Experimental Studies of Positron Interactions in Solids and Liquids

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PHENOMENA associated with the interactions of positrons with matter are currently the subject of a great deal of theoretical and experimental study. Two aspects of these phenomena are responsible for the interest they currently command. First, the theoretical prediction[1] and subsequent discovery of positronium[2] in gases has furnished an atom-like structure in which only electromagnetic forces play a role, there being no nuclear field present. Despite the short lifetime of this atom ($\sim 10^{-10}$ sec) against annihilation, modern experimental techniques have made possible a detailed study of its properties. It has served as an ideal system in which the calculations of quantum electrodynamics can be compared with experimental results. The latest radio-frequency resonance measurements of the fine structure splitting of the positronium ground state to an accuracy of five significant figures established impressively the exactness of the radiative correction computations[3] to terms of order α^5.

The second aspect of positron interactions involves positrons in condensed media, solids and liquids. In this case the primary interest lies in the interactions of the positron with the solid or liquid prior to annihilation, leading to the possibility of bound states formation. Evidence indicates that in metals, for example, positrons reach thermal velocities in a short time, computed[4] to be of the order 10^{-12} sec, and subsequently remain free, annihilating with conduction electrons. On the other hand, in certain insulators an appreciable fraction of positrons form some sort of bound state prior to annihilation, resulting in the appearance of two distinct mean lives against annihilation.

It is to a review of recent experimental work in this second regard that this paper is devoted. The earlier work of Deutsch,[2] Pond and Dicke,[5] and others, establishing the existence and properties of positronium in gases, has been very adequately reviewed elsewhere. We also omit consideration of annihilation in flight[6] where the potentials characteristic of the absorber are relatively insignificant in comparison with the positron energy, and the possibility of the rare event of one photon annihilation[6] in the neighborhood of a nuclear Coulomb field.

ANNIHILATION PROCESS

In a study of positron interactions with matter the only link between experimenter and the positron is the photons proceeding from its annihilation. In order to appreciate the significance of the various measurements performed on these photons, one must be acquainted with the elementary properties of the annihilation process.

An S-state electron-positron pair can exist in the singlet ^1S state of zero-spin angular momentum or in one of three triplet ^3S states of unit spin angular momentum. Using the general symmetry properties of the positron-electron pair and the subsequent 2-photon or 3-photon system, it has been shown that the ^1S state annihilates with 2 photons, whereas the ^3S states have to annihilate via 3 photons. For low relative energies of the pair only these S states lead to annihilation since for higher orbitals the positron and electron wave functions do not appreciably overlap.

In a plane wave approximation Dirac computed the spin-averaged cross section for 2γ annihilation of a pair, the result in the low-velocity limit being

$$\sigma_{2\gamma}=\pi r_0^2(c/v),$$

where r_0 is the classical electron radius. The 3γ-annihilation cross section, being a higher order process, is less probable. Calculations of Ore and Powell for the 3γ process yield a ratio for 2γ and 3γ spin averaged cross sections,

$$\sigma_{2\gamma}/\sigma_{3\gamma}=372. \quad (1)$$

Prior to annihilation a positron can capture an electron to form the hydrogen-like system called positronium. In the ground state the mean lifetimes against annihilation of the 1^1S and 1^3S states are as follows:

$$\tau_1=1.25\times 10^{-10} \text{ sec},$$
$$\tau_3=1.4\times 10^{-7} \text{ sec}.$$

The existence of positronium was discovered in rarefied gases, and it was initially thought unlikely that such a bound system could exist in condensed media. As we shall see, however, recent experiments demonstrate that either positronium or some sort of bound

* Alfred P. Sloan Research Fellow 1955–1956.

[1] A. E. Ruark, Phys. Rev. **68**, 278 (1945); J. A. Wheeler, Ann. N. Y. Acad. Sci. **48**, 219 (1946).

[2] M. Deutsch, Phys. Rev. **82**, 455 (1951); For review articles see: M. Deutsch, Progr. Nuclear Phys. **3**, 131 (1953); S. De-Benedetti and H. C. Corben, Ann. Rev. Nuclear Sci. **4**, 191 (1954).

[3] R. Karplus and A. Klein, Phys. Rev. **86**, 257 (1952); Weinstein, Deutsch, and Brown, Phys. Rev. **94**, 758 (1954).

[4] R. L. Garwin, Phys. Rev. **91**, 1571 (1953); G. E. Lee-Whiting, Phys. Rev. **97**, 1557 (1955).

[5] T. A. Pond and R. H. Dicke, Phys. Rev. **85**, 489 (1952).

[6] Gerhart, Carlson, and Sherr, Phys. Rev. **94**, 917 (1954); J. A. Whalen, Bull. Am. Phys. Soc. Ser. II, **1**, 167 (1956).

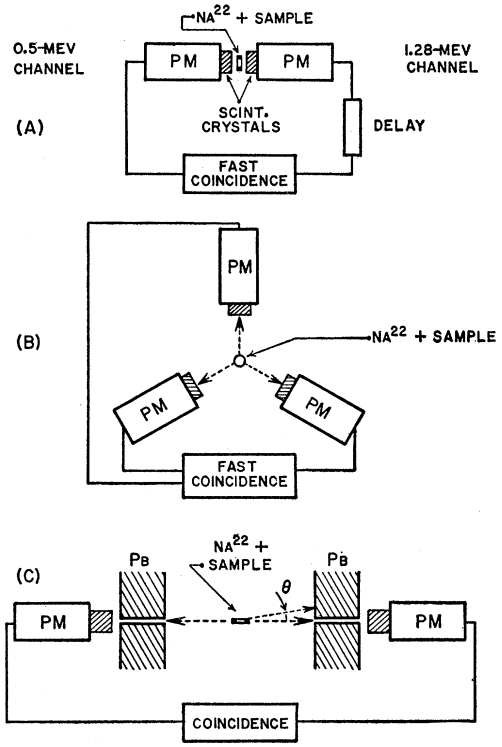

FIG. 1. Schematic scintillation counter coincidence arrangements for observing: (a) the time distribution of 2γ-annihilation events, (b) the 3γ-annihilation rate, (c) the angular correlation of the two photons from 2γ-annihilation. Side-channel pulse-height analysis employed in some experiments is not indicated.

state of positrons does exist prior to annihilation in some liquids and solids.

