the atomic volume would be smaller, whereas at high temperature it would be higher, and the two situations are therefore different.

The phase diagrams (see La to Gd) reflect the relative stability of the hcp, Sm-type, dhcp, and fcc phases under pressure. The stability field of the bcc phase progressively increases from La upwards in the series, with the exception of Ce, for which this field is closed at relatively low pressure. As one moves from La to Gd the crystalline phases step in into the P-T field in the order fcc → dhcp → Sm-type → hcp; pressure of course favors the reverse order. It appears that to get all the possible phases of the sequence for a hcp R.E. metal one has to push higher in pressure. Thus in Gd all four may be expected. McWhan and Stevens's[17] magnetic work on Gd would seem to indicate the appearance of another phase above 50 kbar, which might be the dhcp phase.

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Three-Quantum Annihilation of Positrons in Metals and Insulators

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The three-quantum decay of positrons annihilating in some metals and in some insulators was investigated by using a triple coincidence method. Relative measurements were made by comparing the three-quantum yield in each substance with that of aluminum. Small differences between the three-quantum yields of various metals were found: in Pb, where this effect appears to be the largest, the relative yield is $P/P_0 = 1.16 \pm 0.03$. At present any simple attempt to explain this result is unsuccessful. From the relative three-quantum rates measured in insulators, and on the basis of a simple model, the following information was obtained: The contribution to three-quantum production in insulators due to the positronium atom arises only from the orthostate decaying with a partial lifetime τ_3 equal to that in free space ($\tau_3 = 1.39 \times 10^{-7}$ sec). No evidence was found of three-quantum production arising from interaction of the positronium with matter. The remaining three-quantum annihilations occur with the same yield characteristic of positrons in Al ($P_f/P_0 = 1.00 \pm 0.05$). From the same measurements in insulators, the yield in Al is $P_0 = (2.64 \pm 0.08) 10^{-3}$, in good agreement with the value predicted by Ore and Powell (2.70×10^{-3}).

I. INTRODUCTION

THE time spectrum of the annihilation radiation of positrons in metals is known to be simple according to the results of most of the investigations carried out. In a few cases, however, the decay curve appears to be complex with about 5% of the events having a mean life approximately 5×10^{-10} sec.[1,2,3,4] Weisberg[4] has recently pointed out that the "tail" intensity can depend on sample-preparation techniques, i.e., that at least part of it can arise from annihilation in the source or in impure surface layers of the metal. Any attempt to explain the existence of such a tail meets serious difficulties owing to the fact that the electron-positron system in a metal possesses no "bound state" analogous to positronium, as recently shown by Held and Kahana.[5]

In some solid insulators the time spectrum of the annihilation radiation of positrons is known to be complex, as was shown for the first time by Bell and Graham.[6] The experiments show that at least two distinct components are present with lifetimes of a few times 10^{-10} sec (τ_1) and a few times 10^{-9} sec (τ_2). To the prompt mode of decay there certainly contribute: (1) those positrons which, having survived the slowing-down process, miss the ore gap and annihilate in the free state with emission of two or three quanta; (2) those positrons which have become bound to an electron in parapositronium (this is one-third of the τ_2 percentage). The τ_2 component is due to the formation and decay of orthopositronium. It should be remembered that in parapositronium the positron annihilates with its own electron into two quanta with a mean life of 1.25×10^{-10} sec; this process is forbidden in orthopositronium, which in free space decays only with emission of three quanta ($\tau_3 = 1.39 \times 10^{-7}$ sec). In matter, however, another process prevails over the three-quantum decay, i.e., the annihilation of the positron with an electron of the surrounding molecules, whose spin state relative to it is a singlet ("pick-off" annihilation).

The relative yield of three-quantum events from positrons annihilating when free is equal to 1/372

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according to Ore and Powell[7]; the relative yield from the annihilation of orthopositronium is equal to the ratio between the decay rate λ_3 of a triplet state in free space and the total decay rate λ_t of the same state when it annihilates in matter. The value of the ratio λ_3/λ_t depends on the specimen and is of the order of 10^{-2}.

It follows that a sample showing a long-lived component will yield substantially more three-quantum annihilations than one not showing an appreciable τ_2. This effect has been shown for the first time by Graham and Stewart[8] using a triple-coincidence method similar to one used earlier by De Benedetti and Siegel[9] and by Pound,[10] who detected the three-quantum annihilations by measuring the small defect in the two-quantum annihilation rate as compared with that of a metal. The statistically most significant measurement of the ratio of the three- to the two-quantum yield was reported by Basson[11] for annihilation in aluminum. His result is consistent with the value 1/371 which was predicted for free positrons annihilating with electrons of random spin direction.

