PHYSICAL REVIEW B VOLUME 37, NUMBER 16 1 JUNE 1988

Helium, tritium, and protium NMR studies of tritide-free aged PdT_x

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(Received 13 July 1987)

Pulsed NMR relaxation-time measurements have been performed on PdT_x, aged approximately eight years, after first removing most of the tritium by room-temperature desorption and again after addition of protium to one of these tritide-free samples. Spin-lattice and spin-spin relaxation times T_1 and T_2 were measured for both tritium and ^3He in the temperature range 100–300 K, while T_1, T_2, and the rotating-frame relaxation time $T_{1\rho}$ were obtained for protium in the same temperature range. The relative magnitudes of T_1, the decay time T_{2m} of the Carr-Purcell-Meiboom-Gill signals, and the line-shape decay time T_2^* for ^3He in tritide-free PdT_x, are consistent with the distribution of the helium as microbubbles in the Pd matrix. The increase in the ^3He values of T_1 upon addition of protium to an atomic ratio $[H]/[Pd]=0.68$ is attributed partially to a decrease in the Fermi-level density of states and partially to other internal relaxation mechanisms. Analysis of the dipolar component T_{1d} of T_1, for protons in the sample to which protium was added, gives a value of the diffusion activation energy at temperatures between 230 and 300 K which is in agreement with that for β-PdH_x. Comparison with the triton NMR in tritide-free PdT_x indicates that the residual tritium, rather than forming a dilute solid solution, occupies unusual sites in the Pd lattice, perhaps at internal surfaces surrounding the ^3He microbubbles.

I. INTRODUCTION

The palladium-hydrogen system is probably the most thoroughly studied metal-hydrogen system.[1,2] The phase diagrams, crystal structures, electronic structure, and hydrogen-diffusion behavior of both PdH_x and PdD_x have been investigated experimentally and theoretically by numerous techniques. By comparison, relatively little work on the formation and properties of palladium tritide (PdT_x) has been published.[3-5] However, Lässer has recently determined[6] the pressure-composition-temperature relationship for PdT_x and compared the isotope dependence of the α-β phase boundaries for PdH_x, PdD_x, and PdT_x. It should be noted that most of these studies[4-6] were performed on PdT_x samples with minimal concentrations of the triton β-decay end product: the light helium (^3He) isotope. Since the half-life of radioactive tritium is approximately 12.3 yr, substantial quantities of ^3He can be generated over a few months (e.g., 5.5% of the initial tritium will be converted into ^3He after one year). Schober[7] has reviewed the effects of this decay-generated ^3He on the physical properties of several metal tritides and has noted substantial degradation of crystalline order. In contrast to many metal tritides which irreversibly release substantial quantities of the helium (Refs. 3 and 7), $PdT_{0.6}$ has been found[3] to retain essentially all of the ^3He formed during periods of at least 1300 d. In addition, Thomas and Mintz[8] have clearly demonstrated by transmission electron microscopy that 1.5–2.0 nm diameter helium bubbles and dislocation loops have formed in $PdT_{0.6}$ after only 66 d of aging.

We report here the results of nuclear magnetic resonance (NMR) relaxation-time measurements on aged PdT_x. We were particularly interested in the effects of long-term tritium decay on helium retention in microbubbles as has been inferred in other aged metal tritides,[9-11] and on the tritium solubility, phase composition, and diffusion properties. Due to the nature of the original storage configuration of the nominal $PdT_{0.65}$, the NMR samples had to be prepared after first removing most of the tritium by room-temperature desorption and subsequent encapsulation. In addition, an aged $Pd(H,T)_x$ sample was prepared by the addition of protium to some of this (partially) tritide-free material. Large differences in the ^3He relaxation times were observed between the original aged $PdT_{0.08}$ and the β-$Pd(H,T)_{0.68}$ sample thus produced, which we have attributed to changes in the electronic density of states and the effectiveness of the relaxation process at the bubble wall. The stoichiometries of the tritide-free PdT_x samples were substantially larger than equilibrium compositions measured by Lässer.[6] Furthermore, the tritium diffusion parameters obtained from the triton NMR relaxation times do not agree with the literature results[12,13] for hydrogen isotopes in α-PdH_x. While some of the proton relaxation time data that we obtained from the aged $Pd(H,T)_{0.68}$ sample gave a diffusion activation energy consistent with the published value of 0.23 eV obtained from several NMR studies[14-18] on β-PdH_x, we have seen several anomalous features which include distinct non-Arrhenius temperature behavior. We believe these unusual effects arise because tritium (or protium) can occupy unusual sites in the Pd lattice (e.g., internal surfaces or dislocation cores) that accompany the formation of helium microbubbles as tritium radioactive decay continues. A general mechanism for the self-nucleation of these bubbles as well as the simultaneous creation of interstitial dislocations has been described by others.[19] Hydrogen trapping effects on α-

phase solubility limits and diffusion behavior in cold-worked palladium hydride have been previously attributed[20–23] to dislocations and possibly other unspecified defects. Consequently, similar (or even more extensive) trapping effects are very likely to occur in our aged PdT_x samples.

