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Annihilation of Positrons in Condensed Materials

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An analysis of the experimental results on the annihilation of positrons in condensed materials is suggested, differing from that recently published by Dixon and Trainor. Considerations are offered which make it seem unlikely that excited states of positronium play a significant role. The long lifetime in molecular materials is explained in terms of the formation of 1*s* triplet positronium, while the short lifetime in these materials is interpreted as having a complex origin. The frequency of three-quantum annihilation, the temperature effect of the long lifetime, the angular correlation of the γ rays, and annihilation in superconductors are discussed.

IN the past three years, considerable experimental work has been done on the annihilation of positrons in solids and liquids.[1–8] In a recent paper, Dixon and Trainor[9] have offered an interpretation of the phenomena in question in terms of the formation of excited states of positronium. In the present note, I should like to call attention to serious difficulties in their interpretation, and to suggest an alternative analysis.

Dixon and Trainor's explanation, in terms of an excited 2*s* state of positronium, of the long (τ_2) lifetime found in molecular materials faces two difficulties: (i) the large size of excited-state orbits (the mean particle distance in free 2*s* positronium is ≈ 6.4 A^0), and their weak binding (≈ 1.7 ev for 2*s* and 2*p*) make it seem unlikely that such states could exist in condensed materials, and (ii) if excited states *did* exist, they would certainly not possess the spherical symmetry needed to ensure a sufficiently long lifetime. It is shown in the appendix that an initial *s*-state would very quickly become admixed with *p*-states, which would then be de-excited to the 1*s* state by collision in a time short compared with the annihilation lifetime. Another possibility is, of course, the radiative decay of the *p*-state. This has a lifetime $\approx 3\times 10^{-9}$ second, and is therefore less important than de-excitation by collision.

Dixon and Trainor correctly point out, in their appendix, an inconsistency between the relative intensities of the two components and the corresponding lifetimes, on the basis of a model which allows for decay of positrons only in positronium, with the possibility of conversion from triplet to singlet 1*s* state. This difficulty can, however, be removed without recourse to the hypothesis of excited states, if it is admitted that not all positrons decay while bound to electrons.

Before discussing the processes leading to the two lifetimes, let us note the fundamental difference between the substances which exhibit the long lifetime and those which do not. The latter class of substances, whether they are insulators or conductors, is characterized by the presence of valence binding. The electrons are described by Bloch wave functions extending throughout the crystal. The substances in which the long lifetime appears are molecular materials, either crystalline or amorphous. The motion of electrons takes place predominantly only *within* molecules, which are held together by weak van der Waal's forces. The situation in these materials should then be similar to that in inert gases, except, of course, that the density is that characteristic of a solid.

In the case of metals and valence crystals the fact that the lifetime is fairly independent of the particular substance does not necessarily indicate, as assumed by D.T. and by Bell,[10] that the lifetime must be explained only in terms of positronium formation. In fact, as was pointed out in D.T., the lifetime is several times shorter than would be expected of positronium, since only *singlet* positronium has short lifetime and rapid singlet↔triplet exchange must be assumed. It seems likely, therefore, that whether or not positronium is formed, the polarization of the wave functions of *unbound* electrons must make an important contribution to the shortening of the decay lifetime. It is interesting to note that the work of Green and Stewart[8] on the angular correlation of the emitted γ rays is consistent with the picture of annihilation of the positrons by *free* electrons. It is quite conceivable that the net effect of the polarization will be largely determined by conditions in the immediate neighborhood of the positron and therefore be more or less independent of the substance.

In the case of molecular materials, a considerable proportion of positrons should survive the process of successive electron capture and loss and ultimately annihilate when free. Actually, the generally longer and more variable lifetime of the short (τ_1) component in

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[1] De Benedetti, Cowan, Konneker, and Primakoff, Phys. Rev. **77**, 205 (1950).
[2] R. E. Bell and R. L. Graham, Phys. Rev. **90**, 644 (1953).
[3] S. de Benedetti and S. J. Richings, Phys. Rev. **85**, 377 (1952).
[4] R. L. Graham and A. T. Stewart, Can. J. Phys. **32**, 678 (1954).
[5] W. E. Millett, Phys. Rev. **94**, 809 (1954).
[6] R. Stump and H. Talley, Phys. Rev. **94**, 809 (1954).
[7] Page, Heinberg, Wallace, and Trout, Phys. Rev. **99**, 665(A) (1955).
[8] R. E. Green and A. T. Stewart, Phys. Rev. **98**, 486 (1955).
[9] W. R. Dixon and L. E. H. Trainor, Phys. Rev. **97**, 733 (1955). Hereafter to be referred to as D.T.
[10] R. E. Bell in Siegbahn, *Beta- and Gamma-Ray Spectroscopy* (Interscience Publishers, Inc., New York, 1954), p. 686.

