Systematic Angular-Correlation Studies of Positronium Formation in Silicon Dioxide Powders*

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Positron-annihilation angular-correlation measurements have been made on compressed silicon dioxide powders having mean particle diameters of 50, 120, and 400 Å. The narrow component in the momentum distribution is much more pronounced in the 50- and 120-Å powders than it is in the 400-Å powder. Measurements made in vacuum reveal a narrow component in the momentum distribution which increases with increasing temperature until a saturation temperature is reached. A positronium diffusion constant has been calculated for five temperatures. Similar measurements made in oxygen show an increased narrow component with a nonsaturating temperature dependence. From these measurements a temperature-dependent oxygen enhancement factor has been determined. Both vacuum bakeout and compressing the powder were found to increase the amount of narrow component.

I. INTRODUCTION

When positrons are injected into certain evacuated finely powdered oxides, a substantial amount of positronium (Ps) is formed in the powder grains. The Ps subsequently diffuses into the region between the grains where the orthopositronium (o-Ps) annihilates with a mean lifetime approaching that of free o-Ps in vacuum.[1] Using the results of positron-lifetime measurements, Brandt and Paulin[2] have calculated the Ps diffusion constant for several powders. The value of this constant was observed to be dependent upon the chemical composition of the grains.[2] Additional measurements[3] indicate, as might be anticipated, that the positron lifetime is sensitive to the introduction of gases into the powder and to the surface condition of the grains.

Normal angular-correlation measurements for two-quantum positron-annihilation do not detect the three-quantum decay of o-Ps. However, in the presence of a magnetic field or certain gases such as oxygen, the substates mix and o-Ps can decay by a two-quantum process. In this paper we report positron-annihilation angular-correlation measurements on finely powdered silicon dioxide utilizing either oxygen or an external magnetic field as the o-Ps quenching agent. In particular, certain parameters affecting the fate of o-Ps formed in such powders have been isolated and systematically investigated, namely, the particle size, temperature, environment, surface condition, and density of the sample. Most of the data were taken using compressed powders which had the effect of greatly increasing the amount of narrow component.

II. EXPERIMENTAL TECHNIQUE

The angular-correlation measurement apparatus has been previously described.[4] Silicon dioxide powders[5] having mean particle diameters of 50, 120, and 400 Å were compressed into $\frac{1}{2}$-in.-diam pellets having an approximate density of 0.7 g/cm^3. The pellets were placed in a thin-walled stainless-steel sample chamber whose temperature could be varied from -175 to $+150\,^\circ$C. The sample chamber was connected to a vacuum system and a gas manifold so as to provide a controlled atmosphere during data acquisition. These powders normally possess an outer layer of surface-adsorbed water which is readily removed by a vacuum bakeout. For uniformity, our pellets were given an overnight vacuum bakeout at 106 °C prior to angular-correlation measurements.[6] The angle subtended by the detector slits was set at 0.6 mrad. Higher angular resolution had no effect on the angular-correlation measurements other than reducing the coincidence counting rate. Total coincidence counts at the maximum of each distribution ranged from 10 000 to more than 20 000 counts. Data points are shown in Fig. 1 only. All other angular-correlation measurements were made in a similar fashion.

III. RESULTS AND CONCLUSIONS

Recent positron-lifetime measurements have shown that the amount of o-Ps that diffuses out of the powder grains is strongly dependent on the grain size for sufficiently small particles. As the particle size is decreased from 400-Å mean diameter to 50-Å mean diameter, the number of positrons annihilating as free o-Ps increases by nearly fourfold, while those that annihilate via pickoff are substantially reduced.[1,2]

We have made angular-correlation measurements on particles with mean diameters of 50, 120, and 400 Å. Hereafter we shall simply refer to the powders as 50-, 120-, and 400-Å powders with mean particle diameter being understood. In all cases, the momentum distributions for 50- and 120-Å powders were nearly identical and consequently the data for 120-Å powders are deleted