II. EXPERIMENTAL DETAILS

Several NMR samples were prepared from two batches of aged PdT_x powders that had been previously sealed in stainless-steel containers with sufficient tritium gas to maintain x above 0.60 for several years, given an initial stoichiometry of approximately $PdT_{0.65}$. In order to obtain materials for various experiments, it was necessary to remove most of the tritium from the PdT_x by a room-temperature desorption process until pressures between 10 and 100 mPa were reached. One container had been kept for nearly seven years before this tritium removal was performed, while the second PdT_x batch had been aged an additional period of several months. The actual NMR samples were procured from smaller portions of these two master batches following further storage (but without excess gaseous tritium) in smaller containers for times between a few days to over three years after the original removal of tritium from these master samples. The subsequent differences in residual tritium contents among the NMR samples can be associated with the latter storage time. Compositions at the time when the NMR samples were loaded were obtained by either standard calorimetry analyses or by a volumetric determination on representative portions, using an all-metal Toepler pump and induction heating to a nominal maximum temperature of 1000 °C, with the composition of the evolved gases being analyzed by mass spectrometry. The latter measurements also provided a (destructive) method for determining the trapped ^3He contents in the tritide-free PdT_x materials. Table I provides summaries of the residual [T]/[Pd] atom ratios and helium contents at the time of the NMR measurements.

Since Pd metal and the $Pd(H,D,T)_x$ phases have low electrical resistivities and no effective surface insulating films, special precautions are usually required[14–18] to minimize the various complications that can arise from the radio-frequency skin-depth effects. In the present case, our PdT_x powders were first appropriately sieved by passing through a 100-mesh sieve while being retained by a 400-mesh sieve, and then thoroughly mixed with an approximately equal volume of Al_2O_3 powder of the same dimensions. Weighed quantities of the PdT_x-Al_2O_3 mixtures were sealed in a 7-mm or 9-mm-o.d. evacuated glass tube for the NMR experiments.

The pulsed NMR techniques and spectrometer that were used to measure the tritium and ^3He relaxation times have been described previously.[9,10] Although most of these measurements were performed at a Larmor resonance frequency (ν_0) of 45.7 MHz, some data were also obtained at $\nu_0 = 20.0$ MHz. The spin-lattice relaxation times (T_1) were measured by the inversion recovery method. However, three distinct spin-spin relaxation times[9,10] were routinely determined: T_2^*, the line-shape decay time, usually estimated from the widths of the spin-echo line shapes; $T_{2'}'$, the time constant for the exponential decrease of the two-pulse ($\pi/2$-π) echo maxima; and T_{2m}, the decay of the Carr-Purcell-Meiboom-Gill (CPMG) signals,[9,10] with 200 μsec spacing between the π pulses. The T_1 and T_2 measurements were made between 300 K and about 110 K on the PdT_x samples in the 7-mm-o.d. tubes. However, only room-temperature measurements were made on the 9-mm samples. Nondestructive determination of the ^3He and tritium contents were made at room temperature on all the samples by the NMR spin technique.[9] As shown in Table I, good agreement was found with the volumetric-mass spectrometric results.

A portion of the PdT_x powder, made by removing tritium from the second master container at room temperature, was reacted at ambient temperature with hydrogen gas to a composition $[H]/[Pd] = 0.68$ (as determined by the quantity of gas absorbed during reaction). This powder had been previously mixed with Al_2O_3 and placed in a 7-mm-NMR sample tube (sample 5). When the protium absorption was complete the bottom of the NMR tube was cooled in liquid nitrogen and the tube flame-sealed.

The tritium and ^3He contents in aged $PdH_{0.68}$ (i.e., sample 5), as well as another NMR tube (i.e., sample 6) containing unreacted PdT_x that was processed and sealed at the same time, were determined by NMR spin counts at $\nu = 34.5$ MHz. These results are presented in Table II along with the remeasured values for two previously loaded samples. Since the ^3He contents in samples 5 and 6 are identical within experimental accuracy, there did not seem to be any loss of helium during the addition of protium. However, this does not preclude the possibility of alterations in the microscopic distribution of helium during this treatment, but in the absence of any direct evidence such changes are assumed to be minor. Table II

TABLE I. Residual ^3He concentrations and [T]/[Pd] atom ratios in tritide-free aged PdT_x samples, based on spin count determination (NMR) at 45.7 MHz and gas decomposition and mass spectrometric analysis (PVT).

		[^{3}He] (10^{20}/g)		[T]/[Pd]	
Sample	Tube o.d. (mm)	NMR	PVT	NMR	PVT
1	9	14.7	15.7	0.069	0.078
2	9	15.5	16.3	0.072	0.073
3	7	14.0	15.6	0.072	0.078
4	7	14.3		0.009	

TABLE II. Comparison of tritium and ^{3}He contents in aged PdT_x and $Pd(H,T)_{0.68}$ samples from NMR spin counts at 34.5 MHz.

