PHYSICAL REVIEW B VOLUME 26, NUMBER 5 1 SEPTEMBER 1982

Surface interactions of muonium in oxide powders at low temperatures

Robert F. Kiefl,* John B. Warren, Chris J. Oram, Glen M. Marshall,
Jess H. Brewer, and Dale R. Harshman
Department of Physics, University of British Columbia and TRIUMF, Vancouver, British Columbia V6T 2A6 Canada

Carl W. Clawson
Department of Physics, University of California, Berkeley, California 94720

(Received 12 February 1982)

Measurements of muonium (μ^+e^-) spin relaxation in finely powdered samples of Al_2O_3, MgO, and SiO_2 indicate that the muonium atoms escape the powder grains with a high efficiency, regardless of the ambient temperature of the powder. In Al_2O_3 powder in a pure He (or Ne) atmosphere at low temperature ($T < 30$ K), the muonium spin relaxation rate is proportional to the fraction of the powder surface area not covered by adsorbed He (Ne); it is postulated that a He (Ne) film on the powder surfaces protects muonium against depolarizing collisions with the bare Al_2O_3 surfaces.

I. INTRODUCTION

Surface radicals have long been used as probes of catalytic-oxide surfaces[1] via the technique of electron-spin resonance (ESR). The simplest radical, the H atom, can be stabilized on catalytic-oxide surfaces at low temperature by irradiating the sample with γ rays,[2] which dissociate $(OH)^-$ groups on the surface to form H atoms weakly bound to the surface by van der Waals forces. The chemistry and physics of adsorbed H atoms have been studied previously[3] and are of considerable interest in surface science.

This interest in H atoms on surfaces naturally extends to muonium (μ^+e^- or Mu), effectively a light isotope of H consisting of an electron bound to a positive muon and possessing $\frac{1}{9}$th the mass of a H atom. Mu atoms are formed when energetic positive muons, available at meson facilities such as TRIUMF, are stopped in a suitable target material. It is believed that the muons undergo a series of charge-exchange collisions in the 2-keV to 20-eV region resulting in a neutral fraction (Mu) which subsequently thermalizes within a few picoseconds in condensed matter.[4,5] Polarized Mu atoms are studied by the technique of muon spin rotation (μ^+SR),[4,5] which is somewhat analogous to ESR. One major distinction is that in μ^+SR Mu atoms are studied one at at time, whereas in ESR the H atoms are studied collectively. Thus, while ESR of H atoms may be sensitive to H-H interactions, in μ^+SR there can be no Mu-Mu interactions.

The scientific interest in Mu on surfaces is threefold. First, it is hoped that one may learn about isotopic effects in the chemistry and physics of H atoms on surfaces. The study of Mu chemistry in the gas and liquid phases has been very successful in this regard.[6] Second, certain reactions of Mu on surfaces may be easier to study than the counterpart H-atom reactions. Finally, since Mu atoms are extremely sensitive to impurities and defects, the study of Mu diffusion, trapping, and reactions on surfaces might be useful in characterizing insulator surfaces.

In recent years Mu has been observed in several oxide powders such as SiO_2, Al_2O_3, and MgO (Refs. 7 and 8) at 300 K. There are strong indications that the Mu moves thermally at this temperature in the large free volume between the grains. The principal evidence for this is from measurements of the Mu spin-relaxation rate when paramagnetic O_2 is introduced. The observed rate constant for spin relaxation agrees well with that obtained using an Ar moderator at 300 K.[9] This indicates that the Mu mean velocity is the same in both cases; thus the thermal Mu atom at this temperature spends little time bound to the surface.

In order to study Mu on surfaces it is essential to produce it efficiently in such a way that it comes in contact with surfaces at low temperatures ($kT \ll B_{\mathrm{Mu}}$, where B_{Mu} is the binding energy to the surface). In this siuation the thermal Mu atom may reside on the surface for a large fraction of the muon lifetime (2.2 μs).[10] A difficulty is anticipated with producing such Mu. Until now it was thought that the emergence of Mu from powder grains was a diffusion-controlled process whereby the injected muons form Mu within the grains, diffuse at the ambient temperature to the surface, and are ejected because of a negative work function.[7] According to this model Mu should become trapped inside powder grains at low temperature in materials such as SiO_2 since Mu is static in a bulk sample below 50 K.[11] However, the present results show that the Mu escapes into the voids efficiently even at temperatures as low as 6 K. The results are surprising in this respect and crucially important to future studies of Mu surface physics and chemistry.