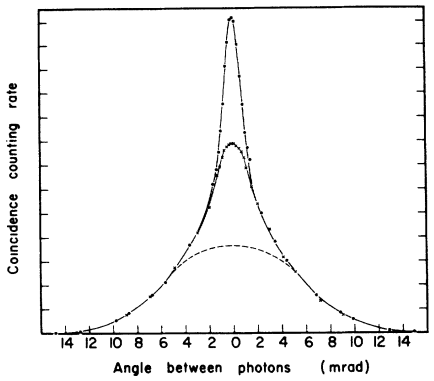

FIG. 1. Effect of variation in powder grain diameter. The upper curve is for a 50-Å powder and the lower curve for a 400-Å powder. These powders were measured in vacuum at 86 °C. The dashed curve for all angular distribution figures is for crystalline quartz (see Ref. 8). The angle between photons actually denotes the angle by which annihilation photons deviate from 180°.

from this paper. Differences occasionally found between the 50- and 120-Å powders when measured under identical conditions were always small and showed no consistent pattern. Apparently, the amount of o-Ps leaving the grains varies rapidly between particle diameters of about 120 and 400 Å and is not strongly dependent on diameter for particles smaller than this. This is consistent with the I_3 data reported by Paulin and Ambrosino.[1] It should be remembered that the diameters quoted are *mean* diameters and that there is considerable spread in the particle size. Thus, both the 50- and 120-Å powders have a number of particles whose mean diameter is between 50 and 100 Å, whereas the 400-Å powder has only a small fraction of particles whose diameter is less than 150 Å. We verified the diameter of the 120-Å particles with an electron micrograph, but were unable to resolve individual particles of the 50-Å powder because of difficulty in dispersing the powder. We did not measure particle diameters for the remaining powder, since the manufacturer[5] supplied an electron micrograph in a descriptive brochure.

The angular-correlation data[7] for 50- and 400-Å powders in vacuum at a temperature of 86 °C are plotted in Fig. 1 along with the momentum distribution for crystalline quartz as reported by Bartenev *et al.*[8] We chose this particular crystalline-quartz distribution because it shows no sign of a narrow component. An 8-kG magnetic field was used to focus the positrons into the target. This field quenches some of the o-Ps by mixing the $m = 0$ substates of singlet and triplet Ps. Thus, both parapositronium (p-Ps) and $m = 0$ o-Ps contribute to a narrow component in the angular distribution. Following Page and Heinberg[9] we define the "narrow component" to be the difference between the powder momentum distribution and the momentum distribution for crystalline quartz. Note from Fig. 1 that the area of the narrow component for the coarse powder is considerably less than it is for the fine powder, indicating that a smaller fraction of the Ps formed in the grains is able to diffuse out prior to annihilation. The full width at half-maximum is larger for the coarse-powder narrow component than for the fine-powder narrow component. This indicates that the average momentum of the annihilating Ps is greater in the coarse powder and suggests that some of the annihilations are occurring in defects in the grains.

In a diffusion-controlled process one naturally anticipates a temperature dependence of the diffusion length. Accordingly, angular-correlation measurements were made on all three powder sizes in a vacuum with a constant magnetic field of 8 kG. The results for the 50-Å powder are shown in Fig. 2. Presumably the temperature effect saturates when a temperature is attained for which all of the Ps formed in the grains reaches the interstices prior to annihilation. Paulin and Ambrosino have made lifetime measurements of the powder in vacuum for temperatures above about 25 °C. Their data show only a slight temperature dependence, since most of their measurements were taken in the range of temperature where the effect is saturated. Our 400-Å powder showed no temperature dependence in vacuum.

In the absence of a magnetic field or any other quenching agent, the narrow component in the angular-correlation distribution comes only from p-Ps. If a strong magnetic field is applied, the narrow component increases in proportion to the amount of $m = 0$ o-Ps which escapes the grains prior to annihilation. The $m = \pm 1$ o-Ps makes no contribution, since these states still annihilate by a three-quantum process. We used an 8-kG mag-

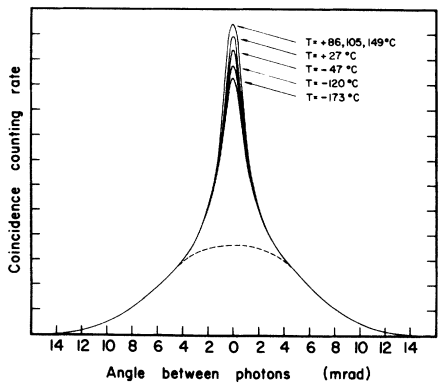

FIG. 2. Effect of temperature on positrons annihilating in a 50-Å powder in vacuum.