Most of the experiments which have been performed involve one of three aspects of a positron's existence and subsequent annihilation in matter. In the following sections the results which have been obtained are reviewed. No effort is made to discuss details of the experimental techniques which are described in the original papers. The three types of experiments involve measurement of (1) the distribution in time of 2γ-annihilation events, (2) the 3γ- or 2γ-annihilation rates, the sum of which must remain constant from substance to substance, and (3) the angular correlation between the two photons in 2γ annihilation. In Fig. 1 scintillation counter coincidence arrangements suitable for each of these measurements are shown schematically.

TIME DISTRIBUTION OF POSITRON ANNIHILATION IN LIQUIDS AND SOLIDS

Following the experiments on the behavior of positrons in rarefied gases, a number of investigators have attempted to measure the annihilation life of positrons in solids and liquids. Most of the available data regarding lifetimes resulted from the investigations of DeBenedetti and Richings, Bell and Graham, and more recently of Berko, Landes, and Zuchelli. All these measurements make use of delayed coincidence methods [see Fig. 1(A)]. Sodium-22 is commonly used as a positron source, and delayed coincidences are counted between the nuclear gamma ray (1.28 Mev) following the positron decay of Na^{22} and one of the annihilation quanta (0.51 Mev) resulting from the 2-photon annihilation of the positrons in the material to be studied. This material usually forms a sandwich around a source deposited on thin foils. The short lifetimes involved (10^{-10} to 10^{-9} sec) necessitate the use of the fastest available coincidence circuitry. Such electronics consists essentially of a shaping circuit (sharp cut-off pentodes or diodes), and a nonlinear element (biased diode) set to accept only true coincidence pulses. These techniques have been greatly improved in the recent years and are subject of many review articles and texts.[7]

The results of the lifetime measurements divide naturally into two groups: annihilation times in metals and mean lifetimes in nonmetals. In their initial experiments, DeBenedetti and Riching[8] have used a comparison method and measured the relative lifetimes in several different metals. They find these mean lives to be equal within 0.7×10^{-10} sec. This surprising independence of the lifetime on the electron density was verified by the more exact measurements of Bell and Graham.[9] Instead of using the Na^{22} nuclear gamma ray as a zero time reference, they passed a beam of positrons through a thin stilbene crystal prior to focusing it on the metal to be studied. This method allowed them to measure the absolute lifetime in the different metals with a result of $\tau=(1.5\pm0.5)\times10^{-10}$ sec for all samples studied.† Minton[10] reported a small difference between annihilation times in Al and Pb [(2.9 ± 0.3) *vs* $(3.5\pm0.3)\times10^{-10}$].

These results are surprising particularly in the view of the experiments on the angular distribution of annihilation radiation in metals (see the last paragraph of this article). These angular distribution experiments can be accounted for, if one assumes that most positrons have slowed down and diffuse essentially freely in the metal, annihilating mainly against the valence electrons of the Fermi band. If one, however, computes the annihilation rate using the simple Dirac formula for free annihilation with plane waves, the predicted absolute magnitude and the variation in lifetime between different metals becomes larger than the corresponding experimental values. To explain this discrepancy, De-

[7] See, for example, I. A. D. Lewis and F. H. Wells, *Millimicrosecond Pulse Techniques* (Pergamon Press, London, 1954).

[8] S. DeBenedetti and H. J. Richings, Phys. Rev. **85**, 377 (1952).

[9] R. E. Bell and R. L. Graham, Phys. Rev. **90**, 644 (1953). See also the review article by R. E. Bell in K. Siegbahn, *Beta and Gamma Spectroscopy* (Interscience Publishers, Inc., New York, 1955), p. 680.

† *Note added in proof.*—Since the preparation of this manuscript, Gerholm [Arkiv Fysik **10**, 523 (1956)] has reported the mean life in metals to be $(2.5\pm0.3)\times10^{-10}$ sec. He has also reported a complex decay curve for aluminum.

[10] G. H. Minton, Phys. Rev. **94**, 758 (1954).

Benedetti and Richings talk about some kind of bound annihilating state, and Bell and Graham are even led to formulate possible positronium formation. Since these lifetime measurements were performed, the evidence from angular correlation experiments has grown stronger that in most metals one has free annihilation. The ratio of the 3-photon to 2-photon rate also supports this evidence. The computation of Lee-Whiting[4] indicates also that the slowing down times of positrons in metals is faster by an order of 10^2 than the measured lifetimes. Recently, Ferrell[11] reported how the discrepancy can be partially resolved by properly taking into account the Coulomb interaction and the screening effect of the electrons. These arguments are presented fully in the following theoretical paper on the subject.

A careful search[12] for the effect of longer mean life in superconducting lead, as announced previously by two investigators,[13] lead to negative results. Following a suggestion by Garwin,[4] Landes, Berko, and Zuchelli[14] have looked for differences in lifetime in highly doped n-type, p-type, and pure germanium. They find these lifetimes to be equal within 0.7×10^{-10} sec. This result was also confirmed by Madansky,[15] who also measured the annihilation life in solid and molten gallium and found no difference. Ferguson and Lewis[16] verified some of the Bell and Graham data, and also looked for a possible difference between magnetized and unmagnetized iron. They find, however, no such difference within 3×10^{-11} sec.

