

Structural implications on positron lifetimes in lamellar polyethylene with chain defects

F. J. Baltá Calleja

Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas Serrano 119, 28006 Madrid, Spain

J. Serna, J. Vicente, and M. A. Segovia

Departamento de Física del Estado Sólido, Universidad Complutense, 28040 Madrid, Spain

(Received 9 July 1984; accepted for publication 19 December 1984)

New positron lifetime data in a series of isothermally crystallized polyethylene pairs with known concentrations of chain defects, having a lamellar structure, have been measured. The materials were characterized by small-angle and wide-angle x-ray scattering techniques. Positron lifetime data were computer analyzed and only three components could be resolved. It is shown that the annihilation mechanisms can be understood in terms of average distance between lamellar crystals (long period), crystal thickness, and chain defect concentration. The present results confirm, in consonance with the conclusions of other authors, the longest component to be due to ortho-positronium pick-off annihilation. The intermediate component may be ascribed to positronium trapped at the crystal-amorphous interface. The application of a three-state trapping model yields a lifetime of about 900 ps for this state. It is suggested that the shortest component may be due to free positron annihilation, para-positronium self-annihilation, and annihilation of positrons from a tightly bound state localized at the chain defects. An approximate calculation provides lifetime values around 250 ps for this short-lived state.

I. INTRODUCTION

Positron annihilation techniques have been widely applied to polymeric solids, particularly to polyethylene (PE). The influence of different physical parameters such as temperature, electric field, etc., has been examined within this context to study phase changes and primarily to identify the origin of the various lifetime components.¹⁻¹⁰ Stevens and Lichtenberger¹ have separated the lifetime spectra of PE into four components, thus emphasizing the complexity of time spectra for positrons annihilating in polymers. Kerr² and Bertolaccini *et al.*³ agreed to identify the longest component with the annihilation via pick-off of ortho-positronium (o-Ps). The studies of Brandt and Wilkenfeld⁴ on a series of five PE, having known densities and crystallinities, show three lifetime components. These authors concluded that the intermediate component arises from the annihilation of positrons trapped in amorphous domains; the short component is more complex and comprises the self-annihilation of para-positronium (p-Ps) pendant of o-Ps, and free positrons. Further experiments carried out by Bertolaccini *et al.*⁵ and Rama Rao, Patro, and Sen⁶ about the influence of an electric field on the positron lifetimes in PE, were compatible with the above interpretation. However, the detailed analysis of the four components of Teflon performed by Kindl and co-workers^{7,8} points to an even more complicated annihilation process than that suggested by Brandt and Wilkenfeld.⁴ According to this analysis, the longest component includes all positrons forming o-Ps and annihilate via electron pick-off; the intermediate long-lived component arises from positrons bound in the amorphous domains; the intermediate short-lived component is exclusively due to free positrons. Finally, the shortest component is partly due to p-Ps self-annihilation and partly to a bound positron state of short lifetime. The existence of this short-lived state had already been pre-

dicted in PE.^{1,2} Dauwe and Motoko Kwete⁹ have further compared their results of three-quantum annihilation yield in γ -irradiated Teflon with the two longest intensities obtained by Kindl, Puff, and Sormann.⁷ The former authors come to the conclusion that the intermediate long-lived component must be also due to a positronium state. Recent results of Kindl¹⁰ favor such an interpretation.

One significant problem that one meets when dealing with positron lifetime data in polymeric materials is the lack of a clear correlation between the results obtained and the microstructure of these materials. In some cases lifetime measurements are performed at varying temperatures and crystallinity is unknown. In other cases, however, parameters such as crystallinity and density are not sufficient to uniquely identify the samples microscopically. It is, thus, important to select a polymer with a well characterized internal structure amenable to yield reproducible annihilation results which can be compared with data from other well characterized polymers. PE supplies a convenient model system in which the stacking of crystalline lamellae a few hundred angstroms thick is featuring the microstructure of the material.¹¹ The lamellae are arranged within spherulites radially growing in all directions. The important parameter of the microstructure is the lamellar periodicity L , the average distance between adjacent lamellar crystals, which can be directly evaluated from small angle x-ray diffraction (Fig. 1). The reciprocal value of L furnishes a measurement of the density of crystalline-amorphous interfaces which can play a relevant role in positron annihilation. Preceding studies¹² on PE containing known amounts of chain defects (branches unsaturations) up to 7 per 10² CH₂ have demonstrated that a fraction of these defects is incorporated into the crystal lattice at interstitial sites. The level of chain defect accommodation within the lattice depends on the size of the defects.¹³ From the above investigations the incorporation of chain