TABLE I. Temperature dependence of the Ps diffusion constant as obtained from angular-correlation measurements on SiO_2 powders. φ is the fraction of o-Ps atoms annihilating inside the particles and D is the diffusion constant in units of cm^2/sec. The powder particle diameter was 50 Å.

T(°C)	−173	−120	−47	+27	+86
φ	0.380 ± 0.030	0.300 ± 0.035	0.244 ± 0.038	0.183 ± 0.041	0.093 ± 0.045
D	$1.01^{+0.20}_{-0.14}$	$1.60^{+0.40}_{-0.29}$	$2.29^{+0.84}_{-0.40}$	$3.7^{+1.7}_{-1.1}$	$9.0^{+11.0}_{-3.3}$

netic field which is sufficiently strong to quench all the o-Ps which escapes the grains[10] but which does not significantly affect the o-Ps annihilation inside the grains. (Basically, the pickoff lifetime is too short to allow the magnetic field to induce much two-quantum annihilation inside the particles.)

By comparing the narrow-component areas with and without magnetic field, the fraction of o-Ps annihilating inside the particles can be measured. Brandt and Paulin[2] have calculated the fraction of o-Ps annihilating inside the particles in terms of a diffusion constant. The results are given by

$$\varphi(\beta) = 1 - \tfrac{3}{2}\beta[1 - \beta^2 + (1+\beta)^2 e^{-2/\beta}],$$

where φ is the fraction of o-Ps annihilating inside the particles and β is given by

$$\beta = (D\tau_2)^{1/2}/R.$$

D is the diffusion constant, τ_2 is the pickoff lifetime, and R is the particle radius.

Using the results of this calculation, together with our angular-correlation data, we obtain the diffusion constants listed in Table I. The errors quoted are worst cases, and in general are probably somewhat high. At the higher temperatures a small error φ corresponds to a large error in the diffusion constant. Our room-temperature value of $(3.7^{+1.7}_{-1.1}) \times 10^{-5}$ cm^2/sec compares favorably with $(5.8 \pm 1.9) \times 10^{-5}$ cm^2/sec as obtained by Brandt and Paulin[2] from lifetime data.

The quenching effect on o-Ps of a paramagnetic gas such as oxygen is well documented.[11] The presence of oxygen in the space between grains of these powders introduces at least two competing effects: pickoff, which adds to the broad component in the angular-correlation distribution, and spin conversion, which adds to the narrow component in the angular-correlation distribution. Angular-correlation measurements were made in a dry-oxygen environment at atmospheric pressure. A focusing magnetic field of 8 kG was used and data were taken at several temperatures between −170 and +143 °C. The results of these measurements for the 50-Å powder are shown in Fig. 3. The angular distributions obtained from positrons annihilating in the 400-Å powder in oxygen for two widely different temperatures are shown in Fig. 4. With the aid of the narrow-component enhancement provided by the oxygen, a slight temperature dependence is visible.

The ratio of the area of the narrow component to the total area of the distribution is plotted in Fig. 5 as a function of temperature for the 50-Å powder both in oxygen and in vacuum. A curve representing the variation in multiplicative factor (enhancement) required to bring the percent narrow components in vacuum and oxygen into coincidence is also shown in Fig. 5.

Both the oxygen and vacuum data of Figs. 2 and 3 were obtained with the powder in an 8-kG magnetic field. As reported in another paper,[10] such a field is sufficiently strong to completely quench

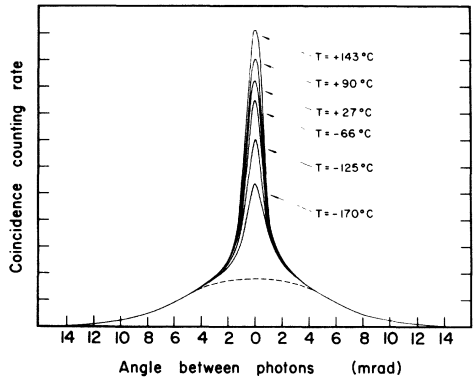

FIG. 3. Effect of temperature on positrons annihilating in a 50-Å powder in oxygen.