these materials suggests that the decay is not exclusively that of singlet positronium. So, in fact, does the intensity ratio of the two components. When electrons are captured in 1*s* positronium at sufficiently low energies ($\lesssim 10$ ev, say), this positronium will predominantly be elastically scattered in successive collisions with the molecules of the substance, which represent closed-shell configurations. If this positronium is singlet, it will have a lifetime $\approx 1.2 \times 10^{-10}$ sec. To this contribution to the short life would be added that of the free positrons, as well as positrons chemically combined with the molecules of the material. In addition to being somewhat longer, this contribution should be expected to show some variations from one material to another, though polarization effects would make these variations proportionately less than the variations in electron density.

The experiments are not inconsistent with the view that the short lifetime has a complex origin in molecular materials.

The long (τ_2) component in molecular materials should then be associated with the formation of 1*s* triplet positronium. Its decay is probably due to "pick-off annihilation" as suggested by Dresden[11]; that is, annihilation during collision with an appropriately oriented electron on a target molecule.

The following comments are offered on other particular aspects of the problem:

THREE-QUANTUM ANNIHILATION

As shown by Graham and Stewart,[4] the three-quantum yield follows naturally from the assumption that the τ_2 component is associated with the formation of triplet 1*s* positronium. D.T.'s explanation of the three-quantum counting rate in molecular materials depends on the assumption of a rather rapid triplet$\rightarrow$ singlet conversion rate in these materials. However, at low energies rapid conversion is not possible. Ore[12] has shown that direct conversion has very long lifetime ($\gtrsim 10^{-5}$ sec). The only other possibility is that of electron exchange. However, this would involve a spin-flip of an electron on the target molecule. Since the ground-state is a closed-shell configuration, this can only be accomplished by excitation of the molecule to a higher electron state with spin 1. This will require considerable excitation energy, and so will not take place in slow collisions.

The results on three-quantum annihilation are consistent with the assumption of slow conversion, annihilation taking place by a process such as that of "pick-off" mentioned above.

THERMALIZATION, TEMPERATURE EFFECT, AND ANGULAR CORRELATION OF γ RAYS

With regard to the temperature effect on the τ_2 lifetime observed by Bell and Graham (lengthening of lifetime with increasing temperature), both the discussion of D.T. ("loosening" of 2*s* states due to thermal excitation) and that of Bell and Graham (increase in number of collisions) assume thermalization of the positronium. Although the thermalization time would be very difficult to estimate, it is by no means certain that it is shorter than the lifetime. At energies high enough to excite electronically the molecules of the substance, inelastic scattering with fairly large energy loss ($\approx$volts) may take place. At somewhat lower energies, inelastic collisions involving vibrational excitation are possible, and at all energies there will occur slight energy losses due to elastic collisions. It should be noted that, neglecting electron exchange, these processes must be second-order ones. For the Coulomb forces acting to produce the collision are antisymmetric in exchange of positron and electron, whereas the initial and final wave functions are symmetrical. Scattering takes place therefore only through the agency of intermediate states (e.g., 2*p*) of the positronium.

A rough estimate of the probability of inelastic scattering with vibrational excitation may be made as follows: the scattering potential is roughly the variation in the potential of the atoms of the molecule over the zero-point oscillations of the atoms. The amplitude of oscillation of the atoms is $(\hbar/2\omega M)^{\frac{1}{2}}$, ω being the vibrational frequency and M the atomic mass. If the mean gradient of the atomic field is $\bar{\epsilon}$ ev per A, the mean perturbing potential of a particular atom is then $H' \approx 0.05\bar{\epsilon}/(E_v A)^{\frac{1}{2}}$ ev, A being the nuclear mass of the atom and E_v the vibration energy in volts, the signs depending on whether it acts on electron or positron. It will be noted that this will be much smaller than the potential involved in elastic scattering, which is $\approx \bar{\epsilon}$.

