Positron annihilation lifetime spectroscopy source correction determination: A simulation study

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ABSTRACT

Positron annihilation lifetime spectroscopy (PALS) can provide sensitive detection and identification of vacancy-related point defects in materials. These measurements are normally performed using a positron source supported, and enclosed by, a thin foil. Annihilation events from this source arrangement must be quantified and are normally subtracted from the spectrum before analysis of the material lifetime components proceeds. Here simulated PALS spectra reproducing source correction evaluation experiments have been systematically fitted and analysed using the packages PALSfit and MELT. Simulations were performed assuming a single lifetime material, and for a material with two lifetime components. Source correction terms representing a directly deposited source and various foil supported sources were added. It is shown that in principle these source terms can be extracted from suitably designed experiments, but that fitting a number of independent, nominally identical, spectra is recommended.

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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]. The ability to identify the type of defect has been markedly enhanced by the development of density function theory (DFT) calculations [1,4–6]. These are capable of accurately predicting positron lifetimes for specific vacancy related defects, which, in turn, has refocused attention on the accuracy of experimentally determined lifetime values obtained by numerical decomposition [4].

PALS measurements are routinely performed using unmoderated radionuclide positron sources, for example, ^{22}Na. The positron source can be deposited directly on to the material under study and a second, nominally identical, piece placed on top; a direct deposit source. Alternatively, the positron source can be deposited on to a thin foil which can then be folded to encapsulate the ^{22}Na crystallites; a foil supported source. The foil source can then be placed between the two, nominally identical, samples. The same foil source can be used repeatedly.

A small fraction of positrons annihilate outside the material under study, these extrinsic contributions are referred to as source correction terms. Annihilations can occur from states within the ^{22}Na crystallites, the 'salt' term, and if a foil supported source is used then annihilations can also occur from within the foil material, the 'foil' term [7–10]. In addition, a third 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 [9,10]. Directly deposited sources minimise the complexity, and the fraction, of annihilations events extrinsic to the material under study. These extrinsic source correction term contributions are normally subtracted from the experimental PALS spectrum to enable accurate deconvolution of intrinsic material component terms [7,11]. Progress has been made in quantifying source correction terms [9,10], nevertheless consensus on the protocols to be adopted in identifying and reporting these is still lacking.

Experimental positron lifetime spectra are numerically deconvolved, normally using well established software packages. These most commonly employ non-linear least-squares fitting to an adjustable model comprising of the appropriate number of lifetime components [12–14]. In addition, they must include fixed terms describing the spectrometer instrument resolution function (IRF), and have the ability to subtract the extrinsic source correction terms, from the raw spectrum prior to the fitting of intrinsic material components. Programmes are also available based on maximum entropy methods, these make fewer model assumptions in the fitting of the material components, but again require the small fraction of extrinsic annihilation events to be subtracted prior to deconvolution [15].

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To experimentally determine the source corrections terms the ideal situation would be to have available convenient, nominally identical, samples that exhibit a single material lifetime component. This could be the bulk, perfect lattice, lifetime of the material, or it could result from saturation trapping at a high concentration of a specific type of open-volume defect. It is normally assumed that low defect content samples exhibiting a single bulk lifetime can be obtained by careful annealing of suitable high purity single crystals or polycrystal metals [9]. Measurements using a directly deposited ^{22}Na source could then allow determination of the material lifetime, and of the salt component lifetime and intensity. The identical material can then be measured using foil supported sources, and the resulting spectra fitted with the material lifetime and the salt lifetime fixed at the values obtained from the direct-deposit source experiments. The procedure may enable the foil lifetime and intensity, and the intensity of the salt component, to be determined. If the same foil-supported source is used for measurements with an unknown sample, the source correction lifetimes would then be known. The intensity of the foil contribution depends on the backscatter coefficient of the material under study for the energy distribution of the ^{22}Na emitted positrons, and hence on atomic number. A multiple scatter model capable of describing the resulting foil intensity has been developed [10,16,17], so it is possible to make an estimate of the foil intensity with a different sample material. For a point ^{22}Na source, the salt component intensity would be independent of sample type, however, for a real source there is evidence for a dependence on atomic number [10].

In practice, it can be difficult to obtain suitable reference sample materials that exhibit a single intrinsic lifetime. However, obtaining material samples giving two lifetimes is more straightforward. In consequence, it is of interest to know if it is possible to measure source correction terms using the above procedure but using a two lifetime reference material.