II. THE μ^+SR TECHNIQUE

The technique of μ^+SR is described elsewhere.[4,5] It suffices to say that the time evolution of the μ^+ spin polarization (both magnitude and direction) is directly observable via the asymmetric decay of the muon ($\mu^+ \rightarrow e^+ + \bar{\nu}_\mu + \nu_e$) in which the positron is emitted preferentially along the muon spin-polarization direction. In transverse-field μ^+SR (used in this experiment), a magnetic field is applied transverse to the initial μ^+ polarization. In vacuum, the muon spin-polarization vector of a bare μ^+ precesses about the applied field at a single Larmor frequency, ν_μ (kHz)$=13.6H$ (Oe), where H is the applied field in Oe. The muon spin polarization in a Mu atom exhibits four discrete precession frequencies. In low fields ($H < 10$ Oe) two of these are of order of the hyperfine splitting (4463 MHz), which is usually too fast to observe. The other two are difficult to resolve and have a mean frequency ν_{Mu} (MHz)$=1.39H$ (Oe) (103 times faster than the free-muon frequency). In matter the muon and Mu precession frequencies are broadened due to interaction with the host, resulting in spin relaxation. The histogram of time delays between an incident muon and its decay positron (the μ^+SR spectrum) is of the following form:

$$N(t)=N_0 e^{-t/\tau_\mu}[1+S_{\text{Mu}}(t)+S_\mu(t)]+\mathscr{B} , \quad (1)$$

with

$$S_{\text{Mu}}(t)=A_{\text{Mu}}R_{\text{Mu}}(t)\cos(2\pi\nu_{\text{Mu}}t+\phi_{\text{Mu}}) , \quad (2)$$

$$S_\mu(t)=A_\mu R_\mu(t)\cos(2\pi\nu_\mu t+\phi_\mu) , \quad (3)$$

where $S_{\text{Mu}}(t)$ and $S_\mu(t)$ are the Mu and free-muon precession signals, $\mathscr{B}$ is a time-independent background, N_0 is the normalization, τ_μ is the muon lifetime (2.2 μs), A_{Mu} and A_μ are the Mu and free-muon precession amplitudes, $R_{\text{Mu}}(t)$ and $R_\mu(t)$ are the Mu and free-muon relaxation functions, and ϕ_{Mu} and ϕ_μ are the Mu and free-muon precession phases. The fitted parameters A_{Mu} and A_μ are used to obtain the Mu and muon fraction by a suitable method of normalization.[8] Much of the interest in a μ^+SR experiment is focused on the spin relaxation of the muon or Mu atom since this phenomenon yields information on the muon-host or Mu-host state.

III. EXPERIMENTAL PROCEDURE AND RESULTS

The experiment was performed in two parts, *A* and *B*. In part *A*, μ^+SR spectra were taken on Al_2O_3, SiO_2, and MgO powder samples in a He atmosphere between 5 and 20 K. The powders were selected on the basis of their high yield of extragranular Mu at 300 K. The properties of the powders are given in Table I. The powder surfaces were not specially cleaned for this part of the experiment due to the preliminary nature of the measurements. The discussion of the results for this part of the experiment is directed at the question: Does Mu emerge from the powder grains at these low temperatures, as previously observed at 300 K? In part *B* a more controlled set of measurements was performed on the Al_2O_3 powder sample in a He or Ne atmosphere, in which careful attention was paid to the condition of the surfaces. This part of the experiment was done first to confirm the conclusions reached from part *A*, and second to investigate the scattering of thermal Mu off Al_2O_3 surfaces with adsorbed He and Ne.

In both parts of the experiment a beam of spin-polarized muons of momentum 28 MeV/*c* produced at TRIUMF was collimated to a 1.9-cm diameter spot and directed into a He-gas-flow cryostat containing the target. The μ^+SR apparatus used in this experiment is described elsewhere.[10,12]

A. μ^+SR measurements in Al_2O_3, SiO_2, and MgO powders in a He atmosphere between 6 and 20 K

Each powder sample was placed in an open-top styrofoam vessel (10.2 cm long by 3.8 cm diameter) equipped with a 12.7-μm aluminized Mylar window to allow entry of the μ^+, and then inserted

TABLE I. Physical properties of the oxide powders.

Powder (Supplier serial no.)	Density ($\mathrm{g\,cm^{-3}}$)	Surface area ($\mathrm{m^2/g}$)	Particle[a] size (diam.) (Å)	Impurities[b]
SiO_2 (Cabot EH5)	0.04	400	70	Na (20–40 ppm) P (<300 ppm) all other elements less than 30 ppm
SiO_2 (Cabot M5)	0.04	200	140	same as above
Al_2O_3 (Davison SMR-7-7563)	0.56	225	75	Fe_2O_3 (1.8 mol %) SO_4 (0.2 mol %) SiO_2 (0.08 mol %) Na_2O (0.03 mol %) Cl (<0.01 mol %)
MgO (Matheson Coleman Bell MX 65-05)	0.12	not available	300	Na (0.5 at. %) Cl (0.01 at. %) Ca (0.05 at. %) Ba (0.005 at. %) SO_4 (0.02 mol %) K (0.005 at. %) NH_4 (OH) (0.02 mol %) Sr (0.005 at. %) In (0.01 mol at. %) Heavy metals (0.003 at. %) Mn (5 ppm)

[a] Estimated from the specific area assuming spherical particles except for the case of MgO where the given size is based on an electron micrograph.

[b] The manufacturer's stated impurities except for the Fe content in Al_2O_3, which was determined by atomic absorption for the sample used in the experiment.

into a He-gas-flow cryostat. In all cases except the 140-Å SiO_2, the powders were not evacuated, so that submonolayer concentrations of O_2 and N_2 (from air in the dead volume of the target vessel) as well as an unknown amount of water vapor were adsorbed on the surfaces. The 140-Å SiO_2 powder was evacuated *in situ* at 270 K to 10^{-1} Torr so that O_2 and N_2 were removed prior to cooling down to 6 K. The effect of these adsorbed gases on the results is discussed later. The residual range of muons entering the target was only 80 $\mathrm{mg/cm^2}$ (of carbon) so, for example, in the Al_2O_3 powder all the muons were stopped before penetrating 1.4 mm into the target. The oxide surfaces of the powders were in direct contact with the cold He gas (at a pressure of 760 Torr) from the cryostat. Temperature measurements were made with a Cryocal 2500H Ge resistor. The temperature was controlled to ± 250 mK.