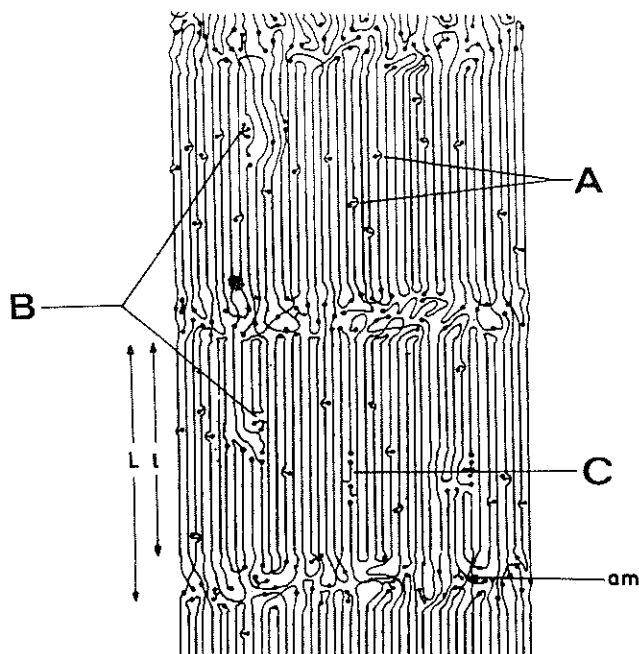


FIG. 1. Schematic representation of the lamellar structure of polyethylene illustrating the periodicity L , the crystal thickness l , and the distribution of chain defects between the "amorphous" layer (am) and the crystals [interstitial (A and C) and amorphous (B)].

sequences, containing branches, in the lattice can be regarded as kind of disorder within the crystals contributing to the enhancement of free volume. According to Brandt and Wilkenfeld⁴ the influence of the latter is notorious on the annihilation parameters. Furthermore, the conspicuous decrease in crystallinity with increasing number of defects has been interpreted as involving the penetration of branches in the crystals through formation of so called "amorphous defects".¹⁴ These can be described as a class of 3-dimensional defects of intermediate size, about 10^3 \AA^3 , which can also contribute to an increase of free volume within the crystals.

The aim of the present work is to report novel positron lifetime data in order to critically investigate the existing correlation between the occurring annihilation mechanisms and the microstructure of PE. For this purpose we have carefully prepared PE samples crystallized under controlled conditions having known concentrations of chain defects.

II. EXPERIMENT

A. Materials and sample preparation

Various commercial samples of PE with molecular weights, \bar{M}_w , ranging from 9600 to 150 000 and varying chain defect concentrations between 0.17–6.9% were investigated.¹² These values were adopted to minimize possible influences of \bar{M}_w on the positron lifetimes.¹⁵ The overall number of chain defects was measured by infrared spectroscopy.¹⁶ The total level of defects ϵ is given as the sum of branches (butyl or longer side groups) plus unsaturations including the chain ends. Two series of samples were prepared (Table I). A first series of linear PE ($\epsilon = 0.17\%$) samples were melted between two cover slides at 160–170 °C within a few minutes and subsequently transferred to a silicon oil bath which was kept at the desired crystallization temperature T_c . Undercoolings of $\Delta T = T_m - T_c$ ($T_m =$ melting point) of 10, 15, 138, and 216 °C were selected (samples 1–4). A second series of samples with varying number of defects ($\epsilon = 1.81$ –6.90%) was prepared by cooling the melt at $\Delta T \sim 10 \text{ °C}$ (samples 5–9). The samples obtained were 2 mm thick and exhibited flat and well defined surfaces, adequate for the experiments of positron annihilation.

B. X-ray diffraction techniques

Wide-angle x-ray diffractograms were obtained at room temperature using a Ni-filtered $\text{CuK}\alpha$ radiation from a tube (40 kV, 30 mA). The working conditions for the diffractometer were selected according to previous line profile studies.¹⁷ One degree divergence and antiscatter, and 0.15 mm receiving slits were used. The radiation was detected with a proportional tube, pulse-height analyzer and counter. The PE diffraction maxima 110, 200, and 020 scanned at a rate of $1^\circ (2\theta)/\text{min}$ were used to calculate the unit-cell dimensions a and b . The standard deviation was found to be 0.01 Å. The unit-cell edge c was assumed equal to 2.546 Å.¹⁸ The 110 and 200 diffraction maxima were also employed in evaluating the volume crystallinity α with help of a computer program by least-squares fitting.¹⁹ The accuracy in the measurement of α lies within 1%. Long periods were obtained by applying Bragg's law to the maxima from small-angle x-ray diffraction recorded photographically with a Rigaku camera using pinhole collimation and filtered $\text{CuK}\alpha$ radiation from a rotating anode source (40 kV, 100 mA). The position of the maxima was recorded photometrically and their accuracy is

TABLE I. Molecular weight, defect concentration, melting temperature, and supercooling of the samples investigated.

