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Quenching of positronium by surface paramagnetic centers in ultraviolet- and positron-irradiated fine oxide grains

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Interactions between positronium atoms and paramagnetic centers on oxide grain surfaces induced by ultraviolet irradiation (254 nm) or positron irradiation from ^{22}Na have been studied with positron annihilation and electron spin resonance (ESR) methods. Oxides studied are silica aerogel heat treated at 200 °C, then heat treated at 800 °C, silica powder (Cab-O-Sil EH-5) and alumina powder (Degussa Alumina C). The positron irradiation from a ^{22}Na of ~10 mCi at low temperatures induced remarkable changes in the angular correlation of the positron annihilation radiation spectra for all the samples studied, showing the spin-exchange reaction of positronium atoms with irradiation-induced paramagnetic centers on the grain surfaces. Remarkable changes in the positron lifetime spectra were also induced by the ultraviolet irradiation on silica aerogel heat treated at 200 °C and Degussa Alumina C, while no change by the ultraviolet irradiation was observed in silica aerogel heat treated at 800 °C and the Cab-O-Sil EH-5. ESR measurements show formation of -OCH_2 radicals on the surfaces of silica aerogel heat treated at 200 °C. The spin-exchange cross section for the collisions between the Ps atoms and the -OCH_2 radicals is estimated to be of the order of $10^{-21}\,m^2$. [S0163-1829(99)05339-4]

INTRODUCTION

Many studies on the interactions between Ps atoms and surfaces[1–11] have been done using aggregates of fine oxide grains that are suitable media to study the Ps-surface interactions. Recently, it has been shown by Dauwe *et al.*[9,10] and by the present authors[11] that Ps atoms formed in the free space between oxide grains[12] react sensitively with irradiation-induced paramagnetic centers on the grain surfaces at low temperatures. These studies indicate usefulness of the positron annihilation techniques for the selective observation of the surface paramagnetic centers, since it is known that Ps atoms between the grains cannot penetrate back into the bulk region of the grains but interact with the surfaces only.[1–8]

In previous works,[9–11] the positrons from β^+ sources were used both to form positronium, and to irradiate the sample. It was, therefore, difficult to control the irradiation. The present authors showed in Ref. 11 that silica aerogel is not damaged by ^{22}Na positron source of ~10 μCi even at low temperatures. This shows that the positron lifetime measurements with other irradiation sources are possible in some material, such as silica aerogel.

In the present paper, we study the effect of the UV irradiation ($\lambda = 254\,nm$) on heat-treated silica-aerogel, silica powder, and alumina powder by using positron lifetime, Doppler broadening of the 511-keV annihilation line, and electron spin resonance (ESR) methods. The ESR is a powerful method for the study of paramagnetic centers. We also measured angular correlation of positron annihilation radiation (ACAR) in these samples. The ACAR was applied only to silica aerogel before.

II. EXPERIMENTAL PROCEDURE

A. Samples

Samples were silica aerogel[13] (Airglass, Sweden), Cab-O-Sil (Cabot Inc. USA), and Degussa Alumina C (Degussa, Germany) as listed in Table I. Silica aerogel has a three-dimensional network of ultrafine particles of amorphous silica; Cab-O-Sil, and Degussa Alumina C are fumed powders. All the silica-aerogel samples were cut from the same monolith whose density was ~0.1 g/cm^3. All the powder samples of the same material were from the same lot.

The silica aerogel is made from $Si(OCH_3)_4$ through the following reactions:

TABLE I. Properties of the samples used in this study.

	Manufacturer	Form	Heat treatment	Surface groups	Mean diameter
Silica aerogel (1)	Airglass	aerogel	200 °C for 2 h	-OCH_3	4 nm
Silica aerogel (2)	Airglass	aerogel	800 °C for 2 h	Si-O-Si	4 nm
Silica aerogel (3)	Airglass	aerogel	none	-OCH_3	4 nm
Cab-O-Sil EH-5	Cabot-Corp	fumed powder	200 °C for 2 h	-OH	7 nm
Degussa Alumina C	Degussa	fumed powder	200 °C for 2 h	-OH	13 nm

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$$Si(OCH_3)_4+4H_2O\xrightarrow[NH_3]{}Si(OH)_4+4CH_3OH \quad (1)$$

$$n\,Si(OH)_4\rightarrow[SiO_2]_n+2n\,H_2O. \quad (2)$$

The water remaining after the reaction (2) is replaced by methanol before the network grows in the solution. The methanol is then removed in an autoclave. Methoxyl groups ($-OCH_3$) remain on the surfaces because of this process. It is known that the methoxyl groups can be removed by heating the aerogel above 500 °C in the air. In the present paper, we used three samples: as-prepared, heat treated at 200 °C, and heat treated at 800 °C. Water on the surfaces are removed in the sample heat treated at 200 °C but $-OCH_3$ groups remain on the surfaces. The samples heat treated at 800 °C do not have the surface $-OCH_3$ groups.