This paper reports the results of an extensive investigation on three-quantum decay of positrons in those metals and insulators for which we have obtained the time annihilation spectra.[12,13] The aim of the experiment was (1) to check whether the three-quantum yield in metals is the same for all metals and is equal to 1/372, as would be expected for annihilation with free electrons; (2) to compare the observed three-quantum yield for various insulators with a simple model which can account for the annihilation in those specimens where positronium formation occurs.

II. EXPERIMENTAL PROCEDURE

The experimental setup used in the present investigation followed conventional lines.[8,14] Three NaI(Tl) scintillation spectrometers were symmetrically located in the same plane as the source; in fact, the total momentum of the quanta being nearly zero, the three photons must be coplanar. The scintillators, each 2 in. thick and $1\frac{3}{4}$ in. in diameter, were shielded by conical lead collimators in order to reduce the spurious coincidences. The three counters were placed at a distance of 10 cm from the source and covered a solid angle of 0.14 sr. The output pulses from the photomultipliers were sent into a triple coincidence circuit having a resolving time equal to 1.7×10^{-8} sec; this coincidence circuit was operated only by the pulses in the energy region 280–410 keV. This energy selection is a consequence of our angular arrangement, which requires the detection of three quanta having nearly the same energy (i.e. $\frac{2}{3}$ mc^2). The details of the measuring apparatus are reported elsewhere.[15]

TABLE I. Experimental data on three-quantum relative yield P/P_0 with respect to Al. R is the ratio between the triple coincidence rates in metals and in Al.

Z	Metal	R	P/P_0
4	Be	0.94±0.04	0.94±0.04
23	V	1.01±0.03	1.01±0.03
26	Fe	0.98±0.03	0.97±0.03
28	Ni	1.14±0.03	1.15±0.03
29	Cu	0.98±0.04	0.97±0.04
30	Zn	1.04±0.03	1.04±0.03
42	Mo	1.05±0.03	1.05±0.03
46	Pd	0.99±0.04	0.98±0.04
47	Ag	1.13±0.02	1.13±0.02
48	Cd	1.10±0.04	1.10±0.04
74	W	1.02±0.03	1.00±0.03
77	Ir	1.06±0.04	1.05±0.04
78	Pt	1.16±0.04	1.16±0.04
79	Au	1.04±0.03	1.04±0.03
82	Pb	1.16±0.03	1.16±0.03

The source of positrons consisted of about 40 microcuries of Na^{22} deposited from a carrier-free solution into a thin Moplefan (polypropylene) foil (1.2 mg/cm^2); the active deposit was 2 mm in diameter. The deposit was covered with an identical foil, then sealed, and the whole source assembly was sandwiched between the targets in which the positrons were to annihilate.

The true triple counting rate when positrons annihilated in Al was equal to 2.40 per minute, while the spurious coincidences were 0.2 per minute only. For the measurement of the spurious coincidences, one of the counters was removed from the plane defined by the source and by the other two, without altering its distance from the source.

The three-quantum yield was obtained by means of relative measurements, i.e., by comparing the triple coincidence rate of positrons annihilating in the specimen under investigation with that in aluminum. In order to minimize any spurious effect due to absorption and scattering of the γ rays, all the targets had the same thickness (200 mg/cm^2, which is sufficient to stop all beta particles) and the same size; further, the sealed source of positrons was put in a composite sandwich of four targets, two of which, i.e., those of Al, operated as standard targets. The measurements consisted of several counting runs taken alternately with the sandwich arranged with the specimen under investigation inside and Al outside, and conversely.

In order to obtain the ratio between the three-quantum annihilation probability P in the specimen under investigation and the same probability P_0 in Al, the measured counting rates (after background subtraction) must be corrected because some annihilation

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TABLE II. Experimental data on positron annihilation in insulators. R is the ratio between the triple coincidence rates in insulators and in Al; P/P_0 is the relative yield of three quantum events in insulators with respect to Al. The second and third columns contain lifetime (τ_2) and abundance (I_2) of orthopositronium. For the explanation of the last column, see Eq. (3).

