22 MAR 1982

TRI-PP-82-
Jan 198

CERN LIBRARIES, GENEVA

- 2 -

TRI-PP 82-3

CM-P00067157

I. INTRODUCTION

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,
Vancouver, B.C., Canada V6T 2A6*

Carl W. Clawson

*Department of Physics, University of California,
Berkeley, California 94720*

Abstract

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 ($T < 30^\circ K$), 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 Mu against depolarizing collisions with the bare Al_2O_3 surfaces.

(Submitted to Physical Review B)

†Current address: Rutherford Laboratory, Chilton, Didcot, Oxon OX1 10QX, U.K.

Surface radicals have long been used as probes of catalytic oxide surfaces¹ 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 previously³ 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 1/9th 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 changing 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 a 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 three-fold. 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 SiO₂, Al₂O₃, and MgO^{7,8} 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 O₂ 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 ($kT \ll B_{Mu}$, where B_{Mu} is the binding energy to the surface). In this situation the thermal Mu atom may reside on the surface for a large fraction of the muon lifetime (2.2 μ s).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 where by 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 SiO₂ 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 muon spin rotation (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) = 13.6 H(0e) where H is the applied field in 0e. The muon spin polarization in a Mu atom exhibits four discrete precession frequencies. In low fields ($H < 10$ 0e) 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) = 1.39 H(0e) (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:

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

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

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

where $S_{\mu}(t)$ and $S_{\mu}(t)$ are the μ and free μ on precession signals, B_0 is a time independent background, N_0 is the normalization, τ_{μ} is the μ on lifetime (2.2 μ s), A_{μ} and A_{μ} are the μ and free μ on precession amplitudes, $R_{\mu}(t)$ and $R_{\mu}(t)$ are the μ and free μ on relaxation functions, and ϕ_{μ} and ϕ_{μ} are the μ and free μ on precession phases. The fitted parameters A_{μ} and A_{μ} are used to obtain the μ and μ on 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 μ on or μ atom since this phenomenon yields information on the μ on-host or μ -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 6°K and 20°K. The powders were selected on the basis of their high yield of extragranular μ 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 μ 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 μ off Al_2O_3 surfaces with adsorbed He and Ne.

In both parts of the experiment a beam of spin polarized μ ons 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°K 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 μ m aluminized mylar window to allow entry of the μ^+ , and then inserted into a He gas flow cryostat. In all cases except the $140 \text{ \AA } SiO_2$, 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 vapour were adsorbed on the surfaces. The $140 \text{ \AA } SiO_2$ 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 μ ons entering the target was only 80 mg/cm² (of carbon) so for example in the Al_2O_3 powder all the μ ons 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 $\pm 250m^{\circ}K$.

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 hour period at an ambient temperature of 6°K. In the case of the Al_2O_3 powder the temperature was varied between 6°K 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 $[\exp(-t^2/t^2)]$ or exponential $[\exp(-\lambda t)]$. Good fits were obtained using a single component Mu relaxation function $[R_{\text{Mu}}(t) = \exp(-\lambda t)]$ except for the case of $140 \text{ \AA SiO}_2$ for which a substantial improvement in the fit was obtained by using a two-component relaxation function

$$R_{\text{Mu}}(t) = \alpha \exp(-\lambda_1 t) + (1-\alpha) \exp(-\lambda_2 t) \quad (4)$$

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 $140 \text{ \AA SiO}_2$ 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 rate of $4.1 \pm 0.7 \text{ } \mu\text{s}^{-1}$, while the remaining fraction relaxes at a much slower rate of $0.16 \pm 0.05 \text{ } \mu\text{s}^{-1}$.

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°K 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.

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 protected 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 $\pm 10\text{m}^\circ\text{K}$.

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 vapour from the surfaces.

The new experimental procedure consisted of (1) admitting a small amount of adsorbate gas (He or Ne) from a standard volume into the target vessel, (2) recording the equilibrated vapour pressure, (3) accumulating a $\mu^+\text{SR}$ spectrum and (4) repeating steps (1) through (3) 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 vapour pressure at constant temperature) was made afterwards by repeating the isotherm with the powder replaced by an equal volume of Al.

The resulting $\mu^+\text{SR}$ 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°K and 10.4°K is

shown in Fig. 4. For comparison, the vapour 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 μ 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 behaviour was observed in the case of Ne adsorbed at 28.7°K and 30.3°K (see Fig. 5).

IV. DISCUSSION

A. Sources of μ spin relaxation

The possible sources of μ spin relaxation are:

1. Random Local Magnetic Fields (RLMF): μ atoms which are inside the powder grains or on their 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 μ 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 μ atoms are 10^3 times more sensitive to RLMF than bare muons.

2. Spin Exchange:^{9,14} If there are unpaired electrons on the surface due to paramagnetic substances such as Fe^{+3} or O_2 , the μ 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.

