

0.98 to about 0.05 that $n=2$. The multiplication was taken as the ratio of the actual collector current to the value obtained by extrapolating (1) into the multiplication range. As can be seen in the particular example shown, there is little change in M before and after bombardment.

It is well known that bombardment by 10^{16} neutrons/cm² produces a very pronounced decrease in mobility as well as recombination time.² Lee *et al.* indicate almost a 50% increase in the field at which a given ionization rate is obtained in some epitaxial material. In a graded collector, a 50% increase in field requires an increase of about 60% in collector voltage. Thus a change in ionization rate tends to be slightly magnified on the voltage scale in the resulting multiplication versus voltage.

² J. W. Cleland and J. H. Crawford, *J. Appl. Phys.* **29**, 149 (1958).

A change of 10% in the field at which a given ionization rate is obtained will be readily seen in our experiment.

We must conclude either that the experiments of Lee *et al.* were erroneous—possibly with respect to determination of area, or else the scattering centers in their crystals have an effect on hot-electron scattering that is not exhibited by neutron damage. It seems that the former explanation must be given serious consideration: particularly since the theory of scattering of charge carriers by charged centers shows that the scattering cross section decreases as the fourth power of the electron or hole velocity.

The possibility that ionization rates are different in different crystals of the same substance must certainly be recognized. There is the possibility that the ionization rates are either greater or less than in the perfect crystal and any instance that is well documented is of interest.

Temperature Dependence of Positron Mean Lives in Polymers*

B. C. GROSECLOSE† AND G. D. LOPER‡§

Department of Physics, Oklahoma State University, Stillwater, Oklahoma

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The mean lives and intensities of positrons decaying by the pickoff mechanism in polystyrene, Lucite, and polyethylene (Marlex 50) have been measured in the temperature interval -200 to $+150^\circ\text{C}$. The mean-life variation with temperature in both polystyrene and Lucite has the same general shape as the specific-volume variation of these materials and may be interpreted as a free-volume effect. However, an observed sharp drop of τ_2 with decreasing temperature below -20°C in Marlex 50 does not correspond to the smooth change in volume of this material in that temperature range.

I. INTRODUCTION

THE decay of positrons in molecular materials is complex, consisting of a short lifetime of the order of 10^{-10} sec due to annihilations from the free state and the bound state of singlet positronium, and a longer lifetime of the order of 10^{-9} sec due to pickoff annihilation from the bound state of ortho-positronium.¹ This latter mean-life component, called τ_2 , depends on the amount of positron-lattice electron wave function overlap, and may be expected to give some information about internal structure. The τ_2 component is temperature-dependent, the lifetime increasing with increasing temperature.² This effect has been qualitatively explained by saying that greater

molecular motion and molecular separations provide more room for the positronium atoms and make pickoff annihilation less likely.³ A theoretical expression for τ_2 as a function of free volume has been derived and has had some success in fitting experimental data.⁴ Most of the pertinent results have been summarized in a review article by Wallace.⁵ The purpose of this investigation was to measure τ_2 and the intensity of this component I_2 in the polymers polystyrene, Lucite, and Marlex 50 in the temperature interval -200 to $+150^\circ\text{C}$, and to correlate this behavior with known changes in other physical properties.

II. EXPERIMENTAL PROCEDURE

The measurements were carried out with typical fast-slow coincidence apparatus, including Nuclear Enterprises NE 102 plastic phosphors, Amperex 56AVP

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† Present address: Lawrence Radiation Laboratory, University of California, Livermore, California.

‡ This paper is part of a thesis submitted as partial fulfillment of requirements for Ph.D. in physics at Oklahoma State University, Stillwater, Oklahoma.

§ Present address: Wichita State University, Wichita, Kansas.

¹ R. A. Ferrell, *Rev. Mod. Phys.* **28**, 308 (1956).

² R. E. Bell and R. L. Graham, *Phys. Rev.* **90**, 644 (1953).

³ P. R. Wallace, *Phys. Rev.* **100**, 738 (1955).