Sample No.	Commercial name	\bar{M}_w	ϵ (%)	T_m^0 (°C) ^a	ΔT (°C)
1	Lupolen 6011 L	150 500	0.17	~138	10
2	Lupolen 6011 L	150 500	0.17	~138	15
3	Lupolen 6011 L	150 500	0.17	~138	138
4	Lupolen 6011 L	150 500	0.17	~138	216
5	Hoechst PA-130	12 000	1.81	120	10
6	Epolene N-12	11 600	2.63	109	10
7	BASF-A WACHS-400	9 600	3.49	108	10
8	EPOLENE C-101	18 300	5.34	107	10
9	EPOLENE C-12	11 000	6.90	88	10

^aData from commercial samples as received.

TABLE II. Unit-cell volume, x-ray crystallinity, lamellar periodicity, and crystalline lamellar thickness of samples investigated.

Sample No.	$V (\text{\AA})^3$	α (%)	$L (\text{\AA})$	$l (\text{\AA})$
1	93.89	80	450	360
2	93.97	75	375	280
3	94.11	71	235	170
4	94.23	68	250	170
5	94.8	72	210	151
6	95.8	66	220	145
7	95.4	65	210	136
8	95.8	50	210	105
9	96.6	31	210	65

estimated to within $\Delta L/L \sim 4 \times 10^{-2}$. The x-ray diffraction measurements were made after the positron annihilation measurements to minimize any possible radiation damage of the samples.⁷ In any case the integral doses of x rays were sufficiently low so that no influence on positron lifetimes was observed.

C. Positron lifetime measurements

The radioactive source was an aqueous solution of $^{22}\text{NaCl}$. A few drops of it were deposited on a nickel foil of 0.89 mg/cm^2 . After evaporation of the water the foil was folded and sandwiched between two identical PE samples ($2 \times 2 \text{ cm}^2$) which had a thickness of 2 mm. The latter was sufficient to ensure a complete absorption of positrons within the sample. The activity of the source was about $30 \mu\text{Ci}$. The experimental setup was a conventional fast-slow constant fraction positron lifetime spectrometer with a resolution of about 300 ps. At least three spectra, each one having a total of approximately 1.5×10^6 counts, were accumulated for each pair of samples. The data were computer analyzed using the program POSITRONFIT EXTENDED,²⁰ without any constraint. The source contribution was taken into account. For deformed nickel the lifetime is 180 ps and an intensity of 1.7% was calculated according to Bertolaccini and Zappa,²¹ taking as the atomic number of PE that of carbon ($Z = 6$). Lifetime experiments were performed with the same source on well polished and carefully annealed germanium single crystals, to calculate the $^{22}\text{NaCl}$ contribution. Positron lifetime for germanium is 230 ps. For $^{22}\text{NaCl}$ a lifetime of 456 ps was obtained, with an intensity of 4.4%. The total positron absorption in the source, 1.7% for nickel and 4.4% for $^{22}\text{NaCl}$, was subtracted in the numerical analysis. Lifetime spectra were evaluated using three- and four-term distributions, but a four-component analysis never converged. Only three lifetime components could be distinctly resolved. All measurements were performed at 21°C .

III. RESULTS

A. Structural parameters derived from WAXD and SAXS

The supercooling temperature ΔT (1st series) and the number of chain defects (2nd series) are the two quantities steering the structural parameters examined in lamellar PE. These include the unit-cell volume V , the x-ray crystallinity α , long period L , and lamellar thickness l . Table II illustrates

