



THERMAL EXCITATION ENERGY OF TRAPPED ELECTRONS AT LOW TEMPERATURE STUDIED THROUGH POSITRON ANNIHILATION LIFETIME SPECTROSCOPY

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Abstract: Positronium (Ps) formation has been studied in high density polyethylene (HDPE) below and around gamma transition temperature (T_g). The increase in ortho-positronium (o-Ps) intensity (I_3) with time due to trapped electrons at different rate has been discussed in terms of different possible models. Some calculation have been performed to find the thermal activation energy of trapped electrons.

Keywords: Positronium formation, trapped electron, high density polyethylene, low temperature, ortho-positronium

Introduction

Temperature dependence of polymer properties constitutes a very important part of polymer studies. From glass transition temperature (T_g) to room temperature, o-Ps intensity (I_3) is known to increase with increasing temperature. It is one of the explanations for these phenomena that the size of intermolecular spaces and their concentration are increased with temperature by micro Brownian motion of molecules. On the other hand below T_g , the I_3 increased along with decreasing temperature. It has been reported that the yield of positronium (Ps) formation at low temperature increased gradually during positron annihilation lifetime (PAL) measurement in materials such as polymers and molecular solids since 1980s (Eldrup *et al.*, 1980; Lightbody *et al.*, 1985; Kindle and Reiter, 1987). At low temperatures this behavior of increase in ortho-positronium (o-Ps) formation is observed and explained in terms of Ps formation occurring from trapped (localized) electrons. Such a dependence has been considered as caused by the freezing of local motion of molecules. Because the pre-existing holes are shielded by local motions at higher temperature, so o-Ps can migrate into the hole only at low temperature after freezing of motions. This effect was confirmed by Hirade *et al.* (1998) who observed the effect of light bleaching of the enhanced o-Ps formation. This effect was studied to investigate the transition and relaxation properties, (Uedono *et al.*, 1997; Suzuki *et al.*, 2003) free volume distribution (Wang *et al.*, 1998), mechanism of positronium formation process (Kansy and Suzuki, 2007) in many works.

It is well known that positron annihilation lifetime spectroscopy (PALS) is an important method to study polymer properties. PAL investigation of polyethylene in the external electric field by Ito and Suzuki (2003) showed that, at a temperature far below the polymer glass

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transition, two different mechanisms of Ps formation were involved. An epithermal positron escapes from the blob may loosely bind to a similarly escaped epithermal electron to form a quasi-free-Ps. This quasi-Ps gradually loses its kinetic energy and finally it forms Ps at some open volume space. This process has been referred to as the slow localization of Ps (SLP) formation (Kansy and Suzuki, 2007) which occurs at all temperatures. Besides this at low temperature (below T_g) Ps can form by interacting with a trapped electron which produces from ionizing positron irradiation (Udeno *et al.*, 1977; Wang *et al.*, 1998; Hirade *et al.*, 1998). This process is referred to as delayed formation Ps (DFP) as it takes time to find a trapped electron. This is the reason for enhancement of o-Ps with elapsed time as the trapped electron increase with time at low temperature. This increase starts at a first rate and becomes slower with time. To explain this phenomenon He *et al.* (2003) suggests that in addition to electron trapping, electron de-trapping due to thermal excitation also occurs during this process.

This paper focuses on o-Ps yield at low temperature using positron annihilation lifetime spectroscopy. The aim of this study is to investigate the thermal excitation energy of electron de-trapping.

Methods and materials

The PALS measurements were carried out using a fast-fast coincidence system with Barium Fluoride (BaF_2) scintillators having a time resolution of 230 ps. Each spectrum contained two million counts per hour. A 30 μ Ci source of spot size 2 mm deposited on a 1.5 μ m thick Al foil was sandwiched between the samples. PALS spectra were analysed using POSITRONFIT.

The HDPE samples used for this experiment were obtained from Goodfellow Metals Ltd (UK). The 1 mm thick HDPE sheet was cut into 10 \times 10 mm² pieces. The HDPE had a quoted crystallinity of 70-80%.