A μ^+SR spectrum of roughly three million events was taken for each sample in a transverse field of 10 Oe over a $(1-2)$-h period at an ambient temperature of 6 K. In the case of the Al_2O_3 powder the temperature was varied between 6 and 20 K.

The resulting spectra were fit to the form given by Eq. (1). The quality of the fits was not sensitive to whether the free-muon relaxation function $R_\mu(t)$ was Gaussian $[\exp(-\beta^2 t^2)]$ or exponential $[\exp(-\lambda t)]$. Good fits were obtained using a single-component Mu relaxation function $[R_{\mathrm{Mu}}(t)=\exp(-\lambda t)]$ except for the case of 140-Å SiO_2 for which a substantial improvement in the fit was obtained by using a two-component relaxation function,

$$R_{\mathrm{Mu}}(t)=\alpha\exp(-\lambda_1 t)+(1-\alpha)\exp(-\lambda_2 t)\ . \tag{4}$$

The χ^2 improved from 401 (for 303 degrees of freedom) in the case of single-component relaxation to 315 (for 301 degrees of freedom) in the case of two-component relaxation. The two-component Mu precession signal obtained from the 140-Å SiO_2 sample is shown in Fig. 1. The results from the two-component fit (given in Table II) indicate that roughly half of the Mu ensemble relaxes at a

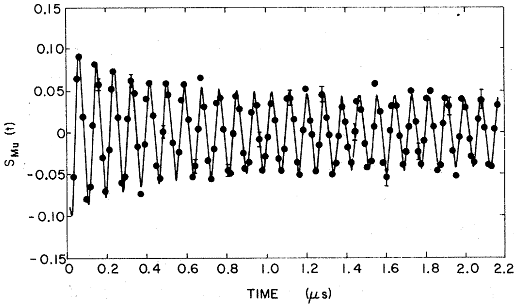

FIG. 1. Muonium precession signal, $S_{Mu}(t)$, in 140-Å SiO_2 powder in a He atmosphere at 6 K. The solid line is the two-component fit to the data.

rate of 4.1 ± 0.7 μs^{-1}, while the remaining fraction relaxes at a much slower rate of 0.16 ± 0.05 μs^{-1}.

In Table II the Mu fraction and spin-relaxation rate at room temperature in evacuated powders are compared with the present low-temperature results in a He atmosphere. Figure 2 shows the temperature dependence of the Mu spin-relaxation rate for Al_2O_3 in a He atmosphere between 6 and 20 K. The spin-relaxation rate rises sharply at a temperature of 12.5 K. At higher temperatures the spin relaxation is so fast that only a lower limit on the relaxation rate is shown.

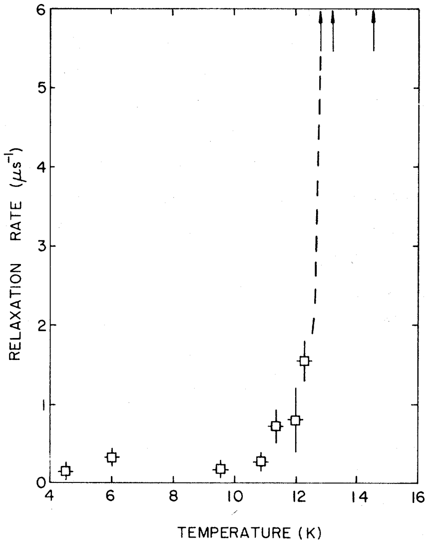

FIG. 2. Temperature dependence of the muonium spin-relaxation rate in 75-Å Al_2O_3 powder in a He atmosphere. The arrows indicate points that are off scale.

B. Mu spin relaxation in Al_2O_3 powder with adsorbed He or Ne

It was hypothesized that the slowly relaxing Mu component observed in all the powder samples at 6 K (see Table II) was due to extragranular Mu pro-

TABLE II. Comparison of room-temperature μ^+SR results for evacuated powders with low-temperature results in a He atmosphere.

Target (Particle size)	Temperature (K)	Muonium fraction (at. %)	Muonium relaxation rate (μs^{-1})
SiO_2 (70 Å)	6	49 ± 3	0.46 ± 0.03
SiO_2 (70 Å)	295	61 ± 3	0.18 ± 0.03
SiO_2 (140 Å)	6	35 ± 5(1)	$4.1\ \pm0.7$(1)[a]
		35 ± 5(2)	0.16 ± 0.05(2)
SiO_2 (140 Å)	295	60 ± 3	0.18 ± 0.03
Al_2O_3 (75 Å)	6	29 ± 3	0.35 ± 0.05
Al_2O_3 (75 Å)	295	35 ± 14	$11.3\ \pm4.4$
MgO (300 Å)	6	12 ± 3	0.22 ± 0.03
MgO (300 Å)	295	15 ± 3	$1.9\ \pm0.5$