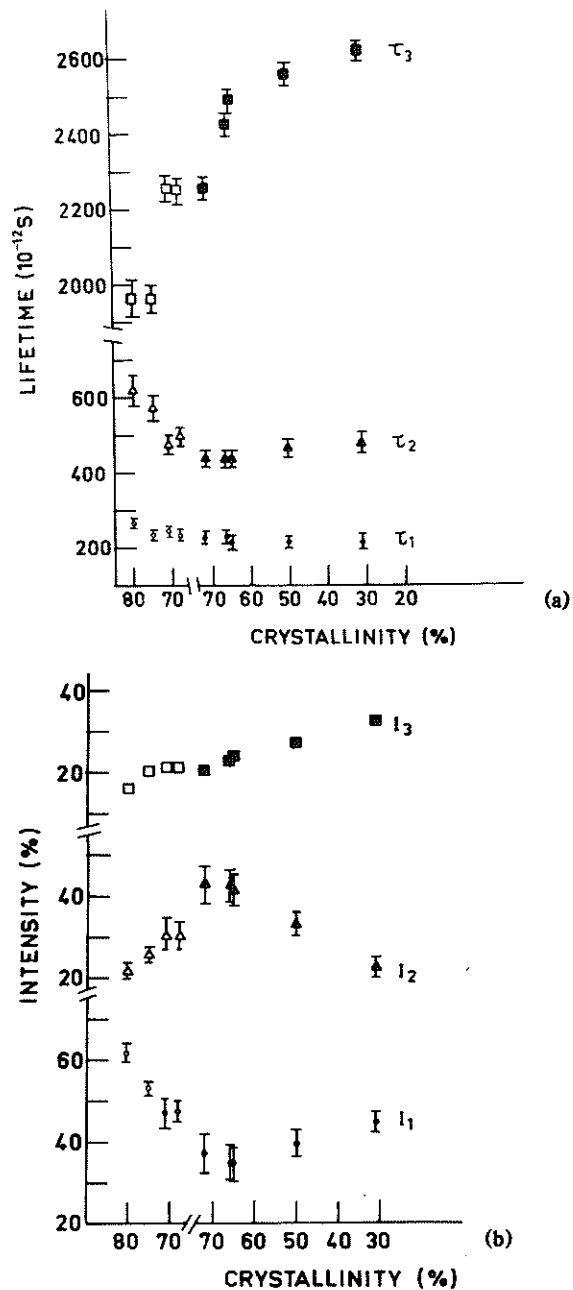


FIG. 2. (a) Lifetimes and (b) intensities of nine pairs of PE samples plotted as a function of crystallinity: 1st series (samples 1-4, open symbols) and 2nd series (samples 5-9, solid symbols), are represented separately to avoid overlapping (see text).

the expansion of the unit-cell volume as function of increasing ΔT and ϵ for the 1st and 2nd series of PE samples, respectively. This expansion can be satisfactorily explained by assuming the generation of step-chain conformational defects (kinks) within the crystal lattice. In case of the 2nd series (samples with increasing number of defects) the chain defects can be accommodated within the crystals at interstitial sites generated by kinks. The data given in Table II indicate that after the initial increase in V (inclusion of chain defects in the lattice), for $\epsilon \geq 2.6\%$ a leveling off in the value of V is detected. The latter is admittedly connected with a substantial rejection of chain defects into the noncrystalline regions.¹² Quantitative calculations of the level of defects incorporated within the lattice core are given elsewhere.¹²⁻¹⁴ Further-

more, the lamellar periodicity decreases as ΔT increases and seems not to be affected by ϵ . The crystal thickness linearly increases with ΔT^{-1} according to kinetic predictions. However, l decreases markedly with ϵ indicating the manifest tendency of a large fraction of chain sequences containing defects to be rejected from the lamellar crystals and, thus, located at the surface layer. Finally, the volume fraction of crystalline material α is a diminishing function of both ΔT and ϵ (Table II).

In summary, low ΔT and small ϵ values yield thick rather perfect crystals providing large lamellar periodicities with a relative low number of interfaces. At the other end, large ΔT and ϵ values yield thin crystals containing very many lattice defects and a large number of crystal-amorphous interfaces offering, as a result, a great variety of positron traps.

B. Positron lifetimes and intensities

Lifetimes and intensity values for the specimen pairs investigated are shown as a function of crystallinity in Fig. 2. The first and second series are represented separately to highlight the structural differences between both series and to avoid overlapping of samples 3 and 4 with sample 5. Thus lifetimes and intensities are plotted from left to right in Fig. 2 to emphasize the variation from the most perfect structures towards the most defective ones. At first sight sample 4, with $\alpha = 68\%$ is apparently less perfect than sample 5, with $\alpha = 72\%$. However, the latter exhibits a defect concentration of $\epsilon = 1.81\%$ and its degree of crystalline disorder is larger than that for the former sample.

Generally, lifetimes and intensity values are different for different specimens as one expects from solids with different structural characteristics. Therefore, any comparison of the present data with other works would be questionable. However, it is worth pointing out that some of the present results are similar to those obtained by Brandt and Spirn²² with PE. These investigators obtained, in fact, one of the highest values for the intensity of the intermediate component, nearly 30%, as in samples 2, 3, 4, and 8 (see Fig. 2). Later data³⁻⁶ furnish values of I_2 which are closer to 10%.

IV. DISCUSSION

Experimental and theoretical studies^{1-10, 22-30} of positron annihilation in condensed molecular substances have shown the possibility of a variety of mechanisms involved. However, despite the attempts existing to identify the origin of the various lifetime components there are, as pointed out above, still certain uncertainties left. Indeed, a clear identification seems rather difficult without the precise structural knowledge of the specimens.