The HDPE samples were taken to low temperature using a '10K EBERA' closed cycle He fridge. Two hours are required to attain the lowest temperature of about 20 K. At each temperature two new pieces of sample were used to avoid any effect due to radical build up. The same positron source was used in each case to assure the dose rate remained the same. A temperature controller (Lakeshore 330) was used to maintain the sample temperature at the correct value.

Results and discussion

Positronium formation in HDPE has been measured at the temperatures 20, 40, 60, 80, 120, 150 and 200 K. PALS data were taken in every hour. In Fig. 1 I_3 is plotted against elapsed time for this temperatures. This measurement has been taken for 4 days. Fig. 1 shows that I_3 increases quickly with time initially and then asymptotically slows down to some saturation value at 20, 40, 60, 80 and 120 K. At 150 K there is a slow rise in I_3 for the whole range, while at 200 K no rise is seen. It is also noted that the 20, 40, 60 K data are close to each other, while for 80 and 120 K the asymptotic values are more quickly diverging.

Electrons produced from the positron source irradiation are trapped at low temperature in shallow potential well (Hirade *et al.*, 2000; Suzuki *et al.*, 2000). Then o-Ps formed through the DFP channel where positron interact with one of the trapped electron and this is the reason for rise in I_3 as shown in Fig. 1.

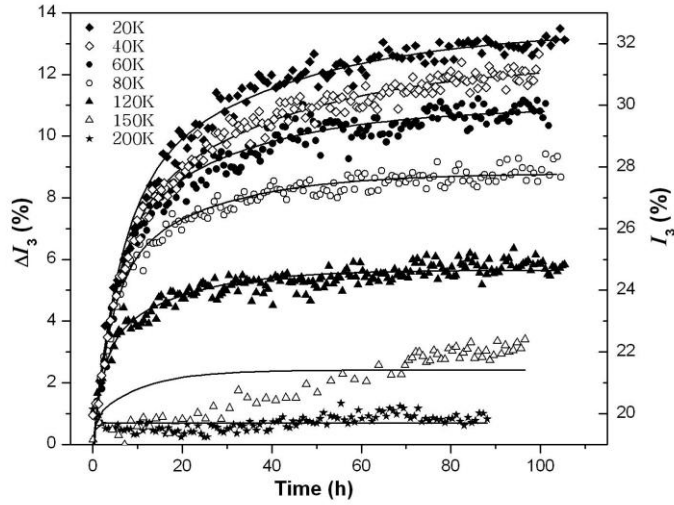


Fig. 1: Time dependence of o-Ps component intensity I_3 at different temperatures for HDPE after fast cooling. ΔI_3 is the increase in o-Ps intensity above the base value of 19%. The curves correspond to the fitting of the two trap model Eq (18).

He *et al.* (2003) explain why the value of I_3 starts at a fast rate and becomes asymptotically slower in terms of the detrapping of the weakly bound electrons at higher temperatures as shown in Fig.1. These authors consider a constant rate of radiation induced electron production and trapping J by the ^{22}Na source. This allows them to write the dynamic equation for the concentration of trapped electrons N_e as

$$\frac{dN_e}{dt} = J - \lambda_d N_e, \quad N_e(0) = 0 \quad (1)$$

where the detrapping rate λ_d is determined by the molecular motions that exist in the vicinity of the trapping site and is written as

$$\lambda_d = \nu_d e^{-E/k_B T} \quad (2)$$

where ν_d is the typical molecular oscillation frequency, E is the activation energy of detrapping (i.e. the trap electron binding energy). The solution of the above equation is

$$N_e(t) = \frac{J}{\lambda_d} [1 - e^{-\lambda_d t}]. \quad (3)$$

From an experimental point of view enhancement of I_3 (ΔI_3) due to trapped electron accumulation is the difference between the value of I_3 at low temperature after measurement time t , and the high temperature value. Thus referencing to Fig.1, the value of ΔI_3 would be written as

$$\Delta I_3 = I_3(t) - 19 \quad (4)$$

It is argued that since ΔI_3 results from epithermal positrons that have escaped the blob interacting with trapped electrons to form Ps (DFP channel), there should be a direct proportionality between ΔI_3 and N_e

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$$\Delta I_3 = CN_e = \frac{CJ}{\lambda_d} [1 - e^{-\lambda_d t}] = CJ\nu_d^{-1} e^{E/k_B T} [1 - e^{-\lambda_d t}] \quad (5)$$