Cab-O-Sil EH-5 and Degussa Alumina C are made through the aerosil method in a hot flame.

Cab-O-Sil:

$$SiCl_4+2H_2+O_2\rightarrow SiO_2+4HCl. \quad (3)$$

Alumina C:

$$4AlCl_3+6H_2+3O_2\rightarrow 2Al_2O_3+12HCl \quad (4)$$

The surfaces of the samples made by this method are covered with hydroxyl groups (-OH).

B. Angular correlation of positron annihilation radiation measurements (ACAR)

We used 1D-ACAR apparatus having three pairs of scintillation detectors.[14] The momentum resolution was adjusted to 0.45×10^{-3} mc. The ^{22}Na positron sources of intensities of ~10 mCi and ~30 mCi were used. The distance between the sample and the source placed outside the Be window of the sample chamber was ~10 mm. The sample, enclosed in a semiclosed inner chamber made of copper[11] with an aluminum window of 10 μm in thickness, was cooled with a closed-cycle helium gas refrigerator down to 30 K.

C. Positron lifetime and Doppler broadening measurements under UV irradiation

To study the effect of UV irradiation on the oxide surfaces, we used positron lifetime and Doppler broadening methods. The ACAR cannot be used for this purpose because the effect of the positron irradiation is too large.

Positron lifetimes were measured with an ordinary fast-fast lifetime spectrometer using modules of EG&G ORTEC. Relatively large (50 mmΦ × 30 mm) BaF_2 scintillators coupled to Philips XP2020Q photomultipliers were used in order to realize a high counting rate. The time resolution of the apparatus was ~280 ps in full width at half maximum. Doppler broadening spectra were measured with a Canberra GL-1520 HPGe detector.

Figure 1 is a schematic diagram of the sample-source assembly. ^{22}Na positron source of an activity ~5 μ Ci was deposited on a quartz-glass plate that was transparent to the UV light. The distance between the source and the sample was ~2 mm. The sample chamber was evacuated to 10^{-7} Torr by an oil-diffusion pump with a liquid-N_2 trap or a turbo molecular pump. The samples were cooled to 30 K with a closed-cycle helium-gas refrigerator. The UV light irradiations (254 nm) were made from the same side as the positron injection. The UV source was a 3-W low-pressure mercury lamp (SP-3-2L, ozoneless type, SEN Lights Corporation, Japan). The luminous intensity on the sample was adjusted to ~1 mW/cm^2 by setting the lamp 2 cm away from the sample.

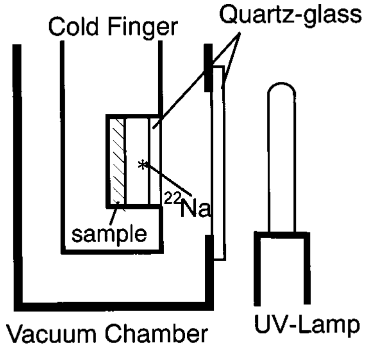

FIG. 1. Schematic diagram of the sample chamber for positron lifetime and Doppler broadening measurements under UV irradiation.

Positron-lifetime measurements with a lower luminous intensity were also performed for silica aerogel heat treated at 200 °C. The distance between the sample and the UV lamp was set to be 7 cm and the luminous intensity was ~0.25 mW/cm^2, which was the same as that in the ESR measurement. The UV irradiations and measurements were made at several temperatures between 30 and 100 K.

D. ESR measurements

ESR spectra were measured with JOEL JES-RE2X spectrometer. A Heritran cryostat system (APD Cryogenics Inc., USA) allows cooling the sample down to 4.2 K. The sample was irradiated by the UV lamp at low temperatures. All the glass tubes and plates surrounding the sample are UV transparent. The distance between the sample and the UV lamp was 7 cm and the luminous intensity at the sample was ~0.25 mW/cm^2. The irradiation and the measurements were made at several temperatures between 15 and 100 K.