From the foregoing discussion it is obvious that an extensive and careful study of lifetimes in metals using improved circuits is very much in order, particularly

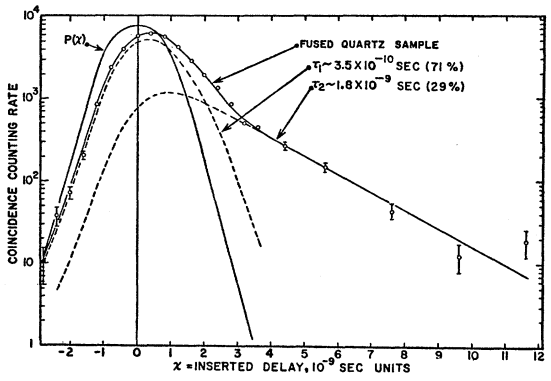

FIG. 2. Positron annihilation in fused quartz. Coincidence resolution curve obtained with a sample of fused quartz; $P(x)$ represents the prompt resolution curve for comparison. Data from Bell and Graham.

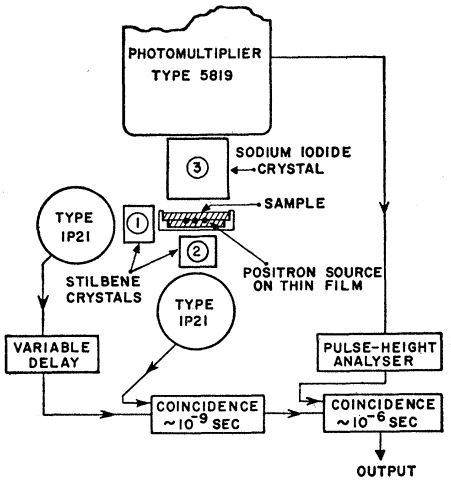

FIG. 3. Arrangement of scintillation counters used by Bell and Graham to compare the spectral and angular distributions of the long-delayed (τ_2) annihilation with those of the more prompt (τ_1) component.

in the light of the recent theoretical computations by Ferrell.[11]

Going to nonmetals, the situation becomes more complex; the results can be summed up as follows:

In simple crystalline materials (crystalline quartz, diamond, NaCl, etc.), Bell and Graham[9] find a positron lifetime behavior similar to that in metals, although the mean life varies over a wider range from sample to sample. In liquids, however, and in some amorphous materials and plastics, they observe a complex time decay that can be analyzed into two distinct lifetimes τ_1 and τ_2. Figure 2 shows such a complex decay scheme (for decay in fused quartz) in the form of a counting rate *vs* delay plot, analyzed into its two components. The curve $P(x)$ stands for the resolution curve of the apparatus (response to prompt coincidences). They also find that the lifetime τ_2 varies strongly from sample-to-sample ranging, for example, from 8.7×10^{-10} sec in fused borax to 3.5×10^{-9} sec in commercial Teflon. In spite of these large variations in τ_2, the analysis of the delay curves shows that the percentage of positrons annihilating via this long component is roughly 30%, seemingly independent of the value τ_2. Table I shows the result of their investigation. In order to verify that the delayed annihilation also represents 2-photon decay, Bell and Graham used the arrangement of Fig. 3. The sodium iodide crystal No. 3 was used to analyze the γ-ray spectrum of the γ ray associated with the 2-photon decay in which its partner was detected by counter 2 forming part of a fast coincidence circuit. This way the pulse-height spectrum of the long delayed (τ_2) annihilation was found to coincide with that of the prompt (τ_1) component.

In order to explain the "anomalous" τ_2 component, Bell and Graham are lead to postulate the formation of bound positron states (positronium) prior to anni-

[11] R. A. Ferrell, Bulletin Am. Phys. Soc. Ser. II, **1**, 138 (1956).
[12] Graham, Paul, and Henshaw, Bull. Am. Phys. Soc. Ser. II, **1**, 68 (1956); B. Green and L. Madansky, Phys. Rev. **102**, 1014 (1956).
[13] W. E. Millett, Phys. Rev. **94**, 809 (1954); R. Stump and H. Talley, Phys. Rev. **96**, 904 (1954).
[14] Landes, Berko, and Zuchelli, Bull. Am. Phys. Soc. Ser. II, **1**, 68 (1956).
[15] L. Madansky (private communication).
[16] A. T. G. Ferguson and G. M. Lewis, Phil. Mag. **44**, 1339 (1953).

TABLE I. Mean lives of positrons in condensed materials.