The cross section will therefore be less than the corresponding one for elastic scattering by a factor $\approx (0.05)^4/E_v^2 A^2$. In most cases $E_v \approx 0.1$–0.5 ev. With a reasonable assumption for the elastic cross section, this mechanism will make a negligible contribution.

In the case of electron exchange, in each case a first-order scattering is possible. The small amplitude of oscillation of the atoms is then less effective in cutting down the inelastic relative to the elastic cross section [ratio $\approx (0.05)^2/E_v A$]. However, the increase in inelastic cross section due to the presence of a first-order matrix element is at least partially compensated by the fact that this matrix element is of the overlap type and is therefore substantially smaller than that for a direct scattering process.

Consider a case which is particularly favorable for slowing-down—that of ice. The main agency for energy transfer will be collision with the hydrogen atoms. There are about 6×10^{22} of these per cc. The velocity of a positronium atom of energy E ev is $\approx 0.4\sqrt{E}\ 10^8$ cm/sec. If we consider a process with a cross section σ, the probability per unit time of that process is $2.4\sqrt{E}\ 10^{30}\sigma$, or the probability that it takes place in 10^{-9} sec

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[11] M. Dresden, Phys. Rev. **93**, 1413 (1954).

[12] A. Ore, Naturvitensk. rekke, Universitetet i Bergen **12** (1949).

is $2.4\sqrt{E}\,10^{21}\sigma$. According to Massey and Mohr,[13] the exchange elastic scattering cross section on hydrogen should be $\pi a_0^2 f = 0.9f\ 10^{-16}$ cm^2 where f is a small number of order unity. Therefore, there will be many elastic scatterings before annihilation. However, inelastic scattering with vibrational excitation should happen less often by a factor $(0.05)^2/E_v$. Possible E_v's for H_2O are ≈ 0.2 ev or ≈ 0.45 ev.

It is evident that this process is of such an order of probability that more careful calculations would be necessary to establish whether or not it would, in 10^{-9} sec, lower the positronium energy below the threshold of E_v in the substances in question. This is particularly the case since the use of Born approximation would overestimate the cross sections, and the case considered (ice) is the most favorable for slowing down.

Below the lowest energy E_v, only elastic collisions with whole molecules are possible. If the molecule has mass A', the mean fractional energy loss per collision will be $4/1840A'$. Reduction of the energy by a factor of 10 (e.g., from 0.25 ev to 0.025 ev) would, assuming constant cross section σ_0, take a time $1840A'/4N\sigma_0 v_0$, v_0 being the thermal velocity and N the number of molecules per unit volume. If $t = 10^{-9}$ sec this would mean $N\sigma_0 = 2.9\times 10^5 A'$. For the most favorable case of ice, this implies $\sigma_0 \approx 2\times 10^{-16}$.

Again, it appears that thermalization might just be possible in the favorable case of ice at ordinary temperatures, but it is less likely in substances with heavier molecules, or at lower temperatures.

It seems, therefore, that a discussion of the temperature effect based on the assumption of thermalization of positronium is open to question. An alternative explanation is the following: it may be assumed that positronium moves adiabatically in the nuclear potential, and should thus be found with highest probability in the larger interstices, near the potential minima. Since, with greater molecular motion, some larger molecular separations appear, the positron intensity will be enhanced in these intermolecular "holes" where the intensity of molecular electrons is least, "pick-off annihilation" is less likely and the observed temperature effect might be expected.

In connection with the question of thermalization of positronium in molecular materials, attention should be drawn to the experiments on angular correlation of annihilation γ rays in these materials by Page, Heinberg, Wallace, and Trout,[7] who found a very narrow component, indicating an energy of the mass center of the annihilating pair of one volt or less, which accounted for about 20% of all decays. If in fact positronium is not thermalized, this might be attributed to a component of the *short* lifetime. An attractive hypothesis would be to associate it with the decay of positrons which have, after slowing down, become bound to molecules of the substance.