Sample	Nominal stoichiometry	[T]/[Pd]	[^{3}He] (10^{20}/g)	[^{3}He][Pd]
3	$PdT_{0.08}$	0.070	17.3	0.31
4	$PdT_{0.01}$	0.011	16.4	0.29
5	$Pd(H,T)_{0.68}$	0.016	14.0	0.25
6	$PdT_{0.055}$	0.045	14.3	0.25

also shows that only one-third of the tritium present in the unreacted PdT_x (sample 6) remains in sample 5 after the reaction with protium. This tritium was presumably displaced with the excess protium in the gas by the isotope exchange process during hydrogen absorption. Due to the very low signal intensity, no triton relaxation time data was obtained from sample 6. However, the proton T_1, T_{2m}, and $T_{1\rho}$ relaxation times for $Pd(H,T)_{0.68}$ were measured between 100 and 300 K, where $T_{1\rho}$ is the rotating frame relaxation time[15] using a spin-locking magnetic field of 7.3 G. All the proton measurements were performed at 34.5 MHz.

III. RESULTS

A. $PdT_{0.08}$

Figure 1 shows the helium relaxation times T_1 and T_{2m} versus temperature in two tritide-free samples (7-mm-o.d. tubes). Also shown is the triton relaxation time T_1 for one of the samples. Figure 2 shows T_1 for ^{3}He over a range of temperatures for tritide-free PdT_x and for $Pd(H,T)_{0.68}$. Figure 3 displays the temperature dependence of the relaxation times for the residual tritium in one of the tritide-free samples. All data in Figs. 1–3 were obtained at 45.7 MHz.

Tables III and IV summarize T_1 and T_{2m} for helium at 300 K for the 9-mm-o.d. samples at 45.7 MHz and 20.0 MHz. Included in both tables is the line-shape decay time T_2^*, determined by analyzing the line shape of spin echoes produced by a $\pi/2$-π pulse sequence.

B. $Pd(H,T)_{0.68}$

Figure 2 shows T_1 for ^{3}He over a range of temperatures for $Pd(H,T)_{0.68}$ at 45.7 MHz. The values of T_1 and T_{2m} at 300 K and 45.7 MHz are included in Table III.

Figure 4 shows T_1 and T_{2m} for the protons as a function of temperature at 34.5 MHz. Also shown are the dipolar component T_{1d} and the rotating-frame spin-lattice relaxation time $T_{1\rho}$. The various curves are from the Bloembergen, Pound, and Purcell (BPP) model[24] and will be discussed in Sec. IV.

Experimentally, the component T_{1d} is obtained from the expression

$$1/T_1 = 1/T_{1d} + 1/T_{1e} , \quad (1)$$

where $1/T_{1e}$ is the contribution of the conduction electrons to the spin-lattice relaxation rate. In Eq. (1), the experimental values of T_1 are used, while T_{1e} is determined at each temperature from[24]

$$T_{1e}T = C . \quad (2)$$

The value of C, constant for a given sample, is determined from the low-temperature limit of the product

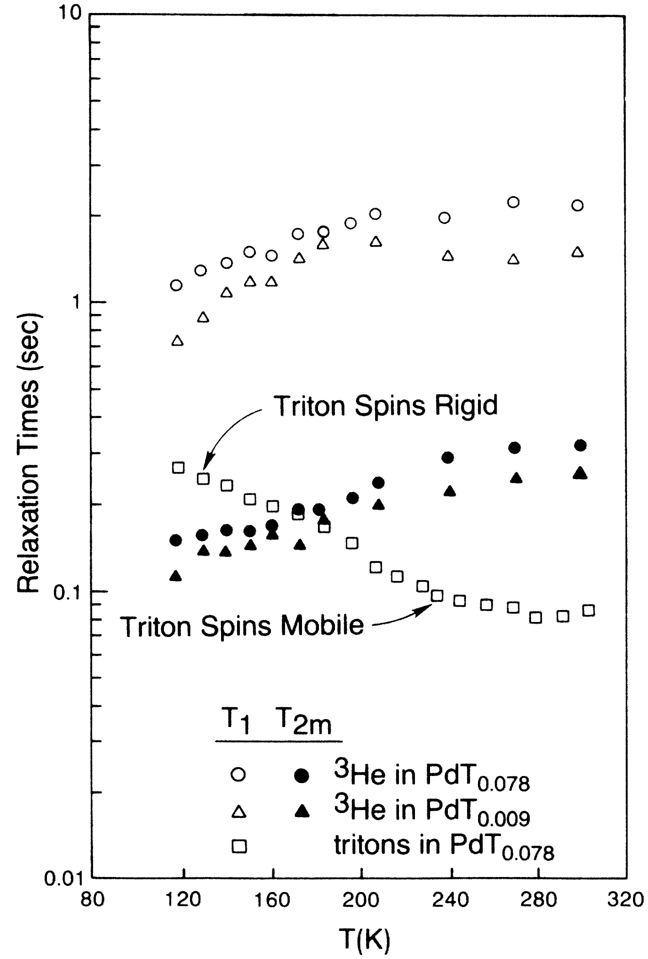

FIG. 1. ^{3}He relaxation times T_1 (open symbols) and T_{2m} (closed symbols) vs temperature in tritide-free aged PdT_x for $x = 0.078$ (circles) and $x = 0.009$ (triangles). Also shown is the triton relaxation time T_1 for $x = 0.078$ (squares). All data were obtained at 45.7 MHz.