[a] The (1) and (2) refer to the two components resolved in the fit.

tected from depolarizing effects of the surfaces by a He film covering the surfaces. In order to test this hypothesis, a second series of measurements were performed on the Al_2O_3 powder, in which controlled amounts of He (99.995% pure) or Ne (99.99% pure) were adsorbed on the powder surfaces at constant temperature while monitoring the Mu spin-relaxation rate. The target-cryostat assembly is shown in Fig. 3. Note that in this second set of measurements the target vessel was isolated from the He atmosphere of the cryostat so that it could be evacuated before insertion into the cryostat and would allow He or Ne to be adsorbed on the surfaces. The temperature of the powder, measured with a Cryocal 2500L Ge thermometer, was controlled to within ±100 mK. Immediately prior to this part of the experiment, the Al_2O_3 powder was baked at 500 K in air for 12 h, sealed in the target vessel, and evacuated at 10^{-5} Torr for a period of 24 h to remove air from the vessel and excess water vapor from the surfaces.

The new experimental procedure consisted of (i) admitting a small amount of adsorbate gas (He or Ne) from a standard volume into the target vessel, (ii) recording the equilibrated vapor pressure, (iii) accumulating a μ^+SR spectrum, and (iv) repeating steps (i) through (iii) until more than a monolayer of adsorbate was on the surfaces. The dead-volume correction to the adsorption isotherm (a plot of amount of adsorbed gas versus pressure at constant temperature) was made afterwards by repeating the isotherm with the powder replaced by an equal volume of Al.

The resulting μ^+SR spectra fitted well to the spectral form given above using a single exponential Mu relaxation function. The Mu relaxation rate versus amount of adsorbed He on Al_2O_3 at 7.3 and 10.4 K is shown in Fig. 4. For comparison, the vapor pressure at each coverage and temperature is also plotted. The number of adsorbed atoms per unit area, n, was determined by using the specific surface area supplied by the manufacturer. The amount of adsorbed gas corresponding to the beginning of the linear portion on the adsorption isotherm is a rough measure of the amount of gas required to complete a monolayer (n_m).[13] Applying this method yields a monolayer coverage $n_m = 10.0 \pm 1.0\ \text{nm}^{-2}$ at 7.3 K and $n = 12.5 \pm 1.0\ \text{nm}^{-2}$ at 10.4 K.

It is clear from Figs. 4 and 5 that the Mu relaxation rate is a decreasing linear function of the density of adsorbed gas below monolayer coverage and quickly levels off at a constant value at higher coverages. Similar behavior was observed in the case of Ne adsorbed at 28.7 and 30.3 K (see Fig. 5).

IV. DISCUSSION

A. Sources of Mu spin relaxation

The possible sources of Mu spin relaxation are as follows:

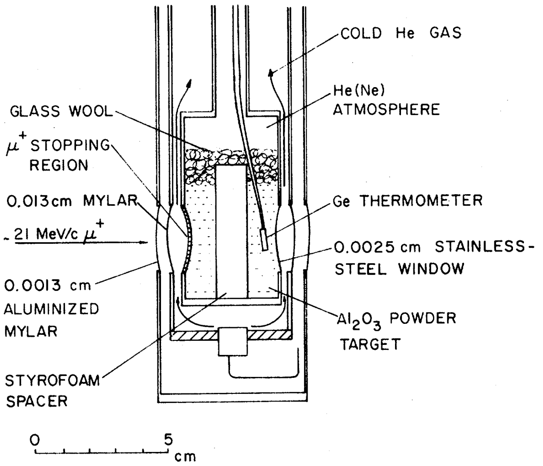

FIG. 3. Target-cryostat assembly for studying the effect of adsorbed He or Ne on muonium spin-relaxation in oxide powders.

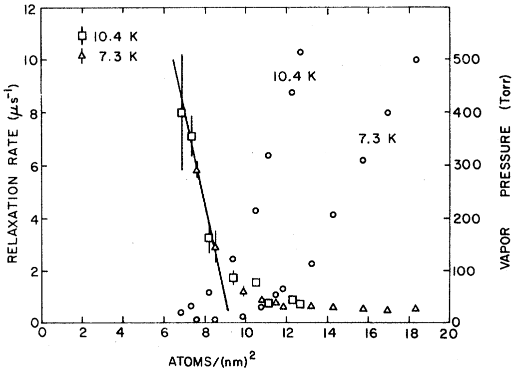

FIG. 4. Muonium spin-relaxation rate vs density of He atoms on the surface of 75-Å Al_2O_3 powder. The circles without error bars are the He vapor pressure at each coverage. The squares and triangles are the muonium relaxation rates measured at 10.4 and 7.3 K, respectively. The straight line is the result of a linear fit to the relaxation-rate data below monolayer coverage.