Positron mobility data in polymeric solids are scarce. Brandt and Paulin³¹ have quoted $\mu_+ \leq 2 \text{ cm}^2/\text{V s}$ for Teflon, and Schiltz³² has obtained $\mu_+ < 1.5 \text{ cm}^2/\text{V s}$ for a commercial polyethylene, with crystallinity between 60 and 80%, and $\rho = 0.95 \text{ g/cm}^3$. Using Einstein's relation the diffusion constants, D_+ , at room temperature are $\leq 5.06 \times 10^{-2} \text{ cm}^2/\text{s}$ and $< 3.97 \times 10^{-2} \text{ cm}^2/\text{s}$. Thus, assuming a lifetime of 300 ps diffusion average lengths of ≤ 945 and $< 825 \text{ \AA}$ are obtained, respectively. Under these circumstances, even for the

specimen with thicker crystals, 360 \AA , and the largest long period of 450 \AA , it may be accepted that a positron which is thermalized at any point of the specimen is capable of reaching any amorphous or crystalline region and annihilates there, if it is not trapped before.

From the foregoing, the origin of the three components and the mechanisms of annihilation are discussed as follows.

A. Third component: Pick-off annihilation of ortho-positronium

Figure 2 illustrates the clear increase of I_3 and τ_3 with increasing crystalline disorder. The lower crystallinity of samples 3 and 4, in contrast to sample 5, is however, compensated by the higher density of chain defects in the latter sample. Thus the annihilation behavior of these three specimens is similar with regard to the lifetime and intensity value of the long component. According to the conclusions arrived independently by other authors in PE and other polymeric materials,²⁻¹⁰ the longest component may be attributed to the pickoff decay of o-Ps. The lifetime of o-Ps becomes, in fact, longer in a larger free volume, as it is obtained here. See also Table II where the increase of the unit-cell volume V with increasing crystalline deficiency is shown for the seven first samples. The anomalous behavior of samples 8 and 9 is evident. Furthermore, the increase of I_3 is in good agreement too with the result of Kindl and Sormann⁸ in Teflon \equiv polytetrafluoroethylene, showing that the probability of Ps formation is higher in the amorphous than in the crystalline phase.

B. Second component: Influence of the crystal-amorphous interface

The intermediate component (I_2, τ_2) has been previously associated to positron annihilation from a bound state in the amorphous regions. This interpretation, first given by Brandt and Wilkenfeld⁴ seems to be, however, inconsistent with their own results. Indeed, these authors obtain a value for the intensity of the second component which is constant, within 9 and 10%, for five different polyethylenes with α values varying between 46 and 80%. The hypothesis of trapping centers localized in the amorphous layer could be valid for the first four samples in Fig. 2, I_2 increasing with $(1 - \alpha)$. This hypothesis is, however, ruled out for the second series because of the evident parallel decrease of α and I_2 . A further difficulty arises if one has to explain the jump in I_2 from sample 4 ($\alpha = 68\%$) to sample 5 ($\alpha = 72\%$).

A better trapping site which could be associated to the intermediate component is the crystal-amorphous interface. At this interface, where a great many molecules are folded, the surface, which is formed by staggered elongated cavities along the [100] direction, can provide the required traps for positrons. Figure 3 illustrates, in support to this assumption, the existing correlation between the intensity of the second component and L^{-1} . The latter is proportional to the density of crystal-amorphous interfaces within the solid. Therefore the larger is the number of interfaces the greater is the number of trapping sites and I_2 increases. The above assumption would explain the jump in I_2 from sample 4 to sample 5, showing that the long period, L , plays an important role in the annihilation mechanism. It is also consistent with the

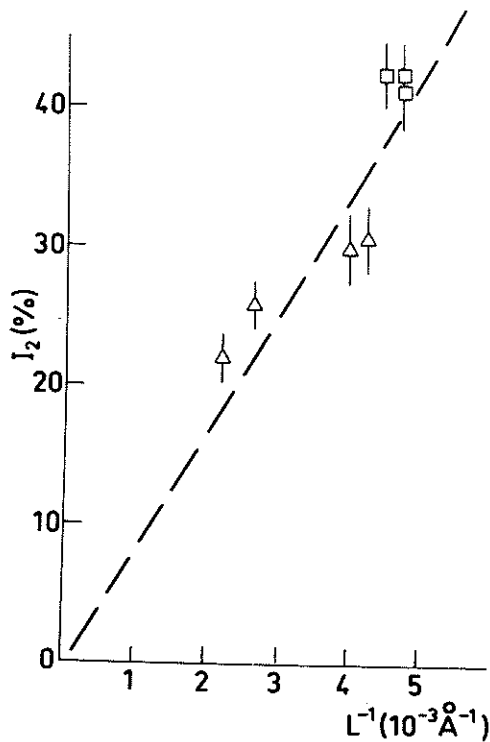


FIG. 3. Intensity of the intermediate component I_2 vs reciprocal lamellar periodicity L^{-1} . The latter is proportional to the density of interfaces. Samples 1-4 (Δ) and samples 5-7 (\square). The anomalous behavior of samples 8 and 9 is explained in the text.

