University of Dundee

Determination of positron annihilation lifetime spectroscopy instrument timing resolution function and source terms using standard samples

Russell, H.; Morton, A.; Keeble, D. J.

[Link to publication in Discovery Research Portal](#)

PAPER • OPEN ACCESS

Determination of positron annihilation lifetime spectroscopy instrument timing resolution function and source terms using standard samples

View the article online for updates and enhancements.

IOP ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Determination of positron annihilation lifetime spectroscopy instrument timing resolution function and source terms using standard samples

H. Russell, A. Morton, and D.J. Keeble*

Carnegie Laboratory of Physics, SUPA, School of Science and Engineering, University of Dundee, Dundee DD1 4HN, United Kingdom

*Corresponding Author E-mail: d.j.keeble@dundee.ac.uk

Abstract. The extraction of material positron lifetime components from positron annihilation lifetime spectroscopy measurements, performed using conventional unmoderated radionuclide positron sources, requires accurate knowledge of both the spectrometer instrument timing resolution function (IRF) and annihilation events extrinsic to the material, the source correction terms. Here we report the results from study of spectrometer performance made using two reference samples, high purity polycrystalline aluminium, and stainless steel supplied by the National Metrology Institute of Japan (NMIJ RM 5607-a). Both prepared with directly deposited ^{22}NaCl positron sources. The IRFs obtained by fitting spectra from both reference samples were monitored with time to evaluate spectrometer stability and to compare methods of IRF determination. Using the aluminium IRFs the analysis of spectra from the NMIJ stainless steel reference samples yielded a single lifetime component with value 106.9(9) ps.

1. Introduction

Positron annihilation lifetime spectroscopy (PALS) enables the detection, and often identification, of open-volume defects in materials, varying in size from monovacancies to large vacancy cluster [1-3]. Vacancy-related defects can influence the properties of a wide range of metals, semiconductors and insulators, both inorganic and organic, and are of particular relevance to the operation of a range of advanced device, and energy, materials. The ability to identify the type of defect detected by PALS has been greatly aided by the development of density function theory (DFT) calculations capable of computing positron annihilation parameters [1, 4-7]. These studies have, in turn, refocused attention on the accuracy of experimentally determined lifetime values obtained by numerical decomposition [5]. Conventional PALS measurements are performed using unmoderated radionuclide positron sources with two identical pieces of the material under study enclosing the positron source. The source is normally sodium-22 in the form of ^{22}NaCl, $C_2H_3{}^{22}NaO_2$ or $^{22}Na_2CO_3$ which can either be directly deposited on one of the samples to be studied, or is more typically deposited on, and enclosed by, a thin supporting and protecting foil material such as 8 μm Kapton, 1 μm Nickel, or 4 μm Titanium. Extraction of positron lifetime components intrinsic to the material under study from the experimental spectrum requires accurate knowledge of both the instrument timing resolution function (IRF) for the spectrometer and of the extrinsic lifetime components resulting from positron annihilation events in the radionuclide source

material and, when used, the support foil material. These lifetime components are called the source-correction terms.

The source correction term accounting for annihilation events in the ^{22}NaCl crystallites has been reported to be described by a single lifetime component with a value in the range 330 – 460 ps [8-11]. If a source support foil is used then it is normally associated with a second lifetime component. The intensity of this 'foil' component can be estimated using a model based on quantifying positron backscatter, transmission and absorption at the foil-sample interfaces [10, 12]. Kapton is a commonly used ^{22}Na source support material foil due to the low atomic number and density, favourable mechanical properties, and its commercial availability as a thin foil. Further, it exhibits a single positron lifetime component which has been directly measured in 8 μm foil by variable energy PALS [13]. In addition, a third very weak extrinsic nanosecond component which is dependent on the nature of the source, the support, and samples is often observed and is assumed to originate from open volume at interfaces [8, 10]. Measurement of the source material component may be extracted from measurements on materials exhibiting a single intrinsic lifetime with a sufficiently short value [8, 14]. However, reliably producing material samples exhibiting a suitable single lifetime component is in practice difficult.