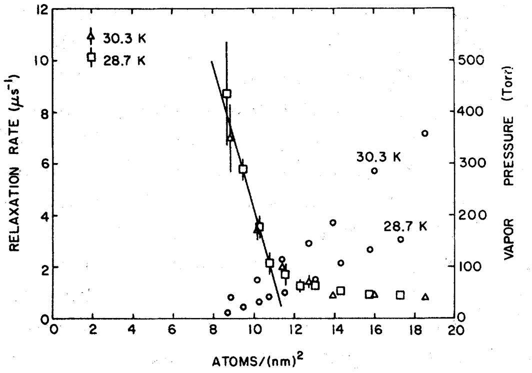

FIG. 5. Muonium spin-relaxation rate vs density of Ne atoms on the surface of 75-Å Al_2O_3 powder. The circles without error bars are the Ne vapor pressure at each coverage. The squares and triangles are the muonium relaxation rates measured at 28.3 and 30.3 K, respectively. The straight line is the result of a linear fit to the relaxation-rate data below monolayer coverage.

a. Random local magnetic fields (RLMF). Mu atoms which are inside the powder grains or on the surfaces may experience (in addition to the applied field) a RLMF produced by nuclear magnetic moments [such as ^{27}Al in the case of Al_2O_3 and H from the surface hydroxyl group $(OH)^-$], or paramagnetic impurities (such as Fe^{3+} within the grains or O_2 on the surfaces). Since the precession frequency depends on the magnetic field at the site of the Mu atom, the presence of a RLMF results in dephasing of the muon spins (or spin relaxation). This is commonly referred to as dipolar broadening of the precession frequency. Note that Mu atoms are 103 times more sensitive to RLMF than bare muons.

b. Spin exchange.[9,14] If there are unpaired electrons on the surface due to paramagnetic substances such as Fe^{3+} or O_2, the Mu atoms will undergo hyperfine transitions during collisions with the surface or while diffusing on the surface. This also results in a loss of coherence between the muon spins.

c. Random anisotropic hyperfine distortion. Mu atoms which are adsorbed on a surface or trapped within a solid may be distorted anisotropically by the host, altering the free-Mu precession frequencies. If there are many nonequivalent trapping sites or even equivalent sites with random orientation, this results in dephasing of the muon spins. For example, the Mu spin-relaxation rate in bulk fused quartz below 50 K (3.3 ± 0.5 μs^{-1}) is attributed to this effect.[11]

d. Chemical reaction. The Mu atoms may react chemically to form Mu compounds which are diamagnetic. In this situation the muon precession frequencies change rapidly at the instant of compound formation. This also results in dephasing of the muon spins or spin relaxation.[6]

In principle, these mechanisms can be distinguished using information from both transverse-field μ^+SR (used in this experiment) and longitudinal-field μ^+SR (where the magnetic field is applied parallel to the muon spin polarization). In the terminology associated with magnetic resonance phenomena, transverse-field μ^+SR measures T_2 relaxation rates whereas longitudinal-field μ^+SR measures T_1 relaxation rates.

B. Effect of adsorbed H_2O, O_2, and N_2

The powder surfaces were not cleaned in part *A* of the experiment. It is of some interest to discuss what effect the condition of the surfaces has on Mu formation, Mu spin relaxation, and the fraction of Mu which escapes from the grains.

Mu formation is most likely a bulk phenomenon since there is no correlation between the Mu fraction and the specific surface area of the sample. For example, the Mu-formation probability in bulk SiO_2 ($79\pm3\%$) (Ref. 11) is nearly the same as in powdered SiO_2 ($60\pm3\%$). Thus, one does not expect the condition of the surfaces to effect Mu formation appreciably.

It will be shown that a fraction of the Mu thermalizes in the void regions of the powder. This extragranular Mu fraction in the Al_2O_3 powder was measured to be the same in parts *A* and *B* of the experiment, despite the varying surface conditions. This is direct evidence that the surface condition has little effect on whether or not Mu finds its way into the void regions of the powder.

However, the surface condition can certainly effect Mu spin relaxation. For example, adsorbed O_2 (known to be paramagnetic on this type of surface[15]) should increase the Mu spin-relaxation rate via spin exchange if the Mu is colliding directly with O_2 on the surface or by RLMF if the Mu is trapped within the powder grains.

C. Extragranular Mu below 30 K

Bearing in mind that there is no Mu formation in He or Ne gas,[16] we propose the following explanation for the data: A large fraction of the Mu which is formed in these powders emerges into the void regions even at a temperature as low as 6 K, and the depolarizing effects of the oxide surfaces are quenched dramatically by the presence of adsorbed He or Ne. There are several observations which support this statement:

(1) The Mu spin-relaxation rate in Al_2O_3 powder at 6 K ($0.35\pm0.05\ \mu s^{-1}$) is much too small to originate from Mu inside the powder grains or adsorbed directly on the surface. Longitudinal field measurements in bulk Al_2O_3 (Ref. 17) indicate that Mu is relaxed rapidly by RLMF (of order 50 Oe), presumably caused by the nuclear magnetic moments of ^{27}Al. This corresponds to a spin-relaxation rate of order 400 μs^{-1}. The 1.8% Fe_2O_3 impurity (see Table I) would also cause spin relaxation at a comparable rate.[10]

(2) Similarly, the slowly relaxing Mu component in SiO_2 powder at 6 K ($0.16\pm0.05\ \mu s^{-1}$) cannot be due to Mu inside the powder grains, since the spin-relaxation rate in fused SiO_2 at this temperature ($3.3\pm0.5\ \mu s^{-1}$) is a factor of 20 faster. It is likely that the fast-relaxing component ($4.1\pm0.7\ \mu s^{-1}$) in the 140-Å SiO_2 powder (see Fig. 1) is due to Mu trapped within the grains. One would not expect to observe such a component in the smaller diameter 70-Å SiO_2 since the relaxation rate would be much faster due to O_2 on the surface. If such a component exists it must be very small in any case, since the observed slowly relaxing component accounts for most of the Mu signal observed at room temperature.

