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Swelling of Aged PdTx During Hydride Phase Cycling

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Abstract

Metal tritides swell with age as a result of the in-growth of helium bubbles within the metal lattice. Nuclear magnetic resonance is used to observe an additional swelling of aged palladium tritide which occurs with hydride phase cycling ($\beta \rightarrow \alpha \rightarrow \beta$). It is shown that the spin-lattice relaxation characteristic of ^3He at room temperature provides good sensitivity to this small change. The observed swelling increase can be quantitatively explained by the lattice expansion which occurs with sample rehydriding.

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Swelling of Aged PdT_x During Hydride Phase Cycling

Introduction

Nuclear magnetic resonance (NMR) provides an accurate means of determining swelling of tritium-containing metals with age. The swelling is generated primarily by the additional volume occupied by ³He, the tritium decay product, within high-pressure bubbles. This volume, in turn, is given by the product of the quantity of helium retained and its average molar volume, V_m . Two independent NMR approaches have been developed to measure V_m and its dependence on age. Abell and Attalla [1] used NMR observation of the solid-liquid melting transition as reflected in the ³He T_1 spin lattice relaxation characteristics, which is sensitive to the ³He atomic motion. The fraction of helium in the fluid phase as a function of temperature is converted to a density distribution by use of the high pressure bulk helium melting curve. Abell and Cowgill [2] determined V_m from direct measurement of the ³He-³He spacing in the rigid solid phase at low temperature. This spacing is fundamentally related to the second moment of the NMR lineshape with no adjustable parameters. The two independent techniques were shown to give the same result for a 7.3 year old PdT_{.65} powder with a helium-to-metal concentration of He/M=.28. A plot of V_m for the helium within PdT_{.65}, extracted from the data in Reference 1-3, is shown in Figure 1. The open circles (o) are the average molar volumes as deduced from the distributions of melting transitions observed for each sample. The closed dots (•) are the same data at room temperature after correction for the differential thermal expansion occurring between RT and the average melting temperature. (Since the thermal contraction of high pressure liquid or solid He is much greater than Pd, pressures in the bubbles drops with decreasing temperature.)

The helium molar volume within the bubbles increases with age. The zero-age intercept, $V_m=4.7 \text{ cm}^3$, reflects the cohesive strength of the metal lattice. It corresponds to a zero size bubble "pressure" of about 12 GPa or a solid helium melting temperature of 295K. This intercept may be compared with the value $V_m=4.3 \text{ cm}^3$ for small bubbles, deduced from precise strain-gauge measurements by Schober [4] of the volume expansion of TaT_{0.74} over the first few months of aging.

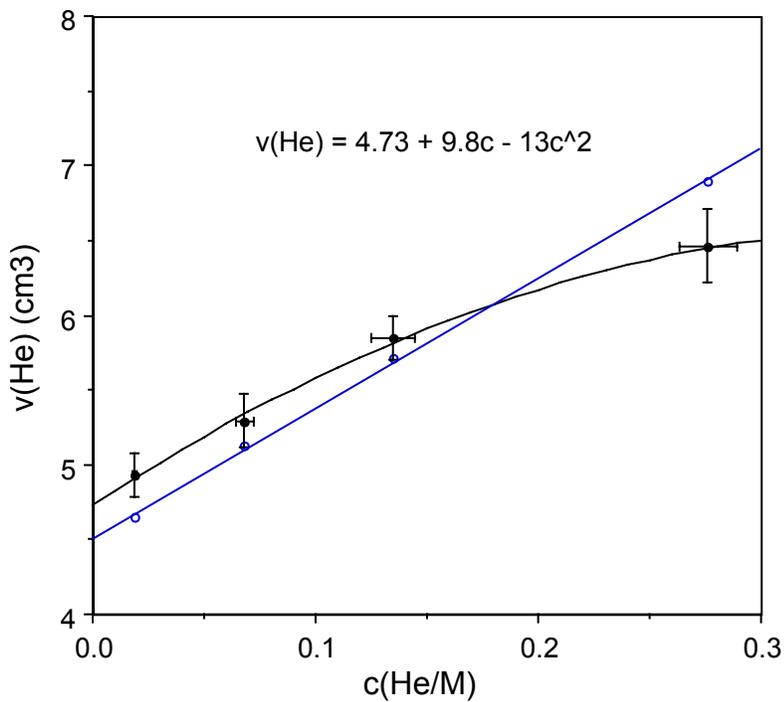


Figure 1. Molar volume of ^3He in small bubbles within aging palladium tritide as a function of He concentration, He/Pd. Open circles (o) were deduced from NMR measurements of References 1-3. Closed circles (•) are the same data corrected for differential thermal expansion.

