Proceedings of the 32nd Polish Seminar on Positron Annihilation, Jarnołtówek 2000

COMMENTS ON THE EFFECT OF γ-IRRADIATION ON POSITRONIUM FORMATION IN POLYMERS AT LOW TEMPERATURES

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Quantitative description of the effect of γ-irradiation of PE and PMMA on positronium formation on the trapped electrons at low temperatures is suggested. The consideration shows that, at least in these substances, the number of the trapping centers is probably enough to localize all *ortho*-positronium, and therefore the intensity of the long-lived positronium component is dependent mostly on the probability of Ps formation but not on the number of the trapping centers.

PACS numbers: 78.70.Bj

1. Introduction

Thus far, there is a problem: has the long-lived Ps component I_3 something to do with the number of o-Ps trapping sites or is this number so high that I_3 is dependent only on the fraction of positrons Q which form Ps in a system [1–5]? The last alternative [4, 5] was proposed recently and it suggests that the o-Ps trapping rate ν_T is much higher than the annihilation rate of free o-Ps λ_f, $\nu_T \gg \lambda_f$. It is likely that a quantitative description of the results [5] on Ps formation on the trapped electrons (their concentration was measured using ESR) in γ-irradiated PE and PMMA gives the first chance to obtain straight argument in favor of the second alternative. Some of our data on thermostimulated luminescence (TSL) glow support the suggested mechanism of Ps formation on the trapped electrons.

2. Experimental

We describe analytically the experimental results [5] consisting in observations of additional o-Ps formation ΔI_3 (relative to $I_3 = 3Q/4$ for a non-irradiated sample) in PMMA and high density PE due to low-temperature γ-irradiation by the ^{60}Co source (Figs. 1, 2). Figure 3 demonstrates TSL glow curves for high density PE (curve A) and PMMA (curve B) measured in this work. Figure 4 shows our TSL results for the two copolymers of the same chemical composition but with different thermal history. One of them was original copolymer poly (methyl methacrylate-*co*-methacrylic acid) with molar feed composition of monomer 70/30 (curve 1). The second one was annealed at 140°C for 0.5 hour (curve 2).

3. Discussion

The increase ΔI_3 of Ps formation in some polymers because of γ-irradiation (either by ^{22}Na source during the experiment or after the exposure to γ-rays from ^{60}Co source) at low temperatures was observed recently by many investigators. The authors of [5] suggested a qualitative explanation, supposing additional Ps formation on weakly bound electrons (trapped electrons) created by γ-irradiation. Essential progress in this study was obtained due to complementary ESR measurements of the trapped electrons concentration N_e. We propose here a quantitative description of the model [5]. The variation ΔI_3 is found from the following equations describing Ps formation (rate ν_{form}) and subsequent Ps trapping (rate ν_T) by the trapping centers (concentration N_3) in the free volume space:

$$\begin{aligned}
&dP_f^+/dt = -(\lambda_f^+ + \nu_{form})P_f^+, && P_f^+(0) = 1 - Q,\\
&dP_f^{Ps}/dt = (3/4)\nu_{form}P_f^+ - (\lambda_f^{Ps} + \nu_T)P_f^{Ps}, && P_f^{Ps}(0) = 0,\\
&dP_T^{Ps}/dt = \nu_T P_f^{Ps} - \gamma_3 P_T^{Ps}, && P_T^{Ps}(0) = 0.
\end{aligned} \tag{1}$$

Q is the fraction of positrons which form Ps without γ-irradiation; the rest of the positrons $(1 - Q)$ escape from the spur and can try to form Ps on the trapped electrons. We shall use P_f^+ as the probability to find free e^+, λ_f^+ as the free e^+ annihilation rate, and λ_f^{Ps} as the annihilation rate of free («pre-localized») Ps; we suppose that $\lambda_f^+ \cong \lambda_f^{Ps} \equiv \lambda_f$. Finally, P_f^{Ps} and P_T^{Ps} are the probabilities to find free and trapped o-Ps, correspondingly. Obviously, o-Ps lifetime in the trapping center is shortened compared to its intrinsic lifetime and equal to $\tau_3 = 1/\gamma_3$. The intensity of this component is denoted as I_3. The solution of Eqs. (1) gives an increase in I_3, ΔI_3, because of additional Ps formation on the trapped electrons

$$\begin{aligned}
\Delta I_3 &= (3/4)(1 - Q)\nu_{form}(\lambda_f + \nu_{form} - \gamma_3)\nu_T(\lambda_f + \nu_T - \gamma_3)\\
&= (3/4)(1 - Q)AB,
\end{aligned} \tag{2}$$

where $B = \gamma_T(\lambda_f + \nu_T - \gamma_3)^{-1}$, $\nu_{form} = 4\pi D_f^+ R N_e = k_{form} N_e$ and $\nu_T = 4\pi D_f^{Ps} R_3 N_3$. D_f^+ and D_f^{Ps} are diffusion coefficients of free e^+ and Ps, correspondingly; R is an effective radius for interaction of e^+ and trapped electron, and R_3 describes an effective size of a trapping center.