(3) In part *A*, measurements of the temperature dependence of the Mu spin-relaxation rate in Al_2O_3 powder in a He atmosphere (see Fig. 2) can be qualitatively explained by the fact that He readily adsorbs on such oxide surfaces at these temperatures and pressures (for example, on TiO_2).[18] One expects (on the basis of adsorption isotherms of He on similar oxide surfaces) that there would be more than a monolayer of He on all these oxide surfaces at 6 K in 760 Torr of He; such a protective film would effectively inhibit depolarization of extragranular Mu. The sharp increase in the relaxation rate above 12.5 K is attributed to the appearance of vacancies in the He film as it evaporates, exposing the bare surface so that depolarization of Mu may occur via adsorption or spin exchange.

(4) In part *B*, measurements of the Mu spin-relaxation rate versus the amount of He or Ne adsorbed at constant temperature on the Al_2O_3 powder surfaces (see Figs. 4 and 5) shows that the relaxation rate is proportional to the fraction of exposed surface area. Below monolayer completion (~ 10 atoms/nm^2), the exposed surface area is to first order a decreasing linear function of the amount of adsorbed gas, since at low coverage and low temperatures adsorbed atoms go primarily into the first layer. The decreasing linear behavior of the Mu relaxation rate in this region is attributed to a linear decrease in the collision frequency of Mu with the exposed Al_2O_3 surface. The rounded nonlinear behavior of the relaxation rate near monolayer coverage is attributed to simultaneous filling of the first and second layers which results in a nonlinear dependence of exposed surface area on the amount of adsorbed gas. When the amount of adsorbed gas has much exceeded that required to complete a monolayer, the collision frequency of Mu with the exposed Al_2O_3 surface is almost nil and virtually independent of the amount of adsorbed gas. This accounts for the small relaxation rate above a coverage of 10 atoms/nm^2 and its insensitivity to the amount of adsorbed gas.

D. Mu scattering off He and Ne adsorbed on Al_2O_3

A simple and slightly quantitative treatment of the He- and Ne-adsorption μ^+SR data was made in order to extract the cross section for Mu to scatter elastically off adsorbed He or Ne. The coverage dependence of the Mu spin-relaxation rate was fitted to the following form for each gas:

$$\lambda(n_1)=\begin{cases} k(1-\sigma^A_{\mathrm{Mu}}n_1)+\lambda_0, & n_1\le 1/\sigma^A_{\mathrm{Mu}} \\ \lambda_0, & n_1>1/\sigma^A_{\mathrm{Mu}} \end{cases} \tag{5}$$

where n_1 is the number of adsorbed atoms per unit area in the first layer only, σ^A_{Mu} is the total elastic cross section for Mu scattering off an adsorbed atom A, $k+\lambda_0$ is the relaxation rate with no adsorbed gas, and λ_0 is a constant relaxation rate unrelated to the Mu-Al_2O_3 surface interaction. λ_0 may be attributed to at least three factors:

(1) In a transverse field of 8 Oe the two observed Mu precession frequencies are actually split by a small amount $\Omega=0.178\ \mu s^{-1}$. The effect of fitting these two frequencies to a single frequency yields an apparent Gaussian relaxation rate $\Omega/2^{3/2}=0.063\ \mu s^{-1}$.

(2) The target vessel was constructed from slightly magnetic stainless steel, giving rise to a small field inhomogeneity over the muon-stopping region.

(3) Impurities in the gas may have caused a small relaxation. The slightly higher value of λ_0 in the case of Ne is attributed to this effect.

At low coverage n_1 is simply the total surface density of adsorbed gas (this explains the linear behavior of $\lambda(n)$ below monolayer completion) whereas at higher coverages, $n_1 \rightarrow n_m$ (the monolayer density) and thus $\lambda(n) \rightarrow \lambda_0$. There was no marked temperature dependence in $\lambda(n)$, and therefore the combined data at both temperatures were fitted to a linear function at low coverage, yielding in the case of He, $k = 32.9 \pm 0.3\ \mu s^{-1}$ and $\sigma_{\mathrm{Mu}}^{\mathrm{He}} = 11.0 \pm 0.2\ \mathrm{\AA}^2$, and in the case of Ne, $k = 31.4 \pm 0.3\ \mu s^{-1}$ and $\sigma_{\mathrm{Mu}}^{\mathrm{Ne}} = 8.9 \pm 0.2\ \mathrm{\AA}^2$.

k may be expressed in terms of more fundamental quantities, such as the sticking probability per collision if it is assumed that the Mu atom depolarizes rapidly during a single dwell time on the surface (i.e., that the mean surface dwell time $\bar{t}$ multiplied by the relaxation rate on the surface, λ_B, is much greater than 1). This will be justified in the next section. In this "strong-collision approximation" k can be expressed as

$$k = \nu_c (P_t + f \sigma_{\mathrm{ex}} m / 2) , \tag{6}$$

where ν_c is the classical collision frequency with the surface, P_t is the probability per collision that the Mu becomes adsorbed, m is the concentration of Fe^{3+} (known to be present in this sample; see Table I) on the surface, σ_{ex} is the corresponding spin-exchange cross section, and f is a factor depending on the spin of the paramagnetic atom ($\frac{8}{9}$ for a spin-1 atom).[14]