It is seen that this equation is successful in explaining the asymptotic behavior of ΔI_3 with elapsed time. Taking logarithms one obtains

$$\ln \Delta I_3 = C + \frac{E}{k_B T} + \ln[1 - e^{-t\lambda_d}], \quad (6)$$

which in the asymptotic limit of $t \rightarrow \infty$ becomes

$$\ln \Delta I_3 = C + \frac{E}{k_B T} \quad (7)$$

A straight line plot of Eq. (7) with a gradient should give the trap energy. Such a plot is shown in Fig. 2, where it is seen that such a straight line has not been obtained. This indicates a problem with this simple theory. This can be seen from the fact that according to Eq. (5) as $T \rightarrow 0$ so $\Delta I_3 \rightarrow \infty$. This is as a result of assuming that the trapped electron concentration is limitless – which results if one has a finite trapping rate J with $\lambda_d=0$ (Eq. (3)). This is clearly an unphysical situation.

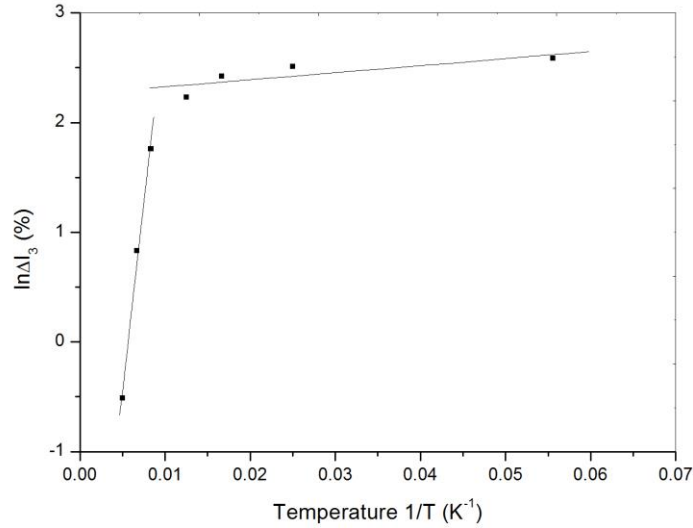


Fig. 2: The plot obtained from plotting $\ln(\Delta I_3)$ against $1/T$ (After He. et.al.2003)

An alternative theory to explain the saturation of ΔI_3 , which does not run into the problem of infinities as $T \rightarrow 0$, has been given by Hirade (2003). Hirade suggests that trapped electrons do not just get released through thermal activation, but in addition have other natural ways of decaying. Whatever the cause, the trapped electron decay rate through this mechanism is temperature independent and is here written as $\lambda_0 N_e$. Eq. (1) is thus rewritten

$$\frac{dN_e}{dt} = J - \lambda_d N_e - \lambda_0 N_e = J - \lambda_{eff} N_e \quad (8)$$

where

$$\lambda_{eff} = \lambda_0 + \lambda_d \quad (9)$$

is the effective decay rate of the trapped electron. The solution of this equation is exactly the same as Eq. (5)

$$\Delta I_3 = CN_e = \frac{CJ}{\lambda_{eff}} [1 - e^{-\lambda_{eff}t}] = \frac{\alpha}{\lambda_{eff}} [1 - e^{-\lambda_{eff}t}] \quad (10)$$

where $\alpha = CJ$. The notable feature of Eq. (10) is that it only contains two fitting parameters α and λ_{eff} . Where the gradient of ΔI_3 with time at $t=0$ is

$$\left. \frac{d\Delta I_3}{dt} \right|_0 = \alpha = CJ \quad (11)$$

Thus the value of α is easily found since, in accordance with the theory, the different temperature data do have very similar $t=0$ gradients. Taking a mean value of the gradient gives $\alpha = 1.32 \pm 0.15h^{-1}$, the only remaining fitting parameter is λ_{eff} . The results of fitting (for 40 h) are shown in Fig 3. The degree of fitting is seen to be quite reasonable showing the fact that such good fitting is found is supportive of the theory of Hirade, particularly since λ_{eff} occurs in two places in Eq. (10) i.e. in both the amplitude (α/λ_{eff}) and in the characteristic rise time (λ_{eff}^{-1}). From Eq. (9) and (2) it follows that

$$\lambda_d = \lambda_{eff} - \lambda_0 = \nu e^{-E/k_B T} \quad (12)$$

from which

$$\ln[\lambda_{eff} - \lambda_0] = \ln(\nu_0) - \frac{E}{k_B T} \quad (13)$$

From this fit λ_{eff} values can be used to determine the trap energy as Eq. (12). λ_0 is the fitted value of λ_{eff} corresponding to the lowest temperature.