The mathematical form of the experimental spectrum is well known. It comprises of the convolution of the IRF with the exponential positron lifetime components, both from the material under study and from the extrinsic source correction terms, and contains an appropriate amount of Poisson noise. These spectra can be readily, and accurately, simulated. Previous studies have used the fitting of realistic simulated PALS spectra to obtain valuable insight [9,11,18–20]. It was clearly demonstrated that an incorrect description of the PALS spectrometer IRF, or estimation of the salt source correction term, can result in significant errors in the deconvolved lifetime components attributed to the material under study [11,21]. The limitations in the ability to deconvolve separate lifetime components have been investigated [18–20]. This depends on number of counts in the spectrum, the peak to background ratio [19], and the separation between the components and the number of components [20]. These studies have enabled apparent inconsistencies in the interpretation of experimental PALS spectra to be resolved [18,20].

In this study simulated spectra are used to evaluate the ability to extract reliable source correction terms from appropriately designed PALS experiments. Two cases are examined; the first assumed single lifetime reference samples were available, while the second investigated the more readily achievable situation of a reference sample with two lifetime components. Spectra simulating the use of a directly deposited source were first studied, then, for the same materials, spectra were generated and analysed to represent the use of various foil-supported positron sources.

2. Methods

Fitting was primarily performed using the non-linearly least-squared based package PALSfit version 2.43 [12,22], but where

appropriate the maximum entropy method programme MELT 4.0 was also used [15]. The simulated spectra were generated using the programme available within PALSfit. All simulated spectra contained 4096 channels with 12.4 ps per channel, and were normalised to contain 5×10^6 counts. The peak to background ratio was approximately 9000:1, and was typical of that observed experimentally using an approximately 400 kBq source. The instrument resolution function was described by three Gaussians with intensity ratios 80:10:10, widths of 216 ps, 157 ps and 300 ps, and with shifts of 0, −30 ps and 30 ps. The resultant IRF has a full width half-maximum (FWHM) of 214 ps. In the simulation experiments described below each type of spectrum was generated 10 times, and these nominally identical spectra were analysed using PositronFit within the PALSFit package with the defined IRF.

In the first set of experiments it is assumed that a single lifetime metal is available. Measurements with a direct deposit source were simulated. An aim was to determine the average lifetime of the salt contribution. All simulated spectra used a salt component intensity of 4%. In PALS experiments, the intensity of this component can vary from batch to batch of supplied radionuclide, nevertheless, a value of 4% typically corresponded to a source activity in the range 400–800 kBq. A series of simulations were performed varying the material lifetime value between 100 ps and 220 ps. This encompassed possible reference materials such as Fe, Cu, and Ni, with bulk lifetimes in the 100–120 ps range, through Al at approximately 160 ps, to silicon with a bulk lifetime of 218 ps. The spectra were fitted without constraints and assuming two components.

Simulation experiments followed with the same 'materials', but using foil-supported sources. Two source correction lifetime components are now required, the salt component and a term representing the average lifetime of the foil material. These simulations were performed for three of the material lifetimes; 100 ps, 160 ps, and 200 ps. The foil lifetime values were varied from 120 ps to 220 ps in 20 ps steps and spanned the typical range observed for thin metal foils. To aid comparison a foil intensity of 8% used for all the simulations. The resulting spectra were fitted assuming three lifetime components, with the material and salt lifetimes fixed at the values obtained from the direct deposit experiments detailed above, all other parameters were unconstrained. In addition, simulations were performed representing the commonly used polyamide film Kapton. The lifetime for Kapton was assumed to be 381 ps foil component lifetime, and was fixed at this value.

A second set of simulation experiments were performed to evaluate the use of a reference material exhibiting two intrinsic material lifetime components. Three model materials were investigated with bulk lifetimes of 100 ps, 160 ps and 200 ps, and with an associated defect component lifetime of 180 ps, 245 ps and 270 ps, respectively, and an intensity of 25%. The resulting two

Table 1
PositronFit results showing the mean and standard deviations obtained from constraint-free analysis of 10 generated spectra using identical input values. The simulated spectra represent a series of materials exhibiting a single lifetime component with a value incremented from 100 ps to 220 ps. The direct deposit source was simulated using a second component with $\tau_{Na}=430$ ps, $I_{Na}=4\%$.

Input values $\tau_{Material}$ (ps)	Fit results			
	τ_1 (ps)	I_1	τ_2 (ps)	I_2
100	100.0(1)	0.960(1)	430(4)	0.040(1)
120	120.0(2)	0.960(1)	430(1)	0.040(1)
140	140.0(1)	0.960(1)	431(4)	0.040(1)
160	159.9(3)	0.960(2)	430(6)	0.040(2)
180	180.0(2)	0.960(2)	430(6)	0.040(2)
200	200.1(3)	0.961(3)	434(8)	0.039(3)
220	219.7(4)	0.957(4)	423(10)	0.043(4)