It is difficult to extract any more information from the present results, such as a value for P_t, without making unjustified assumptions. The contribution to k from spin exchange with the Fe^{3+} on the surface is not known. Further experiments on a sample free of paramagnetic impurities would eliminate this unknown. Furthermore, only an upper limit on the collision frequency with the surface is known, since thermal Mu at low temperatures may scatter off the aggregate structures (composed of primary particles clumped together) rather than off the primary particles. The maximum collision frequency, obtained by assuming a uniform distribution of spherical particle of radius R, can be written

$$\nu_c = \frac{N}{V_F} \pi R^2 v , \tag{7}$$

where N is the number of particles in the sample, V_F is the free volume of the sample ($V - V_{\mathrm{solid}}$), V is the volume of the sample, V_{solid} is the volume of solid in the sample, and v is the mean thermal velocity of Mu. For example, in the $\mathrm{Al_2O_3}$ sample at 10 K, taking R as 37 Å, gives $\nu_c = 5 \times 10^{10}\ \mathrm{s}^{-1}$, which is considerably more than k ($3 \times 10^7\ \mathrm{s}^{-1}$) obtained from the data. This implies P_t is very small or that the clumping effect mentioned above is very important.

E. Thermodynamics of Mu on powder surfaces

The strong-collision assumption ($\lambda_T \bar{t} \gg 1$) can be justifed by applying some simple thermodynamics. Consider the model system in which adsorbed Mu resembles a two-dimensional gas bound to the surfaces by an energy B_{Mu}. The mean surface dwell time (the mean residence time on the surface per adsorption) can be written[19]

$$\bar{t} = \frac{4\Lambda}{vP_t} \exp(B_{\mathrm{Mu}}/kT) , \tag{8}$$

where $\Lambda = (h^2/2\pi mkT)$ is the thermal de Broglie wavelength of Mu. Alternatively, in a tight-binding model in which there are S_0 tight-binding sites per unit area, $\bar{t}$ can be written[19]

$$\bar{t} = \frac{4S_0\Lambda^3}{vP_t} \exp(B_{\mathrm{Mu}}/kT) . \tag{9}$$

This differs from the two-dimensional gas case [Eq. (8)] simply by a factor $S_0\Lambda^2$. For example, if $S_0 = 10\ \mathrm{nm}^{-2}$, then this factor is 40 at 7 K and 1 at 300 K.

In order to proceed further, B_{Mu} must be estimated. B_{Mu} can be expressed in terms of the corresponding binding energy of H atoms, in a somewhat model-dependent manner. The surface potential for both Mu and H is assumed to be represented by the same one-dimensional Morse potential[20]

$$V(z) = D(e^{-2az} - 2e^{-az}) , \tag{10}$$

where D and a^{-1} are the depth and range of the potential, respectively. The binding energy of the deepest bound state of Mu can be written

$$\begin{aligned} B_{\mathrm{Mu}} &= \left[\frac{(2m_{\mathrm{Mu}}D)^{1/2}}{\hbar a} - \frac{1}{2} \right]^2 \frac{\hbar^2 a^2}{2m_{\mathrm{Mu}}} \\ &= \left\{ B_{\mathrm{H}}^{1/2} - \frac{\hbar a}{2^{3/2} m_{\mathrm{Mu}}^{1/2}} \left[1 - \left[\frac{m_{\mathrm{Mu}}}{m_{\mathrm{H}}} \right]^{1/2} \right] \right\}^2 , \end{aligned} \tag{11}$$

where m_{Mu} is the Mu mass, m_{H} is the H mass, and B_{H} is the binding energy of H to the surface (ESR measurements indicate that B_{H} is in the range 500 to 1500 K on silica and alumina surfaces).[2] For example, substituting $B_H = 1000$ K and $a = 0.5$ Å^{-1} (a typical range parameter for this kind of interaction), one obtains $B_{Mu} = 850$ K. Substituting this into Eq. (8), with $P_t \sim 1$, yields a mean surface-dwell time of order 10^{21} s at 10 K. In contrast, at 300 K $\bar{t}$ is only 3 ps. Since the relaxation rate on the surface is estimated at 400 μs^{-1}, the strong-collision assumption ($\lambda_B \bar{t} \gg 1$) is probably very good at the low temperatures in this experiment.

