THE LIFETIMES OF POSITRONS IN OXIDES OF ARSENIC AND ANTIMONY

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Abstract

The lifetimes of positrons in crystalline powders of dimeric oxides of arsenic and antimony, and in trioxymethylene and polyoxymethylene are reported. In As_4O_6 and polyoxymethylene a longer component τ_4 is observed in addition to the usually observed τ_2 component. The variation of τ_4 with temperature and pressure is studied in As_4O_6. On the basis of these results and the X-ray diffraction pictures, it is suggested that ortho-positronium atoms quenched in intercrystallite regions in As_4O_6 gives rise to τ_4.

Introduction

It is well known that the long component τ_2, observed in the lifetime spectra of positrons annihilating in a condensed medium is due to the quenching of the ortho-positronium atoms by the electrons of the medium.[1] τ_2 is usually in the range of 1 to 5 nanoseconds. Recently, however, another longer component, τ_4, of the order of a few tens of nanoseconds, has been observed in some ionic oxides like MgO, Al_2O_3, BeO, etc.[2-4] In most of these cases τ_4 has an intensity (I_4) smaller than the intensity (I_2) of the τ_2 component. The origin of such long components is not clearly understood at present.

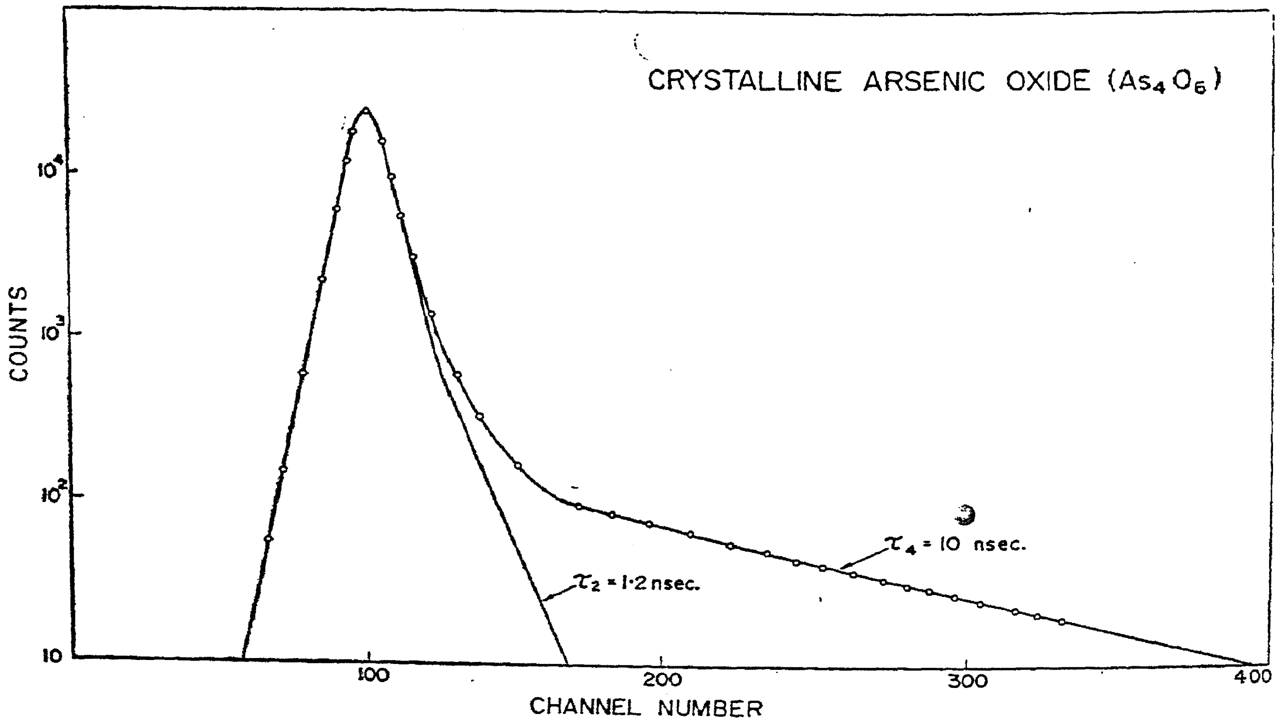
The present paper reports the lifetimes of positrons in crystalline powders of dimeric oxides of arsenic (As_4O_6) and antimony (Sb_4O_6), and in trioxane [trioxymethylene $(CH_2O)_3$] and polyoxymethylene [$H-(CH_2O)_n - OH$]. The longer component τ_4 is observed in As_4O_6, and in polyoxymethylene. The variation of τ_4 in As_4O_6 is studied as a function of temperature and pressure. These results together with the Laue transmission patterns and powder photographs obtained for crystalline and heat-treated samples suggest that τ_4 could arise out of ortho-positronium atoms quenched in intercrystallite regions.