⁴ W. Brandt, S. Berko, and W. W. Walker, *Phys. Rev.* **120**, 1289 (1960).

⁵ P. R. Wallace, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 1.

photomultipliers, a Simms⁶-type transistorized time-to-amplitude converter, and a Nuclear Data (model ND 130) 512 channel analyzer. The resolving time of the apparatus as measured in the two gamma annihilation of positrons in aluminum was 7.9×10^{-10} sec.

Cylindrical plastic samples 1 in. long and 0.438 in. in diameter were machined from rods of the plastics. Polystyrene (atactic) and Lucite, or polymethyl methacrylate, are almost completely amorphous. The Marlex 50 polyethylene, manufactured by Phillips Petroleum Company, is 85 to 93% crystalline.

The Na²² positron source was deposited directly on the samples. At least two identical samples were cut from each piece of plastic. One was used for the high temperatures exclusively, data being taken as the temperature of the sample was increased from room temperature to above the melting point. The other sample was reserved for the low temperatures, data being taken as the temperature of the sample was decreased from room temperature to -196°C .

Temperatures above room temperature were achieved by Ohmic heating of a copper rod provided with a cylindrical hole to hold copper cans in which the plastic samples were placed. Chromel heating wire was wrapped on both sides of this hole and connected to a regulated dc supply. The temperature of the samples was controlled to $\pm 0.5^\circ\text{C}$ with a thermocouple and a millivoltmeter controller. The low-temperature data were obtained by placing the cylindrical samples in a Dewar flask with a narrow flange at the bottom. The samples rested on the bottom of the flange, and cooling mixtures were poured into the Dewar.

An IBM 650 computer was programmed to fit straight lines through fifty points in the tail regions of annihilation time distribution curves, and from the slopes of these lines, to compute τ_2 . The intensity I_2 was determined by extending the line characterizing the tail back to the true zero of time, finding the area under this line, and after multiplying by a correction factor to take into account the finite width of the prompt curve compared with the value of τ_2 , dividing by the area under the entire time distribution curve.⁷

III. RESULTS AND DISCUSSION

Tables I, II, and III present the numerical results of the experiment, and Figs. 1 through 4 are the τ_2 and I_2 versus temperature plots of these results. The τ_2 values quoted in the tables are the most probable values computed for three to ten determinations at each temperature.

The data for both polystyrene and Lucite may be represented by two intersecting straight lines. These plots are similar in shape to specific volume versus temperature data for the two materials, and the temperatures at which the straight lines intersect corre-

TABLE I. Mean lives and intensities in polystyrene.

Temperature in centigrade degrees	τ_2 (10^{-9} sec)	Intensity, I_2 , in %
147.6 \pm 0.5	2.77 \pm 0.08	32 \pm 5
127.2 \pm 0.5	2.59 \pm 0.06	31 \pm 5
108.0 \pm 0.5	2.52 \pm 0.06	32 \pm 5
98.8 \pm 0.5	2.46 \pm 0.05	31 \pm 5
84.0 \pm 0.5	2.21 \pm 0.05	30 \pm 5
72.0 \pm 0.3	2.14 \pm 0.04	30 \pm 5
60.8 \pm 0.3	2.18 \pm 0.05	32 \pm 5
50.0 \pm 0.2	2.07 \pm 0.05	29 \pm 5
39.5 \pm 0.2	2.06 \pm 0.05	31 \pm 5
26.0 \pm 0.5	2.11 \pm 0.05	27 \pm 5
0.5 \pm 0.5	2.13 \pm 0.05	26 \pm 5
-13.0 \pm 0.5	2.10 \pm 0.04	22 \pm 5
-28.0 \pm 2.0	2.07 \pm 0.04	22 \pm 5
-78.5 \pm 0.5	2.00 \pm 0.04	20 \pm 5
-124.6 \pm 2.0	1.92 \pm 0.05	21 \pm 5
-196.5 \pm 0.5	1.72 \pm 0.05	19 \pm 5

TABLE II. Mean lives and intensities in Lucite.

