PHYSICAL REVIEW LETTERS

VOLUME 21 22 JULY 1968 NUMBER 4

POSITRONIUM DIFFUSION IN SOLIDS

Werner Brandt*
Department of Physics, New York University, New York, New York

and

Robert Paulin†
Institut National des Sciences et Technique Nucléaires, Saclay, France

(Received 23 May 1968)

The strong dependence of positron annihilation spectra in solid powders on particle size is shown to be indicative of positronium (Ps) diffusion in solids. Ps diffusion constants and mean annihilation lengths are estimated from measurements on powders of SiO_2, Al_2O_3, and MgO. Because of Ps diffusion, positron emitters suspended in powders of very small particles constitute compact high-yield sources of free o-Ps and of gamma rays with continuous energy spectra.

Recent measurements[1] of positron annihilation spectra on powders (particle size ~100 Å) of SiO_2, Al_2O_3, and MgO have resolved three distinct lifetime components. The components with the two short lifetimes, $\tau_1 \simeq 0.4$ nsec and $\tau_2 \simeq 2$ nsec, are typical of spectra measured on bulk samples. Specifically, the τ_2 component, of relative intensity I_2, can be attributed to the process of electron pick-off by positrons bound in orthopositronium (o-Ps); the τ_1 component, of intensity I_1, combines the annihilation of free positrons and of the parapositronium (p-Ps) pendant of the o-Ps component.[2] By contrast, the new third component is not seen in bulk samples. Its long lifetime τ_3 is equal to that expected for o-Ps annihilation in the ambient gas and approaches the theoretical o-Ps lifetime for 3γ decay in vacuo, $\tau_{3\gamma} = 1.4\times 10^2$ nsec, at gas pressures $<10^{-5}$ Torr. Its relative intensity I_3 increases drastically as the particle size is reduced, at the expense of I_2.

The purpose of our note is to show that this effect can be interpreted quantitatively in terms of Ps diffusion in the solid particles and to report the Ps diffusion constants and Ps annihilation lengths extracted from these data.

We concentrate on a series of measurements on SiO_2 powders produced by a condensation process from $SiCl_4$. Experimental details are reported elsewhere.[1] The particle sizes are determined through absorption isotherms, which yield the area A per unit weight of the powder, combined with electron microscopic sampling. The particles of all powders are nearly perfect spheres, so that their mean radius R is given by $R = 3/A\rho$, where ρ is the density of the particle material. We set $\rho = 2.2$ g/cm^3, the density of amorphous (fused) quartz, because this choice is consistent with the electron diffraction patterns of the powders, with the appearance of the τ_2 component in the annihilation spectra, and with the mean radii measured on the electron micrographs. The distributions of radii about the mean values are close to Gaussian, with half-widths ranging from 0.1 to $0.3R$. Under normal conditions the powders are so fluffy that their apparent density is ~0.05 g/cm^3. This implies that the free volume per particle is some 45 times larger than the particle volume, and we can think of the individual particles as being effectively isolated from one another.

When injected into such a target, positrons are stopped in the particles and can form Ps. If the Ps migrates in the solid, some of it escapes from the particles and annihilates in the surrounding free volume. This process can be detected only for o-Ps because its lifetime outside the particles (τ_3) is some 10^2 times longer than inside the particles (τ_2). If Ps diffusion occurs, I_3 must grow at the expense of I_2 as R decreases. This is what is observed experimentally.[1]