EXPERIMENTAL SET-UP

The standard slow-fast coincidence set-up used in this work to measure the lifetimes of positrons, and the procedure to compute the intensity of the delayed component have been reported earlier.[1] The delayed component τ_2 and its intensity are obtained by subtracting the τ_4 part from the total spectrum, when two delayed components are present.

RESULTS AND DISCUSSION

Text-Figure 1 shows a typical lifetime spectrum obtained for crystalline As_4O_6 at room temperature, showing two delayed components, $\tau_2 = 1 \cdot 2$ ns and $\tau_4 = 10$ ns. The variation in the values and intensities of the delayed components as a function of temperature and pressure is shown in Table I. As the temperature is increased beyond 100° C., τ_4 begins to decrease and at about 135° C., τ_4 disappears irreversibly, *i.e.*, does not reappear on cooling the sample back to room temperature. The experiment was carried out with the sample in vacuum, the tube containing the pellets and the Na^{22} source being evacuated continuously, so as to avoid the effects due to oxygen, and was repeated several times to ensure the irreversible disappearance of τ_4 at about 135° C. When As_4O_6 pellets were



TEXT-FIG. 1. Typical time distribution of positron annihilation quanta in polycrystalline As_4O_6 at room temperature (schematic).

subjected to a pressure of 100 tons/sq. inch, the value of τ_4 decreases. These pellets also exhibit an irreversible disappearance of τ_4 at about 135° C. as seen from Table. I.

TABLE I

Sample	Temperature ° C.	τ_2 ns	I_2%	τ_4 ns	I_4%
As_4O_6	27	1·2±0·1	25±2	10±1	5±1
pellets prepared	100	1·2±0·1	9±2	8±1	16±2
under ·5—·75 tons/sq. inch	150	1·8±0·2	13±2	..	..
	200	1·8±0·2	13±2	..	..
cooled to	27	1·2±0·1	11±2	..	..
As_4O_6	27	<1	..	6·5±1	5±2
pellets prepared	100	<1	..	5±1	5±2
under 100 tons/sq. inch	130	1·3±0·2	6±2	..	..
	200	1·2±0·2	13±2	..	..
cooled back to	27	1·2±0·2	13±2	..	..
Arsenic trioxide glass	27	2·0±0·1	11±1	..	..
Sb_4O_6	27	3·1±0·1	5±1	..	..
Trioxane	27	1·2±0·1	27±2	..	..
Polyoxymethylene	27	2·1±0·1	9±2	13±1	~0·4

Sen and Patro[5] have shown that the longer component τ_4 observed in Al_2O_3 arises out of two photon events. They have observed τ_4 by two different methods, with the standard slow-fast coincidence set-up and also with the triple slow double fast coincidence set-up designed to detect only two photon events, and have obtained the same value (63 ns) for τ_4 in Al_2O_3. From this result they conclude that τ_4 is associated with two photon decay and not with three photon decay. Their work suggests that τ_2 and τ_4 could arise out of ortho-positronium atoms quenched in two different kinds of sites in the medium.