Temperature in centigrade degrees	τ_2 (10^{-9} sec)	Intensity, I_2 , in %
126.0 \pm 0.5	2.35 \pm 0.07	21 \pm 5
119.0 \pm 0.5	2.31 \pm 0.07	22 \pm 5
112.5 \pm 0.5	2.25 \pm 0.07	22 \pm 5
102.4 \pm 0.5	2.21 \pm 0.06	20 \pm 5
93.1 \pm 0.5	2.14 \pm 0.05	20 \pm 5
80.8 \pm 0.4	2.11 \pm 0.06	18 \pm 5
71.6 \pm 0.4	2.01 \pm 0.06	20 \pm 5
61.2 \pm 0.2	2.06 \pm 0.06	20 \pm 5
51.7 \pm 0.3	1.96 \pm 0.06	21 \pm 5
41.2 \pm 0.2	1.99 \pm 0.06	18 \pm 5
32.8 \pm 0.2	1.95 \pm 0.05	20 \pm 5
26.0 \pm 0.5	1.91 \pm 0.04	19 \pm 5
0.5 \pm 0.5	1.94 \pm 0.04	15 \pm 5
-13.0 \pm 0.5	1.91 \pm 0.04	15 \pm 5
-28.0 \pm 2.0	1.95 \pm 0.06	15 \pm 5
-78.5 \pm 0.5	1.79 \pm 0.04	15 \pm 5
-124.6 \pm 2.0	1.77 \pm 0.06	17 \pm 5
-196.5 \pm 0.5	1.62 \pm 0.04	14 \pm 5

TABLE III. Mean lives and intensities in Marlex 50.

Temperature in centigrade degrees	τ_2 (10^{-9} sec)	Intensity, I_2 , in %
152.5 \pm 0.5	3.25 \pm 0.10	24 \pm 5
142.3 \pm 0.4	3.39 \pm 0.12	28 \pm 5
136.8 \pm 0.4	3.23 \pm 0.12	30 \pm 5
128.2 \pm 0.4	3.18 \pm 0.09	25 \pm 5
119.4 \pm 0.4	3.05 \pm 0.10	24 \pm 5
102.7 \pm 0.3	2.78 \pm 0.11	25 \pm 5
90.9 \pm 0.4	2.80 \pm 0.10	23 \pm 5
82.2 \pm 0.4	2.62 \pm 0.06	21 \pm 5
70.5 \pm 0.4	2.48 \pm 0.05	23 \pm 5
59.5 \pm 0.3	2.41 \pm 0.06	21 \pm 5
48.6 \pm 0.3	2.33 \pm 0.07	20 \pm 5
39.6 \pm 0.3	2.42 \pm 0.05	18 \pm 5
26.0 \pm 0.5	2.32 \pm 0.04	19 \pm 5
0.5 \pm 0.5	2.21 \pm 0.04	16 \pm 5
-13.0 \pm 0.5	2.17 \pm 0.05	14 \pm 5
-28.0 \pm 2.0	1.90 \pm 0.06	13 \pm 5
-78.5 \pm 0.5	1.60 \pm 0.04	12 \pm 5
-124.6 \pm 2.0	1.47 \pm 0.06	13 \pm 5
-196.5 \pm 0.5	1.26 \pm 0.04	11 \pm 5

⁶ P. C. Simms, Rev. Sci. Instr. 32, 894 (1961).

⁷ R. E. Green and R. E. Bell, Can. J. Phys. 35, 398 (1957).

spend closely to the glass transition temperatures of these polymers.^{8,9} It seems reasonable to conclude that the τ_2 variation with temperature in polystyrene and Lucite is basically a volume effect, and that positronium is sensitive to the change in free volume which occurs at the glass transition.