III. RESULTS

A. Results of ACAR measurements

ACAR curves for silica aerogel heat treated at 800 °C, Cab-O-Sil, and Degussa Alumina C are shown in Fig. 2. All the ACAR spectra were measured without magnetic field and the UV irradiation. The counts have been normalized to the number of incident positrons. The ACAR spectra for silica aerogel before heat-treatment[13] is also shown for comparison. The open circles (○) show the spectra at room temperature, and the closed circles (●) show those at low temperatures. All the ACAR spectra show remarkable changes on cooling. These changes were reversible; the spectra recover to their initial shapes by heating the samples to room temperature.

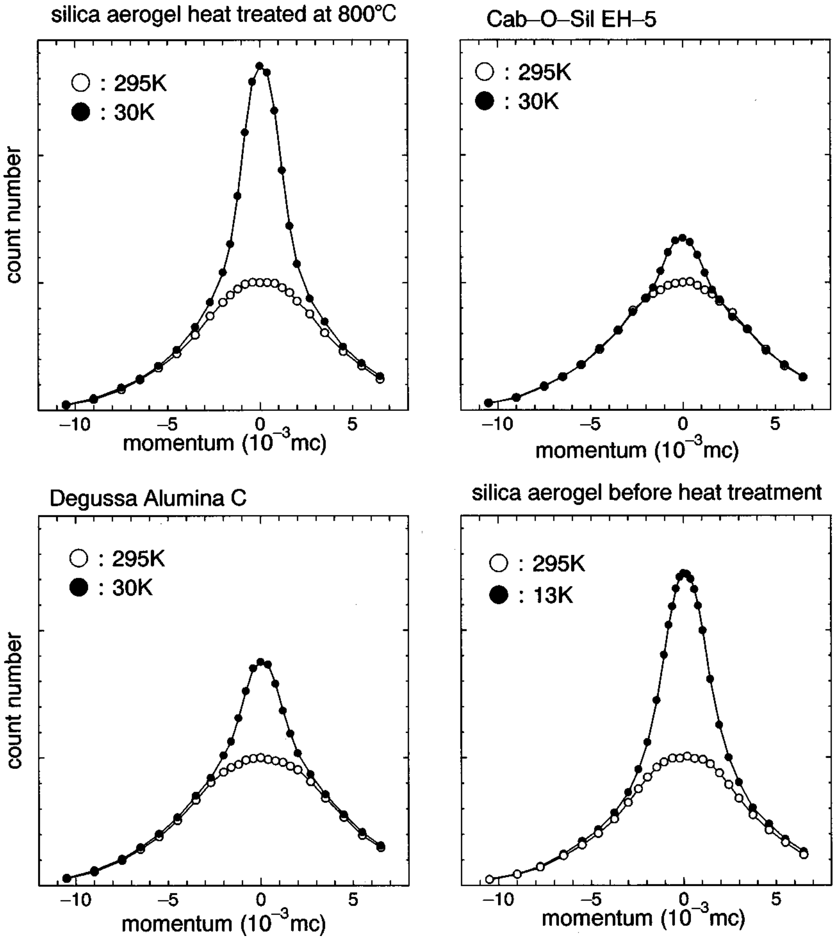

FIG. 2. ACAR spectra for silica aerogel heat treated at 800 °C, Cab-O-Sil, Degussa Alumina C, and silica aerogel as prepared.

B. Results of positron lifetime and Doppler broadening measurements under UV irradiation

Figure 3 shows lifetime spectra for the four samples before (●) and after (+) the UV irradiation at 30 K. The samples were kept at 30 K throughout the measurements. Remarkable changes in the long lifetime component are clearly observed in silica aerogel heat treated at 200 °C [Fig. 3(a)] and Degussa Alumina C [Fig. 3(b)]. In contrast, silica aerogel heat treated at 800 °C [Fig. 3(c)] and Cab-O-Sil [Fig. 3(d)] show no change even after the UV irradiation for more than 10 h. No lifetime spectra before the UV irradiation, even that for alumina powder, changes with time. This indicates that the effect of the irradiation by the positrons from the weak ^{22}Na source for the lifetime measurements (5 μCi) is negligible. Thus, the observed changes in the lifetime spectra are almost solely due to the UV irradiation. Dauwe and Mbungu-Tsumgu[9] reported an effect of the irradiation by a positron source of ~10 μCi on an alumina powder. The difference can be attributed to the fact that the positron source was not in contact with the sample in our setup. In a separate experiment in which the sample and the source were in contact, we observed a decrease of the lifetime of ortho-Ps with time in alumina as reported by Dauwe and Mbungu-Tsumgu.[9]

Figure 4 shows Doppler broadening spectra for silica aerogel heat treated at 200 °C. The closed circles (●) show the data before irradiation and the open circles (○) show those after the UV irradiation for 30 min at 30 K. Effect of the UV irradiation is clear. The Doppler broadening spectra for alumina before and after the UV irradiation, however, were almost identical.