behavior of samples 6 and 7. It does not explain, however, the anomalous decrease in intensity observed for samples 8 and 9, having similar lamellar periodicities (see Table II). This anomaly could be probably related to the high density of chain defects ($\sim 5-7\%$) within the samples 8 and 9 leading to notable deviations of the lamellar structure of polyethylene. These materials are heterogeneous and consist of many microcrystals embedded within the amorphous predominant matrix. Nevertheless, a lamellar stacking, as detected by small angle x-ray diffraction, still prevails, though the total area of crystal-amorphous interface has decreased. According to other results⁹⁻¹⁰ and from the arguments given below, the second component may be ascribed to a positronium state. If this Ps is not tightly bound to the interface, detrapping will be possible and transitions will lead to other states. Free and delocalized Ps is one of the competing states, with an intensity I_3 . Another state is just that of free positrons whose annihilation would contribute to I_1 . These are, however, not the only states competing with trapping at the interface as we shall see below in the discussion of the first component.

The initial decrease in the annihilation lifetime τ_2 for samples 1-5 may be tentatively explained in terms of a three-state model.³³ Let us label the trapping centers at the interface as state 2. Positrons arrive there to form Ps from a free state (state 1) with a transition rate $k_{12} \neq 0$. In the trapped state 2 positronium atoms have annihilation rates λ_{20} and λ_{2p} for o-Ps and p-Ps, respectively. If there is detrapping from the interface positronium will pass to state 3 as free and delocalized positronium, with a transition rate k_{23} and annihilation rates λ_{30} and λ_{3p} corresponding to annihilation via

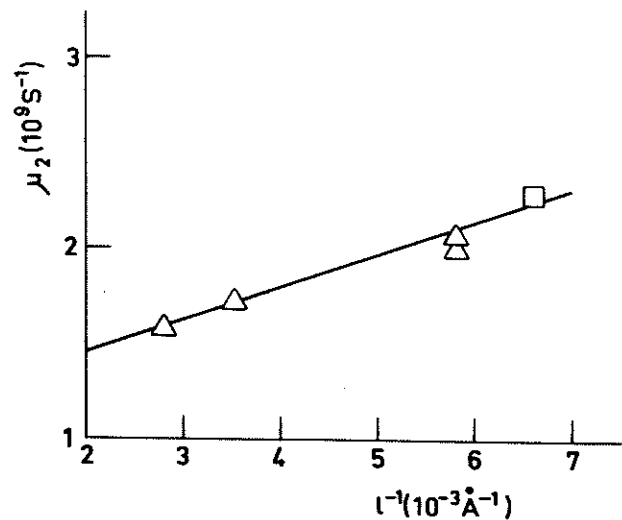


FIG. 4. Plot of μ_2 vs reciprocal lamellar thickness l^{-1} , according to the three-state model, for samples 1-4 (Δ) and 5 (\square). The model is not applicable to the rest of samples where more than three annihilation mechanisms are present.

pick-off of o-Ps and self-annihilation of p-Ps, respectively. From the present results it seems that $\lambda_{3p} \simeq \lambda_{2p}$ but $\lambda_{20} > \lambda_{30}$. This shortening of lifetime at the interface may be explained because o-Ps annihilates there (a) by chemical quenching, (b) by pickoff in a medium¹⁰ other than free o-Ps with an annihilation rate λ_{30} , (c) by another unknown mechanism. If Ps at the interface breaks up into a free positron and an electron, the positrons would contribute to I_1 . This possibility is neither considered in the model³³ ($k_{21} = 0$) nor will be considered here because in the experimental results (samples 1-7) no contribution to I_1 is perceived. On the contrary, I_1 decreases while I_3 increases with I_2 . Despite of the foregoing, the existence of a $k_{21} \neq 0$ may still be possible. The model considers also a transition rate k_{13} from the free positron state to free Ps.

According to the three-state model,³³ the observed lifetime of the second component given in Fig. 2(a) will be $\tau_2 = \mu_2^{-1}$, where $\mu_2 = \lambda_{20} + k_{23}$ and $k_{23} = \nu_{23} \times C_3$, where ν_{23} is the specific positron (positronium in this case) trapping rate or trapping constant, and C_3 is the density of sites where Ps life with annihilation rates λ_{30} and λ_{3p} is possible. It seems plausible⁸ that C_3 could depend on the amount of amorphous material according to $C_3 \sim \alpha^{-1}$. However, we wish to show that the microstructure of polymeric solids plays a more significant role than crystallinity. Thus, since for a lamellar structure, $\alpha \sim l/L$, one may write $C_3 \sim l^{-1}$ and $\mu_2(l^{-1}) = \lambda_2 + A \times \nu_{23} \times l^{-1}$, where A is a proportionality constant. Hence, if one plots μ_2 as a function of l^{-1} (for the first five samples) a straight line is obtained (Fig. 4). This plot extrapolates for $l^{-1} \rightarrow 0$ to the case of an infinitely thick crystal with no amorphous layer. In this case one obtains $\mu_2(0) = \lambda_2 = 1.125 \times 10^9 \text{ s}^{-1}$ yielding a lifetime of 890 ps for positronium trapped at the interface. Indeed, this lifetime seems more appropriate for Ps than for trapped positrons.