The helium-produced swelling is given by $\delta V/V = (\text{He}/M) V_m(\text{He}) / V_m(M)$, where $V_m(M)$ is the molar volume of the metal tritide, $V_m(\text{PdT}_6)=9.821 \text{ cm}^3$, here assumed constant. This swelling is plotted in Figure 2. The plot shows that swelling increases quadratically with He/M. This is in contrast to the early predictions of Wolfer [5] using loop-punching theory, shown by the straight line. Theoretical refinements [6] examined vacancy pipe dislocation diffusion as an additional bubble growth mechanism. More recent work shows that this swelling is explained by dislocation loop punching if the bubble pressure has a $1/R$ dependence throughout the range of bubble radii R [7].

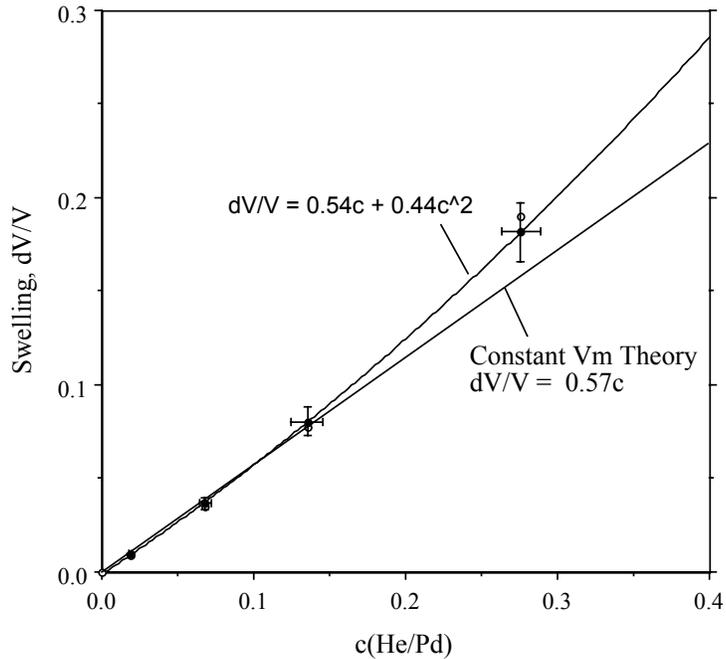


Figure 2. Helium-produced swelling of aging palladium tritide at room temperature calculated using the data from Figure 1. The (\bullet) data are corrected for differential thermal expansion between room temperature and the measurement temperature.

The present paper reports on efforts aimed at determining if sample preparation, specifically hydride phase cycling ($\beta \rightarrow \alpha \rightarrow \beta$) affects the characteristics of the retained helium and thus has potential for affecting these swelling measurements. The hypothesis is that with dehydriding, lattice shrinkage around the effectively incompressible bubbles produces a non-reversible increase in the number of metal atoms on their surface; e.g. punches out additional dislocation loops. Rehydriding should then re-expand the lattice, producing larger bubbles and a concomitant increase in V_m . Under a rigid expansion model, the maximum increase in V_m is expected to be about 11%, the expansion of the metal lattice with hydriding. The measurement of such a small change in V_m using either of the two NMR techniques described above would require considerable signal averaging to obtain data of the required precision. Instead, it is proposed that this change can be deduced from a change in T_1 at room temperature. It is shown below that although this analysis does not produce a determination of the magnitude of V_m , it can provide a sensitive, quantitative measure of its change.

