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Time Distribution of Positron Annihilation in Liquids and Solids

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The time distribution of the annihilation radiation emerging from liquids and solids, following the absorption by the samples of fast positrons, has been studied by the delayed coincidence method. The mean life of positrons in metals is found to be about 1.5×10^{-10} sec, nearly independent of the metal chosen. Some simple crystals behave similarly, but many amorphous substances, both solid and liquid, show a complex time decay in which about $\frac{2}{3}$ of the positrons annihilate with mean life a few times 10^{-10} second, and the remaining $\frac{1}{3}$ with mean life from 0.45×10^{-9} sec to 3.5×10^{-9} sec, depending on the substance. This longer lifetime is shown to decrease, in general, as the sample is cooled. Placing the sample in moderate electric and magnetic fields has no detectable effect. The long-delayed radiation is shown to be similar in energy and angular distribution to the more prompt component. Tentative interpretations of these facts are given, but some points still await a full explanation.

I. INTRODUCTION

A STUDY is being made of the time distribution of the annihilation radiation emerging from samples of condensed materials (solids and liquids) following the absorption by the samples of fast positrons. The time intervals measured thus include the time required for the positrons to slow down to the low energy at which most of the annihilations are generally supposed to take place, as well as the life of the positrons after reaching that energy. The measurements are made by the delayed coincidence method, using scintillation counters and a coincidence circuit[1] of resolving time $2\tau_0\sim2\times10^{-9}$ sec. Results have been obtained for a number of metals, nonmetallic crystals, liquids, and amorphous solids. Many of the materials in the latter two categories show a complex time decay curve which has two distinct components of comparable intensity with different mean lives. Preliminary reports of some of the results described in this paper were given at the 1952 Washington Meeting of the American Physical Society and at the 1952 Quebec Meeting of the Royal Society of Canada.[2]

Following the work of Deutsch and his collaborators[3] on the time decay of the annihilation radiation from positrons absorbed in gases, leading to the discovery of positronium, a number of workers[4-6] have attempted to measure the mean life of positrons in solids and liquids. The lifetimes in liquids and solids are expected to lie in the 10^{-9} to 10^{-10} sec range and hence are more difficult to measure than in the case of gases. Moore[4] has obtained a value of τ (mean life) of positrons in stilbene of $(1.0\pm0.5)\times10^{-9}$ sec. Millett's[5] results on Plexiglas suggest $\tau=1.4\times10^{-9}$ sec. An extensive series of comparison measurements by DeBenedetti and Richings[6] has shown that the difference in positron mean life between various metals is $(0\pm0.5)\times10^{-10}$ sec, but that mean lives in certain amorphous materials and liquids are longer than those of the metals by $(2\text{ to }4)\times10^{-10}$ sec. The actual values of τ were not measured. De Benedetti and Richings did not carry their measured curves out to sufficiently long delays to detect the complex time behavior reported here for some of the same amorphous materials.

II. EXPERIMENTAL ARRANGEMENTS AND RESULTS

(a) Lifetime Measurements

The first measurements in this study were made by a method using a pair of lens beta-ray spectrometers placed end to end,[7] as shown in Fig. 1. The left-hand scintillation counter, shown enlarged in Fig. 1(b) consisted of a stilbene crystal, a short Lucite light-pipe, and a 1P21 photomultiplier, all enclosed in an iron block for magnetic shielding. The stilbene crystal, which was $\frac{1}{4}$ inch in diameter and 50 mg/cm^2 thick, covered a small hole in the Lucite light pipe in which was inserted a source of the positron emitter, Na^{22}. Thus each positron entering the spectrometer from the source had already passed through the stilbene crystal and given a zero of time to the coincidence circuit to which the two scintillation counters were connected. The positrons passed through the left-hand spectrometer, Fig. 1(a), and were focused onto a $\frac{1}{2}$-in. hole in the baffle separating the two spectrometers. The positrons passing through the hole were already selected in energy and trajectory, so that the right-hand spectrometer was not provided with a baffle. The scintillation counter for the right-hand spectrometer used a 1 cm^3 crystal of diphenylacetylene over which the sample under test was placed, as shown in Fig. 1(c). Thus positrons entering the right hand spectrometer could strike no material other than the sample under test. With the sample removed, the focused positrons fell directly on the right-hand scintillation crystal, and the two counters of Fig. 1 then supplied the coincidence circuit with

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[1] Bell, Graham, and Petch, Can. J. Phys. 30, 35 (1952).

[2] R. E. Bell and R. L. Graham, Phys. Rev. **87**, 236 (1952); June Meeting, Quebec, Royal Society of Canada (1952).

[3] J. W. Shearer and M. Deutsch, Phys. Rev. **76**, 462 (1949); M. Deutsch, Phys. Rev. **82**, 455 (1951); **83**, 207 (1951); **83**, 866 (1951).

[4] D. C. Moore, Phys. Rev. **82**, 336 (1951).

[5] W. E. Millett, Phys. Rev. **82**, 336 (1951).

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

[7] R. E. Bell and R. L. Graham, Phys. Rev. **86**, 212 (1952).

coincidences that were prompt, except for the fixed transit time of the positrons through the pair of spectrometers. When the sample was in place, the positrons were absorbed in it and the diphenylacetylene counter detected a fraction of the annihilation quanta emerging from the sample. The coincidence circuit then received coincidences having delays equal to the lifetimes of the positrons in the sample. The measurement of the lifetime properties of positrons absorbed in any particular sample material consisted of a comparison of sample-out (prompt) and sample-in (delayed) conditions by the usual delayed-coincidence method. The methods used for analysis of the coincidence resolution curves so obtained have been described in a previous paper.[1]

The positron energy selected by the spectrometers was 220 kev, kept constant throughout the measurements. The selected positrons had already dissipated about 150 kev in the 50 mg/cm^2 stilbene crystal of the source counter, Fig. 1(b), and so must have left the source with an energy around 370 kev, a point of favorable intensity in the 575-kev β^+ spectrum of Na^{22}. With the sample out the full positron energy, 220 kev, was dissipated in the diphenyacetylene crystal of the sample counter, Fig. 1(c). With the sample in place, this counter registered the Compton recoil electron distribution of a 511-kev gamma-ray, extending from 0 to 341 kev. Since the discriminator for this counter was biased to reject pulses of size corresponding to less than ~150 kev, the average pulse height when counting gamma-rays with the sample in (150–340 kev) was approximately equal to that when counting positrons directly with the sample out (220 kev). Diphenylacetylene was chosen as a phosphor for this counter in preference to stilbene because preliminary measurements showed that the mean time delay for the appearance of the first photoelectron in the photomultiplier ($\bar{t}$, in the notation of reference 1) is smaller by a factor of about 2 for diphenylacetylene than for stilbene. The difference in time delay caused by inequality of the pulse sizes between the sample-out and sample-in conditions is estimated to be less than 2×10^{-11} sec.

