RICE UNIVERSITY

THE DIFFUSION OF POSITIVE MUONS IN PALLADIUM

by

ROBERT T. STEIN

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APPROVED, THESIS COMMITTEE:

S. A. Dodds
Assistant Professor of Physics
Chairman

T. L. Estle
Professor of Physics

H. E. Rorschach
Professor of Physics

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ABSTRACT

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The diffusion of the isotopes of hydrogen in non-magnetic metals has been of interest for many years. Muon spin rotation (\(\mu\text{SR}\)) has permitted the study of the diffusion of the positive muon as a light isotope of hydrogen. This experimental technique has been applied successfully to the diffusion of positive muons in palladium. Classical diffusion theory does not seem to explain the experimental results. A quantum mechanical calculation which explains the results has not yet been made.
Acknowledgments

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I. Introduction

The diffusion of hydrogen and its isotopes in non-magnetic metals is a subject of great physical as well as technological interest.\(^1\) The isotopes of hydrogen have large differences in their relative masses and provide an opportunity to thoroughly test various classical and quantum mechanical diffusion theories. A positive muon (\(\mu^+\)) may also be considered to be a light isotope of hydrogen since it has the same charge, size, and spin as a proton, but only about 1/9 the mass. A study of the diffusion characteristics of the \(\mu^+\) increases the range of mass over which diffusion processes may be examined. Such diffusion studies of the \(\mu^+\) can now be made using the resonance technique of muon spin rotation (\(\mu\)SR). \(\mu\)SR has been used to measure the diffusion properties of the \(\mu^+\) in copper, gold, silver, and various other metals.\(^2,3,4\) This work discusses a measurement of the diffusion of positive muons in palladium.

Palladium is an FCC non-magnetic metal with negligible nuclear moments. The diffusion of hydrogen, deuterium, and tritium in palladium has been measured at temperatures within the range accessible to \(\mu\)SR.\(^5\) A direct comparison of the diffusion characteristics of the \(\mu^+\) with those of the isotopes of hydrogen in palladium is made in this work. Predictions made on the basis of various diffusion theories can then be compared with the experimental evidence presented here.
What is $\mu$SR?

Before examining the theory of $\mu^+$ diffusion in palladium, it is important to first have an understanding of the technique to be used. $\mu$SR is a resonance technique that utilizes the unique properties of the positive muon to probe matter. (Important characteristics of the positive muon are tabulated in Table 1.)

The spin $\frac{1}{2} \mu^+$ possesses a magnetic moment which allows the $\mu^+$ to interact with local magnetic fields in the sample or with applied magnetic fields. It will precess in a uniform applied magnetic field and will couple with nuclear moments, magnetic ions, or conduction electrons.

The $\mu^+$ is not a stable particle. It decays with a half-life of about 2.2 microseconds. It undergoes a parity violating weak decay, of which a neutrino, an anti-neutrino and one positron are the products. The result of the parity violation is that the positron is emitted preferentially in the direction of the muon spin. A polar plot of the angular dependence of the positron momentum direction relative to the spin of the $\mu^+$ is illustrated in Figure 1.

In $\mu$SR a high intensity beam of muons of known polarization is stopped in the metallic sample. The primary mechanism in the process of stopping and thermalization of muons in metals is the scattering of the $\mu^+$ from electrons. The spin dependent parts of the scattering process are weak so that the polarization of the muons is not greatly altered during the stopping process.
Table 1. Properties of the positive muon. (From reference 6.)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Rest Mass</td>
<td>$m_\mu = 106 \text{ MeV} = \frac{1}{9} m_\pi$</td>
</tr>
<tr>
<td>Spin</td>
<td>$S_\mu = 1/2$</td>
</tr>
<tr>
<td>Charge</td>
<td>$q_\mu = +</td>
</tr>
<tr>
<td>Lifetime</td>
<td>$\tau_\mu = 2.1994 \mu\text{seconds}$</td>
</tr>
<tr>
<td>Gyromagnetic Ratio</td>
<td>$\gamma_\mu = 8.5 \times 10^4 \ (\text{sG})^{-1}$</td>
</tr>
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</table>
Figure 1.

Angular dependence of positron emission for muon decay.
It is possible with appropriate detectors and counting logic to ensure that only one $\mu^+$ is present in the sample at any one time. A large number of muons are individually stopped in the sample. Collectively, they make up an ensemble of probes which serve the same purpose as a large number of nuclear moments without the complication of $\mu^+-\mu^+$ interactions. Interaction between spin probes is an important effect in other resonance techniques.