Experimental

To investigate this hypothesis, the NMR T_1 relaxation characteristic of ^3He in aged palladium tritide was observed for two samples of different hydride phase history. The samples were prepared from a single batch of $\text{PdT}_{.65}$ compacted powder, aged 40 months, then D-exchanged at room temperature. The helium concentration in this material is calculated to be $\text{He}/\text{Pd}=.12$, assuming no He loss during aging. One sample was maintained in the beta hydride phase during preparation using a hydrogen-filled glove box. The glove box atmosphere should rapidly H-exchange this powder leaving $\text{T}/\text{H}<0.1\text{ppm}$. A second sample was allowed to de-tritide, prepared in air, then rehydrided with H. Both samples were prepared by chipping or grinding particles from a single sample of compacted powder and mixing with equal volumes of vacuum-dried alumina to reduce inter-particle contact and improve RF penetration. The sample prepared in the hydride phase, designated PC6H, tended to segregate after mixing with the alumina, leaving a salt-&-pepper appearance. Particles from the dehydrided compact mixed uniformly with the alumina, resulting in an overall grey appearance. This sample, designated PC6R, was evacuated at room temperature and rehydrided to the beta phase as indicated by hydrogen uptake. The two samples were then chilled with LN_2 to reduce the hydrogen overpressure and flame-sealed in 7 mm glass tubes. In the NMR probe, sample PC6R produced greater RF coil loading, indicative of higher interparticle electrical contact.

The ^3He NMR signal was observed at 142 MHz using a high-power, pulsed NMR spectrometer with a homemade low temperature probe. A single, narrow resonance line was found for each sample at room temperature, indicating minimal magnetic susceptibility broadening. Since the susceptibility of PdH_x is significantly greater for the alpha and mixed $\alpha+\beta$ phases, these narrow lines signify that both samples were exclusively in the beta-hydride phase. The signal-to-noise ratio for PC6R was about 10:1, roughly one-half that of PC6H

due to probe loading. T_1 decay characteristics for both samples were determined using saturation-recovery techniques with echo formation and 4x signal averaging.

Results and Discussion

The T_1 relaxation for each sample was measured at room temperature and computer-fit to a multi-component exponential decay. A normalized plot of the decays is shown in Figure 3. The data from sample PC6R fits a single component relaxation with a time constant of 8.6 ± 3 s; whereas, sample PC6H requires a 2-component decay with $82 \pm 5\%$ of the helium decaying with 7.1 ± 4 s and $18 \pm 3\%$ with 1.2 ± 3 s. These error bars represent one standard deviation in the fits, where data point weighting was taken proportional to the signal amplitude. In previous studies of the ^3He T_1 in aged tritides, Abell [1] found that a 2-component relaxation can result from coexisting states of solid and liquid helium, where the state ratio varies with temperature. To determine if solid state helium exists in PC6H at room temperature, its T_1 relaxation was also measured at 220 K. These data are plotted in Figure 4 along with three computed multi-component decays. If the faster-relaxing component results from solid state helium, as found in Abell's studies, then at this lower temperature a significantly larger fraction of this component should be found. The best fit to the lower temperature data shows that both components relax somewhat faster (4.5 s and 1.0 s) but remain in the same ratio. This means that for this sample all helium is in the same state. From the discussions below it is concluded that this is the liquid state and that the shortening of the two components results from a similar decrease in motion for all helium atoms. Thus it is concluded that here the 2-component decay must result from the presence of two different helium environments.

The significance of the differing decay times can be understood by considering the interaction producing the T_1 relaxation. From previous studies [1,2] of the temperature

dependence of T_1 , it is clear that at room temperature the liquid state is described by the weak