It becomes obvious that fitting of Eq. (2) to experimental points for PE is possible only with $k_{\mathrm{form}}(\mathrm{PE}) = \nu_{\mathrm{form}}/N_{\mathrm{e}} = 10^{-7}$ cm^3/s and $\nu_{\mathrm{T}} \gg \lambda_{\mathrm{f}}$, i.e. $B = 1$ (Fig. 1). A description of the PMMA results for the highest $N_{\mathrm{e}} = 2 \times 10^{17}$ cm^{-3} [5] is possible by suggesting the two following alternatives:

(a) $\nu_{\mathrm{T}} \gg \lambda_{\mathrm{f}}$, $B = 1$, and $k_{\mathrm{form}}(\mathrm{PMMA}) = (1/50)k_{\mathrm{form}}(\mathrm{PE}) = 0.24 \times 10^{-8}$ cm^3/s. The last ratio probably means that $D_{\mathrm{f}}^{+}(\mathrm{PMMA}) = (1/50)D_{\mathrm{f}}^{+}(\mathrm{PE})$. The diffusion coefficient for PE is known to be about 0.1 cm^2/s, however $D_{\mathrm{f}}^{+}(\mathrm{PMMA})$ is unknown.

(b) ν_{T} andλ_{f} are comparable. Fitting to the highest value of ΔI_3 gives the probability of Ps trapping $B = 0.2$, if the rate constant of Ps formation on the trapped electrons in PE and PMMA are roughly the same: $k_{\mathrm{form}}(\mathrm{PMMA}) = k_{\mathrm{form}}(\mathrm{PE}) = 10^{-7}$ cm^3/s.

A comparison of calculated dependences for the two cases mentioned above is given in Fig. 2.

We have to *conclude* that for PMMA, just as for PE, the alternative (a) gives a much better description of the whole set of points [5] than the alternative (b). And this is the first direct argument in favor of the point of view that in such polymers as PE and PMMA all *ortho*-Ps atoms are probably trapped before annihilation ($B = 1$). It means that in such cases I_3 is dependent mostly on the probability of Ps formation in a substance Q but not on the number of the trapping sites N_3, since the number of Ps traps is too high ($\nu_{\mathrm{T}} \gg \lambda_{\mathrm{f}}$). Further experiments of this type could be useful. In the scope of the further study of the mechanism of Ps formation on the trapped electrons we suggest a comparison of the observed effect with results on TSL glow for the same samples at low tempera-

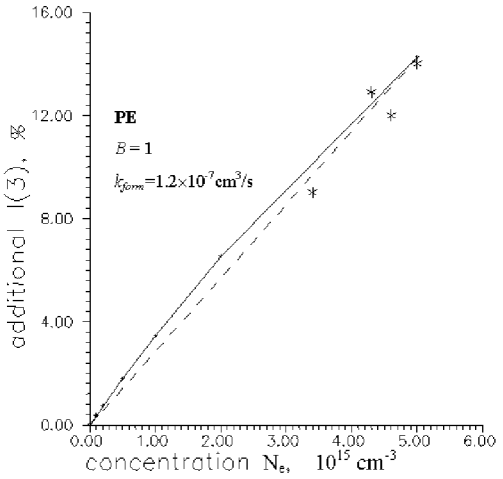

Fig. 1. Additional intensity ΔI_3 of the longest lifetime component in PE as a function of the trapped electron density [5]. The dependence is described (solid line) by Eq. (2) with $k_{\mathrm{form}}(\mathrm{PE}) = 1.2 \times 10^{-7}$ cm^3/s and $B = 1$. The dashed line here and in Fig. 2 represents the linear dependence for comparison.