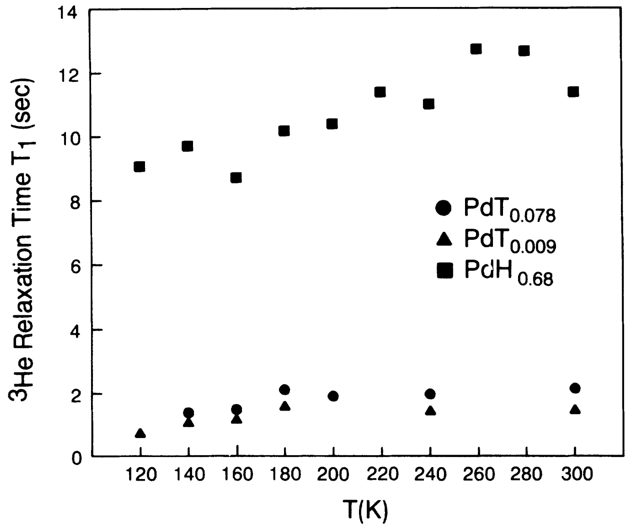

FIG. 2. ^{3}He relaxation time T_1 vs temperature, at 45.7 MHz, in tritide-free aged PdT$_x$ for x —0.078 (circles), x —0.009 (triangles), and in Pd(H,T)$_{0.68}$ (squares).

T_1T, using the fact that $T_1 \rightarrow T_{1e}$ in this limit. For our Pd(H,T)$_{0.68}$ sample, $C = 57 \pm 3$ sec K, compared to 70 ± 3 sec K found by Arons *et al.*[15] for β-PdH$_{0.73}$, and 68 ± 2 sec K given by Cornell and Seymour[17] for β-PdH$_{0.70}$. The difference between our value of C and the latter two values may be due to lattice damage produced in our sample by the tritium decay.

In order to analyze the diffusion behavior in Pd(H,T)$_{0.68}$, the BPP model was applied to extract the jump correlation times, τ_c, from the individual T_{1d} and $T_{1\rho}$ data of Fig. 4 using the procedures described by Korn *et al.*[25] The temperature dependencies of the correlation times from T_{1d} and $T_{1\rho}$ are shown in Figs. 5(a) and 5(b), respectively, along with the apparent activation energies for diffusion, E_a, obtained in regions where the Arrhenius relationship is obeyed. The values of τ_c^{-1} in Fig. 5(a) were adjusted to reproduce the experimental minimum value of T_{1d} and, similarly, the values of τ_c^{-1} in Fig. 5(b) were adjusted to reproduce the experimental minimum in $T_{1\rho}$. It was not possible to fit both the T_{1d} and $T_{1\rho}$ minima with a unique correlation time curve.

IV. DISCUSSION

A. Trapped helium

The rather different temperature behavior of the tritium T_1 values relative to that for helium, seen in Fig. 1, reflects the mobility of the residual tritons in the palladium lattice. In the limit of low temperature, all diffusion processes slow down and T_1 increases. As the temperature is raised the tritons begin to diffuse more rapidly and the effect of this motion is to decrease the spin-lattice relaxation time. At still higher temperatures T_1 will increase again, so the net effect is a minimum in the triton T_1 at some temperature. This general behavior will be discussed further in subsection C. In contrast to this, the helium T_1 (and T_{2m}) values are relatively insensitive to temperature.

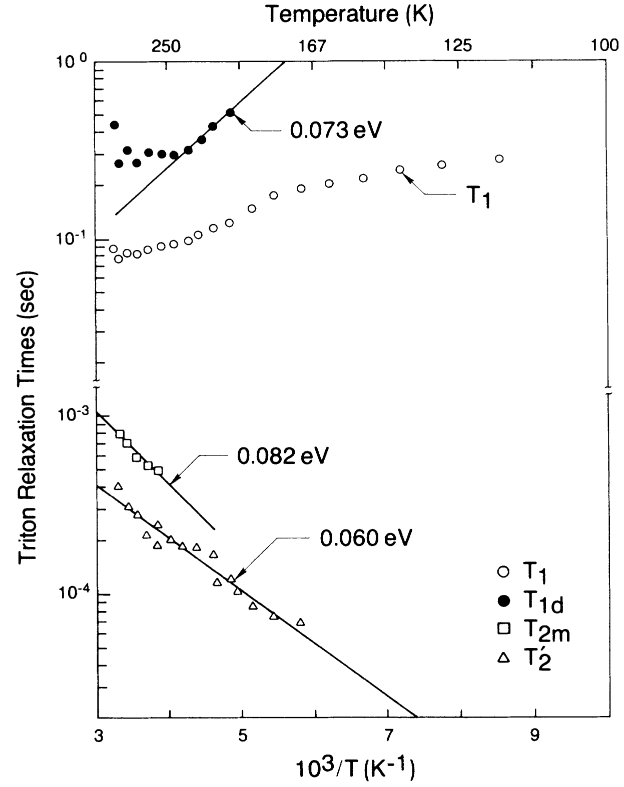

FIG. 3. Estimates of the activation energy for triton diffusion in tritide-free aged PdT$_{0.078}$ obtained from the relaxation times T_{1d} (filled circles), T_{2m} (squares), and T_2' (triangles) at 45.7 MHz.