Sample	$\tau_2\times10^9$ sec	$I_2(\%)$	R	P/P_0	$P/P_0-372I_2\tau_2/\tau_3$
Polyethylene	2.04±0.06	29.5±0.4	2.06±0.09	2.17	0.56±0.11
Teflon	3.22±0.07	21.6±0.7	2.62±0.13	2.79	0.93±0.14
Lucite	1.55±0.01	27.9±1.8	1.81±0.16	1.90	0.74±0.17
Polyvinyl chloride	1.25±0.03	9.5±0.7	1.07±0.02	1.08	0.76±0.07
Nylon	1.39±0.04	22.2±1.0	1.50±0.10	1.56	0.74±0.11
Cellulose acetate	1.85±0.02	24.2±0.9	1.64±0.12	1.71	0.51±0.12
Polyvinyltoluene	1.78±0.05	35.8±0.5	1.97±0.09	2.07	0.37±0.11
Polystyrene	1.60±0.01	45.2±0.1	2.32±0.14	2.46	0.53±0.14
Anthracene	1.16±0.08	6.8±1.2	1.26±0.09	1.29	1.08±0.10
Naphthalene	0.93±0.03	19.1±1.1	1.18±0.09	1.21	0.73±0.09
Acenaphthene	0.84±0.01	23.4±0.5	1.11±0.07	1.13	0.60±0.07
Phenantrene	0.94±0.06	8.5±0.2	0.97±0.08	0.97	0.75±0.08
Crysene	1.50±0.02	4.3±0.2	1.21±0.10	1.23	1.06±0.10
Pyrene	1.25±0.05	1.9±0.1	1.06±0.09	1.07	1.01±0.09
Mica			1.03±0.09	1.04	
Maleic acid			1.02±0.08	1.03	

events occur in the Moplefan foils which support the active deposit.

We now estimate the correction for this effect as follows. The ratio R between the measured counting rates in the specimen and in Al is given by the following equation

$$R=(kP_1+(1-k)P)/(k_0P_1+(1-k_0)P_0) \qquad (1)$$

where P_1 is the fraction of the three-quantum events occurring in Moplefan; k and k_0 are the fractions of positrons annihilating in Moplefan when the sandwich is arranged with the specimen inside and Al outside and when it is arranged with Al inside and the specimen outside, respectively. Contributions to the value of k (and similarly to k_0) are made by: (a) the fraction f of those positrons which are stopped in the Moplefan foil and (b) the fraction of the transmitted positrons which, having suffered a backscattering process from the targets, pass through two Moplefan foils and are absorbed. Then we can write

$$k=f+(1-f)\times b\times 2f$$

where b is the backscattering coefficient. We use for b the experimental relation

$$b=0.0593\sqrt{Z}$$

given by Bisi and Braicovich.[16] The fraction f was obtained by measuring the transmission curve in a conventional way; the curve has a nearly linear trend within the range of thickness to which we are interested. By assembling all data, it results that the k value never exceeds 5×10^{-2} and k_0 is equal to 5.6×10^{-2}.

We are now able to deduce from Eq. (1) the relative yield P/P_0, if we assume for P_1/P_0 the value which can be predicted according to the scheme described in the following section. This procedure is certainly correct owing to the fact that P/P_0 turns out to differ from R by only a few percent.

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III. RESULTS AND DISCUSSION

A. Metals

In Table I we report the measured ratios R, together with the corrected values of P/P_0. As can be seen, most metals show three-quantum yields differing from that in aluminum by not more than one standard deviation. In five cases, however, (Ni, Ag, Cd, Pt, Pb) the deviations of the P/P_0 values from unity appear to be too large to be imputable to experimental errors. In these cases the three-quantum relative yield attains values which are exhibited by some insulators (see Table II, for instance, naphthalene) where positronium formation occurs in appreciable amounts. The time annihilation spectra, however, do not give any evidence at all for a complex decay similar to that in insulators. At present we have no arguments to explain this anomalous behavior, because in our case a high three-quantum production should be associated with a short lifetime, in contrast with the usual behavior.

B. Insulators

In Table II we report the measured ratios R together with the data on positronium decay useful for our discussion (abundance I_2 and mean life τ_2), for various insulators which, for convenience, we classify into two groups. The first group contains a set of polymeric materials in which time annihilation spectra were measured by some of us[13] a few years ago. During the present research, we have reexamined the time spectra of positrons annihilating in the same specimens used for three-quantum measurements. The new data are in strict agreement with the previous ones, with the exception of those for Teflon, for which a specimen obtained from a different manufacturer was used.