Samples 6-9 are not included in the μ_2 vs l^{-1} plot because other annihilation mechanisms can occur and the three-state model is not anymore applicable. The slight increase of lifetimes in samples 8 and 9 is consistent with the

concept of positronium trapped on the amorphous side of the interface and, say, annihilation by chemical quenching. When disorder increases, the amount of overlapping of the trapped Ps and orbital electron wave functions decreases, thus, leading to a lifetime increase.

It is not feasible, at present, to set up energy levels for the three states. However, in doing $k_{21} = 0$ it is assumed that the interface is a shallow trap, compared with the binding energy of Ps. Even more, for Teflon¹⁰ it was deduced that the positron state of the second component (it was the third component in the case of Teflon) cannot be created after the formation of Ps. This supports the above assumption that the particle arriving at the interface to form Ps is a free positron.

C. First component: Chain defects as the origin of a tightly bound state

Lifetime of this short component decreases only slightly in the first two samples and then it remains essentially constant, independent of crystallinity. This behavior is typical for free annihilation of positrons. Perhaps this initial decrease could be explained using the above three-state model³³ associated with the existence of transition rates k_{12} and k_{13} . Unfortunately, these parameters are unknown and any quantitative analysis would be only tentative.

Previous results⁴ suggested that this component is a composite one due to p-Ps self-annihilation, which is statistically one-third of o-Ps, and free positron annihilation. This idea may be accepted for the first six or seven samples. The intensity data obtained for these samples agree, at least qualitatively, with the above interpretation. Indeed, the remarkable decrease of I_1 may be explained partly in terms of a complementary increase of I_3 (the probability of Ps formation increases with increasing thickness of the disorder layer) and partly due to the increase of I_2 (when the density of interfaces increases). For these seven samples there is no indication on whether a fraction of trapped positrons might be included or not in this short component. For the last two samples, 8 and 9, containing a high density of chain defects and showing a large degree of disorder, there is a substantial increase of I_1 , or $I_1 - (I_2 + I_3)/3$. This is, however, at variance with the behavior which one might expect from free positrons in which intensity should decrease with increasing disorder. This unexpected intensity increase may be due to the existence of a short-lived state. Bearing in mind that the only difference in this second series of samples is the density of chain defects, the latter being highest in the last two samples, we suggest that chain defects occluded within the crystal lattice may be the trapping centers responsible of that state.

A bound positron state of short lifetime has been previously detected in PE^{1,2} and in Teflon^{7,8} without specifying the characteristics of the trap. Thus, the bound state at the chain defects may provide an annihilation mechanism that, together with free Ps formation (third component), would compete with trapping at the interfaces. The fact that the influence of this short-lived state has not been observed in the first samples does not preclude its occurrence there. In samples 1-4 of the first series, the concentration of chain defects is extremely low and remains constant. Perhaps in

samples 5, 6, and 7 the defect concentration was not sufficiently high to appreciate their influences in an analysis with only three components. The lifetime of this short-lived state seems difficult to calculate, though a tentative value can be estimated. It was supposed that the first component is a composite one of positrons annihilating in the bulk with a lifetime of 300 ps,^{4,32} p-Ps with annihilation time around 125 ps, and the short-lived state. Furthermore, if the fraction of positrons annihilating in the bulk would depend exclusively on the degree of crystallinity (rough approximation) its percentage could be extrapolated from the first series of samples, where trapping may be neglected, to sample 9. The percentage of p-Ps is readily calculated and thus, the fraction of trapped positrons is deduced, and a lifetime of 250 ps is obtained for the short-lived state. A lifetime of 220 ps was ascribed to this state in the case of Teflon.⁸

V. CONCLUSIONS

Three positron lifetime components have been distinctly resolved on nine samples of isothermally melt crystallized PE with differing chain defect concentrations. It is shown that the annihilation mechanisms can be better understood in terms of lamellar periodicity, crystalline lamellar thickness, and chain defect concentration rather than as a function of crystallinity, a quantity traditionally characterizing these polymeric solids. It is well known that the longest component is due to positrons forming o-Ps subsequently annihilating via electron pickoff. The results of the present investigation agree with previous studies. There is evidence that the intermediate component may be ascribed to positronium trapped at the crystal-amorphous interface where it should not be tightly bound, i.e., detrapping would be possible. The application of a three-state model has allowed the calculation of the lifetime of this long-lived state which is about 900 ps. Finally, it is deduced that the shortest component is due to free positron annihilation, the self-annihilation of the corresponding percentage of p-Ps, and annihilation of positrons from a tightly bound state localized within chain defects. An approximate calculation provides tentative lifetime values around 250 ps for this short-lived state.

