POSITRON ANNIHILATION IN ANNEALED AND QUENCHED TEFLON AND IN SULPHUR

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ABSTRACT

The value (τ_2) and the intensity (I_2) of the delayed component in the lifetime spectra of positrons annihilating in annealed and quenched teflon and in sulphur and crystex (polymer sulphur), at room temperature and at 77° K are reported. These data and the X-ray diffraction patterns for these materials are discussed in terms of the free volume model for the formation and quenching of positronium atoms in molecular materials.

INTRODUCTION

IT is well known that the delayed component, τ_2, observed in lifetime spectra of positrons annihilating in molecular solids and liquids, is sensitive to the structure of the medium.[1, 2, 3] Since τ_2 arises out of ortho-positronium atoms quenched by the electrons of the medium, it depends upon the density of electrons at the site of ortho-positronium atom, and is therefore expected to be sensitive to structural changes such as degree of crystallinity and phase changes such as melting and glass transition. In this paper we report the studies of positron lifetimes in teflon subjected to annealing and quenching, and in two different forms of sulphur. The lifetimes and their intensities, observed at room temperature and at liquid nitrogen temperature are then discussed in terms of the free volume model for the formation and quenching of ortho-positronium atoms, developed in earlier papers.

EXPERIMENTAL SET-UP

The experimental arrangement for studying the lifetime spectra of positrons annihilating in solids and liquids and the method of computing the intensity (I_2) of the delayed component (τ_2) has been reported earlier.[1] The same experimental set-up was used in the present investigation and was arranged to give the slope of prompt resolution curve (obtained with Co^{60}) of 0·18 ns, and the spectra were recorded with the use of a 400 channel multi-channel analyser, the time scale being 1 channel = 0·06 ns. The readings at liquid nitrogen temperature were obtained by immersing the sample holder in a Dewar flask containing liquid nitrogen. Sufficient time was allowed for the samples to attain liquid nitrogen temperature. The spectra were taken at room temperature 300° K and at liquid nitrogen temperature, 77° K, and the values obtained for τ_2 and I_2 are given in Table I.

ANNEALED AND QUENCHED TEFLON

Teflon (Polytetrafluoroethylene) is a well-known thermo-plastic whose degree of crystallinity can be controlled by heat treatment such as quenching or annealing from the softening temperature (350° C.). For this purpose the material must be taken in the form of thin wafers as teflon is an excellent heat insulator. The samples in the form of thin wafers were heated in a glass tube evacuated to high vacuum and sealed, and were annealed from 350° C. at the rate of about 2°/hour. Quenched samples were obtained by transferring the glass tube containing the wafers from the furnace to liquid nitrogen and breaking the vacuum seal of the tube under liquid nitrogen. The wafers were left in liquid nitrogen for a sufficiently long time to ensure quenching throughout the volume of the sample. A large number of such wafers were used to sandwich the Na^{22} source to ensure that all positrons annihilated in the sample.

The effect of annealing thin wafers of teflon is to produce a sample with a high degree of crystallinity, while quenching should increase the amorphous character of the sample. The density of these samples was

TABLE I

Material	Density gm./c.c.	Room Temperature		77° K	
		τ_2 (n. sec)	I_2 (%)	τ_2 (n. sec)	I_2 (%)
Annealed Teflon	2·205	2·2 ± 0·1	13 ± 2	1·2 ± 0·1	12 ± 2
Teflon	2·190	2·9 ± 0·1	17 ± 2	1·5 ± 0·1	13 ± 2
Quenched Teflon	2·150	3·3 ± 0·1	17 ± 2	1·8 ± 0·1	12 ± 2
Sulphur (Orthorhombic)		1·03 ± 0·05	9 ± 1	$\lesssim$ 0·7	..
Crystex (Polymer Sulphur)		1·14 ± 0·05	7·5 ± 1	$\lesssim$ 0·7	..

measured and the values for untreated sample and for annealed and quenched samples are reported in Table I. It is seen that the density of annealed teflon is appreciably higher than that of the quenched variety. A more direct evidence of the changes in crystallinity is the Debye-Scherrer powder photographs taken with CuKα X-rays, shown in Plate I. These pictures show the extent to which the degree of crystallinity has been changed by the heat treatment.