The second group contains almost exclusively materials which were analyzed for the first time in the present research in order to obtain positronium abund-

ance and lifetime. Multicrystalline analytical-reagent-grade chemicals were used in all these cases.

We wish now to examine the simplest possible model of positron decay in order to establish if it can account for the whole set of experimental information. To this end we make the following assumptions: (a) The three-quantum production in orthopositronium arises solely from annihilation of the positron with its bound electron and occurs with a probability equal to τ_2/τ_3. It should be remembered that τ_3 is the lifetime of orthopositronium in free space and that τ_2 is the total lifetime of orthopositronium in matter as results directly from time spectra. (b) The nonpositronium part of annihilation is attributable to positrons which all have the same fate and which behave as if free: their three-quantum annihilation probability is P_f. (c) The parapositronium does not contribute to three-quantum events through any interaction with matter. (d) All the positrons in aluminum have the same fate and behave as if free; their three-quantum annihilation probability is P_0.

We have then

$$P/P_0=(1-\tfrac{4}{3}I_2)(P_f/P_0)+(I_2/P_0)(\tau_2/\tau_3). \quad (2)$$

For a first insight, we can put into the right-hand side of Eq. (2) the values $P_f/P_0=1$ and $P_0=1/372$, and have

$$(P/P_0)-372I_2(\tau_2/\tau_3)=1-\tfrac{4}{3}I_2. \quad (3)$$

We are thus able to display the experimental data in a graph by plotting the experimental value of the left-hand side (i.e., the three-quantum relative yield of the nonpositronium part of the annihilations) as a function of the abundance I_2. These values are also reported in the last column of Table II; their quoted errors are evaluated on the basis of the errors which affect R, I_2, and τ_2. If our model describes correctly the three-quantum production, the points must fit a straight line having a slope equal to $-\frac{4}{3}$ and an intercept on the y axis equal to 1. This straight line is traced in Fig. 1; as can be seen, the maximum deviation of the points from the straight line is equal to two standard deviations and this occurs only in one case.

For a better insight we can put into the right-hand side of Eq. (2) the value $P_0=1/(372K)$ and consider K and P_f/P_0 as unknown; from a least-squares adjustment we obtain:

$$K=1.02\pm0.03, \quad \text{i.e.} \quad P_0=(2.64\pm0.08)\times10^{-3};$$
$$P_f/P_0=1.00\pm0.05.$$

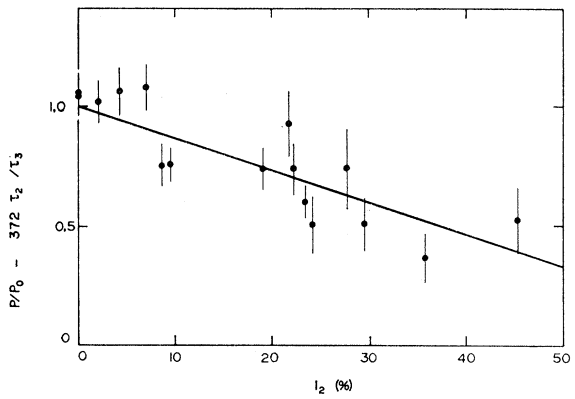

FIG. 1. Three-quantum relative yield of the nonpositronium part of the annihilations in insulators as a function of the abundance I_2 of the positronium.

From the preceding results we can now draw the following conclusions regarding the prominent features of the three-quantum decay of positrons in insulators: (a) The three-quantum annihilation of orthopositronium is described correctly by attributing to it a partial lifetime τ_3 equal to that in free space; (b) No evidence appears to exist for any interaction between a positronium atom and matter leading to an appreciable three-quantum production; (c) The positrons not forming positronium are as effective in producing three quanta as those annihilating in Al.

In addition, the three-quantum relative yield of positrons in Al turns out to be in very good agreement with what can be expected from theoretical predictions on the assumption of annihilation with free electrons.

In conclusion, we wish to mention that quite recently it has been found that the time spectra of positron annihilation in some plastics contain a third component whose lifetime is intermediate between τ_1 and τ_2.[17,18] If this component is present in the time spectra of positrons annihilating in the specimens used by us, and was not detectable because of insufficient resolution, we must conclude that a three-quantum production nearly the same as that due to free positrons will be associated with this component.

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