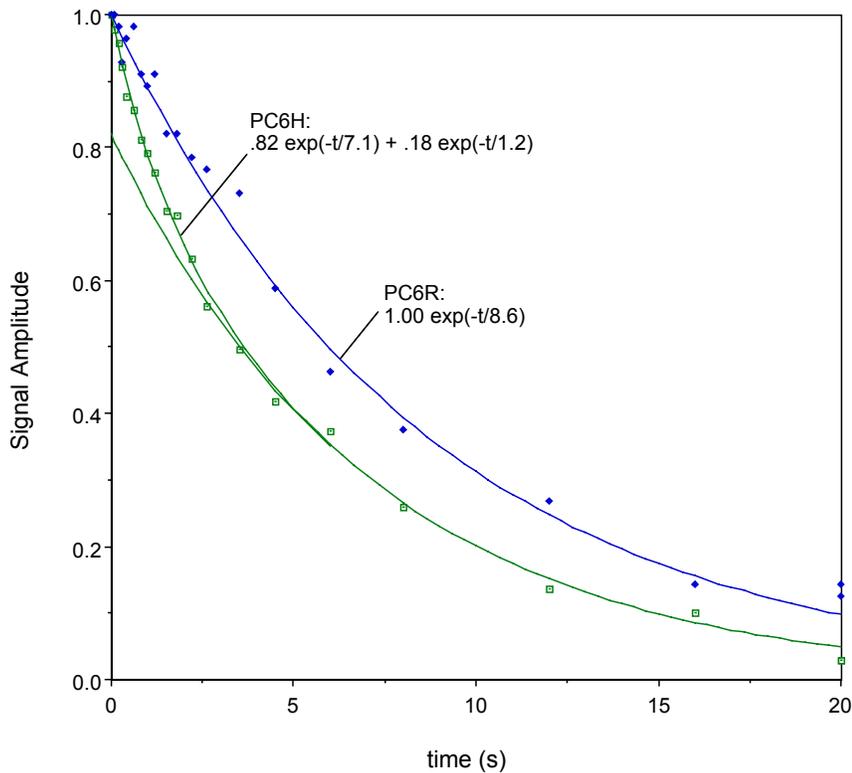


Figure 3. T_1 relaxation data for the two samples at 300 K. Sample PC6H requires two exponential components to fit the data. The dotted line shows the first term alone.

interaction regime, where atomic motion is rapid and many encounters are required to produce relaxation. In this limit, the relaxation rate is proportional to the strength of the magnetic perturbation during the ^3He motion and its fluctuation frequency. The strongest available perturbation is the interaction with H atoms on the bubble interface. These H are the deep-trapped fraction, present at even low hydride stoichiometry. The frequency of interaction with the interface depends on the ratio of bubble surface-to-volume sites in the dense fluid and the helium mobility. Thus, within a given bubble at constant temperature, all variation in T_1 is due to changes in V_m . The strength of the interaction decreases with increasing V_m (increasing ^3He -H spacing) and the fluctuation frequency increases as the mobility increases.

In this weak limit, however, the fluctuations are already too rapid for efficient relaxation; thus both changes decrease the relaxation rate and increase the T_1 decay time.

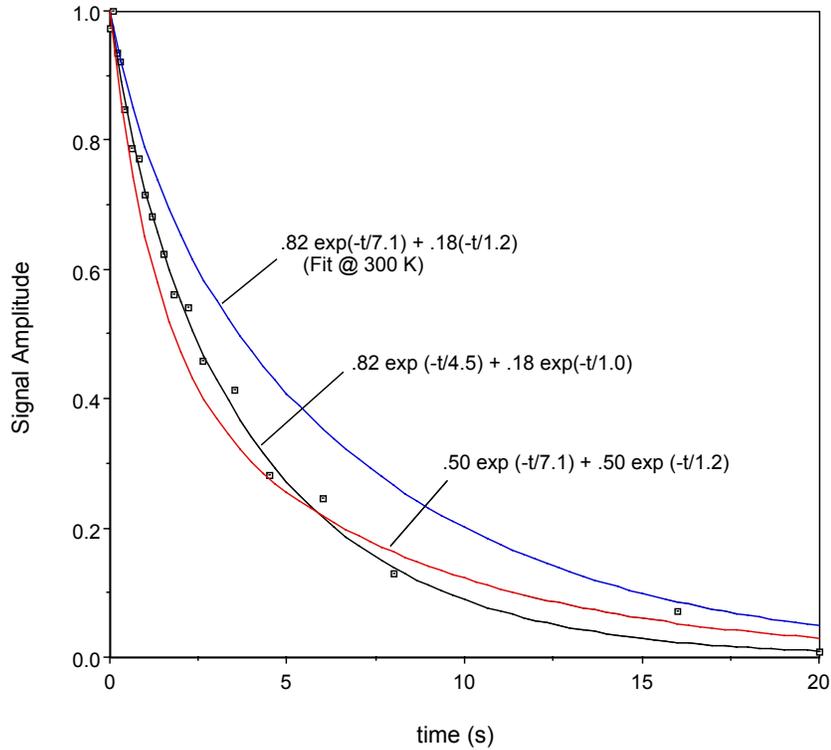


Figure 4. T_1 relaxation data for PC6H at 220 K. The best-fit is generated by using the same component ratio that was found at 300 K.