Given the parity violating decay as well as a large number of polarized muons, it is possible to determine the orientation of the moment of the average $\mu^+$ as a function of time. This is done by detecting the angular dependence of the number of positrons passing through a known solid angle during a time interval between $t$ and $t + \Delta t$ where $t$ is the elapsed time measured from the implantation of each muon into the sample and $\Delta t$ is the width of the interval. A histogram of such time differential data for one direction perpendicular to an applied magnetic field is shown in Figure 2. The sinusoidal oscillations superimposed on the 2.2 micro-second decay curve are due to the Larmor precession of the muon in an applied magnetic field of 150 Oersteds perpendicular to the muon spin direction. The polarization due to the applied field decays because the initially polarized muons relax to the lattice via various mechanisms and the spins become randomly oriented. It is this depolarization rate which is the measurement of interest in the study of $\mu^+$ relaxation and diffusion in metals.
Figure 2.

Time differential \( \mu \)SR data.
If a small number of paramagnetic gadolinium ions are dissolved in palladium, then a diffusing $\mu^+$ will eventually interact with one. The $\mu^+$ experiences a time dependent interaction with the impurity due to fluctuations of the impurity and to the relative motion of the $\mu^+$ and the impurity. The spin of the muon will become random in a relaxation process. The relaxation of an ensemble of muons therefore depends on the diffusion characteristics of the $\mu^+$ in palladium as well as the coupling of the $\mu^+$ with gadolinium impurities. The depolarization due to coupling with palladium nuclei can be calculated using Abragam's formula. Such a calculation shows measurable $\mu^+$-depolarization in pure palladium only at temperatures below those at which the muons begin to diffuse significantly.

Proper analysis of $\mu^+$ relaxation in palladium gadolinium alloys requires the development of a theoretical model that properly accounts for the $\mu$SR data. Several such models are now considered.
II. Theory

A model that describes the diffusion of the $\mu^+$ in palladium must be based on reasonable diffusion processes and $\mu^+$-gadolinium ion interactions. Before a $\mu^+$ diffusion model may be discussed, it is important to examine the long-range $\mu^+$-gadolinium interaction in palladium.

Static $\mu^+$ Relaxation

At low enough temperatures, the $\mu^+$ does not diffuse significantly and the long-range coupling between the $\mu^+$ and impurities will determine the relaxation rate. In such a temperature regime the $\mu^+$ stops at random locations in a sample and couples with randomly located impurity moments. The average $\mu^+$ is fairly far from impurities so that $T_1$ processes due to ion fluctuations are slow compared to the lifetime of the $\mu^+$ and are not observable. The impurity dipoles may be randomly oriented or, if the temperature is very low and the applied magnetic field is large enough, they may be partially polarized. If the ions are only slightly polarized, then at the randomly located $\mu^+$ stopping sites the average impurity induced field is small. The muons will not relax significantly. If, however, the ions are significantly polarized, then the field at stopping sites due to them will no longer be randomly oriented and there will be a significant average component parallel to the applied field. The
magnitude of the impurity field parallel to the applied field at $\mu^+$ sites will vary depending on the site. The random distribution of impurity magnetic fields over interstitial sites will not change the sense of the $\mu^+$ precession, but there will be slight variations in the precession rates causing a general "dephasing," among the ensemble of muons. This dephasing results in a depolarization rate that is measurable using $\mu$SR. The linewidth of the ensemble of static muons in palladium doped with gadolinium can be calculated assuming various long-range $\mu^+$-impurity spin interactions.

R. E. Walstedt and L. R. Walker derive an NMR linewidth for metals with dilute magnetic impurities. Their treatment is easily carried over to $\mu$SR when the $\mu^+$ is not diffusing. The Walstedt and Walker linewidth calculation in the context of $\mu$SR assumes that the $\mu^+$ is not diffusing and is located at some random site, that the impurities are dilute and randomly located, and that $T_1$ relaxation processes due to the impurity fluctuation are negligible. RKKY coupling in palladium gadolinium alloys is negligible compared to dipolar coupling. Therefore the dominant long-range coupling between the $\mu^+$ and gadolinium ions is probably dipolar. Walstedt and Walker show that given the above assumptions, the linewidth for a pure dipolar relaxation mechanism is:

$$\left[\frac{1}{T_2}\right]_{\text{dipolar}} = \frac{8\pi^2 \rho c}{9\sqrt{3}} |B| \langle S_z \rangle_{\text{avg}}$$
where $|B|$ contains the dipolar interaction strength, $\rho$ is the density of sites available to the impurities, $c$ is the fractional concentration of impurities, and $\langle S_z \rangle_{\text{avg}}$ is the thermal average impurity spin component parallel to the externally applied magnetic field. $|B|$ is calculated from classical dipole coupling and is:

$$|B| = 2 \left( \frac{\mu_\mu}{\hbar} \frac{\mu_{\text{Gd}}}{\langle S_z \rangle_{\text{avg}}} \right) = |\hbar \gamma_\mu \gamma_s|$$

where $\gamma_\mu$ and $\gamma_s$ are the gyromagnetic ratios of the muon and gadolinium respectively. Generally, $\langle S_z \rangle_{\text{avg}}$ is calculated from a Brillouin function, but one can easily calculate rough values of the linewidth for fields and temperatures such that