The method just described has the disadvantage of requiring the sample under test to be placed in the vacuum of the spectrometer. It has, however, a number of advantages over simpler arrangements. It gives the value of the mean life absolutely, and not merely by comparison with that of another sample. The method does not depend on the nuclear properties of the source. It is nearly free of chance coincidences, since nearly every true count in the sample counter corresponds to a coincidence event. Unwanted genuine counts due to annihilation in materials other than the sample are negligible because of the double spectrometer arrangement.

The samples used in this method were in the form of disks 1-inch or more in diameter and at least thick enough to stop 220-kev positrons. Finely divided materials were either pressed into the required form or held together by adding about 1 percent by weight of plastic binder.

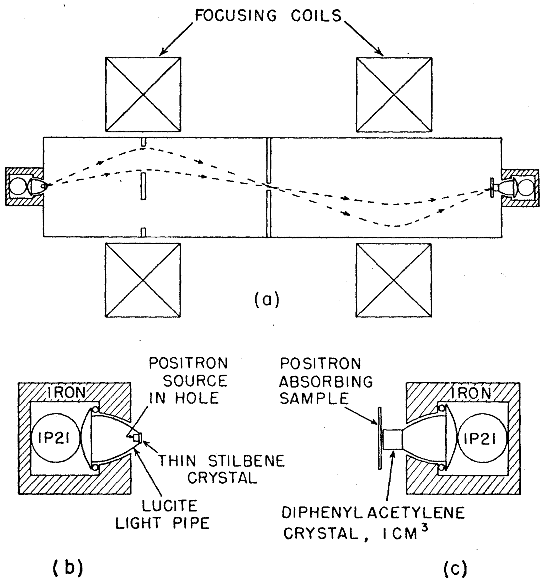

FIG. 1. Pair of identical end-to-end β-ray spectrometers which are operated with the coils in series. Positrons emerging through the stilbene crystal of the left scintillation counter, shown enlarged in (b), are selected in energy and trajectory by the left spectrometer. Positrons, which pass through the hole in the central diaphragm into the right spectrometer, can strike only the sample placed in front of the right hand, γ-sensitive scintillation counter, shown enlarged in (c) or the diphenylacetylene crystal of the counter directly if the sample is removed. The scintillation counters are connected to a coincidence circuit (not shown) of resolving time $2\tau_0=2\times 10^{-9}$ sec.

The results for the first sample, aluminum, are shown in Fig. 2, in the form of a pair of coincidence resolution curves. The procedures used in recording these curves were those of reference 1, the inserted time delay x being provided by the motor-driven helical delay unit described there. The prompt curve $P(x)$ (sample out) yielded a counting rate at its peak of several hundred counts per minute, and was recorded during the daytime hours. The delayed curve, marked "aluminum sample" in Fig. 2, yielded a counting rate about 5 percent as great, and was recorded overnight, the prompt curve being repeated the next day as a check. The two curves have been plotted to the same included area in Fig. 2. The same procedure was followed for all the samples measured by this method. In all cases the $P(x)$ curve was separately determined for each sample and not merely repeated from Fig. 2.

The displacement of the centroid of the aluminum curve (Fig. 2) to the right of that of the prompt curve shows that 220-kev positrons entering aluminum have a mean life τ of about 1.5×10^{-10} sec. The resolution is not sufficient to prove that the time decay is exponential; the result is, however, consistent with this assumption.

A run with a gold sample gave a result similar to that for aluminum, the indicated value of τ being 1.2×10^{-10}

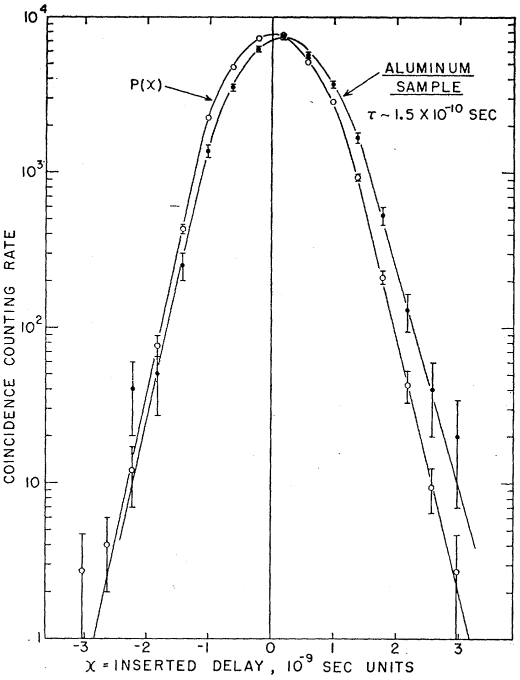

FIG. 2. Coincidence resolution curves. The delayed curve (solid circles) was obtained when the positrons were absorbed in a sample of aluminum, and the prompt curve $P(x)$ was obtained when the sample was removed and positrons were detected directly by the crystal of the right counter in Fig. 1. In this and in Figs. 3 to 8 $P(x)$ is an average of the prompt runs taken immediately before and after the run with sample in position. The standard deviations are shown by vertical bars.

sec. These results and others reported later in this paper support the findings of DeBenedetti and Richings on the near consistency of τ with different metals. The probable error in these values of τ, due to statistics and the uncertainty in $\bar{t}$ mentioned above, is about 0.3×10^{-10} sec, and it is therefore not possible to say definitely whether the mean life in Au is slightly shorter than that in Al.

Figure 3 gives the results for a single crystal of α-quartz (SiO_2).[8] Again we have an apparently simple time decay with $\tau=(2.0\pm 0.3)\times 10^{-10}$ sec. Proceeding to Fig. 4, the sample has been changed from the crystalline quartz of Fig. 3 to fused quartz (a piece of fused quartz laboratory ware). The delayed resolution curve is now seen to split naturally into two components, one of mean life $\tau_1=(3.5\pm 0.5)\times 10^{-10}$ sec, and the other an apparently exponential decay of mean life $\tau_2=(1.8\pm 0.2)\times 10^{-9}$ sec. These values were obtained in the following manner. Taking the value of τ_2 from the slope of the tail and knowing the shape of $P(x)$ the part of the resolution curve due to τ_2 alone was numerically calculated and is shown in Fig. 4 as a broken line; the τ_1 component is obtained by subtraction. The areas under the two separate curves give the relative proportions of positrons annihilating with mean lives τ_1 and τ_2 as (71±5) percent and (29±5) percent, respectively.