ANNIHILATION IN SUPERCONDUCTORS

Stump and Talley[6] found a lengthening of the lifetime of positrons in superconducting lead, as compared with ordinary lead. D.T. attribute this to the tendency of superconducting electrons not to exchange energy with impurities, so that 2*s* positronium, once formed, can be maintained. However, it is difficult to see why, if superelectrons do not react with positronium, they should not be indifferent to slow positrons as well, with consequent inhibition of positronium formation. In fact, such a conclusion is also suggested by the supposed low effective mass of superelectrons. This failure to attract electrons would itself give rise to a lengthening of the lifetime.

APPENDIX

We shall first assume the possibility of 2*s* positronium in a molecular solid, and estimate roughly the probability that it is transformed to the 2*p* state during scattering. Using Born approximation, this probability is

$$\frac{1}{\tau}=\frac{2\pi}{\hbar}|\gamma(\mathbf{k},\mathbf{k}')|^2{}_{E'=E}\,d\Omega(\mathbf{k}')\rho(E). \tag{1}$$

$\rho(E)$ is the density of final states per unit solid angle and the integration is over final directions.

$$\gamma(\mathbf{k},\mathbf{k}')=\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}}\varphi_{2s}(\boldsymbol{\rho})\varphi_{2pn}(\boldsymbol{\rho})\times[V(\mathbf{R}+\tfrac{1}{2}\boldsymbol{\rho})-V(\mathbf{R}-\tfrac{1}{2}\boldsymbol{\rho})]d^3\mathbf{R}\,d^3\boldsymbol{\rho}. \tag{2}$$

Here $\mathbf{k}$, $\mathbf{k}'$ are the initial and final wave-number vectors of the positronium, φ_{2s} and φ_{2pn} the positronium wave functions for the 2*s* state and the 2*p* state with axis $\mathbf{n}$, respectively; $\mathbf{R}$ is the vector specifying the center of mass of the positronium and $\boldsymbol{\rho}$ the position vector of electron relative to positron. The initial and final wave functions are normalized to unit volume, and V is the potential of the electron in the Coulomb field of a scattering molecule. For a rough approximation the effect of the Pauli principle on the electron is ignored.

If $W(\mathbf{K})$ is the Fourier transform of $V(\mathbf{r})$, this integral is easily shown to be

$$\gamma(\mathbf{k},\mathbf{k}')=iW(\mathbf{K})\frac{6K^3a_0^3}{(K^2a_0^2+1)^4}\cos(\mathbf{n},\mathbf{K}), \tag{3}$$

where a_0 is the Bohr radius, and $(\mathbf{n},\mathbf{K})$ is the angle between the axis of the *p*-state wave function and the vector $\mathbf{K}=\mathbf{k}-\mathbf{k}'$.

Summing $|\gamma|^2$ over all possible orientations of the *p*-state wave function, the cosine term will drop out. We may also average over all orientations of the

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[13] H. S. W. Massey and C. B. O. Mohr, Proc. Phys. Soc. (London) **67**, 695 (1954).

molecule, i.e., replace $|W(\mathbf{K})|^2$ by

$$I=\frac{1}{4\pi}\int|W(\mathbf{K})|^2 d\Omega_{\mathbf{K}}. \tag{4}$$

Using the Fourier integral expression for $W(\mathbf{K})$ this yields

$$I=\int V(\mathbf{r})V(\mathbf{r}')\frac{\sin K|\mathbf{r}-\mathbf{r}'|}{K|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}'. \tag{5}$$

We may, for purposes of rough estimation, ignore contributions from $K|r-r'|>\pi/2$. Because this will involve an underestimate, we can replace the $\sin K|\mathbf{r}-\mathbf{r}'|/K|\mathbf{r}-\mathbf{r}'|$ by unity within these limits. But $|6K^3a_0^3/(K^2a_0^2+1)^4|^2$ contributes significantly only in the range $0.4\leq Ka_0\leq 1.4$. Thus, if $|\mathbf{r}-\mathbf{r}'|<(\pi/2)(a_0/1.4)$, over the whole significant range of K we may write approximately

$$I=\int V(\mathbf{r})V(\mathbf{r}')d^3\mathbf{r}d^3\mathbf{r}',$$

the integral being taken over the limits of $|\mathbf{r}-\mathbf{r}'|$ indicated. We shall neglect contributions to I from larger $|\mathbf{r}-\mathbf{r}'|$. Then, without specifying the details of $V(\mathbf{r})$ we see that

$$I\approx\bar{V}^2V_M\pi a_0^3,$$

where $\bar{V}$ is the mean molecular potential, V_M the volume of the molecule.