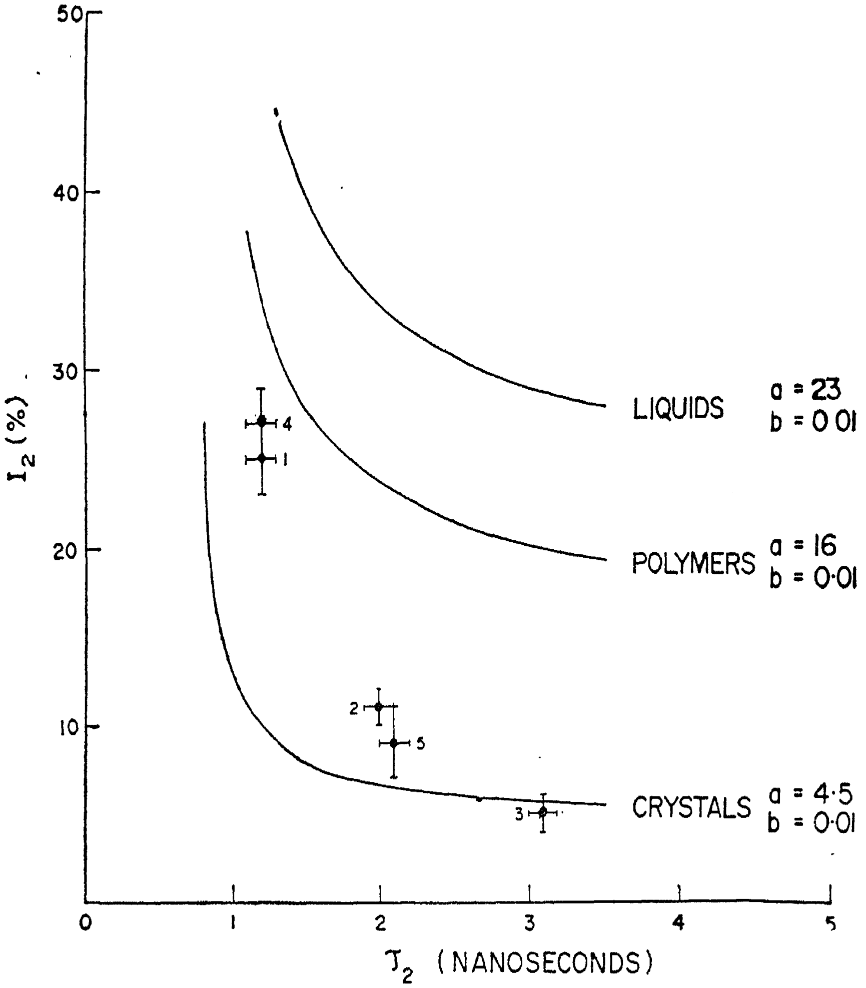
As_4O_6 exists at room temperature in arsenolite phase.[6] This molecular phase is built up from As_4O_6 molecules arranged in such a way that their centroids occupy the lattice points of a diamond structure ($a = 11 \cdot 06$ Å). The basic unit is a three-sided pyramid with the arsenic atom at its apex and the oxygen atoms at the other three corners. Four such units are bonded together through the oxygen atoms, to form a molecular unit, As_4O_6. Weak van der Waals forces bind As_4O_6 units into a crystalline molecular lattice.

The data of lifetimes of positrons in arsenic oxide can be interpreted, if we suppose that the usual slow component τ_2 arises out of ortho-positronium atoms annihilating within the crystallite by the pick-off process, while τ_4 is due to ortho-positronium atoms annihilating in the intercrystallite regions. Above 100° C. As_4O_6 begins to vaporise appreciably, and the size of the crystallite is reduced. The continuous mass thus formed by fusing together of crystallites at about 135° C. has a glassy appearance. It is known that the polished surfaces of arsenolite begin to exhibit roughening[6] when heated beyond 95° C. Arsenic trioxide glass, known to possess a semi-ordered structure, prepared by heating As_4O_6 in vacuum up to 500° C. does not exhibit τ_4.