This complex time-decay phenomenon is observed in a large number of substances, usually, but not always, amorphous or liquid in structure. Figure 5, for example, gives the curve for a polystyrene sample, which yields the result $\tau_1=(3.7\pm 0.5)\times 10^{-10}$ sec (64±5) percent, and $\tau_2=(2.3\pm 0.2)\times 10^{-9}$ sec, (36±5) percent. Behavior similar to that of polystyrene has been observed in paraffin wax, cellulose nitrate, polyethylene, Teflon [polytetrafluoroethylene, $(CF_2)_n$], water, ice, methyl alcohol, and isopropyl alcohol. Not all of these have been measured in great detail and not all by the present method. Further results on some of them are given later.

The three forms of carbon—diamond, "amorphous" carbon, and graphite—were examined, and results are shown in Fig. 6 for the first two. The diamond was in the form of powder and the amorphous carbon was low temperature sugar charcoal. Each shows only a single mean life, and the graphite result (not shown) was similar. The indicated values of τ for diamond, amorphous carbon, and graphite are, respectively, $(1.3\pm 0.3)\times 10^{-10}$, $(4.3\pm 0.4)\times 10^{-10}$, and $(3.0\pm 0.3)\times 10^{-10}$ second, and are roughly inversely proportional to the densities of the substances. No indication of a longer-lived component is seen on any of the carbon curves. The very weak tail on the right-hand part of

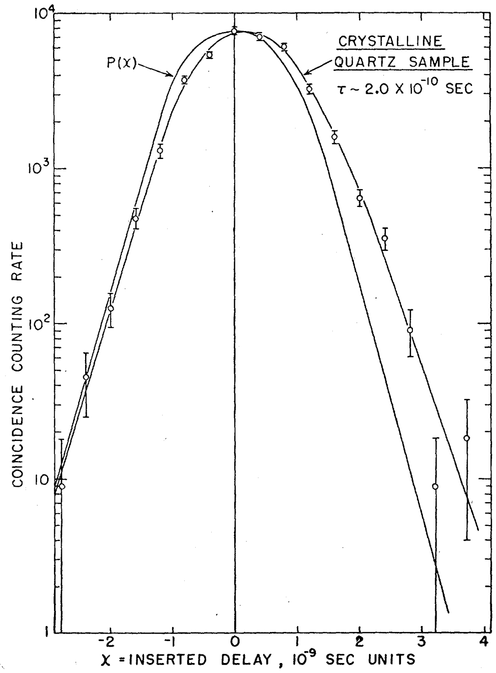

FIG. 3. Coincidence resolution curve obtained with a sample of crystalline α-quartz with a prompt curve $P(x)$ for comparison. Since the prompt curve was always better determined statistically than the delayed curve, the experimental points have been omitted from $P(x)$ here and also in Figs. 4–8. The standard deviations of the points in the delayed curve are shown by vertical bars.

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[8] The α-quartz sample was kindly supplied by Dr. D. G. Hurst.

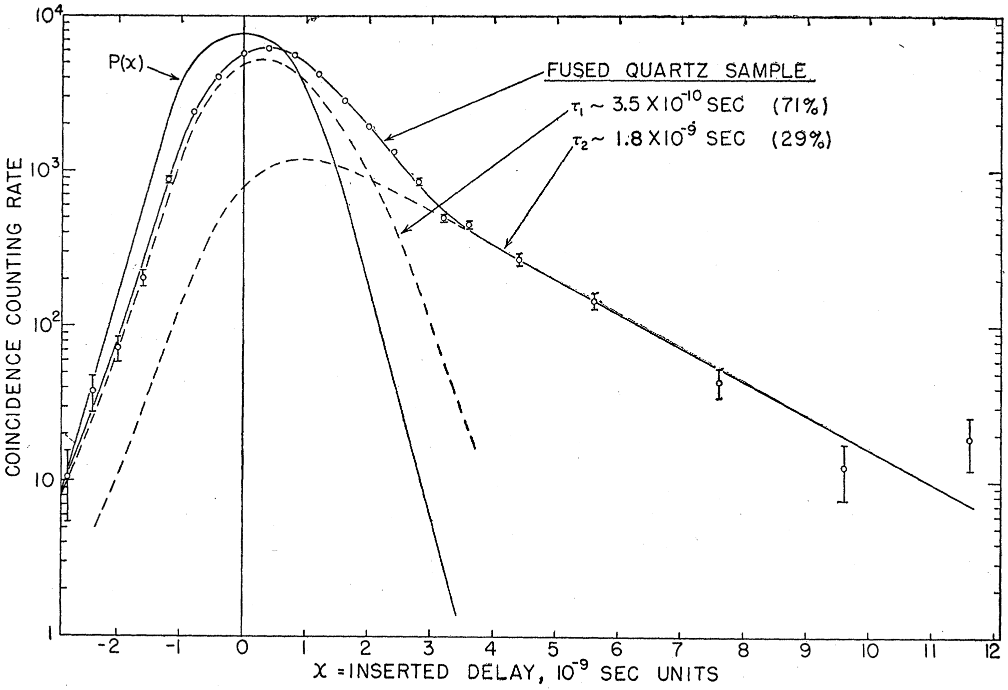

FIG. 4. Coincidence resolution curve obtained with a sample of fused quartz laboratory ware, with a prompt curve $P(x)$ for comparison. The standard deviations are shown by vertical bars.

the curve for diamond can be attributed to the plastic binder used to hold the diamond powder together.

A comparison of monoclinic crystal sulfur with plastic sulfur is shown in Fig. 7. The plastic sulfur was prepared by pouring sulfur heated nearly to its boiling point into cold water. (Plastic sulfur prepared in this way probably contains some sulfur crystals.) It is interesting to see in Fig. 7 that while the crystalline sulfur result is consistent with a single $\tau = 2.1\times10^{-10}$ sec, the plastic sulfur curve is inconsistent with the assumption of any single

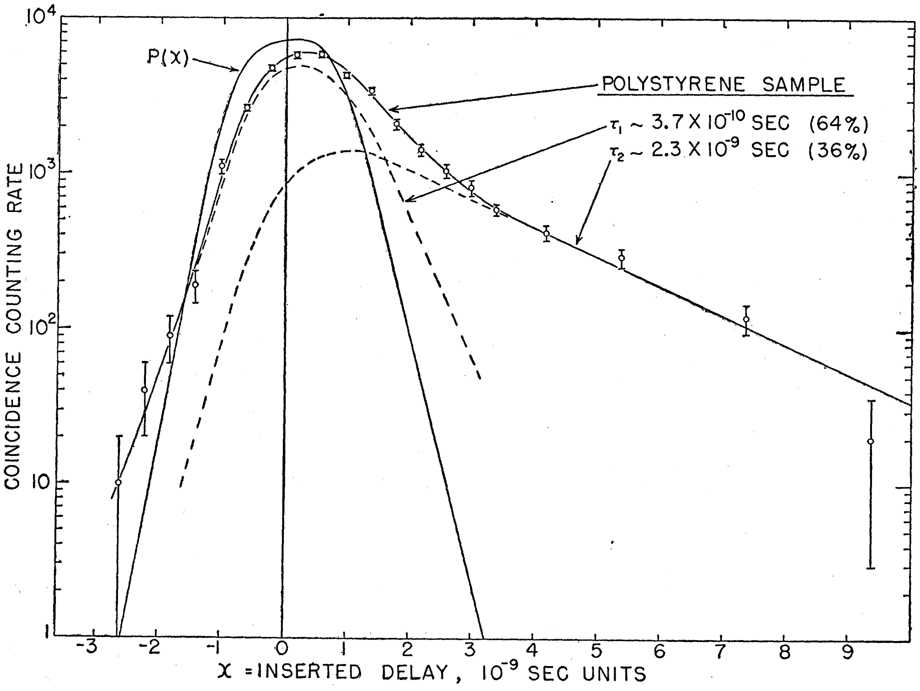

FIG. 5. Coincidence resolution curve obtained with a sample of polystyrene with a prompt curve $P(x)$ for comparison. The standard deviations are shown by vertical bars.