$$\frac{g\mu_B H}{k_B T} \ll 1.$$ 

This is the high temperature limit. In such a limit, $\langle S_z \rangle_{\text{avg}}$ is proportional to $\frac{H}{T}$ and the linewidth is

$$\left( \frac{1}{T_2} \right)_{\text{dipolar}} = 0.383 \frac{cH}{T} (\mu s^{-1})$$

where $H$ is the applied magnetic field in Oersteds and $T$ is the temperature of the sample in degrees Kelvin. With the spectrometer used in our experiments, the largest value of $\frac{g\mu_B H}{k_B T}$ is obtained if $H$ is 5000 Oersteds and $T$ is about 2 degrees Kelvin. With these parameter values

$$\frac{g\mu_B H}{k_B T} = 0.3 < 1.$$
Since .3 is not very small compared with 1, one might expect to see some deviation in measurements of $\frac{1}{T_2}$dipolar from a linear dependence on $\frac{H}{T}$ for high fields and low temperatures. Using the high temperature formula for $\frac{1}{T_2}$ with a field of 5 kilogauss, a temperature of 20°K, and an impurity concentration of 700 parts per million, $\frac{1}{T_2}$ is roughly 3.3x10^{-2} inverse microseconds. By comparing measured static muon depolarization rates to calculated values for the dipolar relaxation mechanism, it is possible to determine whether the long-range coupling between the $\mu^+$ and the impurities is indeed primarily dipolar.

**Diffusing $\mu^+$ Relaxation**

In the treatment of diffusing muons in palladium doped with gadolinium, it is necessary to take into account the discrete nature of the metallic lattice and motion of the $\mu^+$ through it. It is, however, possible and instructive to treat the lattice as a continuum and determine the diffusion of the $\mu^+$ analytically by making certain approximations. By doing this one can gain insight into the physics of the diffusion of the muon.

**Richards' Model**

P. M. Richards approached the problem of diffusion analytically by assuming that the lattice of the metal of interest could be approximated by a continuum and therefore the diffusion of the nuclear moment, or, in the context of
\( \mu SP, \) the diffusion of the \( \mu^+ \) could be described by a continuum model.\(^{12} \) Richards' treatment makes the following assumptions: Any component of the average spin of an ensemble of spins \( \langle I_a(r,t) \rangle_{\text{avg}} \) varies slowly over a distance on the order of a lattice constant; the concentration of paramagnetic impurities is small; the interaction between the impurity and the \( \mu^+ \) is long ranged compared to a lattice constant and is varying slowly spatially; there are only dipolar interactions between the \( \mu^+ \) and the impurity moments; the nuclear moment, or in the present context the \( \mu^+ \) diffuses through the lattice; there is no trapping; and finally, there is no inhomogeneous broadening.

Within the framework of the assumptions and approximations necessary for an analytical treatment of diffusion, Richards' model predicts a linear dependence of the relaxation rate of the \( \mu^+ \) on the concentration of impurity ions. Richards' diffusion model also predicts a "diffusion peak" in a low field depolarization rate vs. sample temperature measurement. At low temperatures the \( \mu^+ \) diffuses slowly if at all and encounters an impurity induced magnetic field rarely. With no strong \( \mu^+ \)-impurity interactions an ensemble of muons does not lose its polarization very quickly. At very high temperatures, the average muon diffuses rapidly and occupies many interstitial sites which are within the influence of spatially varying thermally fluctuating impurity magnetic fields. At such temperatures an average muon experiences a random distribution of field strengths and
orientations. A time average over an average muon lifetime of $\mu^+$-impurity interactions is negligible at high temperatures and the depolarization rate is again small. At intermediate temperatures muons diffuse into interstitial sites near to an impurity and depolarize quickly compared to a $\mu^+$ lifetime and the depolarization rate is high. Depolarization rates for muons in a non-magnetic sample containing magnetic impurities therefore will exhibit a peak as a function of temperature. The position, shape, and height of the peak are determined by the host material and the impurity dissolved in it. Diffusion peaks have been observed with various hosts doped with various magnetic impurities.\(^2\)

There are several serious limitations of Richards' model. The diffusing muon does not actually move through a continuous lattice, but rather hops from interstitial site to interstitial site. It interacts with an impurity moment primarily through a dipole-dipole interaction which falls off rapidly with increasing separation. The muon can therefore hop from an interstitial site where it interacts strongly with an impurity moment to a site where it interacts weakly. This rapid variation in the interaction between the muon and impurity results in inaccuracies in relaxation rates calculated from Richards' continuum model. The result of using a continuum model is that the calculated depolarization rate for a $\mu^+$ is found to be smaller at a given temperature than when a discrete lattice model with the same diffusion parameters is used.\(^2\) Another problem is that the depolarizing mechanism
is not necessarily purely dipolar. In fact, experimental results in gold suggest that some other strong, short-ranged interaction is also present. While a continuum model may be adequate when the muon remains far from an impurity moment, it almost certainly is wrong when the muon is near the site of the impurity. A discrete lattice model would be more accurate, although it could not be treated analytically. Richards does treat a discrete lattice model in his paper, but does not consider any long-range interaction in that case. A discrete lattice diffusion model that takes into account nearest neighbor and dipolar interactions is now presented.