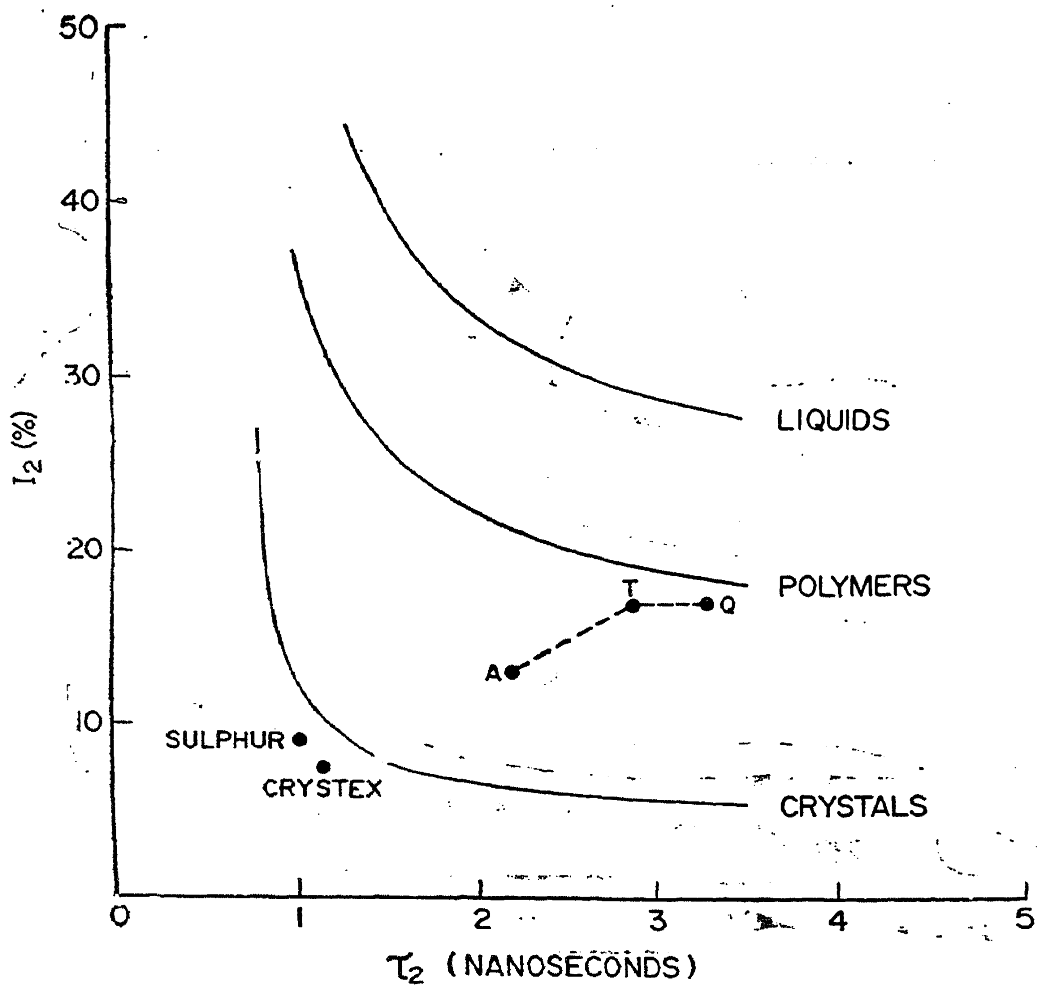

FIG. 1. Observed values of I_2 and τ_2 for T—Teflon, A—Annealed teflon, Q—Quenched teflon, Orthorhombic sulphur and crystex, plotted over the I_2–τ_2 correlation curves.