Determination of the spectrometer IRF can be achieved using measurements on materials exhibiting a well-defined, known, two lifetime component spectrum, but again the use of a true single lifetime reference material simplifies the procedure and improves the accuracy of the obtained instrument function. The stability of the spectrometer over periods of measurements is also of practical concern. The spectrometer IRF may exhibit longer term drift, which may influence the period between reference sample spectrum measurements for IRF determination.

Recently the National Metrology Institute of Japan (NMIJ) have made available stainless steel reference samples for PALS measurements [15]. In this study the timing IRF for a conventional PALS system was determined using two types of materials, both using directly deposited ^{22}NaCl sources, polycrystalline high purity aluminium and NMIJ stainless steel. Measurements were repeated over a period of approximately 150 days. The accuracy and stability of the obtained IRFs is reported. Analysis for the lifetime spectra from the NMIJ stainless steel samples and the aluminium samples is also presented. The measurements also yielded an estimate of the ^{22}NaCl crystallite source correction lifetime component.

2. Experiment
The PALS spectrometer was a conventional analogue fast-fast coincidence system. The start scintillation detector comprised a Bicron BC418 plastic crystal coupled to a Hamamatsu H3348 photomultiplier (PMT) assemble operated at 2270 V, the anode pulses were processed by an Ortec 583 differential constant fraction discriminator (CFD), and the stop detector used a Pilot-U plastic crystal on a Hamamatsu H2241 PMT assemble operated at 1750 V with anode pluses processed by an Ortec 583B CFD. The timing signals triggered an Ortec 566 time to amplitude converter and the resulting spectrum measured using a multichannel analyser. The spectrometer and associated electronics was contained in an environment chamber maintained at 21(1) °C. Measurements were performed using two reference samples, a pair of 3 mm thick stainless steel pieces supplied by the National Metrology Institute of Japan (NMIJ RM 5607-a) with a directly deposited ^{22}NaCl source with approximate activity of 560 kBq, and a pair of 0.5 mm 99.999 % pure polycrystalline aluminium from Goodfellow Cambridge Ltd (AL000650) with a directly deposited source of activity ~650 kBq. The detector separation was maintained at 6 mm for all measurements. Spectra contained 5 x 10^6 counts and were analysed using the Riso laboratory package PALSfit. Spectrometer instrument timing resolution functions (IRFs) were obtained from spectra of both reference sample pairs with directly deposited sources using the RESOLUTION and POSITRONFIT programs with the PALSfit package [16].

3. Results and Discussion
The spectrometer instrument timing resolution functions (IRFs) were obtained by fitting spectra from the aluminium sample pair with a directly deposited source, Al-DD, and also by fitting spectra from the

NMIJ stainless steel pair, SS-DD. In both cases the IRF was assumed to be accurately described using three Gaussian functions with an intensity ratio of 80:10:10. In consequence, the IRF is fully specified by the time shift positions of the latter two Gaussians with respect to the first, and the full width at half maximum (FWHM) values of each Gaussian. It is also useful to compare different IRFs using shape parameters that quantify the sum of the three IRF Gaussians, these are the widths of the resulting function at 1/2, 1/4, 1/10, 1/30, 1/100, 1/500 and 1/1000 of the maximum value.

The spectrometer IRF shape parameter values obtained from 34 Al-DD spectra measured over a period of 153 days are given in table 1, the standard deviations are also shown. Each spectrum was first fitted using RESOLUTION, defining the IRF as described above specifying guess values for the five parameters, and using the three unconstrained lifetime components. The resulting IRF was then used for a series POSITRONFIT runs with three unconstrained lifetime components and a fixed source correction comprising a lifetime of 390 ps with an intensity that was incremented in 0.1 % steps over an appropriate range, which for Al-DD was typically between 1.5–2.5 %. These resulted in a reduced bulk first lifetime component, a second defect lifetime component, and a nanosecond component with an intensity less than 0.2 %. The chi-squared values were found to be approximately constant, the dominant effect of incrementing the intensity of the assumed 390 ps source correction term intensity was to vary the second component lifetime and intensity values. The fit that yielded a value of 245(1) ps was selected and then used to run RESOLUTION again, but with four lifetime components fixed at values obtained from the POSITRONFIT output. The IRF so obtained was assumed to be representative and the average of the shape parameter values are given in table 1.