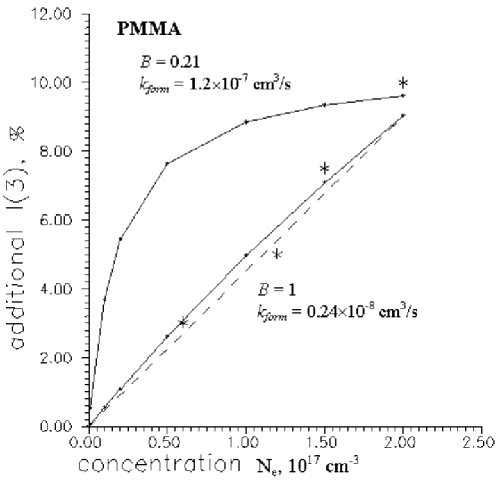

Fig. 2. Additional long-lived component intensity in PMMA as a function of the trapped electron density [5]. Solid curves correspond to different sets of parameters in Eq. (2): $k_{\rm form}$(PMMA) = $k_{\rm form}$(PE) = 1.2×10^{-7} cm^3/s, $B = 0.21$ or $k_{\rm form}$(PMMA) = $(1/50)k_{\rm form}$(PE) = 0.24×10^{-8} cm^3/s, $B = 1$.

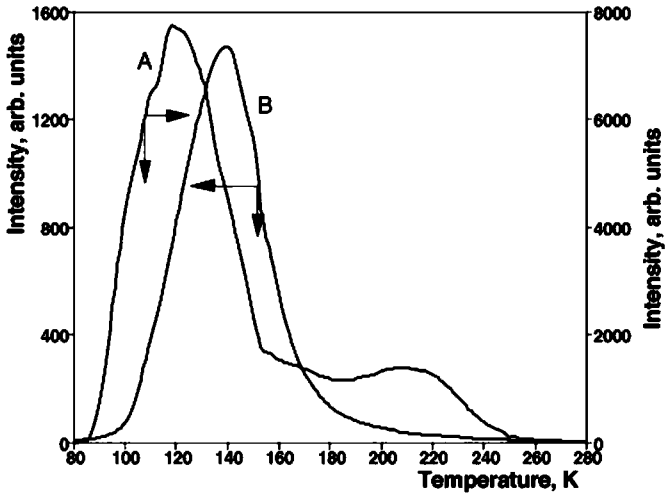

Fig. 3. TSL glow curves for PE (A) and PMMA (B). All curves in this figure and in Fig. 4 are represented in the same relative units.

ture (Figs. 3, 4). Though irradiation dozes normally used in TSL glow experiments are slightly higher (5–10 kGy) than those in PAL study [5], it seems obvious that the mechanisms of the two processes have much in common. Actually, the electrons trapped at low temperature are responsible for the both effects. Both effects can be essentially reduced by bleaching. It is obvious from Fig. 3 that TSL glow

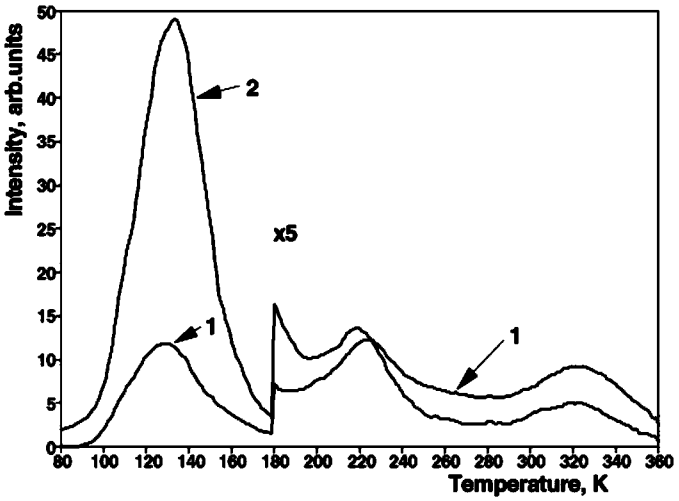

Fig. 4. TSL glow curves for original (curve 1) and annealed (curve 2) MMA-MAC (70/30) copolymers.

of PE is much more intensive than that of PMMA for γ-irradiation with the same dozes (just as the effect of Ps formation on the trapped electrons). A comparison of TSL glow (Fig. 4) for the samples having the same chemical composition but different thermal history (see Sec. 2) and Ps yield at given temperature and dozes would be of special interest.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research, project No.98-03-32859, IR 97-1525, and by the INTAS grant No. 97-1936.

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