Material	°C	τ_1 (sec)	%	τ_2 (sec)	%
Li[a]	20	$(1.5\pm0.6)\times10^{-10}$	(100)		
Be	20	$(1.7\pm0.5)\times10^{-10}$	100		
B "amorphous"	20	$(1.7\pm0.4)\times10^{-10}$	100		
C "amorphous"	20	$(4.3\pm0.4)\times10^{-10}$	100		
C graphite	20	$(3.0\pm0.3)\times10^{-10}$	100		
C diamond	20	$(1.3\pm0.3)\times10^{-10}$	100		
Na[a]	20	$(1.5\pm0.6)\times10^{-10}$	(100)		
Al	20	$(1.5\pm0.3)\times10^{-10}$	100		
S monoclinic crystal	20	$(2.1\pm0.3)\times10^{-10}$	100		
S "plastic"	20	$(1.5\pm0.4)\times10^{-10}$	~70	$(4.5\pm0.6)\times10^{-10}$	~30
K[a]	20	$(1.5\pm0.6)\times10^{-10}$	(100)		
Cu	20	$(1.2\pm0.5)\times10^{-10}$	100		
Ag[a]	20	$(1.5\pm0.6)\times10^{-10}$	(100)		
Au	20	$(1.2\pm0.3)\times10^{-10}$	100		
Hg	20	$(1.2\pm0.5)\times10^{-10}$	100		
Pb[a]	20	$(1.5\pm0.6)\times10^{-10}$	(100)		
Water	20			$(1.7\pm0.2)\times10^{-9}$	~30
Ice	−7			$(1.2\pm0.2)\times10^{-9}$	~30
Ice	−196			$(0.85\pm0.15)\times10^{-9}$	~30
Brine (NaCl)	20			$(1.5\pm0.2)\times10^{-9}$	~30
NaCl crystal	20	$(2.3\pm0.3)\times10^{-10}$	100		
Quartz, α crystal	20	$(2.0\pm0.3)\times10^{-10}$	100		
Quartz, fused	20	$(3.5\pm0.5)\times10^{-10}$	71±5	$(1.8\pm0.2)\times10^{-9}$	29±5
Polystyrene	20	$(3.7\pm0.5)\times10^{-10}$	64±5	$(2.3\pm0.2)\times10^{-9}$	36±5
Polystyrene	−196			$(1.7\pm0.3)\times10^{-9}$	~30
Cellulose nitrate	20			$(2.3\pm0.4)\times10^{-9}$	~30
Teflon	20			$(3.5\pm0.4)\times10^{-9}$	~30
Teflon	−78			$(2.5\pm0.4)\times10^{-9}$	~30
Teflon	−196			$(1.6\pm0.4)\times10^{-9}$	~30
Polyethylene	20	$(3.0\pm0.5)\times10^{-10}$	71±5	$(2.4\pm0.3)\times10^{-9}$	29±5
Borax crystals	20			$(9.0\pm2.0)\times10^{-10}$	~30
Fused borax	20	$(2.6\pm0.5)\times10^{-10}$	68±5	$(8.7\pm1.2)\times10^{-10}$	32±5
Mica	20	$(2.2\pm0.5)\times10^{-10}$	100		
Isopropyl alcohol	20			$(2.3\pm0.4)\times10^{-9}$	~30

[a] Lifetimes for these metals are deduced from the comparison measurements of DeBenedetti and Richings and the absolute lifetime in Al.

hilation. The τ_2 lifetime can be regarded then as a conversion rate from triplet to singlet spin states of the positronium due to collisions with the atoms (electrons) of the sample material. The existence of some sort of bound state prior to annihilation has been substantiated by experiments correlating a 3γ-annihilation rate with the appearance of the τ_2 component.

One of the least understood effects observed for the first time by Bell and Graham is the strong dependence of τ_2 in Teflon and ice on temperature. This dependence is nearly linear, τ_2 decreasing with decreasing temperature. Berko and Landes[14] verified this result for Teflon and extended the data to liquid helium temperatures; they find the τ_2 *vs* T curve to deviate from linearity in this range, leveling off between liquid nitrogen and liquid helium temperature. Annihilation of positrons in liquid helium[12] directly exhibits also a τ_2 component [$\tau_2=(2.7\pm0.3)\times10^{-9}$ sec]. The percentage of positrons annihilating with τ_2 being higher than in most other substances observed so far.

From their data Bell and Graham are lead to the conclusion that the appearance of the τ_2 component is connected with the order-disorder property of the respective solid. In order to check this correlation, Landes, Berko, and Zuchelli[17] have performed a melting experiment on an organic crystal. Napthalene was used, having a melting point at 80.1°C. The results of the experiment are plotted on Fig. 4 in the form of a τ_2-temperature curve. The delay curves exhibit the existence of a τ_2 even in the crystalline state, independent of the temperature below melting. There is a fairly sharp rise in τ_2 at melting, and then a leveling off at a higher absolute value. Besides this phase change, the percentage decaying with the τ_2 component changes also from ~10% below melting to ~30% in the liquid phase. Recent experiments on Teflon carried out by the same group indicate the same order-disorder dependence. They observe the τ_2 dependence of the crystallinity of different Teflon samples that were quenched at various rates from above the 325°C phase point of Teflon to room temperature.

Following a 2-photon rate experiment by Pond,[18] Berko and Zuchelli[19] have reported the quenching of the τ_2 lifetime in benzene with the addition of various percentages of the organic free radical diphenyl picryl hydrazyl (D.P.H.). Figure 5 shows the effect of varying the concentration of D.P.H. on τ_2. From these curves the authors conclude that Bell and Grahams' assumption of positronium formation by a fraction of positrons prior annihilation is the most reasonable picture explain-

[17] Landes, Berko, and Zuchelli, Phys. Rev. (to be published).

[18] T. A. Pond, Phys. Rev. **93**, 478 (1954).

[19] S. Berko and A. J. Zuchelli, Phys. Rev. **102**, 724 (1956).

ing the τ_2 component. Using such a model, and assuming that the effect of the spin unpaired electron of the free radical is to introduce triplet-singlet conversion via spin-exchange collisions, they obtain a triplet-singlet conversion rate of $\sigma=1.2\times10^{-17}$ cm^2. This is in good agreement with Pond's data, and is of the same order of magnitude as the positronium triplet-quenching cross section in gases[2] due to addition of NO. To check the influence of the magnetic field due to the paramagnetism of the free radical, the paramagnetic quenching due to Mn^{++} ions dissolved in water is now being studied. The preliminary results lead to a much lower cross section $\sigma=5\times10^{-20}$ cm^2 for such an effect, although other possible chemical reactions with positronium are not excluded.