Table 1. Average shape parameter widths (ps) from fitted data from the aluminium reference pair with directly deposited ^{22}NaCl source (Al-DD) obtained from 34 spectra. The values obtained from fitting 36 spectra from the NMIJ stainless steel direct deposit pair (SS-DD). All spectra were measured over a 153 day period.

Sample	1/2	1/4	1/10	1/30	1/100	1/500	1/1000
Al-DD	214.1(1.1)	331.8(1.4)	403.4(1.9)	499.6(2.8)	588.2(4.3)	659.0(4.3)	728.7(4.9)
SS-DD	213.2(8)	329.9(9)	400.6(1.1)	496.1(1.3)	585.8(3.7)	657.8(8.4)	730.0(16.0)

The Al-DD derived IRFs were used to analyse adjacent NMIJ stainless steel directly deposited (SS-DD) spectra with POSITRONFIT. The best fits were obtained using three unconstrained lifetime components, the average values obtained from fitting the 36 SS-DD spectra are given in Table 2. The results are in agreement with a single intrinsic lifetime, and the obtained value of 106.7(6) ps is consistent with the supplied value of 106.2(2.4) ps [15]. The second component had an intensity of ~ 4 % and yielded a value of 394(9) ps. This component is attributed to annihilations within the ^{22}NaCl crystallites of the deposited positron source.

Table 2. Average lifetime components parameters of 36 fitted spectra from the NMIJ stainless steel direct deposit sample. A third lifetime component was also obtained with an intensity of 0.10(2) % and a lifetime of 2.3(5) ns.

τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)
106.7(6)	96.0(3)	394(9)	3.8(3)

Instrument resolution functions were also determined from the 36 SS-DD spectra and the average shape parameter values are given in Table 1. The procedure for extracting IRFs from the SS-DD sample spectra was similar, the spectrum was first fitted using RESOLUTION, specifying guess values for the

five IRF parameters and assuming three lifetime components. The resulting IRF was then used for a POSITRONFIT run with three lifetime components, one fixed at a value of 106.2 ps. The fitted lifetime component values were then used as fixed values for a second RESOLUTION run and the resulting IRF was assumed to be representative (table 1). Comparison of the average shape parameters for the IRFs obtained from the aluminium reference with those obtained from the NMIJ stainless steel reference samples assuming a single material lifetime component of 106.2 ps given in table 1 shows them to be consistent. The standard deviations for the dominant shape function widths are slightly narrower for the SS-DD derived IRFs. The obtained IRFs were analysed to see if there was a systematic drift in these parameters over the 153 day period, however, no trend was resolved. It should also be noted that while the standard deviations in the shape parameters widths shown in table 1 are small, the individual IRFs specified by the FWHM values for the three Gaussians and associated two time shift values exhibit larger, the average Al-DD derived values are given in table 3.

Table 3. Instrument resolution functions obtained from 34 Al-DD spectra measured over a period of 153 days, defined by the FWHM values for the three Gaussian functions and the two time shifts with respect to the first Gaussian. All values are in ps.

Gaussian 1	Shift 2	Gaussian 2	Shift 3	Gaussian 3
233.5(1.1)	-42.0(4.5)	129.6(4.7)	32.3(4.0)	132.7(7.1)

The spectra from the aluminium sample with a directly deposited source were fitted using the SS-DD derived IRFs and the results are shown in Table 4. A ^{22}NaCl component assumed to have a lifetime of 394 ps was included. The resulting intensity for this component is smaller than that obtained for the SS-DD sample (table 2) despite the source having a slightly higher activity, however, it should be noted the sources were deposited from different lots of radionuclide. The standard trapping model bulk lifetime values were also calculated (table 4) and are consistent with previously reported values, and with precision DFT calculated values [5, 17]. The defect lifetime component lifetime value (table 4) is lower than, but consistent with, the typically reported range for the monovacancy in aluminium of 237–244 ps [17], and in closer agreement with the DFT values of 227–234 ps [5].