The Shell Model

An algorithm for an approach to $\mu^+$ diffusion in metals doped with paramagnetic ions was developed by Schillaci et al. The model takes into account the discrete nature of the locations that are accessible to a $\mu^+$ near an impurity. Both dipolar as well as nearest neighbor interactions between the $\mu^+$ and impurities are considered. The concentration of the impurity ions is assumed to be small enough so that the $\mu^+$ interacts with only one impurity at any given time. The diffusing muon is assumed to hop from one interstitial site to a nearest neighbor interstitial site. As in Richards' model, the muon is assumed to eventually encounter an impurity with which it couples and depolarizes. It is this model that was used to analyze the relaxation data taken with palladium.
The basic algorithm of this model classifies the sites accessible to the $\mu^+$ according to their radial distance from the closest impurity. Each radius represents a shell of a varying number of sites. The shell with the smallest radius is called the "first shell," the shell with the next larger radius is called the "second shell," and so on. The largest shell considered has a volume equal to or less than the volume per impurity in the sample. When the muons first stop in the sample, the location of the average $\mu^+$ is taken to be random. The mean polarization per interstitial site will be constant throughout the sample. Therefore, the mean polarization contained in a given shell will be proportional to the number of sites in that shell.

That "shell model" assumes that the $\mu^+$ hops only to nearest neighbor interstitial sites so that for a given shell-site, the probability of hopping away or of remaining in the same site during a hopping time $\tau_H$ can be easily calculated. The probability of the $\mu^+$ hopping to any one of the nearest neighbor sites or of remaining at the same site will be independent of the final location. Therefore the probability of the muon hopping from any one shell to any other is proportional to the number of nearest neighbor sites in that destination shell. Spin polarization can diffuse from shell to shell and can be destroyed by the impurity via various relaxation mechanisms.
In a sample with a very low concentration of impurity ions, there are very many shells that must be considered. Fortunately, the field due to the impurity is very weak in outer shells. Because the resulting depolarization rate of a muon in one of these outer shells is small, these shells can be grouped into a smaller number of composite shells each of which includes those shells with interstitial sites which are roughly the same distance from the nearest impurity. In practice the inner six shells were considered separately while shells farther out were combined into groups to simplify calculations. This approximation was found not to greatly affect the calculation of the $\mu^+$ relaxation rate. By assuming reasonable diffusion and interaction parameters and a typical concentration of impurities, it is possible to construct a computer simulation of the relaxation of the diffusing $\mu^+$. Such a simulation was carried out for various shell groupings as well as for the exact case where there was no shell grouping. The approximation resulted in the same calculated relaxation rates as those from the exact calculation. Shell grouping was used in the actual shell model fitting routine to shorten the computation time.

Long-range dipolar interactions affect every shell while nearest neighbor interactions affect only the first shell. The rate of change of the polarization can be written as a number of differential equations, one for each shell:
\[
    \frac{d p_l}{dt} = \frac{1}{\tau_H} \sum_{j \neq l} R_{jl} n_j p_j - \frac{1}{\tau_H} \sum_{k \neq l} R_{lk} n_k p_l - \frac{C n_l p_l}{r^6} - Q n_l p_l
\]

for the first shell and

\[
    \frac{d p_i}{dt} = \frac{1}{\tau_H} \sum_{j \neq i} R_{ji} n_j p_j - \frac{1}{\tau_H} \sum_{k \neq i} R_{ik} n_k p_i - \frac{C n_i p_i}{r^6}
\]

for the other shells. The sums are over the specified shells. \(n_i\) is the number of interstitial sites in the \(i^{th}\) shell. \(p_i\) is the polarization in the \(i^{th}\) shell per interstitial site. \(R_{ij}\) is the probability of the \(\mu^+\) hopping from the \(i^{th}\) shell to the \(j^{th}\) shell. \(C\) is the dipolar coupling coefficient and \(Q\) is the contact coupling coefficient. These coupling coefficients are derived in Richards' paper and are:

\[
    C = \frac{1}{15} (\hbar \gamma S \gamma_\mu)^2 S(S+1) \tau_C \left[ 4 + \frac{3}{1+\omega_\mu^2 \tau_C^2} + \frac{6}{1+\omega_s^2 \tau_C^2} + \frac{1}{1+(\omega_s+\omega_\mu)^2 \tau_C^2} + \frac{6}{1+(\omega_s+\omega_\mu)^2 \tau_C^2} \right]
\]

and

\[
    Q = \frac{1}{3} \frac{(S+1)}{S} (\gamma_\mu H_x)^2 \tau_C \left[ 1 + \frac{1}{1+(\omega_s+\omega_\mu)^2 \tau_C^2} \right].
\]