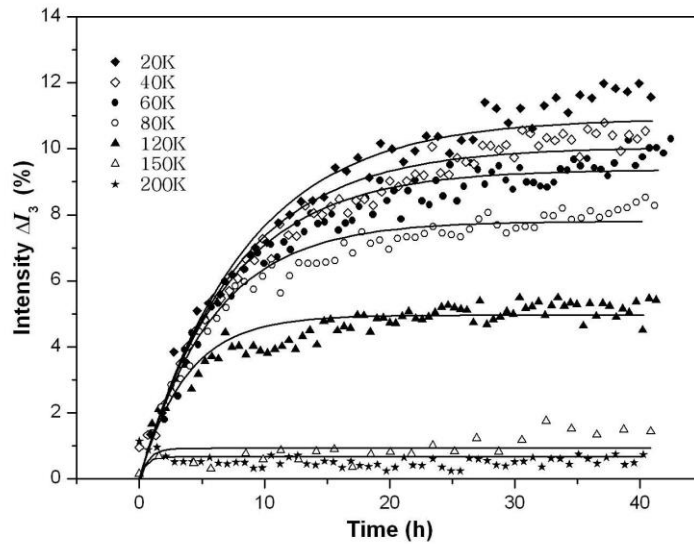


Fig. 3: Least square fitting of the ΔI_3 data for different low temperatures plotted against time for the first 40 h hours of measurement

Thus an Arrhenius plot for λ_d as shown in Fig 4. shows two slopes rather than one. The energies as obtained from the gradients are 0.008 eV at low temperatures (20 – 80 K) and 0.07 eV at higher temperatures (120 – 150 K). At first sight the failure to obtain a straight line on the Arrhenius plot may seem like a break down in theory. It is, however, reasonable to expect more

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than one activation energy in a polymer as a result of the onset of different molecular motions. Moreover, the same effect has been noted in PMMA as noted by Hirade (2003). Two straight line are seen, but these are taken over restricted temperature ranges. For our HDPE data the transition occurs at a much lower temperature of ~ 100 K. This being the case would mean that below ~ 100 K the localized electrons could localize on the HDPE backbone or intermolecular spaces with a trapping energy of ~ 0.008 eV and with increasing temperature the average fraction of trapped electrons in such states would be removed, until at ~ 100 K backbone motion would be so intense that this type of trap was no longer available.

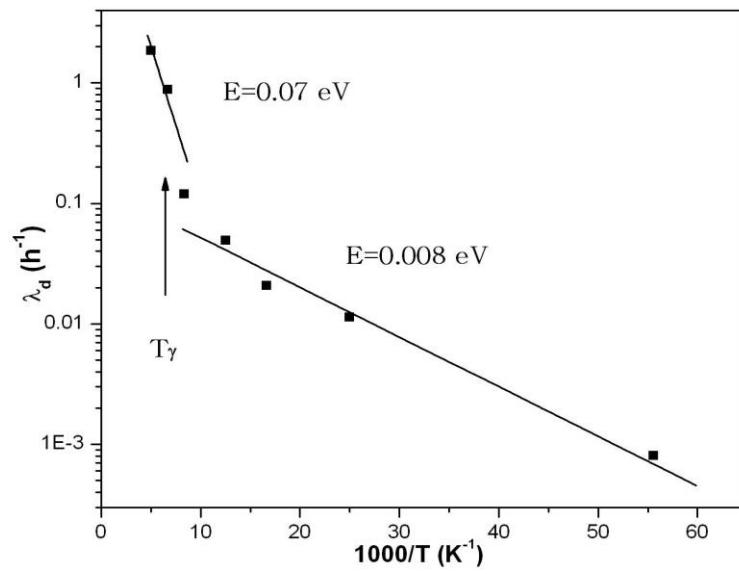


Fig. 4: Arrhenius plot of the thermal de-trapping rate λ_d of trapped electrons in HDPE as determined from Fig. 3 using Eq.(12).