C. Results of ESR measurements

ESR spectra in silica aerogel heat treated at 200 °C are shown in Fig. 5. They were measured at 100 and 15 K after the sample was irradiated by the UV lamp at 30 K. The ESR signal from the H atom with a hyperfine interval of 50.8 mT, which is often seen on silica surfaces,[15] was not found in a separate measurement with a wide range of magnetic field.

The ESR signals for silica aerogel heat treated at 800 °C, Cab-O-Sil EH-5, and Degussa Alumina C were not distinguished from the background, though a weak broad signal were seen in alumina.

Density of the unpaired electrons for silica aerogel heat treated at 200 °C was obtained by comparing the spectra with the signals of Mn+ marker, which is calibrated with solutions of 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxide (HTEMPO). We performed measurements on several samples at several temperatures between 30 and 100 K. The results are averaged and given in the second column of Table II. The errors are estimated from the scattering of the data and the uncertainty of the zero-absorption line.

IV. DISCUSSION

As can be seen in Fig. 2, the low-momentum regions in ACAR spectra for all the samples investigated are enhanced

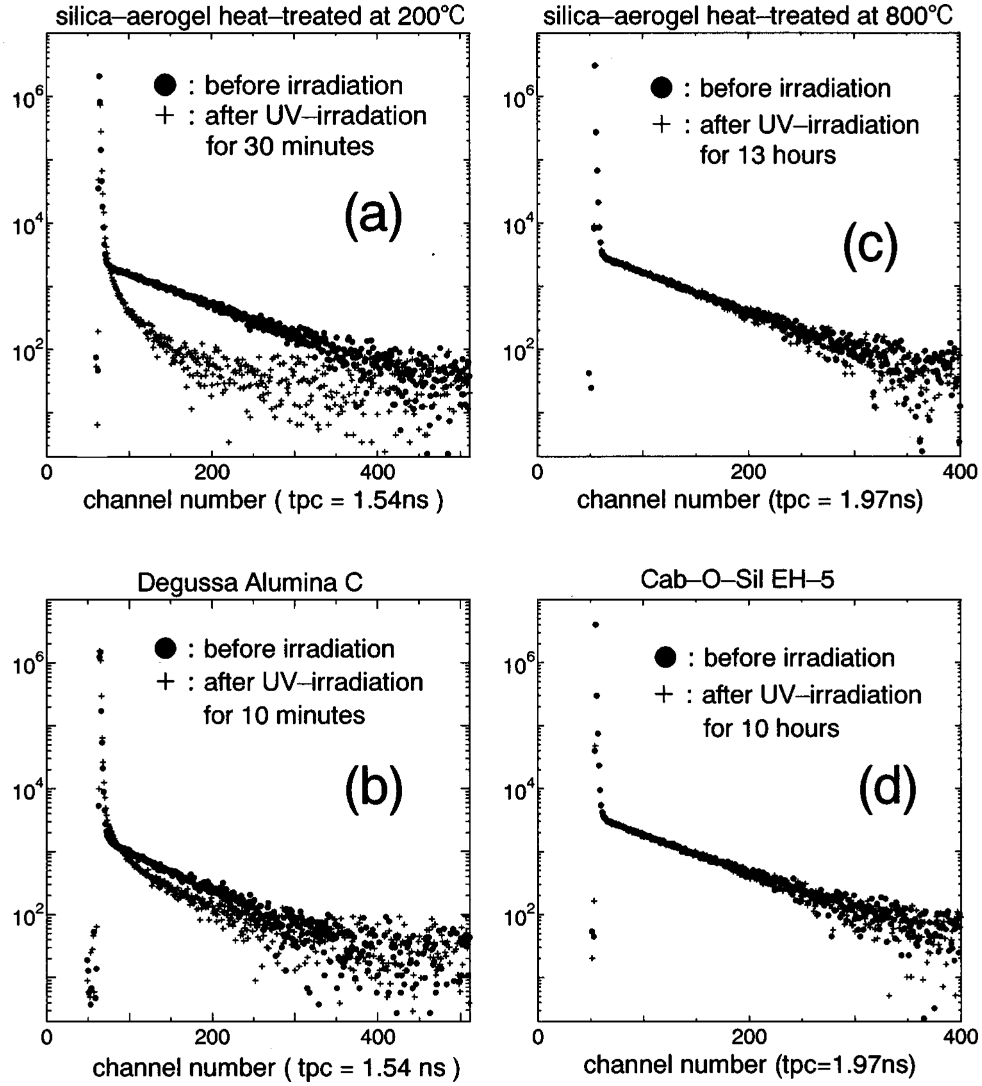

FIG. 3. Positron-lifetime spectra before and after UV irradiation for (a) silica aerogel heat treated at 200 °C, (b) Degussa Alumina C, (c) silica aerogel heat treated at 800 °C, and (d) Cab-O-Sil.

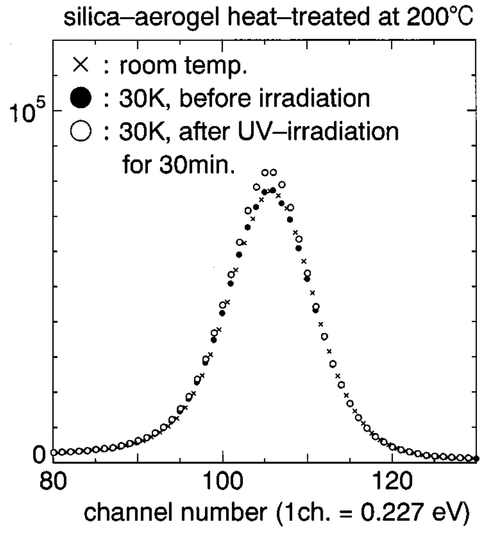

FIG. 4. Doppler broadening spectra before and after UV irradiation for silica aerogel heat treated at 200 °C.

