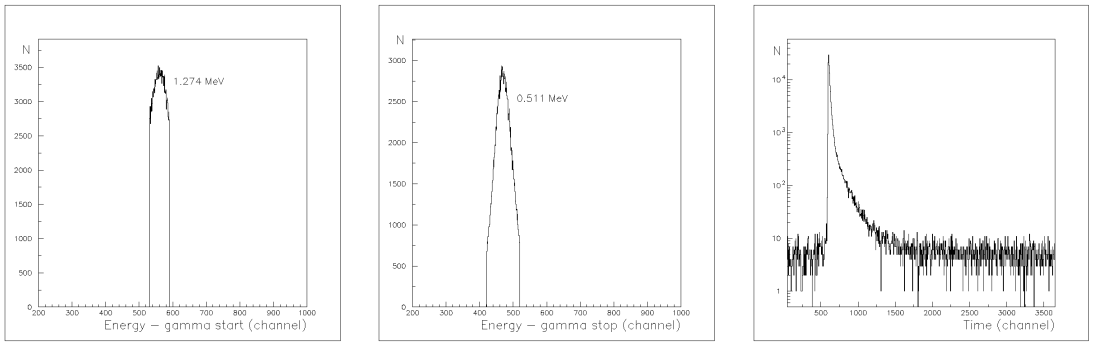

FIG. 3.: The same as Fig. 2, but also with the imposed software cuts on the start and stop energies and corresponding time distribution.

4. Unified Doppler Broadening and Positron Lifetime Spectrometer

After entering the sample (either from beam or radioactive source) positron is very fast slowed down to thermal energies and after short diffusion, eventually annihilates with the electron in the sample. The energies of the annihilating positrons are much smaller than the energies of the electrons on which they annihilate. The reason for this is that there is only one positron at particular time in the sample, and it can slow down almost to zero energy. On the other hand, electrons must obey Pauli principle and have momenta distribution up to the Fermi momentum. Since momentum is conversed in annihilation process, the annihilation gamma rays are also carrying information about the momentum of annihilating electron. This information can be seen in the energies of the annihilation gamma rays and their angles, and both can be measured with Doppler broadening spectroscopy and angular correlation measurements, respectively.

In Doppler broadening spectroscopy the energy of one or both annihilation gamma rays in the window around 0.511 MeV is measured with high-resolution gamma ray detectors usually HPGe. These gamma rays come from direct positron annihilation in the sample or positronium pick-off annihilation. Since the annihilated electron has some momentum, the resulting peak is broadened and this broadening brings some information about annihilation environment (e.g. if voids are present less annihilation occurs on high-momentum core electrons and resulting peak is less broadened). It is possible to perform these measurements only with one detector, single Doppler broadening measurements, but in order to reduce background coincidence measurements with two HPGe detectors or one HPGe detector and one scintillation detector can be performed. Coincidence Doppler broadening measurements provide much better energy resolution and are capable to distinguish chemical environments.
Starting from our digitized positron annihilation lifetime system described in Section 2, we have developed unified PALS and Doppler broadening system, by incorporating HPGe detector in the PALS system and requiring coincidence between all three detectors, Fig. 4. On this way we are performing simultaneously positron lifetime measurements and coincidence Doppler broadening measurements with full correlations of the registered events in PALS and Doppler broadening system. This correlation provides opportunity to connect void sizes and momentum information of the annihilated electrons in particular void.

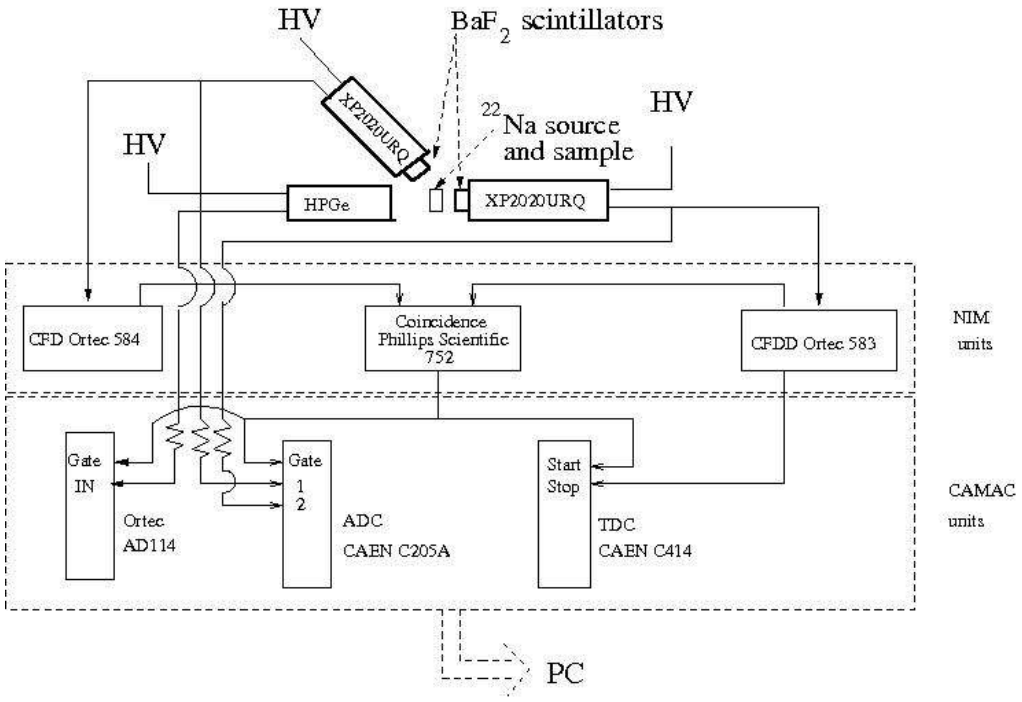

FIG. 4. Unified positron annihilation lifetime and Doppler broadening spectroscopy system.

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