\(S\) is the spin of the impurity. \(\omega_\mu\) and \(\omega_s\) are defined in terms of the applied magnetic field \(H\) as:

\[
    \omega_\mu = \gamma_\mu H \quad \text{and} \quad \omega_s = \gamma_s H.
\]

The correlation time \(\tau_C\) is defined in terms of the ion thermal fluctuation time \(\tau_f\) and the hopping time \(\tau_h\) as
\[ \frac{1}{\tau_c} = \frac{1}{\tau_f} + \frac{1}{\tau_h} \]

The thermal fluctuation time is assumed to be of the form:

\[ \tau_f = \frac{1}{\gamma_s b_s T} \]

as discussed in reference 2. \( b_s \) is the thermal width of the ensemble of impurity ions in the metallic host and \( T \) is the temperature in degrees Kelvin. The hopping time can be related to the diffusion coefficient \( D_\mu \) as

\[ \tau_h = \frac{a^2}{6D_\mu} . \]

\( a \) is the mean hopping distance. \( D_\mu \) is assumed to have an exponential temperature dependence of the form:

\[ D_\mu = D_0 \exp(-\frac{\epsilon}{T}) . \]

\( \epsilon \) is the activation temperature of the \( \mu^+ \) in the sample. \( \tau_h \) can then be written as

\[ \tau_h^{-1} = \nu \exp(\frac{\epsilon}{T}) \]

where
\[
\frac{1}{\nu} = \frac{a^2}{6D_0} .
\]

Only a single diffusion mechanism with a unique activation temperature is assumed to exist in the temperature range of interest.

If in the \( i^{th} \) differential equation the number of sites in the \( i^{th} \) shell is divided into both sides of the equation, one has a system of ordinary differential equations of the form:
\[ \frac{dP_i}{dt} = \sum_{k=1,N} U_{ik} P_k. \]

The solutions of the system of equations are assumed to be of the form

\[ p_i = p_{0i} \exp(-\lambda_i t). \]

This system of equations can be written in matrix form:

\[ \frac{dp}{dt} = UP. \]

The eigenvectors and eigenvalues of this matrix equation are determined numerically using a computer program.\(^\text{15}\) If the \(k^{th}\) eigenvector is \(p_k\) and the \(k^{th}\) eigenvalue is \(\lambda_k\), then the total polarization summed over the \(N\) shells at time \(t\) is given by

\[ p(t) = \sum_{k=1,N} C_k p_k \exp(-\lambda_k t) \]

where the constants \(C_k\) are determined by the assumed uniform polarization distribution at the time \(t = 0\). The elements of \(p(t)\) are the solutions \(p_i\) to the differential equations.

In calculations of the eigenvalues \(\lambda\) for typical values of sample, interaction, and diffusion parameters, only one value was small enough to be measurable with our apparatus. The other values of \(\lambda\) were at least two orders of magnitude larger. The interpretation of this is that the polarization associated with the appropriate fast eigenvectors disappears too rapidly to be seen given the time scale of our time differential data. At the shortest times after the stopping
of the $\mu^+$ when the decay positrons are detected, most of the initial polarization is found to still be present. This is evident from the high initial asymmetries in the time differential data. Even at these short times the faster eigenvalue solutions have vanished. Therefore, the slow eigenvalue solution has a very high amplitude while the fast eigenvalue solutions have small amplitudes. The depolarization rate determined is that for the single slow eigenvector.

Values of the parameters $\varepsilon$, $\nu_o$, $b_s$, and $H_x$ are found for which the model gives the best fit to the $\mu$SR depolarization vs. temperature data. This is done by applying the least square fitting algorithm of Marquardt to the data and shell model.\(^{16}\)

Like Richards' model, the shell model predicts that the linewidth of the ensemble of muons will be proportional to the concentration of magnetic impurities. The model also predicts a diffusion peak with the same interpretations described above.

After the diffusion parameters have been extracted from the experimental data, it remains to interpret them in light of various diffusion theories. There are classical, semi-classical, and quantum mechanical theories of light interstitial diffusion. A good recent review of such theories was done by E. W. Kehr.\(^{17}\)

A purely classical treatment of interstitial diffusion is described by G. H. Vineyard.\(^{18}\) In his paper he concludes
that classical rate theory leads to an interstitial impurity jump rate of the form

\[ \Gamma = v_0 e^{-E/kT} \]

where \( E \) is an activation energy and \( v_0 \) is an effective frequency associated with the vibration of the diffusing particle in an interstitial potential well of the host lattice. Vineyard predicts that \( v_0 \) will be proportional to \( 1/\sqrt{m} \) and that the activation energy will be isotope independent if the interstitial-host interactions are isotope independent.