Limited Trapping Sites Interpretation

In the course of this present study, even though Hirade (2003) interpreted the cause of the saturation of ΔI_3 at ΔI_{3m} as $T \rightarrow 0$, as a temperature independent trapped electron decay, a simpler interpretation considered for the saturation, which seems to be plausible. This is the interpretation of there being a limited density of trapping sites available for localizing electrons. Taking the number of available trapping sites as N_T , the probability of a free electron being trapped depends on the fraction $(N_T - N_e)/N_T$ of sites that do not have trapped electrons and Eq. (1) can be rewritten as

$$\frac{dN_e}{dt} = J \frac{N_T - N_e}{N_T} - \lambda_d N_e \quad (14)$$

$$\text{or, } \frac{dN_e}{dt} = J - \left[\frac{J}{N_T} + \lambda_d \right] N_e = J - \lambda_{eff} N_e \quad (15)$$

$$\text{where, } \lambda_{eff} = \left[\frac{J}{N_T} + \lambda_d \right] \quad (16)$$

So the dynamic equation for N_e is of exactly the same form as that found in Eq. (8), and moreover comparison of Eq. (16) with Eq. (9) shows that the temperature dependence of λ_{eff} is of the same form $\lambda_0 + \lambda_d$, with $\lambda_0 = J/N_T$. This leads to the conclusion that a limited trapping site hypothesis is a reasonable one and will explain the data as effectively as a temperature independent decay rate.

A Two Trap Model

From Fig. 1 it has been shown that the data do not seem to saturate but continue to increase with times greater than 40 h. There could be different reasons to explain this phenomenon. On the limited trapping site model, it could be that some sites are more difficult to access and require more time to fill. The interpretation we have considered here, is that there are two trapping sites instead of one, having different binding energies. In this model ΔI_3 is written as a result of the two populations of trapped electrons, N_{e1} in the first trap and N_{e2} in the second. Then following the same procedure as Eq. (10) ΔI_3 can be written as

$$\Delta I_3 = C(N_{e1} + N_{e2}) \quad (17)$$

where following the same procedures and using the same symbol interpretation as for the single trap model one obtains

$$\Delta I_3 = \frac{CJ_1}{\frac{J_1}{N_{T1}} + \lambda_{d1}} \left[1 - e^{\left(\frac{J_1}{N_{T1}} + \lambda_{d1}\right)t} \right] + \frac{CJ_2}{\frac{J_2}{N_{T2}} + \lambda_{d2}} \left[1 - e^{\left(\frac{J_2}{N_{T2}} + \lambda_{d2}\right)t} \right]$$

which can also be written

$$\Delta I_3 = \frac{\alpha_1}{\lambda_{eff1}} [1 - e^{\lambda_{eff1}t}] + \frac{\alpha_2}{\lambda_{eff2}} [1 - e^{\lambda_{eff2}t}] \quad (18)$$

where for $i=1,2$:

$$\alpha_i = CJ_i, \text{ and } \lambda_{effi} = \frac{J_i}{N_{Ti}} + \lambda_{di} = J_{0i} + \lambda_{di} \quad (19)$$

Eq. (18) contains the 4 parameters α_1 , α_2 , λ_{eff1} , and λ_{eff2} . The values of the 4 fitting parameters are given in Table 1. It is seen that the model fits are significantly better than that had been obtained with just a single trap up to ~100 h. Adding two extra fitting parameters is expected to make a better fit because of the added degrees of freedom. Then it is important to see what physical sense makes this result. Particular observation is that for the 20, 40, 60 and 80 K data the values of α_1 fall in the range between 1.1 and 1.8 h⁻¹, while the values of α_2 also fall randomly between 0.14 and 0.26 h⁻¹. This suggests that to a good approximation α_1 and α_2 may be held constant in order to test the model against a more restrictive two parameter fit. α_1 and α_2 were thus fixed at their mean values of 1.32 and 0.15 h⁻¹. The fitted curves are shown in Fig 1 and are almost as good as those obtained for the four parameter fit. This observation supports the two trap hypothesis. Further a survey of the λ_{effi} ($i=1,2$) fitted parameters as given in Table 2 shows that they follow the expected trend of increase with temperature as expected for electron traps .