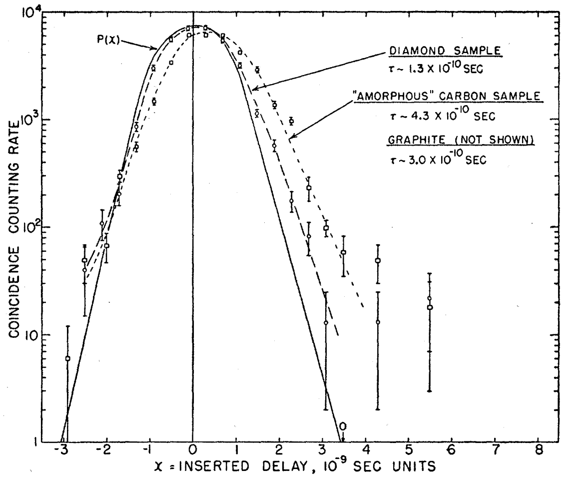

FIG. 6. Coincidence resolution curves obtained with a sample of diamond powder, and a sample of amorphous carbon (low temperature sugar charcoal) together with a prompt curve $P(x)$ for comparison. The standard deviations are shown by vertical bars.

mean life. The curve fails to have its maximum at its intersection with $P(x)$,[9] and the shift of its centroid is inconsistent with the slope of its tail.[1] The plastic sulfur curve could be fitted, as mentioned in Fig. 7, by two components having mean lives $\tau_1 = 1.5 \times 10^{-10}$ sec and $\tau_2 = 4.5 \times 10^{-10}$ sec, the latter decay being at least roughly exponential. These values must be regarded as estimates only, but this observation on the two forms of sulfur is of value as a parallel to the results on the two forms of quartz. Plastic sulfur is the only elementary substance so far tried that shows signs of the longer-lifetime phenomenon.

Figure 8 shows the results for a sample of vitreous $Na_2B_4O_7$ made by melting borax with a glassblowing torch. Here the longer lifetime is clearly present, yielding $\tau_2 = (8.7 \pm 1.2) \times 10^{-10}$ sec, but it is not as long as in the polystyrene and fused quartz cases. The intensity of the τ_2 component, 32 percent, is comparable with that for the previous cases.

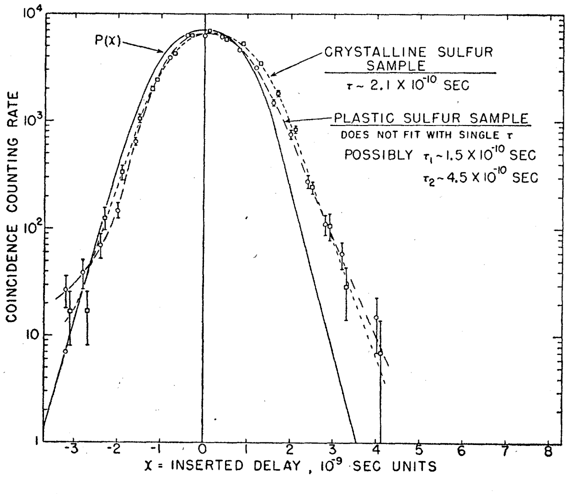

FIG. 7. Coincidence resolution curves obtained with a sample of monoclinic crystal sulfur and a sample of plastic sulfur together with a prompt curve $P(x)$ for comparison. The standard deviations are shown by vertical bars.

A sample of crystalline NaCl gave a result similar in appearance to that for aluminum, the indicated mean life being $(2.3 \pm 0.3) \times 10^{-10}$ sec, with no sign of any longer-lived component.

(b) Factors Influencing the Lifetimes

In order to make the samples more readily accessible, a series of measurements was next made in an arrangement similar to that of De Benedetti and Richings,[6] illustrated in Fig. 9. Here a thin source of Na^{22} sealed between two 2 mg/cm^2 Al foils is sandwiched between layers of the sample material, or immersed in it if it is a liquid. Under these conditions most of the positrons from the source enter the sample material and are stopped there, but a certain fraction of them will be annihilated in the aluminum source envelope. Since this fraction may be expected to vary with the atomic number and density of the sample material, this arrangement is not as suitable for absolute measurements of the intensity of the longer-lived component as the previous one. In addition, it is not convenient in such an arrangement to measure absolute lifetimes, and the result will consist of comparisons of the lifetimes for different substances.

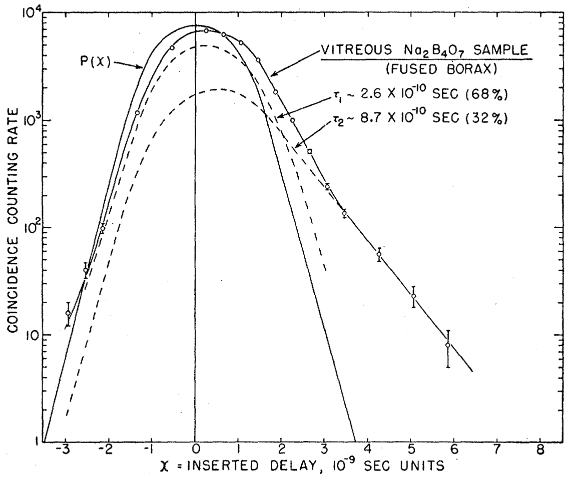

FIG. 8. Coincidence resolution curve obtained with a sample of vitreous $Na_2B_4O_7$ and a prompt curve $P(x)$ for comparison. The standard deviations of the points are shown by vertical bars.

Simple arrangements, not shown in Fig. 9, were made to allow the source and sample assembly to be cooled to dry ice or liquid nitrogen temperature, in order to study the effect of temperature on the phenomena already found.