Experimental results for the various isotopes of hydrogen in palladium, copper, and nickel do indeed show a pre-factor isotope dependence of \( 1/\sqrt{m} \) (except for tritium in Pd for which experimental results are questionable).\(^\text{17}\) The activation energies, however, show a definite isotope dependence which is not explained using a classical diffusion theory. For a positive muon, it is likely that quantum mechanical effects on its diffusion parameters will be much stronger than for a proton because of its small mass.

Flynn and Stoneham\(^\text{19}\) and Stoneham\(^\text{20}\) discuss a general approach to quantum diffusion. They calculate an explicit form for the lattice dilation energy of a proton in a bcc or an fcc crystal lattice. Unfortunately the apparent activation energy for a proton in an fcc lattice is the sum of the lattice dilation energy and a "saddle point energy" \( E_s \) due to a host atom lying on the saddle point of the octahedral
site-octahedral site diffusion pathway. In an fcc metal, $E_s$ is much larger than the dilation energy. To calculate $E_s$ it is necessary to have a knowledge of the interstitial-host lattice interaction which is unavailable at present.

V. G. Grebinnik et al. studied $\mu^+$ diffusion in copper. They derived a diffusion rate for under the barrier tunneling assuming a square well potential. Their theoretical diffusion rate is very sensitive to the barrier width which is in turn sensitive to the exact form of the potential. Without a much better knowledge of the interstitial-host interaction it is impossible to make any conclusive interpretations regarding quantum mechanical tunneling of the $\mu^+$ in Pd.

H. Teichler has done a numerical calculation to determine theoretically the diffusion of the positive muon in copper. His results for copper are reasonable and it would be useful to apply his method to palladium.

Of the remaining theories, most are either similar to those mentioned above or too general or phenomenological in their approach to be of use in predicting experimental results. No adequate theoretical treatment of the diffusion of light interstitials in palladium seems to be available. It is therefore possible only to compare results of $\mu^+$ diffusion measurements with measurements of $H^+$, $D^+$, and $T^+$ diffusion in palladium as well as diffusion results in other fcc metals.
III. Experimental Technique

The diffusion of the positive muon in palladium was measured using the Stopped Muon Channel at the Clinton P. Anderson Meson Physics Facility which is part of the Los Alamos National Laboratory in Los Alamos, New Mexico. In our experiments, the muons are oriented with their spins parallel to their former momentum direction after stopping in a sample. A magnetic field transverse to the original polarization is applied with a set of Helmholtz coils. The muons and their positron decay products are detected with scintillation-photomultiplier tube detector assemblies. The Helmholtz coils and the detector geometries are illustrated in figure 3.

Particles passing through the detectors produce analog pulses which are converted into digital pulses in discriminators. The digital pulses then enter the fast logic system which minimizes background noise and produces the final time differential histograms containing the raw data. Figure 4 depicts a simplified diagram of the $\mu$SR counting logic. A $\mu^+$ stopping in the sample is detected as passing through the Be and M counters, but not being scattered through the FO, LO, or UO detectors. If these conditions are satisfied a digital pulse is produced which is conveyed to a time to analog converter (TAC). The TAC produces an output voltage proportional to the time elapsed after its activation. If another $\mu^+$ stops
1. M-counter
2. BO-counter
3. UO-counter
4. FO-counter
5. LO-counter
6. Cryogenics Can
7. Fl-counter
8. L1-counter
9. Bl-counter
10. Ul-counter
11. F2-counter
12. L2-counter
13. B2-counter
14. U2-counter
15. Be-counter
16. C3-collimator
17. C2-collimator
18. Lead Brick Wall
19. Helmholtz Coils

Figure 3
A side view of the $\mu$SR spectrometer

In the figure, the $\mu^+$ enters the spectrometer from the right. The lead wall and beam collimators are placed so as to minimize the incidence of spurious particles from the beam line in the spectrometer.
A simplified counting logic diagram. Note that only the B-telescope logic is completely illustrated. The other three telescopes have similar logic.
in the sample before the first $\mu^+$ decays and produces a positron, then both the earlier $\mu^+$ as well as the second $\mu^+$ stop are discarded as being "bad" events. This minimizes the possibility of there being more than one $\mu^+$ in the sample simultaneously and ensures that each muon is associated with one positron. This reduces background noise. If no $\mu^+$ "pile ups" occur, the positron emitted in the decay process passes through one of the four positron telescopes. The passage of a positron through, for example, the F telescope is indicated by pulses from the F0, F1, and F2 detectors and no pulses from any of the other telescopes. If these conditions are satisfied, a pulse passes to and stops the TAC. The analog voltage from the TAC is then converted to a digital number by an analog to digital converter (ADC). The digital output of the ADC specifies the channel number of the F histogram which is to be incremented by one. After the positron emission has been recorded in the appropriate histogram channel, the TAC is reset and the process is repeated until sufficient data have been obtained. The final result is four histograms each containing a time differential record of the passage of positrons through a specific solid angle during a time interval centered at a specific time. Each histogram is composed of time channels which represent elapsed time measured from the $\mu^+$-stop. The time range of the data is typically from zero to ten microseconds. The size of each time channel is then about ten nanoseconds for 1024 channels.
There is a possibility that the TAC and the ADC introduce nonlinearities into the relationship between the channel number and the actual elapsed time. To minimize this problem, the channel numbers are related to the elapsed time by fitting a six parameter conversion polynomial to data produced by pulses from a precision time base. The polynomial is then used to convert between time and channel numbers.