3. Random Anisotropic Hyperfine Distortion: μ atoms which are adsorbed on a surface or trapped within a solid may be distorted anisotropically by the host, altering the free μ 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 μ spin relaxation rate in bulk fused quartz below 50°K ($3.3 \pm 0.5 \text{ } \mu\text{s}^{-1}$) is attributed to this effect.¹¹

4. Chemical reaction: The μ atoms may react chemically to form μ 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 $\mu^+\text{SR}$ (used in this experiment) and longitudinal field $\mu^+\text{SR}$ (where the magnetic field is applied parallel to the muon spin polarization). In the terminology associated with magnetic resonance phenomena transverse field $\mu^+\text{SR}$ measures T_2 relaxation rates whereas longitudinal field $\mu^+\text{SR}$ 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 ($79 \pm 3\%$)¹¹ is nearly the same as in powdered SiO_2 ($60 \pm 3\%$). 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 ($0.35 \pm 0.05 \mu\text{s}^{-1}$) 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 $400 \mu\text{s}^{-1}$. 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 ($0.16 \pm 0.05 \mu\text{s}^{-1}$) cannot be due to Mu inside the powder grains, since the spin relaxation rate in fused SiO_2 at this temperature ($3.3 \pm 0.5 \mu\text{s}^{-1}$) is a factor of 20 faster. It is likely that the fast relaxing component ($4.1 \pm 0.7 \mu\text{s}^{-1}$) in the $140 \text{ \AA}$ 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 $70 \text{ \AA}$ 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/nm²), 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 behaviour 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 non-linear behaviour of the relaxation rate near monolayer coverage is attributed to simultaneous filling of the first and second layers which results in a non-linear 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/nm² 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 more 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:

$$\lambda(n_1) = \begin{cases} k(1 - \sigma_{Mu}^A n_1) + \lambda_0 & \left[n_1 \leq \frac{1}{\sigma_{Mu}^A} \right] \\ \lambda_0 & \left[n_1 > \frac{1}{\sigma_{Mu}^A} \right] \end{cases} \quad (5)$$

where n_1 is the number of adsorbed atoms per unit area in the first layer only, σ_{Mu}^A 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 $\Omega^2/2^{3/2} = 0.063 \mu s^{-1}$.
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 behaviour 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 $\sigma_{Mu}^{He} = 11.0 \pm 0.2 \text{ \AA}^2$, and in the case of Ne, $k = 31.4 \pm 0.3 \mu s^{-1}$ and $\sigma_{Mu}^{Ne} = 8.9 \pm 0.2 \text{ \AA}^2$.

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

$$k = v_c [P_t + f \sigma_{ex} m / 2] \quad (6)$$

where v_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 (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 particles of radius R, can be written

$$v_c = \frac{N}{V_F} \pi R^2 v \quad (7)$$

where N is the number of particles in the sample, V_F is the free volume

of the sample ($V - V_{solid}$), 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 Al_2O_3 sample at 10°K, taking R as 37 Å, gives $v_c = 5 \times 10^{10} s^{-1}$, which is considerably more than k ($3 \times 10^7 s^{-1}$) 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 ($\lambda_B \bar{t} \gg 1$) can be justified by applying some simple thermodynamics. Consider the model system in which adsorbed Mu resembles a 2-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 written¹⁹

$$\bar{t} = \frac{4\Lambda}{v P_t} \exp[B_{Mu}/kT] \quad (8)$$

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 written¹⁹

$$\bar{t} = \frac{4S_0\Lambda^3}{v P_t} \exp[B_{Mu}/kT] \quad (9)$$

This differs from the 2-dimensional gas case [Eq. (8)] simply by a factor $S_0\Lambda^2$. For example, if $S_0 = 10 \text{ nm}^{-2}$ 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

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

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

$$B_{\text{Mu}} = \left[\frac{(2m_{\text{Mu}} D)^{1/2}}{\hbar a} - \frac{1}{2} \right]^2 \frac{\hbar^2 a^2}{2m_{\text{Mu}}} = \left[B_H^{1/2} - \frac{\hbar a}{2^{3/2} m_{\text{Mu}}^{1/2}} \left\{ 1 - \left(\frac{m_{\text{Mu}}}{m_H} \right)^{1/2} \right\}^2 \right]^2 \quad (11)$$

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°K to 1500°K on silica and alumina surfaces).² For example, substituting $B_H = 1000^\circ\text{K}$ and $a = 0.5 \text{ \AA}^{-1}$ (a typical range parameter for this kind of interaction) one obtains $B_{\text{Mu}} = 850^\circ\text{K}$. 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, $\bar{\tau}$ is only 3 ps. Since the relaxation rate on the surface is estimated at 400 ps^{-1} , the strong collision assumption ($\lambda \bar{g} \bar{\tau} \gg 1$) is likely 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 $\text{Mu} (\mu^+e^-)$ to $\bar{\text{Mu}} (\mu^-e^+)$ 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 written¹⁰

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

in the 2-dimensional gas model or

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

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 $B_{\text{Mu}} = 850^\circ\text{K}$, one finds that in both the 2-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 free 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 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 μ adsorbed on oxide surfaces such as the binding energy, sticking probability and 2-dimensional diffusion rate. Preliminary results on clean SiO_2 surfaces are very promising. It is clear that the study of μ 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 $\mu^+\text{SR}$ as a method for probing defects and impurities on surfaces.