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Table 1: Four parameter least square fitting results for the ΔI_3 data. The full range of measurement time is fitted .

Temperature (K)	α_1	$\lambda_{\text{eff}1}$	α_2	$\lambda_{\text{eff}2}$
18	1.098	0.171	0.259	0.0387
40	1.167	0.164	0.140	0.0264
60	1.658	0.289	0.200	0.0389
80	1.844	0.363	0.158	0.042
120	0.836	0.169	0.008	-0.003
150	0.079	0.928	0.041	0.0042
200	78.12	178.37	0.005	-0.001

Table 2: Two parameter least square fitting results for the ΔI_3 data plotted against measurement time as shown in Fig. 1. The full range of measurement time is fitted

Temperature (K)	α_1	$\lambda_{\text{eff}1}$	α_2	$\lambda_{\text{eff}2}$
20	1.32	0.169	0.15	0.027
40		0.195	„	0.027
60		0.203	„	0.034
80		0.248	„	0.0438
120		0.436		0.058
150		1.639		0.095
200		2.119		2.114

A further test was carried out on the $\lambda_{\text{eff}i}$ ($i=1,2$) fitting parameters, namely that of performing Arrhenius plots on the thermal dissociation rate $\lambda_{di} = (\lambda_{\text{eff}i} - \lambda_{0i})$ in the same manner as carried out in Fig. 4. These results are shown in Fig 5. The trap energy results for trap 1 are very similar to the energies found from the 40 h data fit of Fig. 3. The activation energy has dropped a little from 0.008 to 0.006 eV below T_γ but above T_γ activation energy has increased a little from 0.07 to 0.086 eV. Furthermore a straight line is obtained below T_γ temperature range with an activation energy of 0.015 eV, which really supports the two trap model. This indicates the presence of a deeper second trap. This all supports the idea that below T_γ there are indeed two electron traps, the first having an activation energy of ~ 0.006 eV and the second ~ 0.015 eV.

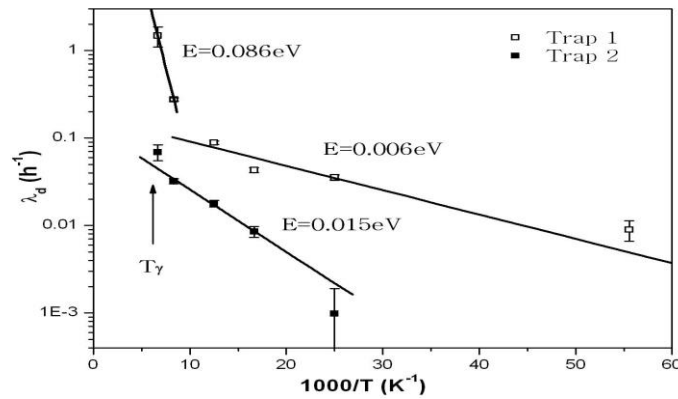


Fig. 5: Arrhenius plot of the thermal de-trapping rate λ_d in HDPE for shallow electron traps 1 and 2. Data derived from the two parameter fit to the data of Fig 1

Conclusion

Positronium formation has been studied in HDPE at low temperature as a function of elapsed time. Below gamma transition temperature the reason of asymptotic slowing of o-Ps intensity has been try to understand through different model. According to the explanation of dynamic equilibrium between the trapping rate of electron and their thermal detrapping rate (He *et al.*, 2003) and some other non thermal process (Hirade, 2003) of detrapping our data has been explained. In addition, two other possibilities has been proposed. A limited trapping site has been suggested in place of non thermal detrapping, which gives the same dynamic equation. To explain the saturated values of o-Ps two trap model has been proposed. With this model thermal detrapping energy has been estimated on time scale greater than 40 h. This investigation finds two trap energy of ~0.006 eV and ~0.015 eV below gamma transition indicating the presence of a deeper trap.

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