From Tables III and IV, the magnitudes of T_1, T_{2m}, and T_2^* for helium at 300 K are seen to satisfy

$$T_2^* < T_{2m} < T_1 \ . \qquad (3)$$

Figure 1 shows that the inequality $T_{2m} < T_1$ exists over the entire temperature range investigated. By contrast, for a rigid spin lattice one would expect[10]

$$T_2^* \sim T_{2m} \ll T_1 \ , \qquad (4)$$

TABLE III. Summary of ^{3}He NMR relaxation times at 300 K and 45.7 MHz.

Sample	Phase	T_2^* (msec)	T_{2m} (msec)	T_1 (msec)	T_{2m}/T_1
1	α	0.081	365	2120	0.172
2	α	0.077	178	2190	0.081
5	β		1680	11 350	0.148

TABLE IV. Summary of ^{3}He NMR relaxation times at 300 K and 20.0 MHz. Both samples were α phase.

Sample	T_2^* (msec)	T_{2m} (msec)	T_1 (msec)	T_{2m}/T_1
1	0.176	700	2540	0.28
2	0.187	500	2265	0.22

while for a bulk fluid one would have[10]

$$T_2^* < T_{2m} \sim T_1 \ . \tag{5}$$

That inequality (3), rather than (4) or (5), is satisfied, is consistent with what has been observed in several aged tritides in which the ^{3}He is distributed as microscopic bubbles.[26,27] Direct evidence for such bubbles in aged PdT$_x$ was obtained by Thomas and Mintz,[8] who inferred a mean bubble diameter of 1.5–2.0 nm from transmission electron microscopy on 66-d old PdT$_{0.6}$. Table V lists the ratio T_{2m}/T_1 for ^{3}He in several aged metal and alloy tritides at room temperature.

In Fig. 2 it is seen that the helium T_1 values increase by a factor of from 5 to 10 upon addition of protium. Phenomenologically, the spin-lattice relaxation rate for helium microbubbles may be written,[10]

$$T_1^{-1} = T_{1w}^{-1} + T_{1B}^{-1} \ , \tag{6}$$

where T_{1w}^{-1} is the relaxation rate at the bubble wall and T_{1B}^{-1} that in bulk helium. It has been proposed[9,10] that T_{1w}^{-1} generally dominates in metal tritides, so that T_1 should be sensitive to the electronic structure and chemical composition of the host. Our results are consistent with this, since the protiding reaction would not be expected to change T_{1B} but does change the host characteristics. For example, the value of $T_{1e}T$ [Eq. (2)] changes from 32±1 sec K for tritons in PdT$_{0.08}$ to 57±3 sec K for protons in Pd(H,T)$_{0.68}$, indicative of a decrease in the density of states at the Fermi level,[24] and hence, a decrease in the contribution of the conduction electrons to T_{1w}^{-1}. This would increase the helium T_1 by about 50%, which is, however, much less than the observed increase. Other processes, such as direct spin coupling between ^{3}He and the protons or tritons may be contributing, but it is difficult to make quantitative estimates in the absence of good models for surface relaxation mechanisms.

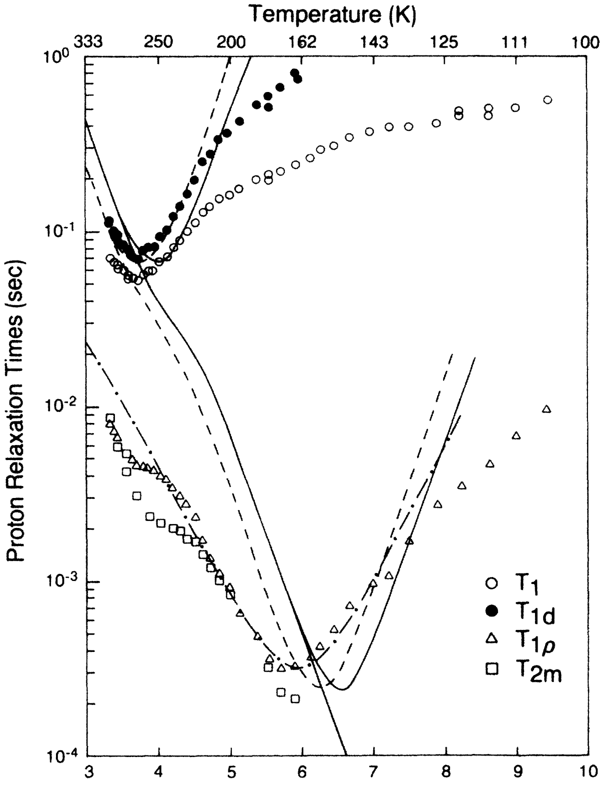

FIG. 4. Proton relaxation times T_1 (open circles), T_{1d} (filled circles), $T_{1\rho}$ (triangles), and T_{2m} (squares) for Pd(H,T)$_{0.68}$ at 34.5 MHz. The curves are a fit to the BPP model: ——, from the NMR diffusion parameters for β-PdH$_x$ (Ref. 16); — — —, from the correlation times obtained from T_{1d}; —·—·—·, from the correlation times obtained from $T_{1\rho}$. (See the discussion in Sec. IV.)