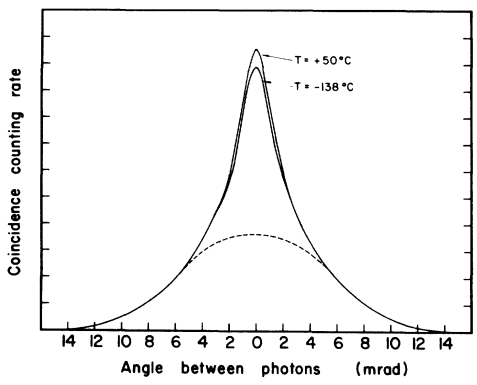

FIG. 4. Effect of temperature on positrons annihilating in a 400-Å powder in oxygen.

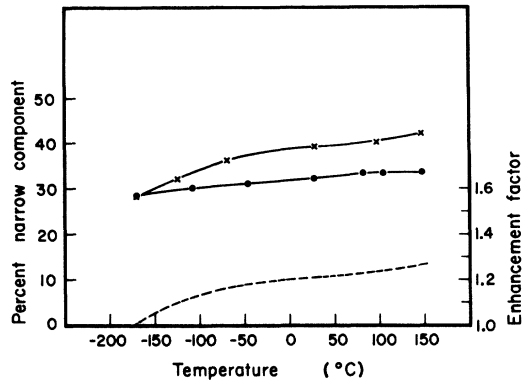

FIG. 5. Effect of the addition of oxygen to a 50-Å powder. The uppermost curve shows the temperature variation of the narrow component in oxygen, while the curve immediately below shows the temperature variation in vacuum. The enhancement factor (dashed line) is the number by which the percent narrow component in vacuum must be multiplied in order to yield the corresponding percent narrow component in oxygen.

the $m = 0$ substate of o-Ps. Accordingly, the 50-Å powder was remeasured in a dry-oxygen atmosphere, but in the absence of an external magnetic field. The application of an 8-kG external magnetic field in the presence of oxygen produces no discernible effect. The magnetic interaction of oxygen with Ps is far too little to account for the quenching,[12] and yet in the presence of oxygen there is no longer any enhancement of the narrow component by the presence of an 8-kG external magnetic field. This leads one to believe that oxygen completely quenches all three substates of o-Ps. In vacuum in the presence of a saturation magnetic field the narrow component would be due to annihilations of the $m = 0$ substates of both o-Ps and p-Ps, and thus represents half the total Ps. In oxygen, all substates of Ps would contribute to the narrow component. Thus, one would anticipate an oxygen enhancement factor of 2 (above that due to the field alone). We attribute the reduction in enhancement factor below the factor of 2 to a competing process—most probably pickoff. The increase in enhancement factor with temperature suggests that the relative effectiveness of oxygen pickoff decreases with increasing temperature. A possible cause of this is the low-temperature surface absorption of Ps predicted by Brandt and Paulin.[2] Note that most of the temperature dependence of the enhancement factor takes place below $-100\,^{\circ}$C. Between -100 and $+150\,^{\circ}$C the enhancement factor only varies from 1.15 to 1.25.

For the sake of completeness, data were taken on the 50-Å powder in dry air. As might be anticipated, the effect of introducing air was similar to that of oxygen but not quite as pronounced.

To examine the effects of surface conditions, the 50-Å powder was measured in dry air before and after a 24-h bakeout at 106 °C. As can be seen in Fig. 6, the presence of surface-absorbed water reduces the amount of narrow component. This is consistent with the reduction in I_3 caused by the absorption of water in silica gel.[13] We conclude that although the temperature and particle size effects support the viewpoint that Ps is formed in the powder grains and diffuses out, one cannot discount the presence of surface interactions.

All the powders discussed so far were prepared in a pellet press with a pressure of about 4 ton/in.^{2}. Measurements were made on a pellet prepared from the 50-Å powder using the maximum available pressure of 40 ton/in.^{2}. The resultant pellet had a definite glassy sheen and a density of 1.1 g/cm^3. For comparison, the density of fused quartz is

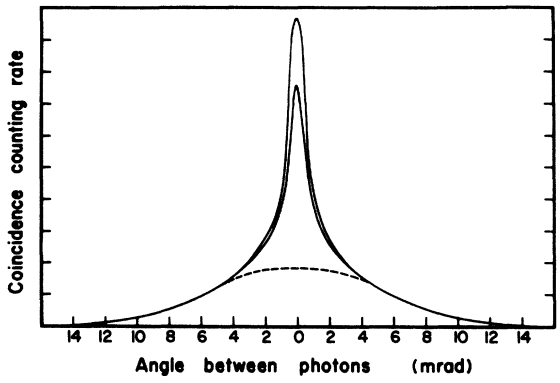

FIG. 6. Effect of vacuum bakeout on a 50-Å powder. The upper curve was taken from a powder which had undergone our standard overnight bakeout at 106 °C. The lower curve was obtained with an untreated powder. Measurements were made at room temperature in dry air.