In Fig. 9, stilbene counter 1 is biased so as to count only the 1.28-Mev nuclear gamma-ray accompanying

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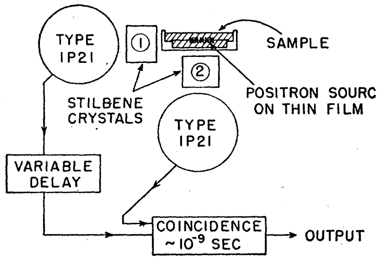
[9] T. D. Newton, Phys. Rev. 78, 490 (1950) and reference 1.

the emission of each positron from the Na^{22} source. Stilbene counter 2 is biased to count annihilation gamma-rays from the sample, and coincidences between counters 1 and 2 can be analyzed for delayed events in the same way as previously, except that now a comparison sample (usually aluminum) must be used in addition to the sample under study.

A series of results for four metals is shown in Fig. 10. The results are all very similar for beryllium, aluminum, copper, and liquid mercury. The latter shows no sign of the long-lifetime effect in spite of the fact that it is a liquid. Small arrows in Fig. 10 mark the centroids of the resolution curves. The centroids shift to the right by about 0.5×10^{-10} sec as we go from mercury to beryllium. This shift is hardly outside the limits of error, but if it is real it would suggest that the mean life of positrons in light metals is very slightly longer than that in heavier metals. The outstanding feature of Fig. 10, however, is the similarity of the four curves, and we summarize the results with metals by saying that the mean life for metals is constant ±25 percent, independent of the metal chosen.

Results with water are shown in Fig. 11. Here we have plotted the curves for water at room temperature, brine (saturated NaCl solution) at room temperature, ice at $-7°C$, and ice at $-196°C$, with an aluminum curve for comparison. One might have expected water and ice to yield results similar to those obtained for fused and crystalline quartz. In fact, however, all the forms of water and ice show the long-lived effect, the value of τ_2 changing from 1.7×10^{-9} sec (water, room temperature) to 1.2×10^{-9} sec (ice, $-7°C$), to 0.85×10^{-9} sec (ice, $-196°C$). The intensity does not seem to be altered much by temperature changes. The brine result, $\tau_2=1.5\times10^{-9}$ sec, shows that any slight impurity of the water used is unlikely to introduce any serious error in the result for water, and is interesting because crystalline NaCl has already been shown not to display the longer lifetime.

FIG. 9. Arrangement of scintillation counters for examining liquid as well as solid samples.



The effect of variation of temperature of a sample of fused quartz is shown in Fig. 12. It may be seen that there is little difference in either lifetime or relative intensity of the longer lived component between 20°C and $-196°C$. In Fig. 13 a similar set of curves is shown for a teflon sample, which has the longest τ_2 at room temperature of any substance so far tested. Teflon shows a marked variation in τ_2 with temperature, the values being $\tau_2=3.5\times10^{-9}$ sec at 20°C, $\tau_2=2.5\times10^{-9}$ sec at $-78°C$ and $\tau_2=1.6\times10^{-9}$ sec at $-196°C$. The intensity of the τ_2 component remains unchanged at about 33 percent throughout these temperature changes. Polystyrene shows a temperature effect intermediate between fused quartz and Teflon; the measurements, not shown in a diagram, give $\tau_2=2.3\times10^{-9}$ sec at 20°C and $\tau_2=1.5\times10^{-9}$ sec at $-196°C$, the intensity again being roughly independent of temperature.

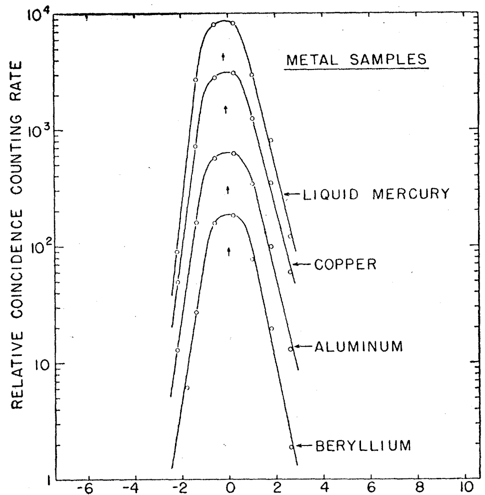


FIG. 10. Coincidence resolution curves obtained with metal samples.

In further experiments using apparatus similar to that of Fig. 9, it was shown that the τ_2 component in Teflon and polystyrene is not markedly affected by the application to the sample of either an electric field of 15 kv/cm or a magnetic field of 3500 gauss.

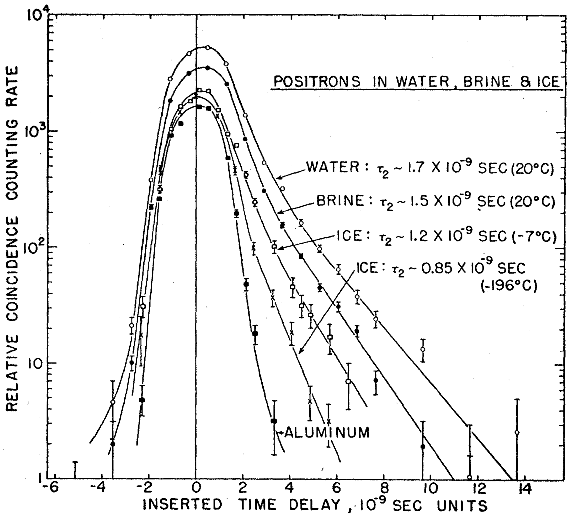


FIG. 11. Coincidence resolution curves obtained with samples of water brine and ice. The standard deviations are shown by vertical bars.

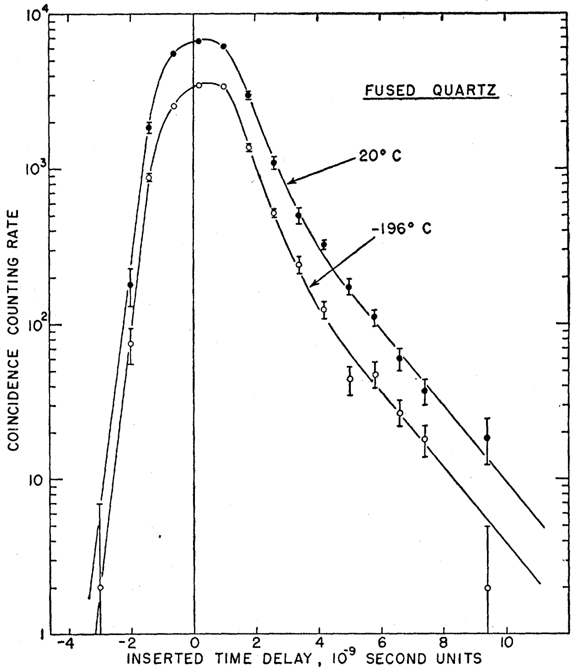


FIG. 12. Comparison of the coincidence resolution curves obtained with a fused quartz sample at two temperatures. The standard deviations are shown by vertical bars.