Although these experiments substantiate the existence of positronium in some liquids and solids and its interaction with the atoms and atomic fields in these substances, many aspects of the behavior of τ_2 component remain unexplained. Further experiments are therefore needed to bring about an understanding of the parameters influencing the anomalous lifetime of positrons annihilating in these solids.

3-PHOTON AND 2-PHOTON ANNIHILATION RATES

Three-photon annihilation in gases was first observed by Deutsch,[2] the results yielding $2\gamma/3\gamma$ ratios as low as 3, considerably less than that expected for annihilation of free positrons [Eq. (1)]. This confirmed his earlier work, indicating abundant positronium formation in some gases. Pond and Dicke,[5] observing variations in the 2γ rate from gas to gas, obtained similar results. It was initially thought that in solids and liquids, positronium formation would be highly improbable and that positrons should remain free, the $2\gamma/3\gamma$ ratio being the same for different substances and of the order of 372. However, the discovery of the τ_2 component and the Bell-Graham[9] postulate of its origin necessitated modification of these ideas. If the Bell-Graham mechanism is correct, those substances exhibiting a τ_2 component should yield increased 3γ-annihilation rates. On the other hand, substances showing

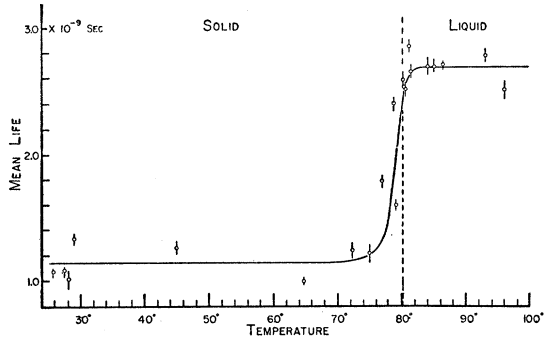

FIG. 4. The "anomalous" positron annihilation lifetime component, τ_2, in napthalene, plotted against temperature. Melting point is at 80.1°C. Results of Landes, Berko, and Zuchelli.

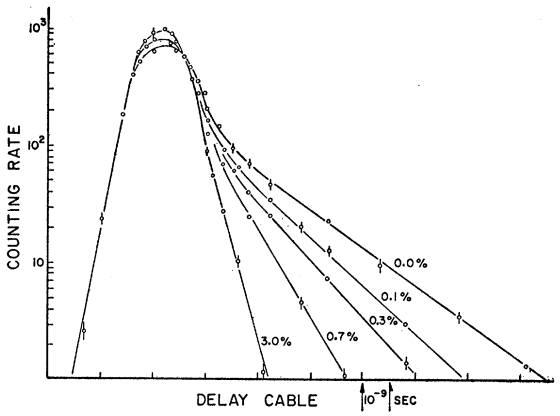

FIG. 5. Delay curves exhibiting the change in lifetime of positrons in benzene as a function of concentration of added organic free radical diphenyl picryl hydrayl. Results of Berko and Zuchelli.

no τ_2 component should yield a constant $2\gamma/3\gamma$ ratio of about 372.

Comparison of the 3γ rates in different substances can be achieved either by direct triple coincidence detection or by observation of the 2γ rate. Under conditions of constant source strength, the sum of these two rates must remain constant for different substances. Since in solids and liquids the $2\gamma/3\gamma$ ratio is of the order of 372, most investigators have employed direct 3γ detection, which yields large percentage changes in counting rates. Without exception the experiments have been performed with fast scintillation counter coincidence circuits either with or without side channel pulse-height analysis, as indicated in Fig. 1(b).

Rich[20] first reported observation of 3γ annihilation in a solid, observing the $2\gamma/3\gamma$ ratio in aluminum and finding rough agreement with the value 372. Subsequently, DeBenedetti[21] and his co-workers confirmed this result and carried through a thorough investigation of the energy distributions for 3γ annihilation, demonstrating conservation of energy and momentum.

Basson[22] has reported the most statistically significant measure of the $2\gamma/3\gamma$ ratio. For annihilation in aluminum his results yield for the ratio of the spin averaged cross sections,

$$\sigma_{2\gamma}/\sigma_{3\gamma}=406\pm50.$$

The agreement with the value 372 is again evidence that positrons remain free in a metal annihilating with electrons of random spin direction. This is entirely consistent with the appearance of a single lifetime in metals as described in the preceding section.

Turning now to the comparison of different substances, Graham and Stewart[23] have demonstrated a correlation between τ_2 and the 3γ annihilation rate.

[20] J. A. Rich, Phys. Rev. **81**, 140 (1951).
[21] S. DeBenedetti and R. Siegel, Phys. Rev. **94**, 955 (1954).
[22] J. K. Basson, Phys. Rev. **96**, 691 (1954).
[23] R. L. Graham and A. T. Stewart, Can. J. Phys. **32**, 678 (1954).

TABLE II. Observed three-quantum decay rates in condensed materials.

Material	Three-quantum rate at 20°C (counts/min)	Positron mean lives (sec) τ_1	τ_2
Beryllium	0.14±0.05	$(1.7\pm0.5)\times10^{-10}$	···
Aluminum	0.20±0.05	$(1.5\pm0.3)\times10^{-10}$	···
Crystalline quartz	0.22±0.05	$(2.0\pm0.3)\times10^{-10}$	···
Fuzed quartz	0.41±0.10	$(3.5\pm0.5)\times10^{-10}$	$(1.8\pm0.2)\times10^{-9}$
Polystyrene	0.47±0.12	$(3.7\pm0.5)\times10^{-10}$	$(2.3\pm0.2)\times10^{-9}$
Teflon	0.68±0.10	Not quoted	$(3.5\pm0.4)\times10^{-9}$

Their data clearly show a greater triple rate in substances exhibiting a τ_2 component (see Table II). Similarly there is correlated with the dependence of τ_2 upon temperature (preceding section) a dependence of the 3γ rate upon temperature. Figure 6 shows the results of Graham and Stewart[23] and of Wagner and Hereford[24] in this connection. An immediately obvious feature of the results is the absence of a temperature effect in zinc, which again is consistent with free positron annihilation in metals. For the other substances, all of which exhibit a τ_2 component, the lifetime data are not sufficient to make a detailed comparison between τ_2 and the 3γ rate. No simple relation between the quantities is expected since the triple rate will depend strongly upon the fraction of positrons annihilating with the longer lifetime. Whereas, experiments initially indicated that this fraction was constant from substance to substance, it is now known that this is not necessarily the case.