The data are analyzed by fitting an eight-parameter model to the time differential data using Marquardt's least squares fitting algorithm. The model is of the form:

\[ P(t) = X_1 + X_2 t + X_3 \exp\left(-\frac{t}{X_4}\right)[1+X_5 \exp(-tX_6)\cos(X_7 t+X_8)] \]

where the unknown parameters \( X_i \) are defined as:

- \( X_1 \) = constant background;
- \( X_2 \) = linear background coefficient;
- \( X_3 \) = number of events in \( t = 0 \) time bin;
- \( X_4 \) = \( \mu^+ \) half life fixed at 2.20 \( \mu \)seconds;
- \( X_5 \) = asymmetry;
- \( X_6 \) = depolarization rate;
- \( X_7 \) = \( \mu^+ \) Larmor precession frequency; and
- \( X_8 \) = the phase of the precession.

Once the parameters have been extracted from the time differential data for a range of temperatures, the shell model fitting algorithm is applied. Diffusion parameters are extracted and conclusions can be drawn.
Measurements were made on two palladium samples doped with gadolinium impurities. Each sample was prepared by arc melting a small piece of palladium with gadolinium and then adding enough palladium to obtain the final dilution. The final alloys were melted, turned over, and then melted again fourteen or more times. They were rolled and then annealed at 1000°C for eight hours and then quenched rapidly in water. The concentration of one sample was measured to be 260 parts per million ± 10 parts per million. This concentration proved to be too low for the acquisition of adequate depolarization rate data. The concentration was therefore increased to roughly 1000 parts per million. A precise measurement of the gadolinium concentration in the second sample is pending.

The applied transverse magnetic fields ranged from 150 Oersteds to 5000 Oersteds. The field was homogeneous across the sample to better than one part in $10^5$. The field varied during the acquisition of data less than one tenth of one Oersted. The magnitude of the field was known to an accuracy of one Oersted.

The temperature of the sample was controlled by fixing the sample to a liquid-helium-cooled cold finger. The sample was thermally isolated by a metal heat shield and by being placed under a high vacuum. The temperature was measured to an accuracy of better than one percent by means of a carbon glass resistor thermally fixed to the sample. The
temperatures at which data were taken ranged from 2.5°K to 300°K. During the acquisition of data the temperature was held constant to within one percent of the target temperature.
IV. Results and Conclusions

The measured low temperature muon spin depolarization rates in Pd-Gd are shown in figure 5. At temperatures on the order of a few degrees Kelvin, the positive muon is not diffusing significantly during its lifetime. Depolarization rate data taken at such low temperatures can therefore be compared to the static $\mu^+$ linewidth predictions of Walstedt and Walker. The Walstedt and Walker static $\mu^+$ linewidth for 700 p.p.m. gadolinium in palladium is superimposed on the data in figure 5. The data fall very nearly along the theoretical prediction. A concentration of 700 p.p.m. gadolinium is not far from the intended 1000 p.p.m. Such a concentration is also consistent with the best fits of diffusing $\mu^+$ data obtained using the shell model.

The low field muon spin depolarization rate data for both the 260 p.p.m. and 700 p.p.m. Pd-Gd samples are shown in figure 6. The higher impurity concentration data scale with the 260 p.p.m. data by a factor of about three. Assuming a gadolinium concentration of 700 p.p.m. resulted in the best shell model fit to the high Gd concentration data. These results considered along with the static $\mu^+$ depolarization data and a linear dependence of the diffusing $\mu^+$ linewidth on impurity concentration are consistent with a high impurity concentration sample with 700 p.p.m. gadolinium, a low concentration sample with 260 p.p.m. gadolinium and a dipolar long-range $\mu^+$-impurity interaction.
Figure 5

Static $\mu^+$ data in Pd-Gd (700). The straight line is the Walstedt and Walker calculation using a Curie law approximation of the average impurity spin. The approximation is not significantly different from the exact value in the range of H/T considered.
Pd-Gd Relaxation Rate Data

Figure 6.

