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Trapping Rate of Positrons, DBAR line shape parameters and Calculation of Free Volume Hole Size in Polymeric materials using PALS Data

Priyanka I[1], Asha J K[1], Preeti B Hammannavar[1], Arati M[1], Basavarajeshwari M B[1], V Ravindrachary[2] and Blaise Lobo[1]*

[1]Department of Physics, Karnatak Science College, Karnatak University, Dharwad 580001, Karnataka, India
[2]Department of Physics, Mangalore University, Mangalagangothri 574199, Karnataka, India.

***Corres.author: blaise.lobo@gmail.com**

Abstract: The calculation of different parameters of positron annihilation in polymeric materials, to determine parameters like free volume hole size, positronium (Ps) formation probability, DBAR line-shape parameters, and positron trapping rates in ordered and disordered regions of semi-crystalline polymers are discussed. The programs are validated with data from standard, well cited research papers. The computer source codes have been written in Fortran-77.
Keywords-Trapping Rate; Free Volume Hole Size; Positronium; Polymeric Materials; Positron Annihilation Spectroscopy; DBAR; Line shape parameters; PALT.

Introduction and Experimental:

Positron Annihilation Spectroscopy (PAS) refers to a group of techniques used to study materials, wherein positron is used as a nano-probe [1-4]. The ability of PAS to study free volume in polymers arises from the fact that the Ps atom (a positron-electron-bound state) is trapped in free volumes, and annihilates there with a much longer lifetime when compared to the crystalline regions of the polymeric material. The para-positronium (p-Ps) decays with a lifetime of 125 pico-seconds (ps), but the ortho-positronium (o-Ps) lives for a longer time, especially in open or vacant spaces like the free volume holes in polymers, annihilating with a lifetime between 1 nano-seconds (ns) and 5 ns. A semi empirical equation between the measured ortho-positronium (o-Ps) lifetime and free-volume hole radius (R) has been first given by Tao [5], and later elaborated by Eldrup [6].

$$\tau_3 = 0.5\left[\left(1-\frac{R}{R_o}\right)+\frac{1}{2\pi}\sin 2\pi\left(\frac{R}{R_o}\right)\right]^{-1} \qquad (1)$$

In equation (1), R_O=R+ΔR and ΔR is empirical parameter which is determined by the fitting of observed o-Ps life time τ_3 with known hole and cavity sizes. The best fitted value of ΔR from all known data is 1.656 Å.

Results and Discussion:

The positron parameters like free volume hole size (V), Ps formation probability (P), fractional free volume (F) of semi-crystalline polymers has been computed using Fortran 77 code. The raw positron data is first analyzed using the POSITRONFIT (PATFIT-88) program to extract the lifetime components (τ_i) and corresponding intensity components (I_i) using 3 component (i=3), free fit analysis [7]. The following code is validated with results presented by Nakanishi and Jean [8].

```
C   COMPUTATION OF R, V, P and F
      REAL DR, R, R0, T3, S3, I3, V, F, P, C
      REAL X1, X2
      DR=1.656E-10
      R=0.01E-9
      WRITE (*,*)'ENTER THE VALUES OF t3 IN ns AND I3 IN %'
      READ (*,*) T3, I3
      WRITE (*,*)'ENTER THE VALUE OF STRUCTURAL CONSTANT C'
      READ (*,*) C
      DO   30   I=1, 100000
      R0=R+DR
      X1=1-(R/R0)
      X2= (SIN(6.283*(R/R0))/6.283)
      S3=0.5/(X1+X2)
      IF (S3.GE.T3) THEN
      WRITE (*,*)'THE VALUE OF O-Ps LIFE t3 (in ns) IS'
      WRITE (*,10) S3
 10 FORMAT (E14.5)
      WRITE (*,*)'THE FREE VOLUME HOLE RADIUS (in m) IS'
      WRITE (*, 20) R
 20 FORMAT (E14.4)
       GO TO 100
       END IF
       R=R+0.00001E-9
 30  CONTINUE
100 WRITE (*,*)'ASSUMING SPHERICAL SHAPE FOR HOLE'
       V= (4.0/3.0)*3.14159*(R**3)
       P= (4.0/3.0)*I3
       F=C*I3*V
       WRITE (*,*)'FREE VOLUME V (in cubic meter) =',V
       WRITE (*,*)'POSITRONIUM FORMATION PROBABILITY, P=',P
       WRITE (*,*)'FREE VOLUME FRACTION, F (%) =',F
       STOP
       END
```

The trapping rates [9, 10] in the ordered and disordered regions of a semi-crystalline material can be determined in a straight-forward manner, starting from Goldanskii's kinetic relations [11]. Positrons are trapped in voids in the crystalline (ordered) regions of a semi-crystalline polymer, and positronium (Ps) in the free volume holes, the dynamic open spaces in the amorphous (disordered) regions. The trapping rates in the ordered and disordered regions of the polymeric material are indicated by ν_o and ν_d respectively, and are given by equations (2) and (3).

$$\nu_o = [I_2/(1-I_2)] \times (1/\tau_1 - 1/\tau_2) \quad (2)$$

$$\nu_d = [4\times I_3 \times (1/\tau_1 - 1/\tau_3)] / [3-(4\times I_3)-(3\times I_2)] \quad (3)$$

We have also written a program written in Fortran-77 to analyze the DBAR spectra of polymeric materials and determine the line shape parameters (S- parameter, W- parameter etc., reflecting annihilation of positrons with low and high momentum electrons in the material) [4], the details of which will be published elsewhere.

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