at low temperatures. This is due to the spin-exchange reaction of positronium in the free space between the grains.[11] Para-Ps (spin-singlet) and ortho-Ps (spin-triplet) are formed in the ratio of 1:3 and para-Ps atoms normally annihilate into two γ rays in vacuum, while ortho-Ps atoms annihilate into three γ rays. The self-annihilation rate of para-Ps ($8\times10^9\,\mathrm{ns}^{-1}$) is much higher than that of ortho-Ps ($7\times10^6\,\mathrm{ns}^{-1}$). In the ACAR measurements, the samples are irradiated by an intense positron source (a few tens of mCi). Paramagnetic centers are formed at low temperatures by the positron irradiation and the Ps atoms in the free space between the grains exchange their spins with the centers on the surfaces. This reaction increases the intensity of the para-Ps component in the low-momentum region in the ACAR spectra, because ortho-Ps, which normally annihilate into three γ rays, converts to para-Ps and annihilates into two γ rays.

Temperature dependencies of the ACAR spectra are due to the change in the rate of annealing of the paramagnetic centers. The spin exchange of the Ps atoms is not observed at room temperature because the annealing rate of the paramagnetic centers at room temperature is so high that the equilibrium concentration of the paramagnetic centers are negligibly low.

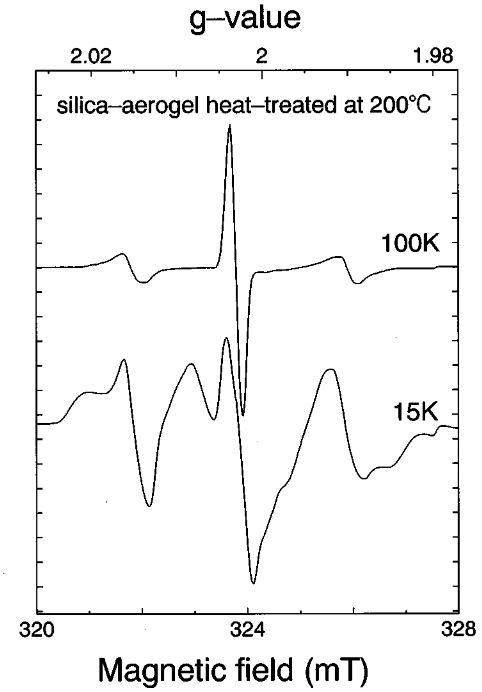

FIG. 5. ESR spectra for silica aerogel heat treated at 200 °C. The sample was irradiated by UV at 30 K and measured at the temperatures indicated.