Several interesting features of the 3γ *vs* T°K results are worth citing. First, there is no apparent relation between the magnitude of τ_2 and the strength of the $\tau_2(T)$ dependence. Teflon exhibits a larger value for τ_2 than glycerine, but the percentage change of the 3γ rate with temperature is much greater in glycerine. Second, the strong temperature effect in glycerine is reminiscent of its strong viscosity *vs* temperature dependence. Finally, the data for water (plus $Na^{22}Cl$) show a leveling off of the 3γ rate with increasing temperature near the melting point. A similar leveling off of the 3γ rate in glycerine at about the melting point (310°K) has recently been observed by Hughes and Hereford (unpublished). This behavior may be connected with the change of τ_2 near the melting point, as observed for annihilation in naphthalene (see preceding section).

No satisfactory mechanism predicting the quantitative features of the temperature effect has been given. It is even more difficult to specify which temperature dependent properties of materials are pertinent. It appears in ice where the crystallinity is temperature dependent and in Teflon where it apparently is not. Further measurements of both lifetime and the 3γ rate in a variety of substances are much needed.

Free radical quenching of the 3γ annihilation rate has been observed by Pond[18] by measurement of the increase in the 2γ rate, upon addition of D.P.H. to benzene. Analysis of the data yielded a cross section in agreement with the value obtained subsequently by Berko and Zuchelli in their observations on the τ_2 component in benzene+D.P.H.

Recently, Telegdi[25] has observed a decrease in the 3γ rate in Teflon with the application of an external magnetic field. This phenomenon is analogous to the magnetic quenching of positronium in gases.[26] The quenching mechanism is the magnetic mixing of the singlet state and the $m=0$ triplet substate which enables the triplet state to undergo 2γ annihilation. His results are generally consistent with the assumption that positronium is formed in Teflon.

The same effect was recently observed by Deutsch,[27] measuring directly the quenching of the τ_2 component with applied magnetic field on Teflon.

2-PHOTON ANGULAR CORRELATION

The 2γ annihilation of a positron-electron pair at rest in a laboratory system results in two photons of energy mc^2 at a relative emission angle of π radians. If the annihilating pair has a finite momentum and energy, then the two photons must carry away this additional momentum and energy. In the case of a random distribution of the momentum direction, mo-

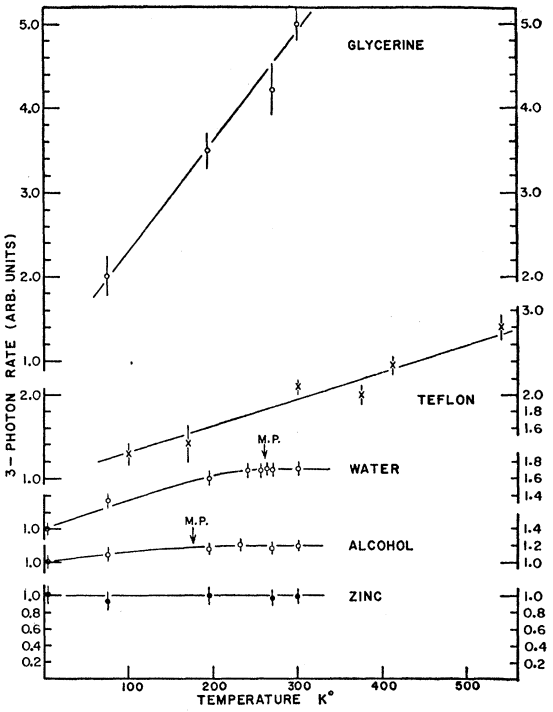

FIG. 6. Variation of the 3γ-annihilation rate with temperature (°K) for annihilation in various materials. ●—Wagner and Hereford (unpublished); ○—Wagner and Hereford[24] ×—Graham and Stewart.[23] The curves are arbitrarily normalized at 0°K.

[24] R. T. Wagner and F. L. Hereford, Phys. Rev. **99**, 593 (1955).

[25] V. Telegdi, Bull. Am. Phys. Soc. Ser. II, **1**, 168 (1956).

[26] M. Deutsch and E. Dulit, Phys. Rev. **84**, 601 (1951).

[27] M. Deutsch (private communication).

mentum conservation leads to photon pair emission at relative angles differing from π, and energy conservation to a broadening of the mc^2 gamma line. Thus observation of either of these two phenomena yields information about the state of the electron pair just prior to annihilation. DuMond[28] and his co-workers have observed the Doppler line broadening, and the angular distribution has been studied by a number of workers. These latter measurements have been performed with arrangements similar to that shown schematically in Fig. 1(c).

The first measurements made with sufficiently high angular resolution to be of interest were those of DeBenedetti[29] *et al.*, who observed that for annihilation in gold the average momentum of the electron pairs is 1.2 $mc/137$. The Doppler line width observed for annihilation in copper gives a value of the same order of magnitude. This figure is in rough agreement with the momenta of conduction and valence electrons $\approx mc/137$. Hence, these data indicate that the positrons reach very low velocities and annihilate primarily with conduction electrons in a metal.