B. Trapped tritium

The equilibrium composition of α-PdT$_x$ under the conditions at which tritium was removed from our samples (see Sec. II) is $x < 0.01$ (Ref. 6). However, the stoichiometries of the tritide-free PdT$_x$ samples shown in Table I are nearly an order of magnitude larger than this (with the exception of sample 4, which was prepared from tritide-free material which had been stored without excess tritium for an additional three years). The excess tritium must evidently exist at trapping sites which are likely associated with the formation of the helium microbubbles. Bubble formation may be considered a form of "cold-working," and a general mechanism for self-nucleation of these bubbles with the simultaneous creation of interstitial dislocations has been described by

TABLE V. Summary of T_{2m}/T_1 ratios for ^{3}He NMR in several aged metal and alloy tritides at room temperatures and 45.7 MHz.

System	Age (d)	T_{2m}/T_1	Reference
Pd	~3000	0.15	this work
Li	815	0.01	27
Ti	1346	0.060	26
U	1108	0.35	26
V	1825	0.024	26
Mg$_2$Ni	1281	0.042	26
ZrNi	1330	0.014	26

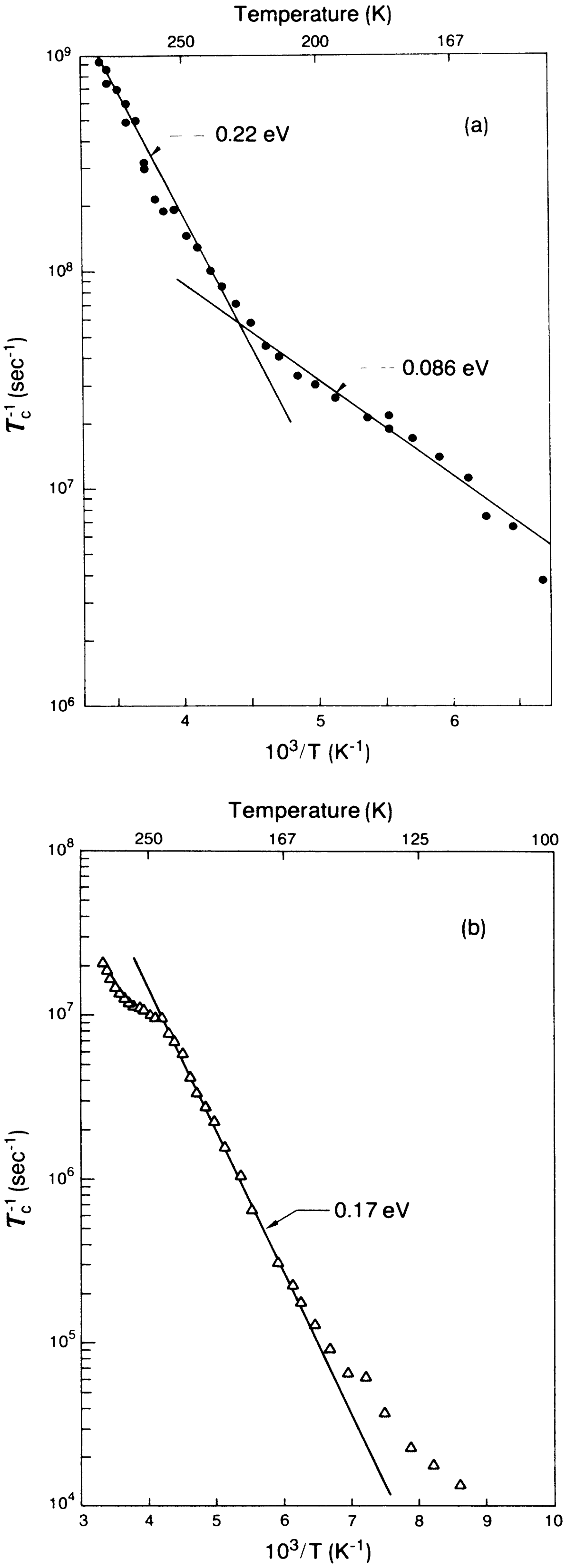

FIG. 5. Arrhenius plots of the inverse of the BPP correlation time τ_c for proton diffusion in Pd(H,T)$_{0.68}$: (a) obtained from the relaxation time T_{1d} (circles); (b) obtained from the relaxation time $T_{1\rho}$ (triangles).