Unpaired electrons sometimes induce chemical quenching of Ps atoms[16] through oxidation or formation of Ps compounds. This diminishes the narrow para-Ps self-annihilation component in the ACAR spectrum and enhances the broad component. The intensity of the broader components in the ACAR spectra in Fig. 2 are almost unchanged. This shows clearly that the Ps atoms does not undergo the chemical quenching in any of the samples investigated but undergo the spin-exchange reaction. This discrimination is not possible by the positron lifetime or 3γ annihilation fraction measurements because both spin-exchange reaction and chemical quenching cause shortening of the lifetime of ortho-Ps and decrease of the 3γ annihilation fraction.

The UV irradiation effect is most prominent for silica aerogel heat treated at 200 °C as manifested in the positron lifetime spectra shown in Fig. 3(a). The mean lifetime of ortho-Ps at 30 K is plotted against the UV irradiation time is shown in Fig. 6. When the temperature is raised, the mean lifetime of the ortho-Ps begins to increase at around 150 K and approaches its initial value before the UV irradiation as is seen in Fig. 7. Doppler broadening spectra in silica aerogel heat treated at 200 °C (Fig. 4) shows modest enhancement in the central part after the UV irradiation at 30 K.

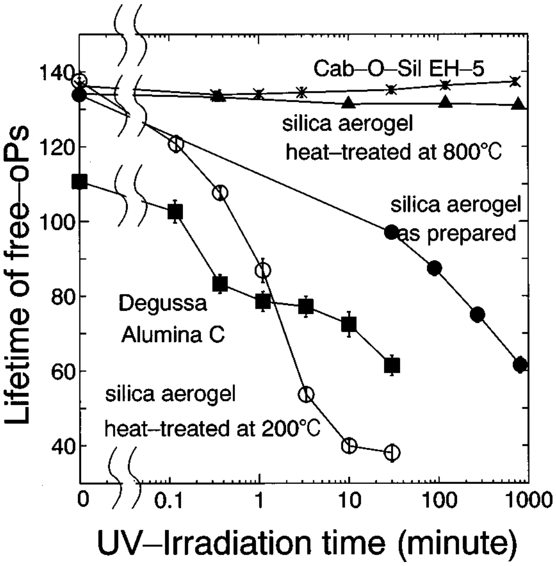

FIG. 6. Lifetime of ortho-Ps versus irradiation time. The luminous intensity of the UV light at the sample was about 1 mW/cm^2.

These results are interpreted in a similar way as that for the case of positron irradiation. Paramagnetic centers are formed on the grain surfaces by the UV irradiation and the Ps atoms undergo spin-exchange collisions with the centers. The recovery of the lifetime of ortho-Ps above 150 K can be attributed to the annealing of the irradiation-induced centers.

The ortho-Ps lifetime in Cab-O-Sil and silica aerogel heat treated at 800 °C were unchanged during the UV irradiation for more than 10 h as seen in Figs. 3(c) and 3(d) and 6, indicating that surface paramagnetic centers are not created by the UV irradiation. This is in clear contrast to the results of the ACAR measurements which show the formation of the paramagnetic centers in these materials. This is because the energy of the positrons from ^{22}Na (maximum 0.54 MeV) is many orders of magnitude higher than that of the UV light used (4.9 eV) and thus the former can make various kinds of paramagnetic centers.

In the alumina powder the mean lifetime of ortho-Ps showed a remarkable shortening induced by the UV irradiation as seen in Figs. 3(b) and 6, indicating that Ps atoms undergo spin-exchange reaction or chemical quenching on the surfaces. The fact that the ACAR measurements show no chemical quenching induced by the positron irradiation suggests that Ps atoms undergo only spin-exchange reaction also in alumina powder under the UV irradiation; if centers that induce chemical quenching were created by the low-energy UV irradiation (4.9 eV), it would be created by positron irradiation with much higher energy. The Doppler broadening

TABLE II. Unpaired electron density after the UV irradiation at low temperatures in silica aerogel heat treated 200 °C, orthopara conversion rate, and orthopara conversion cross section.

