

Nature of Positron Annihilation in Liquids and Solids

W. R. DIXON* AND L. E. H. TRAINOR

Department of Physics, Queen's University, Kingston, Ontario, Canada

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An interpretation of the experimental results on positrons stopping in liquid and solid media is presented in terms of annihilation from excited states of positronium. It is assumed on an empirical basis that the $2S$ states of positronium have sufficient stability in certain materials for direct annihilation.

I. INTRODUCTION

AN experimental study of two-quantum annihilation of positrons in liquid and solid materials has been reported by Bell and Graham.¹ In metals, they observed a single lifetime $\tau_1 \cong 1.5 \times 10^{-10}$ sec, roughly independent of the particular metal employed. In some insulating materials (usually with crystalline structure), the results were the same as for metals, while in others (usually liquids and amorphous solids) 70 percent of the annihilations occurred with a short lifetime τ_1 and 30 percent occurred with a lifetime τ_2 which was five to ten times longer, depending on the material used. Moreover, the lifetime τ_2 was observed to increase with temperature in some nonmetals. Bell and Graham offered an explanation of the τ_2 component in terms of the conversion rate of triplet to singlet positronium. As they have pointed out, this explanation is not entirely free from objections. The purpose of the present paper is to offer a possible explanation of the τ_2 component in terms of annihilation from excited states of positronium.

There is evidence for the formation of positronium in both metals and nonmetals. This seems to be the most reasonable interpretation of the observation of Madansky and Rasetti² that no thermal positrons diffuse from metallic and nonmetallic surfaces surrounding a positron source. Indirect evidence that positronium is formed in metals, as Bell and Graham have pointed out, is the independence of τ_1 on the metal used, and hence the independence of τ_1 on the electron density. In nonmetals, the occurrence of the two components τ_1 and τ_2 , is difficult to explain unless some positronium is formed. It should be noted that if positronium has a stable binding in solid media, then its formation is a highly nonequilibrium process. Once the positronium atom is formed it has a high probability of persisting until annihilation takes place, since the ionization energy required to free the positron is not readily available.

The discussion of the Bell and Graham experiment below is based on the assumption that the rate of formation of positronium in condensed matter is considerably faster than the rate of annihilation of free positrons. The conversion interpretation then leads to

serious difficulties with the magnitude of the τ_1 lifetime and with the intensity ratio of the two components.

The difficulty with the τ_1 lifetime arises as follows. In nonmetals where the conversion rate has been assumed slow, the observed lifetime τ_1 should correspond to the lifetime $\tau(1^1S)$ for two-quantum annihilation from the singlet state of positronium. However, in metals where the conversion rate has been assumed rapid, τ_1 ought to be *four* times the lifetime $\tau(1^1S)$, as pointed out by Garwin.³ Since the observed lifetime in metals is $\lesssim 1.5 \times 10^{-10}$ sec, it follows on this basis that in metals $\tau(1^1S) \lesssim 0.4 \times 10^{-10}$ sec, in serious disagreement with the theoretical value of 1.25×10^{-10} sec for free positronium⁴ and with the observed values of 2.5 to 3.5×10^{-10} sec for those nonmetals exhibiting a τ_2 component. Such a serious disagreement seems unlikely. If one abandons the explanation of the τ_2 component in terms of the conversion rate, one can either suppose that the conversion rate is slow ($\lesssim 10^8$ /sec) in all materials, or that it is rapid in all materials ($> 10^{10}$ /sec). In the former case the disagreement among lifetimes disappears; in the latter case the theoretical lifetime must be modified by a factor of 2 to 3 in all materials.

The other serious difficulty with the conversion interpretation arises when one attempts to account for the observed intensity ratio. An elementary analysis of this problem is given in the Appendix. From Table I it is seen that no choice of the conversion rate gives a satisfactory interpretation both of the two lifetimes and of their relative intensities. More generally, the observed constancy of the intensity ratio I_1/I_2 despite large variations in τ_2 is not consistent with the conversion interpretation. Again this is illustrated by reference to Table I.