A decrease in the volume of the intercrystallite sites can also be achieved by subjecting the material to sufficiently high pressures. As_4O_6 pellets prepared under a high pressure of 100 tons/sq. inch (as compared to 0·5 to 0·75 tons/sq. inch, used normally) show a measurable decrease in τ_4. The irreversible disappearance of τ_4 at about 135° C. is reproduced for these samples also.

The Laue transmission patterns obtained with Mo Kα radiation for crystalline As_4O_6, As_4O_6 heated up to 200° C., and arsenic trioxide glass are shown in Plate I, Fig. 1. The pattern for crystalline As_4O_6 consists of discrete spots, which merge into continuous rings in the pattern for the arsenic trioxide glass, the sample heated up to 200° C. showing an intermediate pattern.

The powder photographs for these samples obtained with Cu Kα radiation are shown in Plate II, Fig. 2. The large angle scattering, seen for crystalline As_4O_6, shows a decrease in intensity for the sample heated up to 200° C. and is nearly absent for the arsenic trioxide glass. These results show[7] that the crystallite size of the sample decreases upon heating and that the arsenic trioxide glass is in a semi-ordered crystalline form. These results and the observed variation of τ_4 with temperature and pressure are consistent with the suggested origin of τ_4.



TEXT-FIG. 2. Observed values of I_2 and τ_2 for (1) Polycrystalline As_4O_6, (2) Arsenic Trioxide (glass) heated to 500° C., (3) Polycrystalline Sb_4O_6, (4) Trioxane, (5) Polyoxymethylene plotted over the I_2-τ_2 correlation curves.

ANTIMONY OXIDE (Sb_4O_6)

Antimony oxide has a structure similar to that of arsenic oxide,[6] but the sample is composed of crystallites very much smaller in size, as indicated by the Laue transmission pattern and the powder photograph for Sb_4O_6 shown in Plates I and II respectively. Sb_4O_6 exhibits only one delayed component $\tau_2 = 3 \cdot 1$ ns with an intensity $I_2 = 5\%$. The values of τ_2 and I_2 do not change when the sample is heated in vacuum up to 500° C. The Laue pattern and the powder photograph for Sb_4O_6 heated up to 500° C. are found to be similar to those obtained for Sb_4O_6 shown in Plates I and II. It is interesting to note that the X-ray patterns and positron lifetime studies are together useful in investigating such structural changes.

TRIOXANE

Crystalline trioxane has the property that it polymerises in the solid state[8] under irradiation by γ-rays, and retains a highly crystalline character even in the polymer phase. The crystalline character of these two phases has been studied extensively by Okamura *et al.*[8] by X-ray diffraction. Trioxane in polymer phase (polyoxymethylene) was obtained by irradiating polycrystalline trioxane monomer with γ-rays from a 22·5 KC source of Co^{60}. The polymer phase is separated from the monomer phase by dissolving the monomer in methyl alcohol. The results of lifetime measurements of positrons in both these phases of trioxane, given in Table I, show that the monomer phase exhibits only one delayed component $\tau_2 = 1 \cdot 2$ ns with an intensity of 27%. The polymer phase exhibits two delayed components, the longer one $\tau_4 = 13$ ns having a much smaller intensity $I_4 \simeq 0 \cdot 4\%$.

A correlation between the value (τ_2)and the intensity (I_2) of the delayed component based on a free volume model for molecular materials has been reported earlier.[1, 9] Here the intensity is plotted against τ_2 for molecular materials in different states of aggregation, and three distinct curves are obtained for fully amorphous solids and liquids, semi-crystalline polymers and crystals. The point for Sb_4O_6 lies on the crystal curve. The point, corresponding to crystalline As_4O_6, lies near the crystal curve, while that corresponding to semi-ordered arsenic trioxide glass lies between the curves for crystals and polymers. The points corresponding to trioxane monomer and trioxane polymer fall very close to the crystal curve.