ACKNOWLEDGEMENTS

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.

REFERENCES

- 1 J.H. Lunsford, Adv. in Cat. 22, 265 (1972).
- 2 V.B. Golubev, Russian Journal of Physical Chemistry 39, 1395 (1965).
- 3 G.V. Pariiskii and V.B. Kasanskii, Kinetika i Kataliz 5, 96 (1964).
- 4 J.H. Brewer, K.M. Crowe, F.N. Gyax and A. Shenck, *Muon Physics*, Vol. II, edited by V.W. Hughes and C.S. Wu, Academic Press, New York, 3 (1975).
- 5 J.H. Brewer and K.M. Crowe, Ann. Rev. Nucl. Sci. 28, 240 (1978).
- 6 D.G. Fleming *et al.*, Advances in Chemistry Series 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, Hyperfine Interactions 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, Department of Physics, University of British Columbia, (1981).
- 11 J.H. Brewer, Hyperfine Interactions 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, Hyperfine Interactions 8, 337 (1981).
- 15 S.A. Surin, G.M. Zhidomirov, B.N. Shelimov and V.B. Kazanskii, Teoreticheskaya i Eksperimentalnaya Khimiya 6, 353 (1970).
- 16 D.G. Fleming, R.J. Mikula and D.M. Garner, Hyperfine Interactions 8, 307 (1981).
- 17 E.V. Minaichev *et al.*, Sov. Phys.-JETP 31, 849 (1970).
- 18 J.G. Aston, S.V.R. Mastrangelo and R.J. Tykoidl, J. Chem. Phys. 23, 1633 (1955).
- 19 S.B. Crampton, Journal de Physique, Colloque C7 41, C7-249 (1980).
- 20 F.R.S. Lennard-Jones and C. Strachan, Proc. Roy. Soc. 150, 442 (1935).
- 21 G.M. Marshall, J.B. Warren, C.J. Oram and R.F. Kiefl, to be published in Phys. Rev. D, (1981).

Table I. Physical properties of the oxide powders

Powder (Supplier serial #)	Density (g/cc)	Surface area (m ² /g)	Particle ^b size (diam) (Å)	Impurities ^a
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 ₂ O ₃ (Davison SMR-7-7563)	0.56	225	75	Fe ₂ O ₃ (1.8%) SO ₄ (0.2%) SiO ₂ (0.08%) Na ₂ O (0.03) Cl (<0.01%)
MgO (Matheson Coleman Bell MX 65-05)	1.12	not available	300	Na (0.5%) Ca (0.05%) SO ₄ (0.02%) NH ₄ (OH) (0.02%) In (0.01%) Heavy metals (0.003%) Mn (5 ppm)

^aThe manufacturer's stated impurities except for the Fe content in Al₂O₃, which was determined by atomic absorption for the sample used in the experiment.

^bEstimated from the specific area assuming spherical particles except for the case of MgO where the given size is based on an electron micrograph.

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 (%)	Muonium relaxation rate (ns ⁻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) 35 ± 5(2)	4.1 ± 0.7(1) ^a 0.16 ± 0.05(2)
SiO ₂ (140 Å)	295	60 ± 3	0.18 ± 0.03
Al ₂ O ₃ (75 Å)	6	29 ± 3	0.35 ± 0.05
Al ₂ O ₃ (75 Å)	295	35 ± 14	11.3 ± 4.4
MgO (300 Å)	6	12 ± 3	0.22 ± 0.03
MgO (300 Å)	295	15 ± 3	1.9 ± 0.5

^aThe (1) and (2) refer to the two components resolved in the fit.

FIGURE CAPTIONS

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

2. The temperature dependence of the muonium spin relaxation rate in $75 \text{ \AA}$ Al_2O_3 powder in a He atmosphere. The arrows indicate points that are off scale.

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

4. The muonium spin relaxation rate versus density of He atoms on the surface of $75 \text{ \AA}$ Al_2O_3 powder. The circles without error bars are the He vapour pressure at each coverage. The squares and triangles are the muonium relaxation rates measured at 10.4°K and 7.3°K respectively. The straight line is the result of a linear fit to the relaxation rate data below monolayer coverage.

5. The muonium spin relaxation rate versus density of Ne atoms on the surface of $75 \text{ \AA}$ Al_2O_3 powder. The circles without error bars are the Ne vapour pressure at each coverage. The squares and triangles are the muonium relaxation rates measured at 28.3°K and 30.3°K respectively. The straight line is the result of a linear fit to the relaxation rate data below monolayer coverage.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5