These difficulties could be circumvented if the τ_1 component could be largely accounted for by the annihilation of free positrons in flight, although this seems unlikely. The τ_2 component might then be attributed either to triplet-singlet conversion or, as suggested by Garwin,³ to the annihilation of positrons in collisions between triplet positronium and electrons of appropriate spin on neighboring molecules. One still

* On leave of absence from the National Research Council of Canada, Ottawa, Canada.

¹ R. E. Bell and R. L. Graham, *Phys. Rev.* **90**, 644 (1953).

² L. Madansky and F. Rasetti, *Phys. Rev.* **79**, 397 (1950).

³ R. L. Garwin, *Phys. Rev.* **91**, 1571 (1953).

⁴ J. Pirenne, *Arch. Sci. phys. et nat.* **28**, 273 (1946) and **29**, 121 (1947).

would not seem to have a satisfactory explanation of the temperature effect.

A possible explanation of the Bell and Graham results, in which free positrons do not play a dominant role, is presented in Sec. II.

II. ANNIHILATION FROM EXCITED STATES OF POSITRONIUM

The constancy of the intensity ratio I_1/I_2 despite large variations in τ_2 among nonmetals suggests that in order to explain the τ_2 component, one requires a mechanism of formation (of the state decaying with lifetime τ_2) which is relatively insensitive to environment, even though the lifetime τ_2 itself is sensitive to environment. Such a possibility exists in terms of the annihilation from excited states of the positronium atom, a process which was considered by Ore and Powell⁵ for positrons in gaseous media, but which seems to have been ignored or considered unlikely in liquids and solids. It was pointed out by Ore and Powell that the excited $2S$ states normally possess unusual stability against radiative de-excitation. The transition 2^1S-1^1S is absolutely forbidden, and the transitions 2^3S-1^1S and 2^1S-1^3S are extremely slow, since the space wave functions are very nearly orthogonal (in contrast to magnetic dipole absorption of the deuteron, which occurs because the nuclear forces are strongly spin-dependent⁶). It might at first be thought that this stability would be lost for positronium in solid media through collisional de-excitation. In metals such de-excitation will take place rapidly through collisions with conduction electrons. In nonmetals, however, the electrons are firmly bound to their atomic stations so that rapid de-excitation may not be possible. In both cases, coupling with the lattice is very small since the energy transferred in de-excitation must be several electron volts. The possible stability of the 2^1S state then provides a mechanism to explain the occurrence of the τ_2 component in some nonmetals.

It is improbable that states of higher angular momentum will be bound for positronium in solid media. Assuming the effective potential of the electron-positron system is a strongly shielded Coulomb potential, the level sequence is $1S$, $2S$, $2P$, etc. with a relatively large $2S-2P$ separation. For simplicity we will assume here that the $2P$ state is not bound. If it is bound, its role is limited to indirect effects such as influencing the intensity ratio I_1/I_2 . This follows from the observation of Ore and Powell⁵ that the probability of annihilation from a P state is negligible since the internal wave function vanishes for electron-positron coincidence.

With these assumptions we can now construct the following picture for positrons slowing down in solid and liquid media. In both metals and insulators posi-

trons slow down rapidly, via the usual processes (ionization, Auger effect, etc.), to energies where the probability for the formation of positronium is large. In metals the $2S$ states, if bound, are rapidly de-excited by nonradiative collisions with conduction electrons and a single lifetime τ_1 for two-quantum annihilation is observed. If the 2^1S state is bound in insulators and has sufficient stability, then it decays by two-quantum annihilation directly, so that one observes a second lifetime τ_2 . One can even understand in a qualitative way why the τ_1 component has a greater intensity. In insulators, electron pickup from the lattice by the positron is likely to be an endothermic reaction for the formation of the $2S$ states, but even exothermic for the $1S$ states.

The above picture for positrons slowing down in solid media is capable of explaining the following experimental facts:

(i) There exists a short lifetime τ_1 in all materials, and a second lifetime τ_2 in some nonmetals.

(ii) The magnitudes of τ_1 and τ_2 are essentially determined by the lifetimes for two-quantum annihilation, $\tau(1^1S)$ and $\tau(2^1S)$, respectively. Since the probability density for electron-positron coincidence decreases as the cube of the principal quantum number for S states,⁵ $\tau_2 \approx 8 \times \tau_1 \approx 10^{-9}$ sec.