These results seem to suggest that the second long component (τ_4) observed in the lifetime spectrum of positrons in arsenic oxide is probably due to ortho-positronium atoms annihilating by the pick-off process in inter-crystallite sites. This conclusion seems to be justified by the observed changes in τ_4 in arsenic oxide as a function of temperature and pressure and by the X-ray diffraction patterns.

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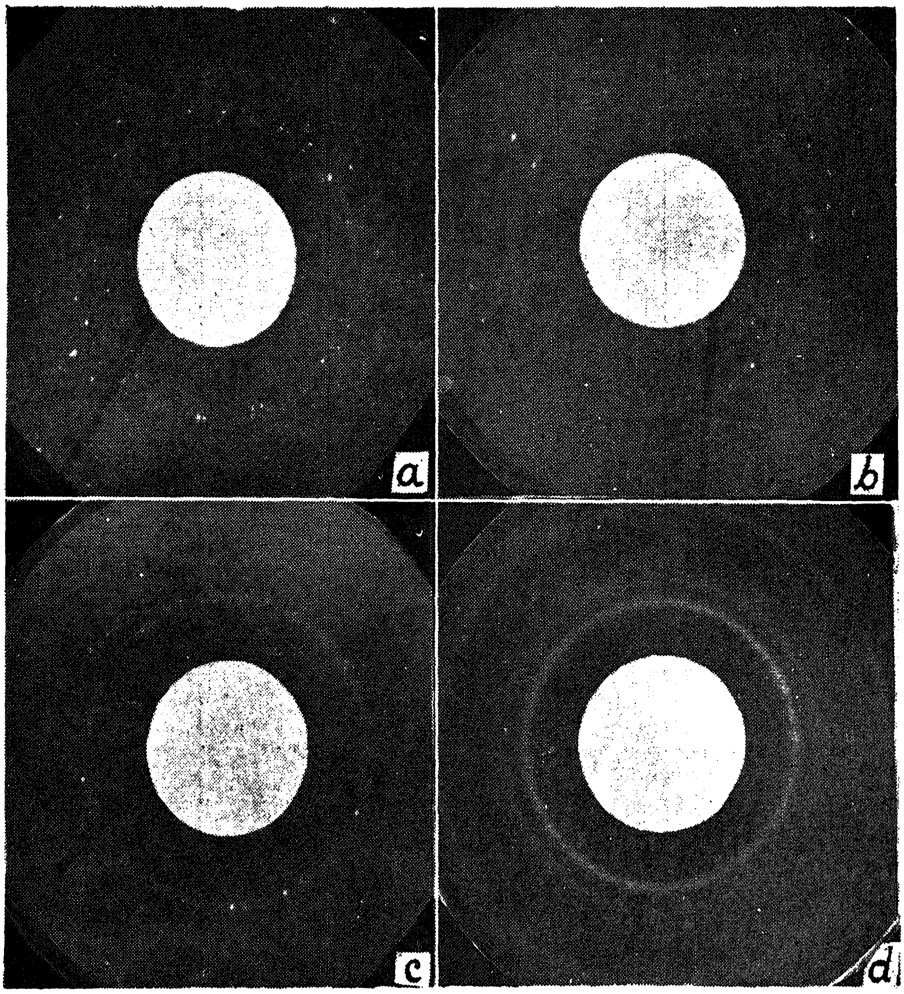