Temperature (°K)

\( \frac{F(t) - T}{T} \)

pd-Gd (260)

pd-Gd (700)
The solid curves in figure 6 represent depolarization rates calculated using the shell model with the best fit diffusion parameters from the 700 p.p.m. data analysis. The calculated curve does not quite pass through the 260 p.p.m. Pd-Gd data. This is probably due in part to errors in the concentration of gadolinium in the high concentration sample. The 260 p.p.m. Pd-Gd data are therefore consistent with the 700 p.p.m. diffusion results.

The 700 p.p.m. Pd-Gd diffusion parameters from the best fit of the data are tabulated in Table 2. Also listed are diffusion parameters for the proton in Pd as well as for the muon and proton in copper, gold and silver.

It is clear that Vineyard's classical diffusion theory does not explain the diffusion of positive muons in palladium. The prefactor $v_0$ extracted from the experimental data is much too small for the $\mu^+$ in palladium. A $1/\sqrt{m}$ isotope dependence would predict that $v_0$ be about four orders of magnitude greater given the proton prefactor in Pd. The measured activation energy for the $\mu^+$ is much smaller than that measured for the proton in palladium.

The qualitative results of diffusion studies of palladium are similar to those for copper. They both show large reductions in the prefactor $v_0$ when the muon is compared with the proton. The activation energies for muons in copper and palladium are also much less than those measured for protons.

It is interesting to compare diffusion results in palladium and copper with results in gold and silver. Diffusion
Table 2. Fitted parameters for muons and protons in various hosts.

<table>
<thead>
<tr>
<th>Host</th>
<th>$v_0$ (s$^{-1}$)</th>
<th>$\epsilon$ (K)</th>
<th>T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^a$</td>
<td>$10^{7.46 \pm .04}$</td>
<td>551 $\pm$ 15</td>
<td>80-250</td>
</tr>
<tr>
<td>Ag$^a$</td>
<td>$10^{13.7 \pm .5}$</td>
<td>3400 $\pm$ 200</td>
<td>200-500</td>
</tr>
<tr>
<td>Au$^a$</td>
<td>$10^{13.5 \pm .5}$</td>
<td>1350 $\pm$ 100</td>
<td>85-230</td>
</tr>
<tr>
<td>Pd$^b$</td>
<td>$10^{9.8 \pm .5}$</td>
<td>850 $\pm$ 200</td>
<td>100-300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Host</th>
<th>$v_0$ (s$^{-1}$)</th>
<th>$\epsilon$ (K)</th>
<th>T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^a$</td>
<td>$(1.04\pm.08)\times10^{14}$</td>
<td>4640 $\pm$ 30</td>
<td>720-1200</td>
</tr>
<tr>
<td>Ag$^a$</td>
<td>$6.1\times10^{13}$</td>
<td>3620</td>
<td>950-1120</td>
</tr>
<tr>
<td>Au$^a$</td>
<td>$4.0\times10^{12}$</td>
<td>2840</td>
<td>770-1200</td>
</tr>
<tr>
<td>Pd$^a$</td>
<td>$4.2\times10^{13}$</td>
<td>2740</td>
<td>230-700</td>
</tr>
</tbody>
</table>

**Measurement** | Gd Thermal Fluctuation Time in Pd (ns-K)
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$SR$^b$</td>
<td>6.2 $\pm$ 1</td>
</tr>
<tr>
<td>EPR$^c$</td>
<td>6.1 $\pm$ .26</td>
</tr>
</tbody>
</table>

$^a$Reference 23.

$^b$This work.

$^c$J. Moret *et al.*, reference 11.
results in these two metals are qualitatively different than those in palladium and copper. The diffusion rate prefactors for muons and protons in gold or silver may be roughly isotope independent. The difference in examined temperature ranges for the two interstitials makes a definitive statement difficult. The activation energies measured in each metal are not so strongly dependent on the mass of the interstitial as is the case for copper and palladium. An explanation for the qualitative differences and similarities between these four fcc metals is not apparent.

The results of the above experiment show that positive muons in palladium do not diffuse significantly at sample temperatures below about 100K. Classical diffusion theory does not account for the diffusion parameters extracted. A complete quantum mechanical calculation with which experimental results may be compared has not yet been carried out for muons in palladium. When such a calculation has been made it will be possible to estimate the effects of quantum mechanical mechanisms on the diffusion of positive muons and light interstitials in palladium.
V. References

7. See for example J. J. Sakurai, Advanced Quantum Mechanics (Addison-Wesley, 1976).
11. In palladium the RKKY interaction was found to be about two orders of magnitude weaker than the dipolar interaction. Approximate calculations were made using the low temperature EPR value for impurity spin-conduction electron coupling [J. Moret et al., Phys. Rev. B 11, 2002 (1975)] and the Knight shift of the muon in Pd at 75°C [F. N. Gygax, Hyperfine Interactions 8, 487 (1981)].
22. J. A. Mydosh, private communication.