(iii) The relative constancy of τ_1 compared with the wide variations in τ_2 in different materials follows from the strong binding of the 1^1S state and the weak binding (and hence greater sensitivity to environment) of the 2^1S state.

(iv) The lifetime τ_2 depends rather sensitively upon the small binding energy of the $2S$ state, whereas the intensity ratio I_1/I_2 is determined by the more gross parameters of formation such as the $1S-2S$ binding energy difference. Hence I_1/I_2 is relatively more independent of environment than τ_2 .

(v) The long lifetime τ_2 is temperature-dependent. As the temperature is raised, the 2^1S states become less firmly bound so that the wave function for the relative separation of electron and positron "spreads out." The probability density at coincidence then decreases and the lifetime increases contrary to normal expectation.¹ A similar but smaller temperature effect might be anticipated for τ_1 .†

The situation in superconductors is uncertain from both experimental and theoretical points of view. A complex decay scheme is indicated by the experimental results.⁷ This might be understood by means of arguments similar to those used by Dresden⁸ concerning the inability of the electrons to exchange energy with the lattice or with impurities (positronium). Such a

† Footnote added in proof.—One can interpret the results of Graham and Stewart [Can. J. Phys. 32, 678 (1954)] on the temperature dependence of the three-quantum annihilation rate as evidence for such an effect.

⁷ W. E. Millett, Phys. Rev. 94, 809 (1954); H. Talley and R. Stump, Phys. Rev. 94, 809 (1954).

⁸ M. Dresden, Phys. Rev. 93, 1413 (1954).

⁵ A. Ore and J. L. Powell, Phys. Rev. 75, 1696 (1949).

⁶ See, for example, similar arguments in J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley and Sons, Inc., New York, 1952), pp. 603-604.

prohibition of collisional de-excitation would imply the stability of the 2^1S state of positronium and lead to a complex decay scheme analogous to that found in some insulators.

The hypothesis that excited states of positronium are responsible for the τ_2 component is not inconsistent with the experimental results of De Benedetti and Siegel.⁹ They have found that the three-quantum counting rates are greater in materials exhibiting a τ_2 component, by an amount consistent with the conversion interpretation of τ_2 . However, an explanation of these results also follows from the excited-state interpretation of τ_2 , provided that the conversion rate is assumed rapid ($\gtrsim 10^{11}$ /sec) in metals, and moderately rapid ($\gtrsim 10^{10}$ /sec) in nonmetals. This follows from the elementary analysis in the Appendix and from the experimental observation that τ_1 is lengthened in those materials showing a τ_2 component. Thus for fast conversion, the experimental lifetime τ_1 is to be identified with $1/\lambda_2$, and the expected ratio of the three-quantum rate in Teflon to that in aluminum is

$$\frac{\lambda_2(\text{aluminum})}{\lambda_2(\text{Teflon})} = \frac{\tau_1(\text{Teflon})}{\tau_1(\text{aluminum})} \cong 2 \text{ to } 3,$$

in agreement with the measured ratio. (The inclusion of the $2S$ states in the analysis of the Appendix would not materially change this result, of course.) The results of Pond¹⁰ on the ratios of the two-quantum annihilation rates in various pairs of materials are also consistent with the excited-state interpretation.

According to the excited-state hypothesis, if the $2S$ states have sufficient stability against transition to the $1S$ states, one should observe the lifetime of the 2^3S as well as of the 1^3S state in experiments of the kind performed by Deutsch¹¹ with gases. It might be profitable to look for such an effect, although the longer lifetime and expected smaller intensity of the 2^3S component would make it difficult to observe experimentally.

Finally, let us remark on the question as to whether there is enough room in the solid lattice to accommodate the "orbits" of the $2S$ states of positronium. In this connection it might be noted that the effective atomic size of the positronium atom is likely to be smaller within solid material. Moreover, the validity of the hypothesis actually requires that the $2S$ states be bound only in amorphous solids. Also, positronium need not exist as such in the literal sense; for example, it may appear in the form of a molecular compound. Despite the greater complexity then involved, one might anticipate some of the same general features as discussed above.