An empirical relation between a change in T_1 and a change in V_m can be obtained from Bowman's [8] T_1 measurements on 7-8 year old material. He measured T_1 versus temperature for three samples with different H/Pd, all rehydrated from the same batch of aged material. (In terms of the ^3He T_1 relaxation, tritium and hydrogen produce very similar effects and thus the isotope change is of no significance.) The temperature dependence of his data shows the relaxation to be in the weak limit as described above. The room temperature T_1 values for this material are plotted as a function of hydride stoichiometry, $x=\text{H/Pd}$ in Figure 5. Here, it is argued that the observed increase in T_1 with x results from an increase in the helium motion, which in turn results from the reduction in helium density as the metal lattice expands. Also plotted in the figure is the change in helium V_m with x , calculated assuming the helium bubble expansion is the same as the palladium lattice expansion with

hydriding. Values for the hydriding expansion were taken from x-ray measurements [9] and the V_m line is normalized to agree with the previously determined molar volume shown in Figure 1. Since only a small change in V_m occurs with hydriding, both these sets of data may be fit with linear approximations. Normalizing these changes using their absolute values, allows scaling this calibration from the older material to PC6 where slightly different ranges of V_m and T_1 values exist, but where the same relaxation mechanism holds. At $x \approx 0.65$, the linear fits in Figure 5 produce the expression

$$(\delta V_m / \delta x) / V_m \approx 0.1167 (\delta T_1 / \delta x) / T_1, \quad (1)$$

valid for hydrided or tritided (but not deuterided) palladium at room temperature.

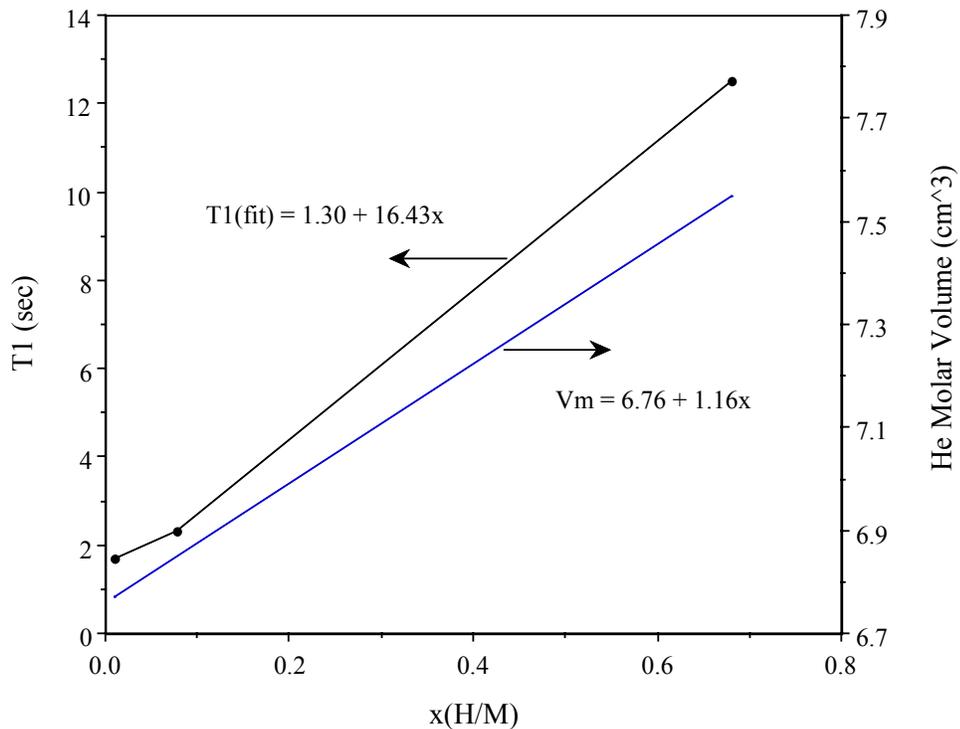


Figure 5. Calibration curves relating a change in T_1 to a change in molar volume used to generate Eq. (1). The T_1 data are from Reference 8. The molar volume change is assumed to follow the lattice expansion results from Reference 9.