It is also of some interest to estimate the fraction of time thermal Mu spends on the surfaces of a powder at room temperature in the above model, since a recent search for the conversion of Mu ($\mu^+ e^-$) to $\overline{\text{Mu}}$ ($\mu^- e^+$) has been performed in targets composed of 70-Å SiO_2 powder.[21]

The analysis hinges upon the fact that Mu spends most of its time in the desorbed states, moving freely in the void regions of the powder. Using simple thermodynamics,[19] the fraction of time spent on the surface, α, can be written[10]

$$\alpha = \frac{1}{1+\exp(-B_{Mu}/kT)V_F/A\Lambda} \tag{12}$$

in the two-dimensional gas model or

$$\alpha = \frac{1}{1+\exp(-B_{Mu}/kT)V_F/S_0\Lambda^3 A} \tag{13}$$

in the tight-binding model, where A is the surface area of the powder sample. For example, in 70-Å SiO_2 powder of density 0.04 g cm^{-3} at 300 K with $B_{Mu} = 850$ K, one finds that in both the two-dimensional model and tight-binding model, the Mu spends only 7.7% of the time on the surface. The effect of clumping, mentioned above, could only decrease this fraction. This agrees well with the experimental results on O_2 quenching of Mu in this powder at 300 K, which indicate that Mu moves essentially freely in the void regions of the powder.[7] The situation at 10 K is very different since the mean surface-dwell time far exceeds the muon lifetime so that once the Mu is adsorbed it remains there for the duration of the muon lifetime.

V. CONCLUSION

In conclusion, we are now confident that a considerable fraction of the Mu emerges from the surfaces of these oxide powders at temperatures even as low as 6 K. This suggests that there exists a mechanism for Mu to escape from the powder grains that is not diffusion controlled, under the conditions of this experiment. One possibility is that a fraction of the Mu thermalizes directly in the void regions of the powder because of a negative work function of order 2 eV and the presence of He and Ne in the voids.[10] However, care must be taken not to generalize this result to all temperatures and experimental conditions. For example, the room-temperature results in evacuated 140-Å SiO_2 (Ref. 7) still indicate that at least part of the Mu escapes by diffusion.

With these experiments, a new technique has been demonstrated for studying the properties of catalytic surfaces and adsorbed atoms on these surfaces.

Experiments now in progress will measure fundamental properties of Mu adsorbed on oxide surfaces such as the binding energy, sticking probability, and two-dimensional diffusion rate. Preliminary results on clean SiO_2 surfaces are very promising. It is clear that the study of Mu chemistry, already successful in the gas and liquid phases, can now be extended to surfaces. Future experiments will also attempt to evaluate the utility of μ^+SR as a method for probing defects and impurities on surfaces.

ACKNOWLEDGMENTS

This research was supported by the Natural Sciences and Engineering Research Council of Canada. We would like to express our gratitude to C. A. Fry for his assistance during the second part of the experiment.

---

*Present address: Physik-Institut der Universität Zürich, Schönberggasse 9, CH-8001 Zürich, Switzerland.

[1] J. H. Lunsford, Adv. Catal. 22, 265 (1972).
[2] V. B. Golubev, Russ. J. Phys. Chem. 39, 1395 (1965).
[3] G. V. Pariiskii and V. B. Kasanskii, Kinet. Katal. 5, 96 (1964).
[4] J. H. Brewer, K. M. Crowe, F. N. Gygax, and A. Shenck, in *Muon Physics*, editd by V. W. Hughes and C. S. Wu (Acadmic, New York, 1975), Vol. II, p. 3.
[5] J. H. Brewer and K. M. Crowe, Ann. Rev. Nucl. Sci. 28, 240 (1978).
[6] D. G. Fleming *et al.*, Adv. Chem. Ser. 175, 279 (1979).
[7] G. M. Marshall, J. B. Warren, D. M. Garner, G. S. Clark, J. H. Brewer, and D. G. Fleming, Phys. Lett. 65A, 351 (1978).
[8] R. F. Kiefl, J. B. Warren, G. M. Marshall, C. J. Oram, J. H. Brewer, D. J. Judd, and L. D. Spires, Hyp. Int. 6, 185 (1979).

[9] D. G. Fleming, R. J. Mikula, and D. M. Garner, J. Chem. Phys. 73, 2751 (1980).

[10] R. F. Kiefl, Ph.D. thesis, University of British Columbia, 1981 (unpublished).

[11] J. H. Brewer, Hyp. Int. 8, 375 (1981).

[12] R. F. Kiefl, J. B. Warren, G. M. Marshall, C. J. Oram, and C. W. Clawson, J. Chem. Phys. 74, 308 (1981).

[13] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. 60, 309 (1938).

[14] D. G. Fleming, D. M. Garner, and R. J. Mikula, Hyp. Int. 8, 337 (1981).

[15] S. A. Surin, G. M. Zhidomirov, B. N. Shelimov, and V. B. Kazanskii, Teor. Eksp. Khim. 6, 353 (1970).

[16] D. G. Fleming, R. J. Mikula and D. M. Garner, Hyp. Int. 8, 307 (1981).

[17] E. V. Minaichev *et al.*, Zh. Eksp. Teor. Fiz. 58, 1586 (1970) [Sov. Phys.—JETP 31, 849 (1970)].

[18] J. G. Aston, S. V. R. Mastrangelo, and R. J. Tykoidi, J. Chem. Phys. 23, 1633 (1955).

[19] S. B. Crampton, J. Phys. (Paris) Colloq. 41, C7-249 (1980).

[20] F. R. S. Lennard-Jones and C. Strachan, Proc. R. Soc. London 150, 442 (1935).

[21] G. M. Marshall, J. B. Warren, C. J. Oram, and R. F. Kiefl, Phys. Rev. D 25, 1174 (1982).