Table 4. Average lifetime components parameters from 34 fitted aluminium direct deposit (Al-DD) spectra. The ^{22}NaCl component was fixed at 394 ps. A fourth lifetime component was also obtained with an intensity of 0.11(2) % and a lifetime of 2.1(5) ns. The calculated bulk aluminium lifetime is also given.

τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	τ_B (ps)
142(6)	69(9)	228(21)	28(8)	394	2.3(7)	161(1)

4. Concluding Remarks

Positron annihilation lifetime spectra from a commercial polycrystalline aluminium sample pair, and from a stainless steel reference sample pair supplied by the National Metrology Institute of Japan (NMIJ RM 5607-a), both using directly deposited ^{22}NaCl positron sources, were repeatedly measured over a period of 153 days. Both samples were used to extract spectrometer instrument timing resolution functions (IRFs). These were compared and found to be in good agreement. The spectrometer IRF was found to be stable over the period of the study. The aluminium derived IRFs were used for the deconvolution of the NMIJ stainless steel spectra. A single intrinsic material lifetime of 106.7(6) ps was obtained, which is consistent with the supplied value of 106.2(2.4) ps. The aluminium sample spectra were deconvolved using the

stainless steel derived IRFs and yield a defect lifetime consistent with the experimental, and DFT calculated, values reported for the monovacancy. Similarly, the intrinsic bulk lifetime value obtained was in agreement with previously reported experimental and DFT calculated values. An experimental value for the lifetime due to positron annihilation events with the ^{22}NaCl source crystallites of 394(9) ps was obtained.

References

[1]   Tuomisto F and Makkonen I, 2013. *Rev. Mod. Phys.* **85**, 1583.
[2]   Keeble D J, Brossmann U, Puff W and Wurschum R, in *Characterization of Materials*, edited by
         E.N. Kaufmann. (John Wiley & Sons, Hoboken, N.J., 2012), pp. 1899
[3]   Krause-Rehberg R and Leipner H S, *Positron Annihilation in Semiconductors*. (Springer-Verlag
         Berlin, 1999)
[4]   Wiktor J, Jomard G and Torrent M, 2015. *Phys. Rev. B.* **92** 125113.
[5]   Kuriplach J and Barbiellini B, 2014. *Phys. Rev. B.* **89** 155111.
[6]   Ishibashi S, 2014. *J. Phys. Conf. Ser.* **505**, 012010.
[7]   Torsti T, Eirola T, Enkovaara J, Hakala T, Havu P, Havu V, Hoynalanmaa T, Ignatius J, Lyly M,
         Makkonen I, Rantala T T, Ruokolainen J, Ruotsalainen K, Rasanen E, Saarikoski H and Puska
         M
           J, 2006. *Phys. Status Solidi B.* **243**, 1016.
[8]   Staab T E M, Somieski B and Krause-Rehberg R, 1996. *Nucl. Instrum. Meth. A.* **381**, 141.
[9]   Djourelov N and Misheva M, 1996. *J. Phys. Condens. Mat.* **8**, 2081.
[10]   McGuire S and Keeble D J, 2006. *J. Appl. Phys.* **100**, 103504.
[11]   Weisberg H and Berko S, 1967. *Phys. Rev.* **154**, 249.
[12]   Saoucha A, 1999. *J. Appl. Phys.* **85**, 1802.
[13]   Kanda G S, Ravelli L, Loewe B, Egger W and Keeble D J, 2016. *J. Phys. D.* **49** 025305.
[14]   Kanda G S and Keeble D J, 2016. *Nucl. Instrum. Meth. A.* **808**, 54.
[15]   *https://www.nmij.jp/english/service/C/crm/20/5607a_en.pdf*.
[16]   Olsen J V, Kirkegaard P, Pedersen N J and Eldrup M, 2007. *Phys. Status Solidi C.* **4**, 4004.
[17]   Campillo Robles J M and Plazaola F, 2003. *Defect Diff. Forum.* **213-215**, 141.