FIG. 1. X-Ray Laue Transmission Patterns

(*a*) Polycrystalline As_4O_6 (*c*) Arsenic trioxide Glass

(*b*) As_4O_6 heat-treated upto 200° C. (*d*) Polycrystalline Sb_4O_6

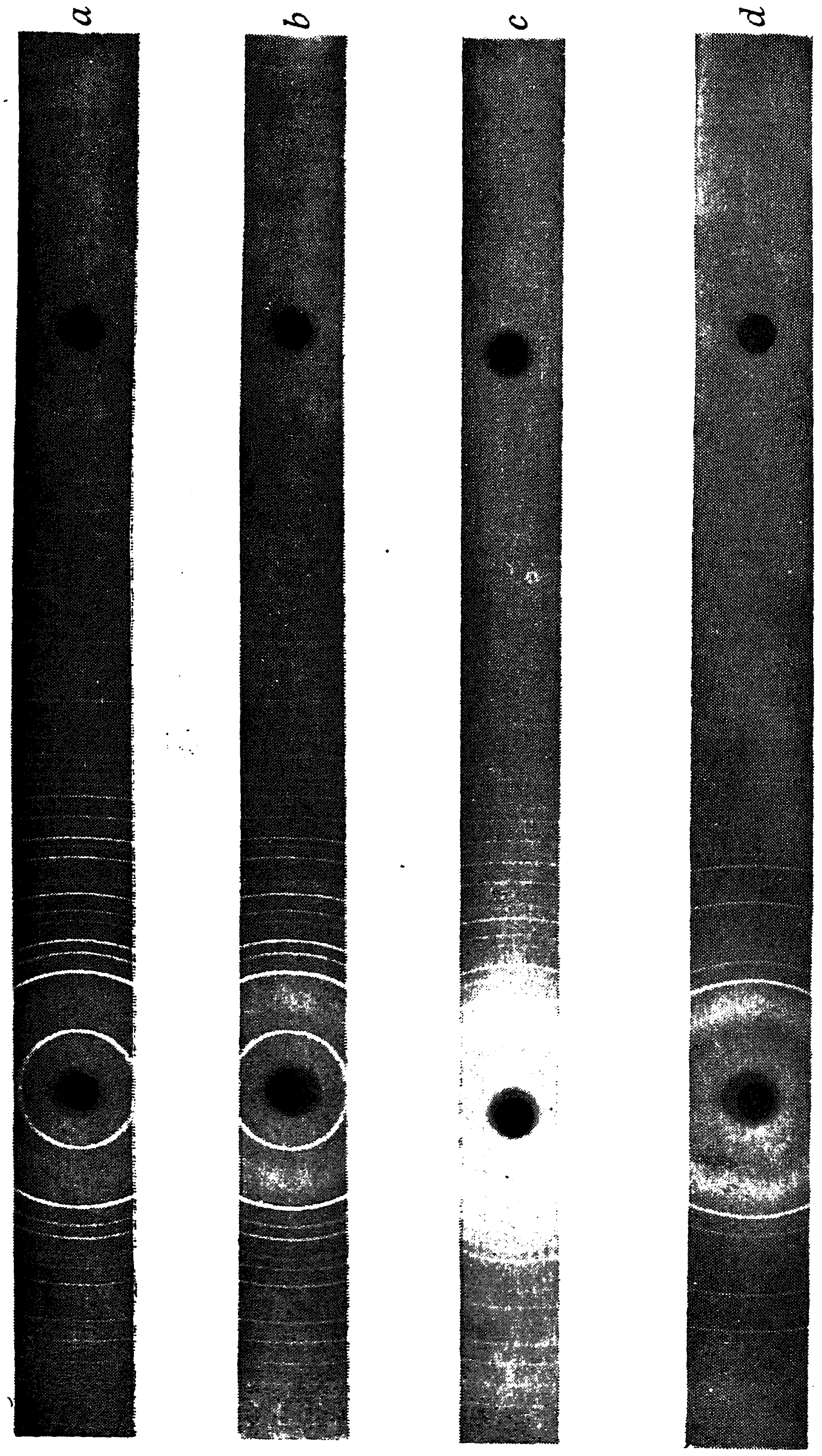

FIG. 2. X-Ray Powder Patterns

(a) Polycrystalline As_4O_6

(b) As_4O_6 heat-treated upto 200° C.

(c) Arsenic trioxide Glass

(d) Polycrystalline Sb_4O_6

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