ACKNOWLEDGMENTS

Grateful acknowledgment is due to Comision Asesora de Investigacion Cientifica y Tecnica (Spain) for the support of this investigation. One of us (J.S.) is greatly indebted to Dr. A. H. Schiltz for providing unpublished data, and to the late Dr. R. Paulin for interesting and enlightening discussions.

¹J. R. Stevens and P. C. Lichtenberger, Phys. Rev. Lett. **29**, 166 (1972).

²D. P. Kerr, Can J. Phys. **52**, 935 (1974).

³M. Bertolaccini, A. Bisi, G. Gambarini, and L. Zappa, J. Phys. C **7**, 3827 (1974).

⁴W. Brandt and J. Wilkenfeld, Phys. Rev. B **12**, 2579 (1975).

⁵M. Bertolaccini, A. Bisi, G. Gambarini, and L. Zappa, Appl. Phys. **17**, 203 (1978).

⁶M. Rama Rao, A. P. Patro, and P. Sen, Appl. Phys. **22**, 317 (1980).

⁷P. Kindl, W. Puff, and H. Sormann, Phys. Status Solidi (a) **58**, 489 (1980).

⁸P. Kindl and H. Sormann, Phys. Status Solidi (a) **66**, 627 (1981).

⁹C. Dauwe and Motoko Kwete, in *Positron Annihilation*, edited by P. G. Coleman, S. C. Sharma, and L. M. Diana (North-Holland, Amsterdam, 1982), p. 663.

- ¹⁰P. Kindl, *Phys. Status Solidi (a)* **81**, 293 (1984).
- ¹¹B. Wunderlich, *Macromolecular Physics* (Academic, New York, 1975), p. 232.
- ¹²J. Martinez Salazar and F. J. Baltá Calleja, *J. Cryst. Growth* **48**, 283 (1980).
- ¹³F. J. Baltá Calleja and R. Hosemann, *J. Polym. Sci. Polym. Phys. Ed.* **18**, 1159 (1980).
- ¹⁴M. E. Cagiao and F. J. Baltá Calleja, *J. Macromol. Sci. Phys.* **B21**, 519 (1982).
- ¹⁵D. H. D. West, V. J. McBrierty, and C. F. G. Delaney, *Appl. Phys.* **7**, 171 (1975).
- ¹⁶D. R. Rueda, F. J. Baltá Calleja, and A. Hidalgo, *Spectrochim. Acta* **35A**, 847 (1979).
- ¹⁷J. Gonzalez Ortega and F. J. Baltá Calleja, *Ann. Fis.* **70**, 92 (1974).
- ¹⁸G. T. Davies, R. K. Eby, and G. M. Martin, *J. Appl. Phys.* **39**, 4973 (1968).
- ¹⁹J. Martinez Salazar, J. C. Gonzalez Ortega and F. J. Baltá Calleja, *An. Fis.* **73**, 244 (1977).
- ²⁰P. Kirkegaard and M. Eldrup, *Comput. Phys. Commun.* **7**, 401 (1974).
- ²¹L. Bertolaccini and S. Zappa, *Nuovo Cimento* **52B**, 487 (1967).
- ²²W. Brandt and I. Spirn, *Phys. Rev.* **142**, 231 (1966).
- ²³G. D. Loper, J. P. Wayne, and J. W. Giles Jr., *Phys. Lett.* **30A**, 403 (1969).
- ²⁴Yu. V. Zelenev and A. I. Filip'ev, *Sov. Phys. Solid State* **18**, 787 (1976).
- ²⁵A. Bisi, G. Gambarini, and L. Zappa, *Lett. Nuovo Cimento* **31**, 58 (1981).
- ²⁶I. K. MacKenzie and B. T. A. McKee, *Can. J. Phys.* **44**, 435 (1966).
- ²⁷J. R. Stevens and R. M. Rowe, *J. Appl. Phys.* **44**, 4328 (1973).
- ²⁸G. M. Bartenev, A. P. Buchikhim, V. I. Gol'danskii, and A. D. Tsyganov, *Sov. Phys. Dokl.* **19**, 447 (1975).
- ²⁹W. Brandt and J. H. Fans, *Phys. Rev. B* **2**, 1425 (1970).
- ³⁰S. J. Tao, *Appl. Phys.* **10**, 67 (1976).
- ³¹W. Brandt and R. Paulin, *Phys. Rev. B* **15**, 2511 (1977).
- ³²A. H. Schiltz, Ph. D. thesis, Eidgenoessischen Technischen Hochschule, Zürich (1983).
- ³³M. Bertolaccini, A. Bisi, G. Gambarini, and L. Zappa, *J. Phys. C* **4**, 734 (1971).