Marlex 50 has a first-order transition at about +130°C and a second-order transition in the neighborhood of -20°C.^{10,11} The data for this material may be explained as a slow melting out of the crystalline regions in the interval +20 to +130°C, with a leveling off of τ_2 above melting, corresponding to the leveling off of specific volume above melting. The magnitude and direction of the change of τ_2 around -20°C is difficult to understand; the change in volume associated with the second-order phase transition is not great. A possible explanation is that the long chain molecules were oriented to some degree during manu-

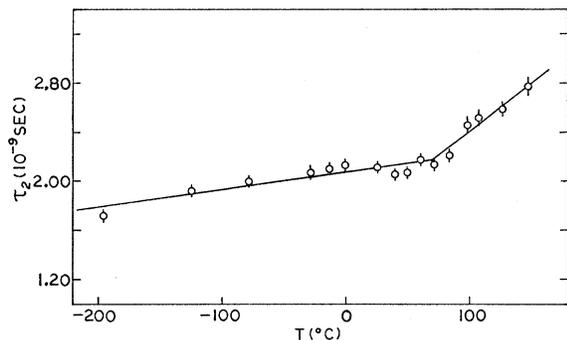


FIG. 1. Mean life (τ_2) of positrons decaying by pickoff versus temperature in polystyrene. Vertical lines represent the standard deviation.

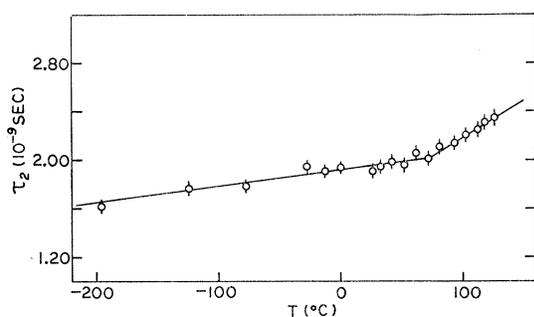


FIG. 2. Mean life (τ_2) of positrons decaying by pickoff versus temperature in Lucite.

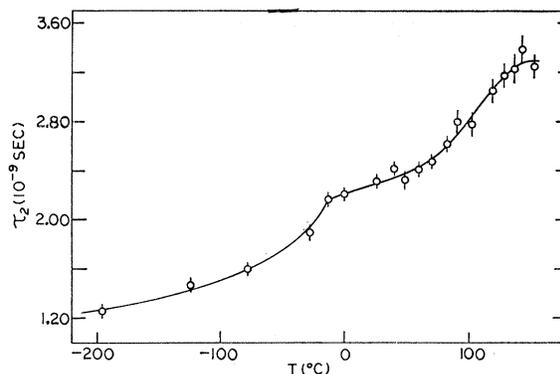


FIG. 3. Mean life (τ_2) of positrons decaying by pickoff versus temperature in Marlex 50.

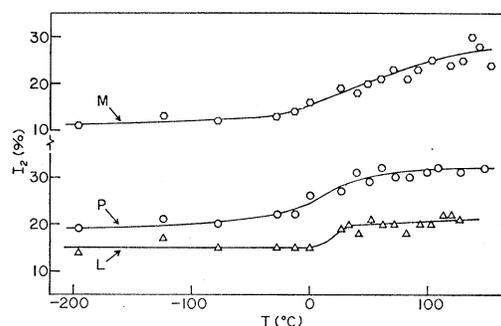


FIG. 4. The intensity of the τ_2 component versus temperature in polystyrene (P), Lucite (L), and Marlex 50 (M). The error in all cases is $\pm 5\%$.

facture of the samples, which allowed closer packing below -20°C, and hence the observed drop off of τ_2 .

The changes in I_2 in all three samples are small, but there is a general increase in I_2 with increasing temperature. The lines drawn through the points in Fig. 4 are a visual fit. No large change in I_2 occurs at -20°C in Marlex 50.

A third lifetime component, shorter than τ_2 but longer than the free-state or singlet-positronium lifetime and with an intensity comparable to I_2 , has recently been reported for amorphous materials and plastics.^{12,13} This intermediate lifetime component is evident in the present data and a paper now in preparation will report on the temperature dependence in polystyrene, Lucite, and Marlex 50. The presence of this additional component has no effect on the τ_2 lifetimes and intensities reported herein.

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