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APPENDIX

The dependence of the observed lifetimes and intensities for two-quantum annihilation of positronium upon the 1^3S-1^1S conversion rate can be illustrated as follows. Let P_S be the probability of finding a positronium atom, once formed, in the 1^1S singlet state, and P_T be the corresponding triplet state probability. Then the rate of change of probability can be expressed by the equations:

$$dP_S/dt = -(3\gamma + \lambda_S)P_S + \gamma P_T,$$

$$dP_T/dt = 3\gamma P_S - (\gamma + \lambda_T)P_T,$$

where γ is the rate of conversion between the singlet state and any one of the three triplet states, λ_S is the two-quantum annihilation rate for the singlet state, and λ_T is the three-quantum annihilation rate for the triplet state. Simultaneous solution of these equations yields

$$P_S = C_S \exp(-\lambda_1 t) + D_S \exp(-\lambda_2 t),$$

$$P_T = C_T \exp(-\lambda_1 t) + D_T \exp(-\lambda_2 t),$$

where

$$\lambda_{1,2} = \alpha \pm (\alpha^2 - \beta^2)^{1/2},$$

$$2\alpha = 4\gamma + \lambda_S + \lambda_T,$$

$$\beta^2 = \gamma\lambda_S + 3\gamma\lambda_T + \lambda_S\lambda_T.$$

Since $\lambda_S P_S$ is the rate of two-quantum annihilation, one has two lifetimes, a short lifetime $1/\lambda_1$ and a long lifetime $1/\lambda_2$. By integrating from the time of formation to infinity, one gets for the relative intensities of the two components:

$$I_1/I_2 = C_S \lambda_2 / D_S \lambda_1.$$

The constants C_S and D_S are determined by the initial conditions:

$$P_S(t=0) = \frac{1}{4}, \quad P_T(t=0) = \frac{3}{4}.$$

TABLE I. Lifetimes for two-quantum annihilation and their intensity ratio as a function of the triplet-singlet conversion rate.

3γ (per sec)	$1/\lambda_1$ (sec)	$1/\lambda_2$ (sec)	I_1/I_2
∞	0	5.0×10^{-10}	0
10^{12}	7.5×10^{-13}	5.0×10^{-10}	6.7×10^{-6}
10^{11}	7.2×10^{-12}	5.2×10^{-10}	6.4×10^{-4}
10^{10}	5.0×10^{-11}	7.6×10^{-10}	3.7×10^{-2}
10^9	1.1×10^{-10}	3.3×10^{-9}	0.25
10^8	1.2×10^{-10}	2.5×10^{-8}	0.39
10^7	1.25×10^{-10}	9.6×10^{-8}	1.0
10^6	1.25×10^{-10}	1.3×10^{-7}	7.5
0	1.25×10^{-10}	1.4×10^{-7}	∞

⁹ S. De Benedetti and R. T. Siegel, Phys. Rev. **94**, 955 (1954).

¹⁰ T. A. Pond, Phys. Rev. **93**, 478 (1954).

¹¹ M. Deutsch, Phys. Rev. **82**, 455 (1951); **83**, 866 (1951).

It follows that

$$C_S = (\lambda_1 - 4\gamma - \lambda_T)/4(\lambda_1 - \lambda_2),$$

$$D_S = (-\lambda_2 + 4\gamma + \lambda_T)/4(\lambda_1 - \lambda_2).$$

Table I gives the expected lifetimes for two-quantum annihilation and their relative intensity I_1/I_2 for various possible choices of the conversion rate γ , assuming that the triplet three-quantum annihilation rate is $\lambda_T = 7.14 \times 10^6/\text{sec}$ as given by Ore and Powell⁵ and that the singlet two-quantum rate is $\lambda_S = 8 \times 10^9/\text{sec}$.⁴ As noted in the text, the assumption of rapid conversion would require that these rates be increased by factors of about 2 or 3. For rapid conversion one then obtains $1/\lambda_2 \approx 2 \times 10^{-10}$ sec in agreement with the experimental lifetime τ_1 .