Wilson *et al.*[19] Hydrogen trapping effects on solubility limits and diffusion behavior in cold-worked α-PdH$_x$ have been observed and attributed to dislocations and possibly other unspecified defects.[20–23] While dislocation cores can serve as trapping sites, one may also consider the internal surfaces defined by the ^{3}He bubbles as possible trapping centers. From the bubble sizes and densities reported by Thomas and Mintz, we estimate that the number of internal surface sites associated with the microbubbles is about 10% of the bulk lattice sites of the sample. Thus, with respect to site availability, internal surface sites could easily accommodate the residual tritium via internal chemisorption. We are currently pursuing a rigid-lattice second-moment analysis and deuteron exchange experiments on the PdT$_{0.08}$ sample, which appears to support the idea of internal chemisorption.

C. Diffusion behavior

The occurrence of a minimum in the proton T_{1d} (and T_1) as a function of temperature, seen in Fig. 4, is indicative of long-range motion of the spins through the lattice. In the BPP formulation of NMR relaxation-rate theory,[24] the dipolar field correlations are assumed to decay as $\exp(-t/\tau_c)$, where τ_c is the correlation time. For a diffusing species, $\tau_c=\tau_d/2$, where τ_d is the mean time between jumps, and the minimum in T_{1d} occurs when $\omega_0\tau_c\sim 1$, where $\omega_0/2\pi$ is the Larmor resonance frequency ν_0. Similar considerations[25] hold for the variation of $T_{1\rho}$. The minimum value of T_{1d} is proportional to ω_0 and shifts to higher temperatures as ω_0 is increased; at low temperatures ($\omega_0\tau_c \gg 1$) T_{1d} varies as ω_0^2 at fixed temperature. Our T_{1d} values for Pd(H,T)$_{0.68}$ are in general agreement with those of Refs. 15 and 17 for β-PdH$_x$ when allowance is made for the different resonance frequencies used. The BPP variation of T_{1d}, $T_{1\rho}$, and T_{2m} with temperature, calculated using a single correlation time curve based on the NMR diffusion parameters measured for β-PdH$_{0.70}$ by Seymour *et al.*,[16] is shown by the solid curves in Fig. 4. The BPP value of T_{1d} at the minimum has been adjusted to agree with our observed value.

However, these calculated curves do not closely correspond to the proton relaxation times obtained from the aged Pd(H,T)$_{0.68}$ sample: (1) the experimental T_{1d} and $T_{1\rho}$ minima occur at temperatures approximately 20–25 K above their respective minima on the solid curves; (2) the experimental $T_{1\rho}$ minimum is about 30% larger than the value predicted by the BPP mode even though the latter value has been fit to the T_{1d} minimum; (3) the experimental T_{1d} and $T_{1\rho}$ exhibit large negative deviations from the BPP curves at temperatures below their minima; and (4) for temperatures above 160 K, the experimental $T_{1\rho}$ and T_{2m} data are substantially below the BPP-model predictions. These high-temperature deviations have *not* been previously observed[14,15] in proton relaxation times for β-PdH$_x$ samples that were conventionally prepared, i.e., not reacted with tritium, producing helium impurities, or extensively cycled through the two-phase region, producing dislocations.[21,22] Also shown in Fig. 4 (as dashed lines) are the BPP values for the proton T_{1d} and $T_{1\rho}$ when calculated from the Arrhenius line of Fig. 5(a) corresponding to 0.22 eV activation energy. This fit to the measured T_{1d} data is much better (as would be expected), but for temperatures below 210 K an apparently lower activation energy process[28] influences the proton relaxation rate.[17,18] Although this BPP fit shifts the calculated $T_{1\rho}$ curve upwards in temperature, the previously mentioned discrepancies (2), (3), and (4) remain. In fact, a unique set of correlation times that satisfactorily fits both the T_{1d} and $T_{1\rho}$ data for $\mathrm{Pd(H,T)}_{0.68}$ was not found. Using the Arrhenius line of Fig. 5(b) to calculate the BPP values only of $T_{1\rho}$ results in the dot-dashed line shown in Fig. 4. While the E_a value of 0.17 eV from $T_{1\rho}$ is slightly smaller than the value 0.22 eV from T_{1d}, different absolute τ_c values are required to describe the T_{1d} and $T_{1\rho}$ proton relaxation times in $\mathrm{Pd(H,T)}_{0.68}$. The greater width of the $T_{1\rho}$ results (dot-dashed line) directly reflects a smaller E_a value.

The most likely explanation for the unusual proton relaxation times found for the aged $\mathrm{Pd(H,T)}_{0.68}$ sample, as compared to previously published NMR studies[14–18,29,30] on β-PdH_x, is some form of trapping associated with the lattice damage that accompanies helium bubble formation. Proton diffusion and relaxation processes can be greatly altered[21–23] in the presence of one or more locations with increased stability relative to the normal interstitial sites. In $\mathrm{Pd(H,T)}_x$, either the bubble surfaces or the dislocations generated by their formation could act as these traps. A major effect of trapping would be a slower "average" mobility, which would be manifested as a shift of the proton relaxation minima to higher temperatures. This is exactly the behavior observed for $\mathrm{Pd(H,T)}_{0.68}$ in Fig. 4 when compared with the BPP curves (solid lines) derived from the diffusion parameters of Seymour *et al.* The inflection points near 260 K in the experimental $T_{1\rho}$ and T_{2m} may be due to exchange processes[31] between protons in traps and normal interstitial sites. But the absence of detailed information on the nature and distribution of these traps makes quantitative estimates of their effect difficult.