(c) Properties of the Delayed Annihilation Radiation

An experiment was next performed to compare the spectral distribution and angular distribution of the long-delayed (τ_2) annihilation radiation with those of the more prompt (τ_1) component. The apparatus, shown in Fig. 14, is similar to that of Fig. 9, with the addition of the sodium iodide counter 3, connected to a single-channel pulse-height analyzer whose output is placed in slow coincidence (resolving time = 1 μsec) with the output of the 10^{-9} sec coincidence circuit. As before, stilbene counter 1 detects 1.28-Mev nuclear gamma-rays from the Na^{22} source, and counter 2 detects the annihilation radiation from positrons decaying in the sample material. Now, however, in the interests of higher counting rate, the discriminator bias on counter 1 was lowered, so that it counted more of the 1.28-Mev gammas and hence also annihilation quanta. This meant that counters 1 and 2 were equivalent so far as the fast coincidence circuit was concerned, since annihilation quanta and 1.28-Mev gamma-rays were counted by both and the resulting resolution curves showed the τ_2 component on both sides, when it occurred. The τ_2 component on the right-hand side, however, still corresponded to detection of 1.28-Mev gamma-rays by counter 1 and of annihilation quanta by counter 2, as before. For normal annihilation radiation, in which the two quanta are strongly correlated at 180°, counter 3 will detect a large fraction of the coincident partners of the annihilation quanta whose delay is being measured by counter 2. The apparatus of Fig. 14 allows us to measure the delay of one member of a pair of annihilation quanta detected by counter 2 and the pulse-height spectrum of its coincident partner detected by counter 3. This complex arrangement could be avoided if a phosphor material were available which had both the absorption coefficient and light output of NaI and the speed of the organic phosphors.

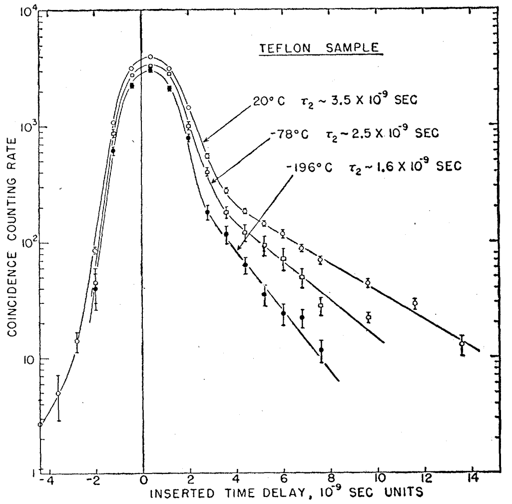


FIG. 13. Comparison of the coincidence resolution curves obtained with a sample of Teflon at three temperatures. The standard deviations of the points are shown by vertical bars.

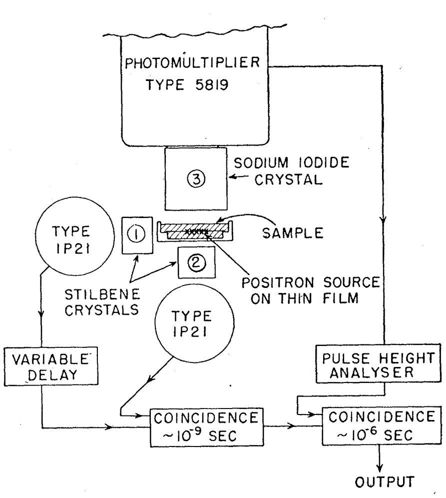


FIG. 14. Arrangement of scintillation counters used to compare the spectral and angular distributions of the long-delayed (τ_2) annihilation with those of the more prompt (τ_1) component.

The results of an experiment with an Al sample are shown in Fig. 15(a) and (b). Here (b) shows the resolution curve observed in the usual way for coincidences between counters 1 and 2. The delay chosen for pulse-height selection is indicated by an arrow in Fig. 15(b), and is near the peak of the aluminum curve. For these conditions Fig. 15(a) shows the total and coincidence pulse height spectra observed in counter 3. The spec-

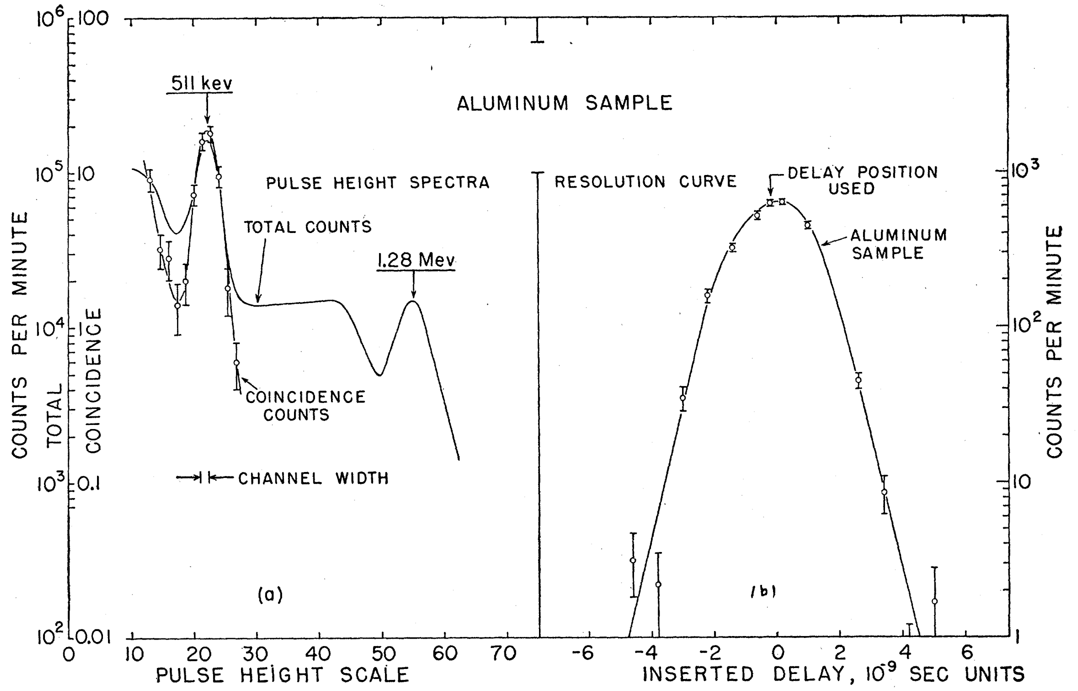


FIG. 15. (a) Comparison of the gross pulse-height spectrum (solid line) obtained in counter 3, Fig. 14, with that (open circles) obtained in coincidence with the prompt decay component using a sample of aluminum. (b) Coincidence resolution curve obtained with counters 1 and 2 Fig. 14. Standard deviations are shown by vertical bars.

trum of total counts shows peaks at 1.28 Mev and 0.511 Mev, while the coincidence spectrum shows only the peak at 0.511 Mev, as expected.