DISCUSSION

A detailed account of the free volume model for the formation and quenching of positronium atoms (Ps) in molecular materials has been published in an earlier paper.[1] According to this model, the formation and quenching of Ps atoms is confined to the free volume, V_f, of the material. $V_f = V - V_{exc}$ where V is the specific volume and V_{exc} the excluded volume. In a molecular medium V_f may be considered to be divided into a number of sites or cavities, of average volume 'V' occupied by Ps atoms which are subsequently quenched by pick-off process. In this model τ_2

is then dependent on v, while the intensity I_2 is proportional to V_f/v. When the amorphous character of the medium and the degree of disorder increases, both V_f and v would increase though not necessarily in the same proportion. It is seen from Table I and Fig. 1 that compared to teflon, annealed teflon having a higher degree of crystallinity exhibits a smaller τ_2 with a lower intensity while the quenched sample which is more amorphous shows a higher τ_2. These changes in τ_2 and I_2 are consistent with the expectations of the free volume model.

It was shown in earlier papers[1, 4] that the I_2–τ_2 correlation for molecular materials is represented by three distinct curves corresponding to fully amorphous solids and simple liquids, semi-crystalline polymers and molecular crystals (*see* Fig. 1). The I_2–τ_2 point corresponding to semi-crystalline teflon lies near the polymer curve. It is interesting to note that the point corresponding to annealed teflon shifts towards the curve for crystals.

It has been shown in an earlier paper, that polyethylene[5] subjected to irradiation by γ-rays from Co^{60}, becomes more amorphous, and τ_2 increases with the dose of irradiation. Samples of polyethylene of two different densities, subjected to various doses of irradiation by γ-rays from Co^{60}, were obtained from Dr. A. Charlesby's laboratory in Harwell. The studies of positron lifetimes in these samples essentially reproduced our ealier results. It is significant, however, to note that the low density polyethylene exhibited a higher τ_2 than the high density polyethylene which is consistent with the variation of τ_2 with density in teflon shown in Table I. For the same material, higher density implies smaller 'v' giving rise to smaller τ_2.

Wilson, Johnson and Stump[6] have studied the effect of externally applied pressure on I_2 and τ_2 in teflon. They have shown that both I_2 and τ_2 show a decrease when samples are subjected to pressure. This is understandable in terms of the free volume model since applied pressure will tend to decrease the free volume V_f. In this process the average volume of the site 'v' decreases and some sites may even be squeezed out. A similar effect can be expected if contraction is achieved by decreasing the temperature, provided no phase changes occur within this temperature interval. It is known that teflon does not undergo any phase changes from 300° K to 77° K. The effect of the thermal contraction on all the three varieties of teflon is shown in Table I. In each case there is a sharp decrease in τ_2 on cooling. The decrease in free volume V_f brought about either by pressure or by thermal contraction is expected to decrease I_2 only if some of the sites are squeezed out, *i.e.*, they are no longer available for Ps formation.

SULPHUR AND CRYSTEX

We have studied Positron lifetimes in crystalline orthorhombic sulphur and polymerised sulphur sold under the trade name Crystex.[7] Polymer sulphur is obtained by the opening out of the S_8 rings in crystalline sulphur to form long chain molecules. Crystex thus formed is quite stable at about 20° C., the rate of reversion to crystalline sulphur being less than 1% per month. The values of τ_2 and I_2 in crystalline sulphur and crystex at 300° K and 77° K are given in Table I. The Debye-Scherrer powder photographs for sulphur and crystex are given in Plate IV. Crystalline sulphur exhibits a delayed component of 1·03 ns with an intensity of 9%. The point corresponding to orthorhombic sulphur lies very near the curve for crystals in the I_2–τ_2 correlation curves shown in Fig. 1. It has been reported that monoclinic sulphur does not exhibit a delayed component.[8] Polymerised sulphur (crystex) is also highly crystalline in nature as seen from the powder photograph in Plate IV, and the point corresponding to it ($\tau_2 = 1 \cdot 14$ ns, $I_2 = 7 \cdot 5\%$) also falls very near the curve for crystals. Crystex at room temperature is well below its glass transition temperature (T_g = 75° C.).[7] It does not show any EPR signal indicating that no unpaired electrons are present in the sample. On cooling to 77° K, τ_2 decreases to $\lesssim$ 0·7 ns for both sulphur and crystex.