To obtain the total probability per unit time $1/\tau_0$ for scattering from a $2s$ to a $2p$ state we then multiply (1) by $1/V_M$, the number of molecules per unit volume, and get

$$\frac{1}{\tau_0}=\frac{2\pi}{\hbar}\bar{V}^2\pi a_0^3\frac{1}{4\pi^3}\frac{mk}{\hbar^2}\int\frac{36K^6a_0^6}{(K^2a_0^2+1)^8}d\Omega. \tag{6}$$

To do the integral over direction, we use the fact that

$$\begin{aligned}K^2a_0^2&=2k^2a_0^2(1-\cos\theta)\\&=2(E/W_0)(1-\cos\theta)=2\eta(1-\cos\theta).\end{aligned}$$

W_0 being the energy of the $1s$ state of positronium. For $\eta\approx 1$, the integral in (6) is approximately $9\pi/35\eta$. Thus, finally,

$$\frac{1}{\tau_0}=\frac{9}{280\eta^{\frac{1}{2}}}\frac{\bar{V}}{W_0}\frac{\bar{V}}{\hbar}. \tag{7}$$

This gives a time of the order of 10^{-14}–10^{-15} sec.

Consider next scattering with de-excitation from a $2p$ state to the $1s$ state. The matrix element is similar to that of (2), except that $\varphi_{2s}(\rho)$ is replaced by $\varphi_{1s}(\rho)$, and in addition $|\mathbf{k}'|$ is no longer equal to $|\mathbf{k}|$ since energy is gained on collision. On evaluating we find

$$\gamma'(\mathbf{k},\mathbf{k}')=iW(\mathbf{K})\frac{24\cos\alpha}{\sqrt{2}}\frac{Ka_0}{(K^2a_0^2+8/3)^3}, \tag{8}$$

α being the angle between $\mathbf{K}$ and the axis of the $2p$ wave function. Averaging $|\gamma'|^2$ over all possible directions for this axis, we can replace $\cos\alpha$ by $1/\sqrt{3}$. This time $k'^2=k^2+(4m/\hbar^2)\frac{3}{4}W_0$ or $k'^2a_0^2=k^2a_0^2+\frac{3}{4}$, from which it follows that

$$K^2a_0^2=2\eta+\tfrac{3}{4}-2[\eta(\eta+\tfrac{3}{4})]^{\frac{1}{2}}\cos\theta. \tag{9}$$

The range of Ka_0 over which $(Ka_0)^2/(K^2a_0^2+8/3)^6$ has significant values is comparable to that of the previous calculation; by similar arguments therefore

$$\frac{1}{\tau'}=\frac{2\pi}{\hbar}\bar{V}^2\pi a_0^3\frac{1}{4\pi^3}\frac{mk'}{\hbar^2}\int\frac{96K^2a_0^2}{(K^2a_0^2+8/3)^6}d\Omega \tag{10}$$

approximately. The integral can be evaluated, and yields

$$\frac{8\pi}{5[\eta(\eta+\frac{3}{4})]^{\frac{1}{2}}}\left\{\frac{(77/4)+30\eta-30[\eta(\eta+\frac{3}{4})]^{\frac{1}{2}}}{[(41/12)+2\eta-2(\eta(\eta+\frac{3}{4}))^{\frac{1}{2}}]^5}-\frac{(77/4)+30\eta+30[\eta(\eta+\frac{3}{4})]^{\frac{1}{2}}}{[(41/12)+2\eta+2(\eta(\eta+\frac{3}{4}))^{\frac{1}{2}}]^5}\right\}. \tag{11}$$

This expression varies with η, though not too rapidly in the interesting energy range ($\eta\approx 1$). Writing $\frac{1}{5}$ of the curly bracket as $F(\eta)$

$$\frac{1}{\tau'}=\frac{1}{\sqrt{\eta}}\frac{\bar{V}}{W_0}\frac{\bar{V}}{h}F(\eta). \tag{12}$$

At $\eta=1$, $F(\eta)=0.0114$, so that the mean time for this transition at this energy is about three times that for $2s\rightarrow 2p$ conversion, and is therefore still very short compared with the lifetime.

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