The dependence of the total rates for two- and three-quantum annihilation on the triplet-singlet conversion

rate can be calculated in a similar manner. In the differential equations one replaces the probabilities P_S and P_T by the populations N_S and N_T , respectively, introduces constant rates of formation ($\frac{1}{4}$ for the singlet state and $\frac{3}{4}$ for the triplet state), and finally equates the derivatives to zero. This gives for the total rates:

$$\lambda_S N_S = \lambda_S(4\gamma + \lambda_T)/4\beta^2 \quad (\text{two-quantum}),$$

$$\lambda_T N_T = 3\lambda_T(4\gamma + \lambda_S)/4\beta^2 \quad (\text{three-quantum}).$$

For λ_T small compared to γ and λ_S , one finds

$$\lambda_S N_S \approx 1 - 3\lambda_T/4\lambda_2,$$

$$\lambda_T N_T \approx 3\lambda_T/4\lambda_2.$$

For very rapid conversion, $\lambda_2 \rightarrow \lambda_S/4$, and hence

$$\lambda_T N_T \rightarrow 3\lambda_T/\lambda_S.$$

Matrix Elements in Superaligned Transitions*

MARK BOLSTERLI† AND EUGENE FEENBERG

Wayman Crow Laboratory, Washington University, St. Louis, Missouri

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The nuclear matrix element for superallowed transitions between two states of an isobaric spin multiplet can be expressed in terms of a diagonal matrix element of the spin operator difference $\mathbf{S}_n - \mathbf{S}_p$. Known theoretical results on the nuclear matrix element in image transitions are summarized and the methods which have proved useful in the study of image transitions are extended to superallowed transitions within the lowest $T=1$ isobaric spin multiplet in the $4n$ series.

Experimental results indicate the actual occurrence of such transitions in Na^{20} , Al^{24} , P^{28} , Cl^{32} and Sc^{40} .

1. INTRODUCTION

THE known superallowed transitions now include the following types:

$$\begin{aligned} a: & \Delta I=0, & T_i=T_f=\frac{1}{2} & (A=4n\pm 1), \\ b: & \Delta I=\pm 1, & T_i=T_f=\frac{1}{2} & (A=7), \\ c: & \Delta I_i=\pm 1, & \Delta T=\mp 1 & (A=4n+2), \\ d: & I_i=I_f=0, & T_i=T_f=1 & (A=4n+2), \\ e: & \Delta I=0, & T_i=T_f=1 & (A=4n). \end{aligned} \quad (1)$$

Types *a* to *d* are well known, but only recently has experimental work on short-lived radioactivities in the $4n$ nuclear series¹⁻⁵ indicated the actual occurrence of type *e*.⁶ The list *a* to *e* does not exhaust the possible

types of superallowed transitions. To see that others may occur, consider the approximation of spin- and charge-independent forces. In the $4n$ series the lowest supermultiplet containing a $T=1$ isobaric spin multiplet has the basic structure shown in Table I. Thus there are seven different final states coupled to the initial ($T_3=-1$) state by nonvanishing Gamow-Teller matrix elements.

Now, by introducing a spin-dependent force, the seven distinct final states are spread out into a spectrum as illustrated in Fig. 1. The Fermi matrix element vanishes in all but the *e*-type transition. Other transitions with $\Delta T=0$ may occur, but they involve smaller decay energies and smaller decay matrix elements; hence they may be neglected in a preliminary discussion. The remaining three final states (those with $T=0$

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† Shell fellow 1952-1954; now National Science Foundation pre-doctoral fellow.

¹ N. W. Glass and J. R. Richardson, Phys. Rev. **93**, 942 (1954).

² Glass, Jensen, and Richardson, Phys. Rev. **90**, 320 (1953).

³ Brackon, Henrikson, Martin, and Foster, Can. J. Phys. **32**, 223 (1954).

⁴ A. C. Birge, Phys. Rev. **85**, 753 (1952).

⁵ L. W. Alvarez, Phys. Rev. **80**, 519 (1950).

⁶ M. Bolsterli and E. Feenberg, Phys. Rev. **95**, 612 (1954).

TABLE I.

T	S	$I (L \neq 0)$
1	1	$L-1, L, L+1$
1	0	L
0	1	$L-1, L, L+1$