Irradiation time	Unpaired electron density (10^{17} spins/g)	Ortho-para conversion rate (ns^{-1})	Ortho-para conversion cross section (10^{-21} m^2)
10 min	1.6 ± 0.8	1.5 ± 0.5	4^{+6}_{-2}
30 min	6.3 ± 3.7	3.3 ± 0.7	2^{+4}_{-1}
Averaged			3^{+6}_{-2}

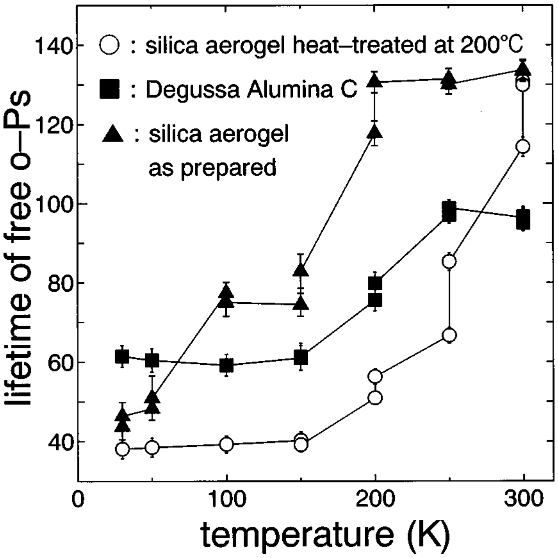

FIG. 7. Lifetime of ortho-Ps with elevating temperature after UV irradiation at 30 K.

spectra are insensitive in this case. This is probably because large part of positrons annihilate in the region where the UV irradiation is unreachable.

The ESR spectra for the silica aerogel heat treated at 200 °C (Fig. 5) show formation of -OCH_2 radicals. The triplet splitting in the spectrum at 100 K indicates that two protons exist close to the unpaired electron. The g value and hyperfine splitting observed are 2.002 and 20 G, respectively. These values are close to those reported for $\cdot CH_2OH$ in the literature, which are 2.001 (Ref. 17) for g value and 17 ± 2[17] 19,[18] or 17.2 G (Ref. 19) for the hyperfine splitting. The spectrum at 15 K in Fig. 7 resembles ESR spectra for $\cdot CH_2OD$ observed at 77 K in a frozen matrix by Sullivan and Koski.[20] The change in the shape of the ESR spectrum on cooling to 15 K is interpreted as due to freezing of the rotation of -CH_2.

The simplest reactions that create the -OCH_2 radicals are

$$\text{-}OCH_3 + h\nu \rightarrow \text{-}OCH_2\cdot + H\cdot \tag{5}$$

or

$$\text{-}OCH_2^- + h\nu \rightarrow \text{-}OCH_2\cdot + e^-. \tag{6}$$

Reaction (5), however, is unlikely because (i) it is known that CH_3OH, which is the simplest molecule containing -OCH_3 does not absorb the 254-nm light, and (ii) ESR lines from H atoms were not observed in our measurements. The reaction from a precursor as described by Eq. (6) is more likely.

The third column of Table II shows ortho-para conversion rate obtained in the same irradiation condition as the ESR measurements. The conversion rate was obtained from one-component fit to the lifetime spectra in the time region from 20 ns after the prompt. Since the temperature dependence is not larger than the scattering of the data, the averaged values in the temperature range between 30 and 100 K are listed.

Using the conversion rate from the positron-lifetime measurements and the unpaired electron density obtained from ESR in Table II, we estimate the ortho-para conversion cross section for positronium collisions with -OCH_2 radicals. We assume that silica grains are spheres of radius r, that all the paramagnetic centers exist on the surfaces of the grains, and that the conversion cross section is independent of the angle between the positronium velocity (V_{ps}) and the surface of the grains. When a Ps atom collides with a grain, the surface paramagnetic centers on the backside are not effective for the spin-exchange collision. Therefore, the effective number of paramagnetic centers per grain is $n_s \times 4\pi r^2/2$, where n_s is the surface density of the paramagnetic centers. The ortho-para conversion rate c is thus given by

$$c = \frac{\sigma \cdot n_s \cdot 4\pi r^2/2}{\pi r^2} \cdot \frac{V_{\mathrm{Ps}}}{l} \tag{7}$$

and hence, the conversion cross section σ is

$$\sigma = \frac{c \cdot l}{2 \cdot V_{\mathrm{Ps}} \cdot n_s}, \tag{8}$$

where l is the mean distance between the grains.