The high-temperature activation energy of 0.22 eV obtained from T_{1d} [Fig. 5(a)] agrees closely with values found by others for β-PdH_x using T_{1d}.[15,17,29,30] The value of 0.086 eV observed below about 230 K is also consistent with earlier findings,[17,29,30] and with the general conclusion that the low-temperature side of the T_{1d} (and $T_{1\rho}$) minimum yields τ_c values which are inconsistent with the high-temperature side.[14,15] This apparent breakdown of the BPP model may be a result of short-range motion of the spins becoming important as the temperature is lowered. Such motion may be influenced by tunneling and therefore not well described by the present BPP model.[25]

BPP analysis of our $T_{1\rho}$ data yields $E_a = 0.17$ eV from about 250 K to 150 K [Fig. 5(b)], compared to the value 0.225 eV obtained by Arons *et al.*[15] for β-PdH_x between 300 K and 170 K using a similar analysis. The discrepancy in our values of E_a and τ_c, compared with our high-temperature T_{1d} analysis, and with the $T_{1\rho}$ analysis of Arons *et al.*, is likely associated with the presence of lattice damage referred to earlier. Below about 150 K (the low-temperature side of the $T_{1\rho}$ minimum), our BPP analysis of $T_{1\rho}$ results in non-Arrhenius behavior.

Figure 3 shows the temperature dependence of the relaxation times obtained at 45.7 MHz for the residual tritium in one of the tritide-free samples. Although the T_{1d} minimum is evident, the scatter in the data precludes a BPP analysis for τ_c. An estimate of E_a in this case was obtained using the fact that, in virtually all formulations of relaxation-rate theory involving a jump time τ_d, the magnitude of the slope of the plot of $\ln T_{1d}$ versus $\ln(1/T)$ far from the minimum is just E_a. A similar result holds for T_{2m} (and $T_{1\rho}$). Because of scatter on the high-temperature side, the low-temperature side of the T_{1d} data was used, yielding $E_a = 0.073$ eV. The high-temperature side of the T_{2m} data gives 0.082 eV. Also shown is the estimate 0.060 eV from the spin-spin relaxation time T_2'.

A diffusion activation energy lying between 0.06 and 0.08 eV for the residual tritium is much less than the value 0.248 eV for protons in α-PdH_x (very close to the value found in β-PdH_x), determined from an analysis of permeation and internal-friction data.[32] This is an indication that the distribution of the tritium cannot be described simply as a dilute solid solution among octahedral sites in the Pd lattice. Furthermore, numerous studies[12,13,16,18,32] of the macroscopic diffusion coefficients in PdH_x have indicated that E_a is nearly constant (i.e., 0.21 eV $< E_a <$ 0.25 eV) in both the α and β phases, which corresponds to a range of hydrogen concentrations up to $x = 0.75$, and that the coefficients scale by a simple site blocking factor $1-x$. This latter observation implies that, in this concentration range, there is little correlation between successive diffusion jumps. Consequently, the low triton activation energy found in $\mathrm{PdT}_{0.08}$ probably corresponds to short-range motion of the trapped tritium atoms.

V. CONCLUSIONS

The relative magnitudes [Eq. (3)] of the ^{3}He NMR relaxation times when tritium is removed from PdT_x after approximately eight years as a tritide, agree with those found in several other aged metal and alloy tritides, and are consistent with the ^{3}He being distributed in microbubbles in the Pd lattice. The increase in the T_1 values for ^{3}He upon addition of protium to one of the tritide-free samples, is attributed partially to a decrease in the Fermi-level density of states brought about by the addition of protium, and partially to the presence of other internal relaxation mechanisms.

Analysis of proton T_{1d} values for the jump correlation time τ_c in the sample containing protium, yields an activation energy E_a for diffusion, between 300 K and 230 K, in close agreement with similar analyses in nontritided

β-PdH$_x$. However, analysis of the proton $T_{1\rho}$ gives results inconsistent with this, which is likely to be a result of lattice damage associated with helium bubble formation.

The triton relaxation times in tritide-free PdT$_{0.08}$ indicate a value of E_a much less than that for protons in α-PdH$_x$. This suggests that the tritium is not distributed uniformly among octahedral sites. The low activation energy may be associated with short-range motion of trapped tritium, perhaps at internal surfaces surrounding the ^{3}He microbubbles.

ACKNOWLEDGMENTS

Thanks to R. H. Steinmayer for preparing the NMR samples and W. E. Tadlock for providing the aged material. This work was supported by the Chemical Sciences Division, Office of Basic Energy Science, U.S. Department of Energy, and by the DOE-Mound Research Participation Program. The Mound Facility is operated by Monsanto Research Corporation for the U.S. Department of Energy under Contract No. DEAC04-76-DP00053.

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