We assume that a thermalized o-Ps atom is formed in a particle at some point $\vec{x} = \vec{x}_0$ with a probability $g(\vec{x}_0)d^3x_0$ and normalize such that $\int_{\text{particle}} g(\vec{x}_0)d^3x_0 = 1$. In first approximation the particle surface at $\vec{x} = \vec{R}$ acts as an absorbing boundary in the sense that once Ps has crossed the surface it has a negligible probability for electron pick-off from the solid before it annihilates in the large free volume. Inside the particle, o-Ps disappears at a rate $q_p(t) = \gamma_p \exp(-\gamma_p t)$, where $\gamma_p \simeq \tau_2^{-1}$ is the electron pick-off rate. Following Chandrasekhar[3] we calculate the disappearance rate through the particle surface $s(\vec{R})$, with the normal direction $\vec{n}(\vec{R})$, in terms of a Ps diffusion constant D:

$$q_s(t, \vec{x}_0) = \int ds(\vec{R}) \frac{(\vec{R}-\vec{x}_0)\cdot \vec{n}(\vec{R})}{2\pi^{3/2} t (4Dt)^{3/2}} \times \exp\left[-\frac{|\vec{R}-\vec{x}_0|^2}{4Dt} - \gamma_p t\right]. \tag{1}$$

The fraction of all o-Ps atoms annihilating inside the particle becomes

$$\Phi_2 = \int g(\vec{x}_0) d^3x_0 \int dt\, [q_p(t) - q_s(t, \vec{x}_0)]. \tag{2}$$

For a spherical particle and $g(\vec{x}_0) = \text{const}$, we obtain

$$\Phi_2(\beta) = 1 - \tfrac{3}{2}\beta[1 - \beta^2 + (1+\beta^2)\exp(-2/\beta)], \tag{3}$$

where $\beta \equiv (D\tau_p)^{1/2}/R$. In a powder with a Gaussian distribution of radii with half-width (Δ/R) about a mean R one observes the mean value

$$\langle\Phi_2\rangle = \Phi_2(\beta) + 0.27(\Delta/R)^2\beta[\beta^2 - 6\beta^4 + (2 + 6\beta + 11\beta^2 + 12\beta^3 + 6\beta^4)\exp(-2/\beta)]. \tag{4}$$

The escaping o-Ps fraction becomes $\langle\Phi_3\rangle = 1 - \langle\Phi_2\rangle$. In the experiments under discussion the difference $\langle\Phi_2\rangle - \Phi_2$ is less than 1 % and can be neglected.

If the surface were to act as a potential barrier, the second term in Eq. (3) would be multiplied with the transmissivity of the barrier $T < 1$. One estimates, however, that Ps presumably experiences a drop in the potential in passing through the surface, which does not affect the diffusion equations and therefore is equivalent to $T = 1$. At larger distances from the surface the potential rises to form a van der Waals-type potential. At low temperatures it can give rise to an absorption of free Ps on the particle surface. The zero-point amplitude of Ps in this potential is large and therefore the electron pick-off from the solid remains small, i.e., even "adsorbed" Ps has effectively the same lifetime as free Ps in the voids. These subtle surface interaction effects can be studied through the dependence of the hfs interval of Ps on temperature and the apparent density of the powder.

Figure 1 compares Eq. (3) with the experimental values $I_2/(I_2 + I_3)$ on SiO$_2$ powders. The best fit is obtained for $D = (5.8 \pm 1.9)\times 10^{-5}$ cm^2 sec^{-1}. We have measured Φ_2 on two powders between 120 and 440°K. It is consistent with a temperature dependence of the diffusion constant ~$\exp(-\Theta/T)$, where $\Theta = (180 \pm 100)$°K $= (1.5 \pm 0.8)\times 10^{-2}$ eV/k_B. In terms of a mean annihilation length $\lambda(\tau) \equiv (2D\tau)^{1/2}$, o-Ps migrates in SiO$_2$ over $\lambda(\tau_2) \simeq 46$ Å before annihilating by electron pick-off; p-Ps can cover only $\lambda(\tau_{2\gamma}) \sim 12$ Å before 2γ self-annihilation ($\tau_{2\gamma} = 0.125$ nsec). Table I lists the con-