The results for polystyrene are shown in Fig. 16(a) and (b). Here (b) shows the resolution curve for the polystyrene sample, with the previously observed

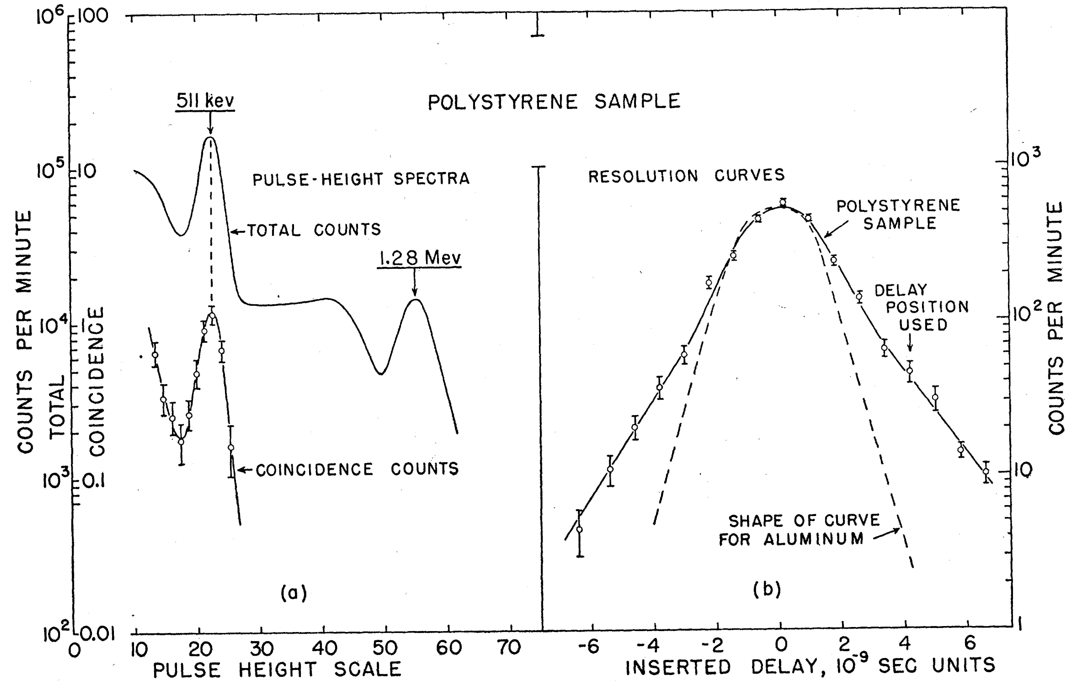


FIG. 16. (a) Comparison of the gross pulse-height spectrum in counter 3, Fig. 14, with that part of it which coincides with the longer lived (τ_2) component using a sample of polystyrene. (b) Coincidence resolution curve obtained with counters 1 and 2, Fig. 14. Standard deviations are shown by vertical bars.

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 (reference 6) and the absolute lifetime in Al obtained here.

aluminum curve for comparison. At the selected delay position shown in Fig. 16(b), the coincidence counting rate is down by a factor of 15 from its peak value, and the coincidences are at least 95 percent due to the τ_2 component in polystyrene. The corresponding pulse-height spectra in counter 3 are shown in Fig. 16(a). The coincidence spectrum again shows the clean peak at 0.511 Mev, with an intensity lower than that in the aluminum case, Fig. 15(a), by a factor of 15. The yield of triple coincidences per recorded double coincidence is therefore equal for the aluminum and polystyrene samples.

We conclude from these results that the long-delayed (τ_2) annihilation quanta have an energy equal to that of the more prompt (τ_1) annihilation quanta, to an accuracy estimated at ±3 percent, and that the long-delayed (τ_2) component consists mainly of pairs of quanta strongly correlated at 180°; the angular resolution with which this observation was made was about ±20°. There is therefore no evidence from this experiment that the long-delayed component of the annihilation radiation differs from the more prompt component in anything but mean life.

III. DISCUSSION

A summary of the lifetime measurements of positrons in various materials is presented in Table I. Where the simple experimental arrangement of Fig. 9 was used and the resolution curve was found to be complex, only the longer τ_2 mean life is reported; estimates of the relative intensities of the two components and hence of τ_1 are unreliable as remarked above. In all such cases, however, the intensity of the τ_2 component is consistent with the figure of ~30 percent found in the double spectrometer experiments. Absolute lifetimes of positrons in five metals not tried here are deduced from the comparison measurements of DeBenedetti and Richings[6] and the absolute lifetime of Al found here.

Two main sets of experimental facts have appeared in this study:

(i) The mean life of positrons in a metal is, within ±25 percent, independent of the metal chosen, and is near 1.5×10^{-10} sec.

(ii) Some substances, usually, but not always, liquid or amorphous, show a longer-lived component whose mean life τ_2 can be as long as 3.5×10^{-9} sec, and whose relative intensity is always about $\frac{1}{3}$, in addition to a shorter-lived component having a mean life τ_1 equal to a few times 10^{-10} sec and an intensity about $\frac{2}{3}$. The value of τ_2 varies from substance to substance over wide limits, and it is possible that all substances including the metals would show the double lifetime effect if the time resolution of the apparatus were sufficiently good. In most cases the value of τ_2, but not the intensity of the τ_2 component, is reduced by lowering the temperature of the sample. Moderate electric and magnetic fields do not seem to have a detectable effect. The annihilation radiation emitted with the longer delay is similar in energy and angular distribution to the more prompt component.

In order to try to explain result (i) we may attempt to predict the mean life of positrons in a metal from the Dirac cross section[10] for the annihilation of slow positrons by a free electron,

$$\sigma = \pi r_0^2 c/v, \tag{1}$$

where r_0 is the classical electron radius and v is the velocity of the positron relative to the electron. The mean life of slow positrons in a medium of free electron density D is given by

$$\tau = [\pi r_0^2 cD]^{-1}. \tag{2}$$

The total electron density of a material of mass density ρ, atomic number Z, and mass number A is

$$D_e = (N_0 \rho Z/A) \text{ cm}^{-3}, \tag{3}$$

where N_0 is Avogadro's number. Thus if all the electrons in a substance are regarded as free, the predicted mean life for positrons in it is

$$\tau = [\pi r_0^2 c\rho N_0 Z/A]^{-1} = 2.2\times 10^{-10}(A/\rho Z) \text{ sec.} \tag{4}$$

The results of DeBenedetti *et al.*[11] on the angular correlation suggest that only valence electrons or conduction electrons take part appreciably in the annihilation process. In that case, instead of Z, the effective number of electrons per atom is N_e, a number lying perhaps between 1 and 4, depending on the valence of the atom. Equation (4) now becomes

$$\tau = 2.2\times 10^{-10}(A/\rho N_e) \text{ sec.} \tag{5}$$

Taking N_e for Al as 3, for example, we get

$$\tau_{\text{Al}}(\text{calc}) = 7.5\times 10^{-10} \text{ sec,} \tag{6}$$

a value five times greater than the observed one. If N_e is taken to be less than 3, the magnitude of the disagreement is increased. The fact that all the metals tried showed the same value of τ within ± 25 percent, means that on the above analysis $A/\rho N_e$ should be constant to the same degree. If we take N_e as the number per atom of electrons having binding energy less than, say, 15 ev, the quantity $A/\rho N_e$ varies widely for different metals, being 2.44 for Be and 23.7 for Na, for example. The above simple analysis therefore is unable to account for either the shortness of the mean life in metals, or its constancy from metal to metal.