V_{ps} was estimated from the lifetime spectra in the presence of paramagnetic centers at various temperatures. The spectra show that lifetime of the ortho-Ps was unchanged between 30 and 100 K. This indicates that Ps atoms are not thermalized below 100 K in the silica aerogel whose density was ~0.1 g/cm^3. Here, we assumed that V_{ps} is the thermal velocity at 100 K for the Ps between 30 and 100 K. The cross sections obtained are listed in Table II. The averaged value is $3^{+6}_{-2} \times 10^{-21}\,\mathrm{m}^2$.

To the authors knowledge, there are no data reported in the literature for the spin exchange of Ps atoms with -OCH_2 radicals. We can only compare the present results with those reported for gas molecules[21,22] and for ions in solutions.[23–27] The cross sections for paramagnetic gases are $(1.0\pm 0.3) \times 10^{-23}\,\mathrm{m}^2$ (O_2, elastic),[21] $5\times 10^{-21}\,\mathrm{m}^2$ (O_2, inelastic) (Ref. 21), and $8.45\times 10^{-23}\,\mathrm{m}^2$(NO).[22] Our result is comparable to that for the inelastic collision with O_2. Very large conversion cross section ($\sim 10^{-17}\,\mathrm{m}^2$) for phosphorescent gases (SO_2 and benzaldehyde) excited by UV light were once reported by Brandt *et al.*[28,29] However, their results were not supported by later works.[30,31] The conversion cross sections are also reported for ions in solutions. The values are $1.3 \times 10^{-21}\,\mathrm{m}^2$ for $e-_{NH3}$ (Ref. 23), $5.9\times 10^{-23}\,\mathrm{m}^2$ for Ni^{++} (Ref. 24), $2.4\times 10^{-23}\,\mathrm{m}^2$ for Cu^{++} (Ref. 25), $0.15 \times 10^{-23}\,\mathrm{m}^2$ for an electron in a series of lanthanide ions ($Ce^{3+} \sim Gd^{3+}$),[26] $0.4\times 10^{-24}\,\mathrm{m}^2$ for an electron in another series of lanthanide ions ($Yb^{3+} \sim Tb^{3+}$).[27] These values may be underestimated because the velocity of the Ps atoms, which are actually diffusing in the solutions, is assumed to be the thermal velocity. Theoretical calculations have been made by several workers for Ps spin exchange with the H atom,[32–38] Li atom,[39,33] and an electron.[33,40–42] Results of almost all the theoretical calculations range above $10^{-20}\,\mathrm{m}^2$, larger than the present result. The only comparable value with the present result is shown in Ref. 37 for the spin exchange of Ps with a H atom around the thermal energy, which is about $10^{-21}\,\mathrm{m}^2$.

As ortho-para conversion rate of Ps is proportional to the surface density of the paramagnetic centers, the Ps spectroscopy offers a detection method for them. The sensitivity of the Ps method for the detection of the surface paramagnetic centers depends on the velocity of Ps. When Ps, which exists in the vacant space between the grains, has the thermal velocity at 295 K ($V_{\mathrm{Ps}} = 8 \times 10^4$ m/s), and that the lifetime of Ps is measured with an accuracy of a few percent, the detection limit is estimated to be $\sim 10^{16}$ spin/cm^3. This is as high as that of a typical superconducting quantum interface device magnetometer. Of course the ESR method has much higher sensitivity. Relaxation of the spins, however, often broaden the ESR spectra and make them invisible. The Ps method is free from the relaxation of the spins.

The existence of the paramagnetic centers on the surfaces is often demonstrated by observing changes in the ESR spectra on introducing gases.[43] This procedure, however, sometimes leaves ambiguousness about the location of the paramagnetic centers due to the diffusion of the gas molecule into the bulk. The Ps method, which has surface selectivity, affords a complementary and unique tool for the detection of paramagnetic centers.

V. CONCLUSIONS

Effects of the irradiations by positrons and UV lights on oxide grains at low temperatures were studied using positron annihilation and ESR methods. It was shown that the sufficiently high-positron irradiation (10–30 mCi) form surface paramagnetic centers at low temperatures in all the oxide samples investigated and that Ps atoms exchange their spins with them. On the other hand, the effect of weak positron sources ($\sim$10 μCi) was negligible. The UV irradiation of $\sim$1 mW/cm^2 forms the surface paramagnetic centers only in silica aerogel heat treated at 200 °C and alumina. In both cases spin exchange is the dominant effect on the Ps. Formation of -OCH$_2$ radical is observed in the silica aerogel heat treated at 200 °C. The spin-exchange cross section for the collisions between the Ps atoms and the -OCH$_2$ radicals are estimated to be of the order of 10^{-21} m^2.

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