Later results reported by Cloizeaux and Ambrosino[30] indicated that the average momenta of annihilating pairs in copper were definitely larger than that expected for conduction and valence electrons. These workers suggested that the larger value of momentum was due to positron annihilation with "core" electrons (e.g., d electrons). These early measurements were not sufficiently precise to compare the shape of the angular distribution with that predicted by the electron theory of metals.

For annihilation in a free-electron gas one can easily predict the expected shape of the angular distribution. Consider, for example, thermalized free positrons ($\approx 1/40$ ev), annihilating in a free-electron gas of a given Fermi energy. The momenta of the pairs derive from the electron momenta, k, which are distributed uniformly about an origin in momentum space, filling a sphere of radius k_F (Fig. 7). A photon pair at $\pi \pm \theta$ radians must originate from an electron pair with

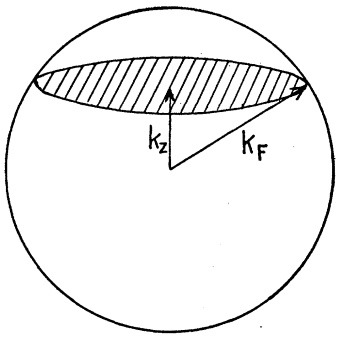

FIG. 7. The shaded area shows the slice through the momentum distribution which is sampled by counting photon pairs at a relative angle $\pi \pm \theta$, corresponding to a given z component of electron momentum.

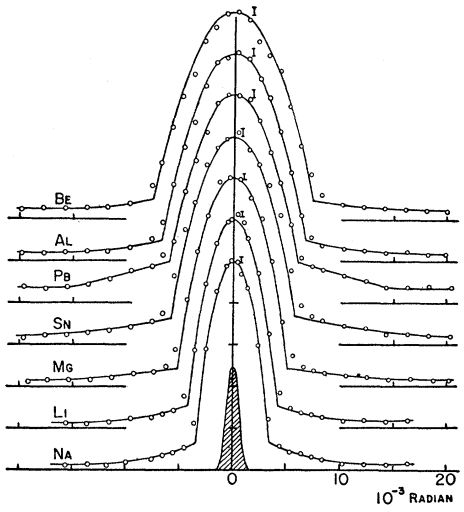

FIG. 8. The 2γ angular correlations observed by De Benedetti *et al.* in the substances indicated.

transverse momentum component $k_Z = \theta(mc)$. The number of such pairs will be proportional to the area of a slice through the sphere at k_Z as in Fig. 7. The area of this slice and hence the rate of photon pairs emitted between θ and $\theta + d\theta$ is then

$$dn/d\theta = \text{const}(k_F^2 - k_Z^2)$$

or

$$dn/d\theta = \text{const}(k_F^2 - \theta^2 m^2 c^2).$$

Thus one expects an inverted parabola for a Fermi electron gas. In any case, the 2-photon rate at a given relative angle samples a slice through the momentum space of those electrons which the positron selects for annihilation. The measurement then yields information about the momentum distribution of those electrons.

Recently, three groups of workers have studied the 2γ angular resolution with improved resolution. In Fig. 8 are shown the experimental distributions for a number of metals reported by DeBenedetti[31] and his coworkers. Very similar curves have been obtained by Stewart.[32] The parabolic parts of the solid curves are the computed values of k_Z for electrons of a Fermi gas of density equal to the free electron density for the various metals shown. The tails are simply drawn through the experimental points. The points fit the parabolas very well except for the regions of larger angles (higher momenta) where "tails" appear. It is interesting that in transition and noble metals where the cores are closer together[31] the tails are more pronounced, suggesting annihilation with core electrons.

Results obtained by Stewart[32] show similar effects. After correcting for finite angular resolution he has extracted from the data the momentum distribution $N(k)$ of the annihilating pairs, presumably to be

[28] DuMond, Lind, and Watson, Phys. Rev. **75**, 1226 (1949).
[29] DeBenedetti, Cowan, Konneker, and Primakoff, Phys. Rev. **77**, 205 (1950).
[30] J. Des Cloizeaux and G. Ambrosino, Compt. rend. **237**, 1069 (1953).
[31] Lang, De Benedetti, and Smoluchowski, Phys. Rev. **99**, 596 (1955).
[32] A. T. Stewart (private communication).

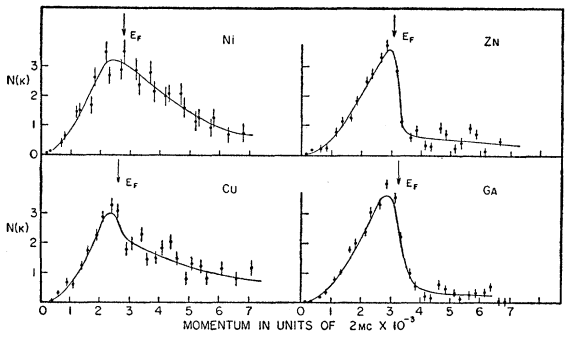

FIG. 9. Momentum distribution of electrons participating in 2γ annihilation. Results of Stewart.

identified with the electron momentum distribution. Figure 9 shows his results for Ni, Cu, Zn, and Ga. The progressive decrease in the tail in this series may be correlated with the filling of the *d* shell and the addition of *s* electrons.

In certain nonmetals Page *et al.*[33] and Stewart[34] have observed that the angular distribution has a broader base and sharper peak than is the case with metals. The sharper peak is thought to be due to annihilation of positronium or some sort of bound system. In particular Page and his co-workers found a narrow component in fused quartz but none in crystalline quartz, which may be related to the presence of a τ_2 component and increased 3γ rate in fused quartz. Analysis of their data indicated that the narrow component involved about 20% of the positrons undergoing annihilation.