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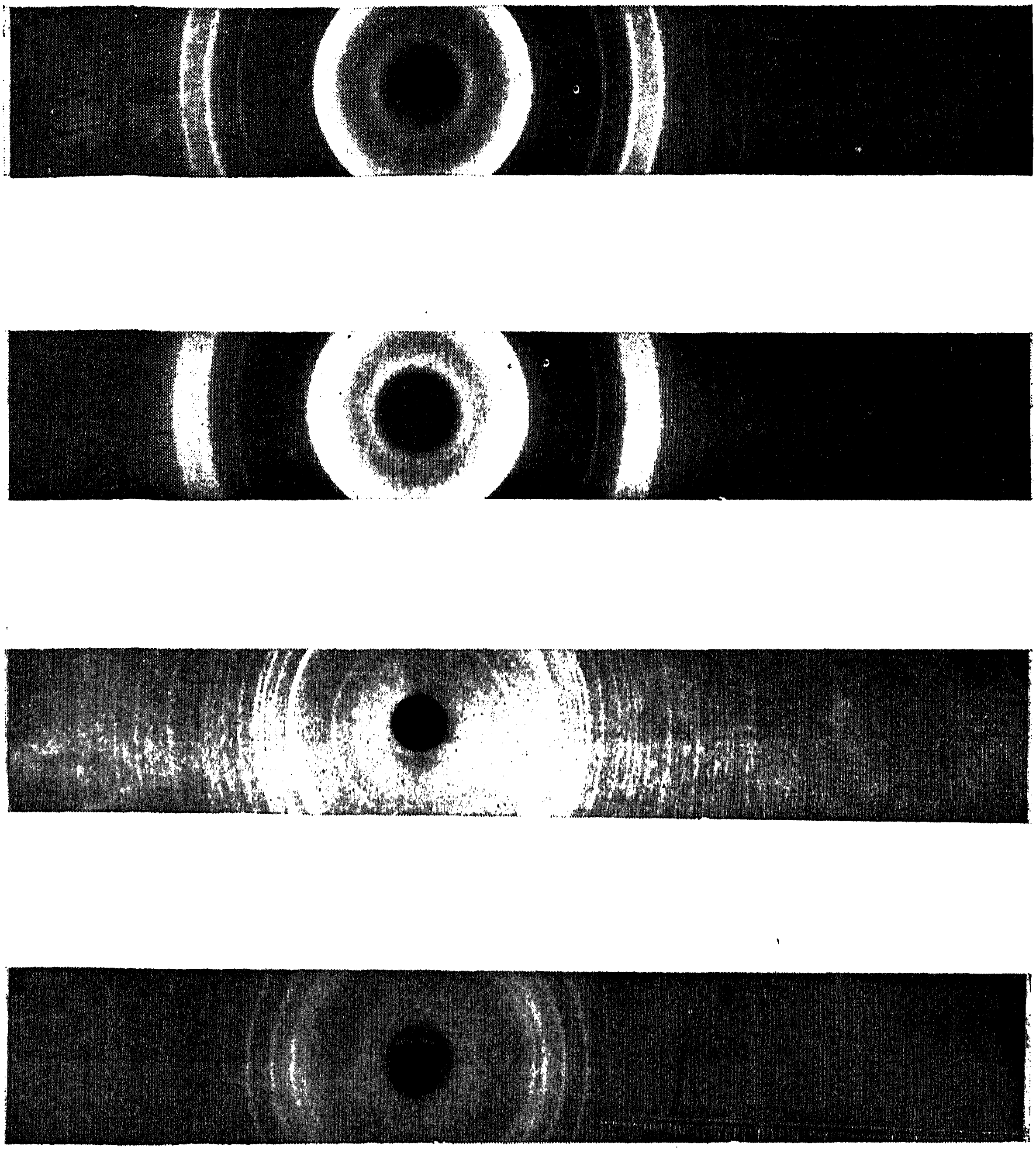

(*a*)

(*b*)

(*c*)

(*d*)

X-Ray Powder Patterns

(*a*) Annealed Teflon.
(*b*) Quenched Teflon.
(*c*) Orthorhombic Sulphur.
(*d*) Polymer Sulphur (Crystex).

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