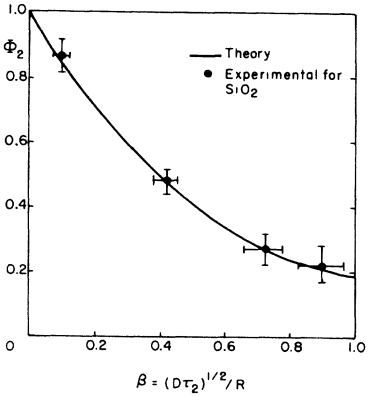

FIG. 1. Comparison of ϕ_2, Eq. (3), with experimental data of $I_2/(I_2 + I_3)$ in four SiO$_2$ powders (Ref. 1). With $\tau_2 = 1.8 \pm 0.2$ nsec and the mean-particle radii R (in Å) 273, 76, 45, and 36, respectively, the best fit yields $D = (5.8 \pm 1.9)\times 10^{-5}$ cm^2/sec.

Table I. Ps diffusion constants, as estimated by Eq. (3) from annihilation spectra of positrons in powders of three different solids.[a]

Powder	A^b (m^2/g)	R (Å)	Φ_2	τ_2 (nsec)	D (10^{-4} cm^2/sec)	λ_2 (Å)
SiO_2	180 ± 20	76 ± 8	0.48 ± 0.04	1.8 ± 0.2	0.6 ± 0.2	46 ± 7
Al_2O_3	130 ± 15	77 ± 8	0.14 ± 0.02	3.5 ± 0.5	2.6 ± 1.3	140 ± 40
MgO	110 ± 15	82 ± 8	0.05 ± 0.02	2.8 ± 0.4	14 ± 7	270 ± 80

[a] Ref. 1.

[b] SiO_2 by Degussa, Germany; Al_2O_3 by Touzart and Matignon, France; MgO by Prolabo, France. We are grateful to Miss R. Lucas for A determinations by the Branauer-Emmett-Teller technique.

stants estimated from the annihilation spectra in other powders. Their large variations pose interesting questions on the dynamics of Ps atoms in solids.

The experiments have shown that, depending on the particle radii and the Ps diffusion constants, up to 95% of all o-Ps formed in a powder (corresponding to 20-30% of all positrons injected) can diffuse into the free volume surrounding the particles and annihilate by 3γ decay. In this sense, powders act as catalysts, in that positron emitters suspended in powders of particle size $<\lambda(\tau_2)$ become compact high-yield sources of free o-Ps and of gamma rays with continuous energy spectra. Such sources should find many experimental applications.[4]

---

*Work supported by the U. S. Atomic Energy Commission and the Defense Atomic Support Agency.

†Work supported by the French Atomic Energy Commission.

[1] R. Paulin and G. Ambrosino, J. Phys. 29, 263 (1968).

[2] For general references, see, Positron Annihilation, edited by A. T. Stewart and L. O. Roellig (Academic Press, Inc., New York, 1967).

[3] C. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).

[4] The authors benefited from discussions with A. Schwarzschild on this point.

STIMULATED INFRARED EMISSION FROM OPTICAL PHONONS*

J. P. Biscar, R. Braunstein, and S. Gratch
Department of Physics, University of California at Los Angeles, Los Angeles, California

(Received 27 May 1968)

The first observation of infrared stimulated emission associated with the optical phonons of a liquid is reported at 5 μ from benzene. The variation of the 5-μ output, as a function of the temperature of the benzene, is the same as the large period of the thermospectrum of the 8050-Å stimulated Raman line, which involves the same optical phonons.

We report the generation of stimulated infrared radiation at 5 μ by phonons from benzene excited by a Q-switched laser. The radiation observed corresponds to 1984 cm^{-1}. The carbon-carbon vibration in the plane of the molecule, 992 cm^{-1}, and its harmonic, 1984 cm^{-1}, have been shown to be strongly active in second order[1-3] and multiphonon[4] stimulated Raman generation.

The experiments were performed with a ruby laser Q switched by a rotating prism. The single pulse output had a half-width of 40 to 50 nsec. We used two different configurations in these experiments. In all runs, the parallel output beam of the laser was used. The temperature of the benzene was controlled by temperature-regulated water circulating in a jacket surrounding the Raman cell.

The first set of runs were performed with a cell, 69 cm long, having a quartz input window