A temperature effect in the angular distribution in Teflon has been observed by Stewart (Fig. 10). His data indicated a strong peak in the distribution at 525°K which was not present at 77°K, again reminiscent of the increase of τ_2 and the 3γ rate at higher temperatures. According to Stewart, it is difficult to determine whether the fraction of positrons contributing to the narrow component increases at higher temperatures, or whether the width of the narrow component decreases.

The influence of applied magnetic fields upon the angular distribution for annihilation in materials exhibiting a τ_2 component has been observed by Page *et al.*[33] In Teflon, for example, with a field of 15 kilogauss they detected a transfer from broad to narrow component of roughly 4% of the total intensity (Fig. 11). In interpreting this result, they assume the narrow component to arise from positronium annihilation. Presuming that some triplet state positronium systems normally annihilate in collisions with no triplet-to-singlet conversion involved, they suggest that the magnetic field enables some of these ^3S pairs to undergo singlet annihilation through mixing of the ^1S state with the $m=0$ triplet substrate. This is undoubtedly related to the magnetic quenching of the 3γ rate[25] and of the τ_2 component.[26]

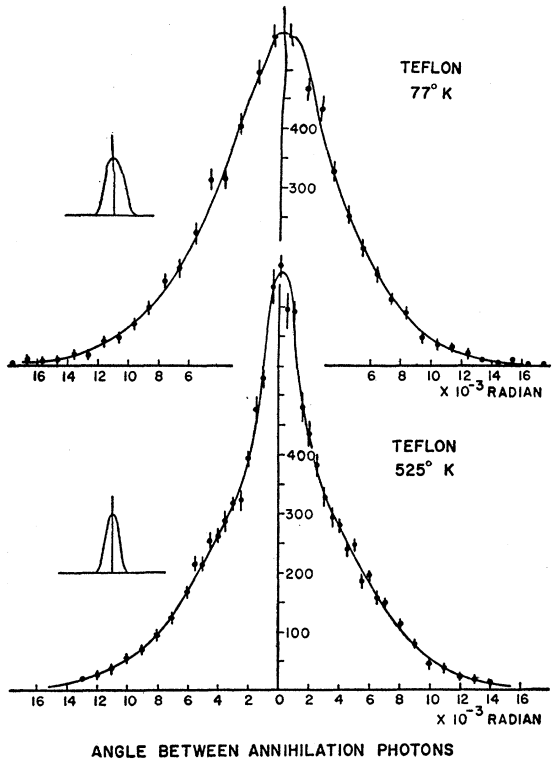

FIG. 10. The 2γ angular correlation in Teflon at two temperatures. Results of Stewart.[34]

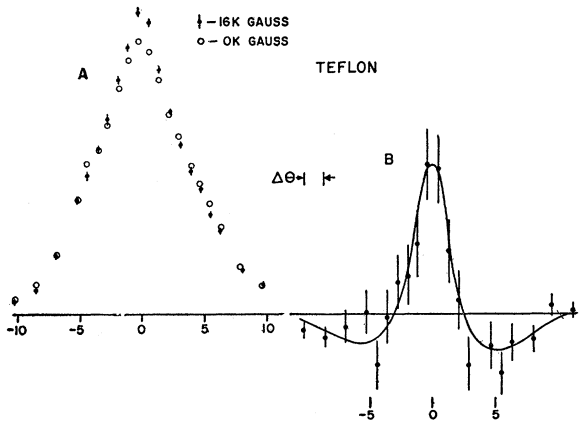

FIG. 11. Effect of magnetic field on the 2γ angular correlation. Results of Page *et al.*[33] Curve *B* is the difference between the field-on and field-off angular distributions.

SUMMARY

As we have seen in the foregoing review, the problem of positron annihilation in solids and liquids has been studied by several investigators using three different

[33] Page, Heinberg, Wallace, and Trout, Phys. Rev. **98**, 206 (1955).
[34] A. T. Stewart, Phys. Rev. **99**, 594 (1955).

methods: lifetime measurements, 2γ or 3γ annihilation rate detection, and 2γ angular correlation. These methods are complimentary in giving information about the behavior of the positrons prior to annihilation. The materials in which annihilation has been studied can be classified with regard to these measurements as follows:

Category I: (a) No complex decay scheme (absence of τ_2).
(b) $2\gamma/3\gamma = 372$.
(c) No complex angular distribution (absence of narrow component).

Category II: (a) Well-defined τ_2 lifetime.
(b) $2\gamma/3\gamma < 372$ (increased 3-photon decay rate).
(c) Narrow component in the 2γ angular correlation.

All metals and most crystals studied fall into the first category, some amorphous solids, plastics and liquids form the second category.

The most reasonable interpretation of these results is that in materials of class I, positrons, upon slowing down rapidly, annihilate freely with the electrons of the solid. In the materials of class II, there are at least two independently annihilating states. Experiments on magnetic quenching, free radical interaction and larger 3γ rate indicate the formation of bound positron states, most probably positronium.

Many effects, such as that of temperature and phase change are not yet understood theoretically and should be further investigated. Careful lifetime measurements in metals are necessary in order to observe possible variation of τ_1 with the density of conduction electrons. Ionic crystals have been studied in terms of the 2γ angular correlation, but very few lifetimes have been measured. The exact correlation between the τ_2 component and the narrow angular distribution should be further investigated, since it represents the most important clue as to the nature of the annihilation mechanism from triplet positronium states via the τ_2 lifetime.

Many authors have voiced their hope that once understood, these annihilation phenomena could form a useful tool in the study of the solid and liquid state of matter. It is obvious however, that before this can be the case, much more data are required in order to formulate a more complete theory of positron interaction in matter.

ACKNOWLEDGMENTS

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