It now appears that the present picture of the slowing down and annihilation of positrons in metals is in need of revision. Positrons were formerly supposed to slow down to thermal energies and spend some time diffusing through the metal before being annihilated.[11] The mean time for slowing down has been calculated by DeBenedetti *et al.*[11] as 3×10^{-10} sec for metallic gold. Both the fact that the total mean life of fast positrons in gold is only about 1.2×10^{-10} sec, and the fact of the nonappearance of thermal positrons in the experiment of Madansky and Rasetti[12] suggest that most of the positrons are annihilated in a metal before they have slowed down to thermal energies. It seems likely that fast positrons in a metal slow down rapidly to energies of a few ev, where they have a high probability of forming singlet positronium, whose mean life is 1.25 $\times 10^{-10}$ sec.[13] In support of this idea, no sample has shown an experimental mean life shorter than 1.25 $\times 10^{-10}$ sec within experimental error.

Turning to result (ii), the appearance of two distinct mean lives in some substances means not only that two different annihilation processes are present, but also that these two processes are mutually exclusive. Positrons decaying with the longer mean life are somehow prevented from participating in the faster process. The effect is reminiscent of that observed by Deutsch *et al.*,[3] in which a fraction of the positrons absorbed in a gas forms triplet positronium decaying with a mean life of 1.5×10^{-7} sec (extrapolated to zero gas pressure). This fraction has been measured by Pond[14] for various gases, the result varying with the gas from 0.11 (N_2) to 0.19 (H_2) in the presence of a magnetic field. Using the dependence upon magnetic field found by Pond and Dicke,[15] we find that the fraction to be expected with zero magnetic field is from 0.16 (N_2) to 0.26 (H_2), which is slightly less than the intensity of the longer lived component found here. Deutsch[16] found that in freon 12 (CCl_2F_2) the mean life of triplet positronium could be represented by

$$\tau = (6.8\times 10^6 + 0.3\times 10^6 p)^{-1} \text{ sec,} \tag{7}$$

where p is the gas pressure in atmospheres, and the second term of (7) represents a shortening of the mean life due to collisions with gas atoms. If we now regard one of our amorphous condensed materials as equivalent to a gas at, say, 1000 atmospheres, the value of τ deduced from (7) is

$$\tau \sim 3\times 10^{-9} \text{ sec,} \tag{8}$$

agreeing in order of magnitude with the values found for τ_2.

A possible explanation of the τ_2 component found in the experiments is then as follows: Positrons slowing down in the sample form triplet positronium in some

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[10] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, London, 1944), p. 208.

[11] DeBenedetti, Cowan, Konneker, and Primakoff, Phys. Rev. **77**, 205 (1950).

[12] L. Madansky and F. Rasetti, Phys. Rev. **79**, 397 (1950).

[13] A. Ore and J. L. Powell, Phys. Rev. **75**, 1696 (1949).

[14] T. A. Pond, Phys. Rev. **85**, 489 (1952).

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

[16] M. Deutsch, Phys. Rev. **83**, 866 (1951).

fraction of the cases, according to our results about $\frac{1}{3}$. This triplet positronium is destroyed mainly by conversion to the short-lived singlet state[13] ($\tau = 1.25\times10^{-10}$ sec) in collisions with atoms of the sample material. The triplet positronium thus has its own lifetime shortened, as suggested by (7) and (8), by a factor of 50 or more. On this view, less than 2 percent of the τ_2 component observed in the experiments would consist of three-photon annihilations, a fraction which would have escaped detection in any of the experiments reported here. The absence of an observable τ_2 component in metals and some crystals might then be explained by assuming that electrons in energy bands determined by the crystal structure are effectively free so far as positrons or positronium are concerned. These electrons would rapidly convert the triplet positronium to the singlet state by collision, in much the same way that the odd electron in NO destroys triplet positronium in a gas.[14,16]

This explanation is not free of objections. In the first place if the magnitude of τ_2 is determined mainly by "gas collisions," it might be expected to increase as the temperature is reduced, whereas the opposite is observed. Secondly, the intensity of the τ_2 component formed here, $\sim\frac{1}{3}$, is somewhat greater and more constant than the values measured for the formation of triplet positronium in gases.[14,16] On the other hand, the above picture is consistent with the independence in the observed effect of moderate fields. Certainly the rate of conversion of triplet positronium to singlet positronium due to the magnetic fields used here is expected[14,15] to be much less than that previously estimated due to collisions.

Some light may be thrown on the temperature variation of τ_2 by noting that in all the samples a connection seems to exist between regularity of structure and shortness of τ_2. Generally speaking, lowering the temperature of a substance tends to make its structure more regular. The observations presented on the various forms of water, Fig. 11, show that τ_2 shortens with increase of regularity of structure. Ice is not completely regular,[17] being "crystalline only in the position of its molecule . . . glass-like in their orientation,"[18] but is more so than water. Brine is also more regular than water because the presence of small ions in solution increases the regularity of the water solvent.[18] Ice at a low temperature may be expected to be more regular than ice near room temperature. There is a suggestion in these remarks that experiments of the kind reported here might form a useful tool in the experimental study of the solid and liquid state. Before this is possible, however, the interpretation of the effects observed must be placed on firmer ground.

If the analysis given here is substantially correct, a sample showing a long τ_2 would yield substantially more three-quantum events than one not showing an appreciable τ_2. Thus, in an experiment designed to detect the three-quantum effect, such as those reported by Rich[19] or DeBenedetti and Siegel,[20] the replacing of a metal sample by a Teflon sample would give a large increase in the three-quantum counting rate. An experiment of this kind is now being planned in this laboratory.

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[17] Wollan, Davidson, and Shull, Phys. Rev. **75**, 1348 (1949).
[18] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).
[19] J. A. Rich, Phys. Rev. **81**, 140 (1951).
[20] S. DeBenedetti and R. Siegel, Phys. Rev. **85**, 371 (1952).