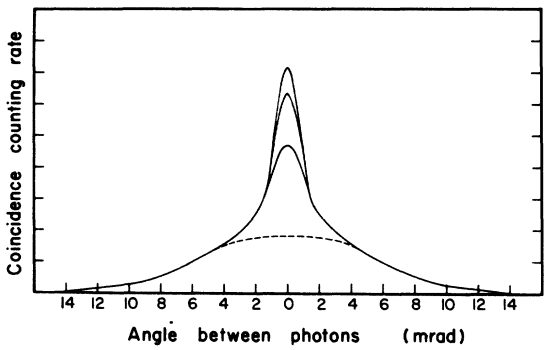

FIG. 7. Effect of pellet density on positrons annihilating in a 50-Å powder. The highest curve corresponds to 1.1 g/cm^3, the intermediate to 0.7 g/cm^3, and the lowest curve to 0.08 g/cm^3. Measurements were made at 90 °C in vacuum.

2.2 g/cm^3. Measurements were also made on the same powder contained in a thin-walled cup and subjected to only a light tamping. (Precautions were taken to ensure that positrons did not annihilate in the containing vessel.) The density of the powder in the cup was 0.08 g/cm^3. The effects on the momentum distribution of these density variations are shown in Fig. 7. The authors had anticipated that increasing pressure would decrease the free surface through which the Ps could reach the interstices and thereby reduce the amount of narrow component. Moreover, Ps that did escape the grains would be confined to a smaller free volume which would broaden the momentum distribution. We offer no explanation for the reverse phenomena shown in Fig. 7. The pellets were prepared in vacuum so there was no chance of sealing in air during compression. One might argue that the positron depth of penetration in the lowest-density powder is sufficient to adversely affect the instrumental resolution. This reduction in resolution would produce a reduction in peak height and a broadening in the narrow component *such that the total area of narrow component remained constant*, which is clearly not the case. Further, we limited the maximum target thickness exposed to the detectors by the use of adjacent lead slits. In any case, the positron depth of penetration is insufficient to affect the instrumental resolution at the higher densities shown in Fig. 7.

The area of the narrow component for the tamped powder was about 26% of the total area of the distribution. Since the data were taken at a saturation magnetic field, about half or 13% of the narrow component area was from p-Ps annihilations. The lifetime data predict a narrow-component area in the range of about 8–14%[1,3] in agreement with our result.

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[5]Obtainable commercially from Degussa, Inc.

[6]The manufacturer reports this temperature range to be adequate to remove surface-absorbed water.

[7]Unless otherwise indicated, all powders were measured with a pellet density of 0.7 g/cm^3 and in a magnetic field of 8 kG. Multiple-distribution graphs have been normalized to the same amplitude at angles equal to or greater than 3 mrad.

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Multipole Relaxation in the Presence of Radio-Frequency Fields

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It is shown that, in general, the damping constants measured in angular-correlation experiments are modified in the presence of a rf field. Restricting to cases in which a transformation to the "rotating frame" allows an exact treatment of the time-dependent field, we give expressions for the perturbation factors and explicit formulas for multipole relaxation constants.

I. INTRODUCTION

In view of the growing number of nuclear-spin-relaxation studies via radiative detection of nuclear magnetic resonance (NMR), e.g., by measuring the angular distribution perturbed by NMR (PAD/NMR), it is worthwhile to reconsider the theory of multipole relaxation in the presence of a rf field. The present paper is based on a recently published theory of perturbed angular correlations.[1,2]

The method of (partially) destroying the anisotropy of the γ radiation emitted from aligned nuclear-spin systems by NMR finds its main field of application in in-beam experiments. The interpretation of the experimental data usually ignores[3]