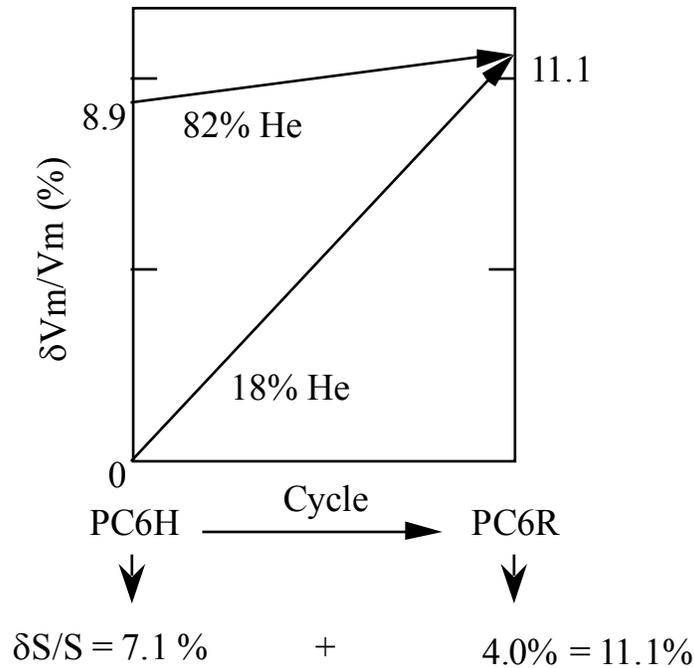


Figure 6. Diagram summarizing the effect of the hydride cycle on the helium bubbles in PC6. The split distribution of molar volumes is transformed into a simple distribution with an increased average value and a concomitant increase in swelling, as described in the text.

The effect of the rehydride cycle on the aged PC6 material, determined using Eq. (1) is shown schematically in Figure 6. It appears that within the hydride sample PC6H, 82% of the helium has a molar volume which is 8.9% greater than the remaining 18%. Hydride cycling produces sample PC6R, which has all the helium with an average V_m of 11.1% greater than the more dense 18% within PC6H. That is, the hydride cycle expanded 82% of the helium by 2.2% and the remaining 18% by the full 11.1%. This is consistent with the idea that dehydrating compresses all helium to a single limit determined by the metal lattice, after which it all appears the same. Rehydrating then expands the helium to a single, larger average V_m , with a single, longer relaxation time. In terms of swelling, this picture implies that the initial hydride sample PC6H has an average swelling which is 7.1% higher than would be expected if all the helium was present at the higher V_m value. To this initial state, the hydride cycle produces an additional swelling of 4.0%, with 2.2% coming from the initially-compact 18% He and 1.8% coming from the initially-expanded 82% He. This

amounts to a total apparent swelling increase of 11.1%. This value indicates that the effect of the hydride cycle is just the rehydriding expansion as hypothesized. It is reminded the calibration from the older sample currently assumes the bubble expansion rigidly follows that of the lattice with no allowance for the lattice relaxation that may result from the changing helium pressure within the bubbles. If such relaxation occurs, it will reduce the swelling increase. However, such a correction will affect both processes the same, maintaining the agreement .

Although the cause of the bimodal distribution for the uncycled sample PC6H remains unknown, several possibilities were investigated. First, during aging the PC6 material was stored with sufficient tritium overpressure to resupply decaying tritium for only half its life. During the remaining aging, the sample is expected to phase-segregate and only bubbles within the shrinking tritium-rich, β -phase region will continue to grow. This would result in bubbles with a continuous distribution of effective ages; whereas, a bimodal distribution of V_m is observed. Additionally, the overall helium reduction due to such aging is calculated to be only about 4%, much too small to produce the observed difference in T_1 . Second, temperature or stress transients occurring during sample grinding operations in the glove box may have resulted in partial phase-cycling of the sample. The observed relaxation times are very close to what one would expect if 82% of the PC6H sample had inadvertently experienced the $\beta \rightarrow \alpha \rightarrow \beta$ phase cycle. Third, the longer time constant could result from a large quantity of deuterium remaining in the sample on the bubble interfaces, reducing the magnetic interaction. A dilution calculation shows that after several hours of H_2 exposure in the glove box, the sample should possess <1 ppm D/H, unless the isotope exchange is inhibited by surface contamination or deep-trapping. The rapid rehydriding of PC6R indicates no such contamination. If produced by deep-trapped D, this would mean that exchange for these traps at 300 K is much slower than for the bulk hydride sites. Finally, such a bimodal distribution may be intrinsic to the sample, e.g., as a consequence of the

presence of both defect and self-trapping of ^3He , or of two competing bubble growth mechanisms.

Conclusions

There is an apparent increase in swelling of aged palladium tritide with hydride phase cycling ($\beta \rightarrow \alpha \rightarrow \beta$). The magnitude of this increase agrees with the simple idea of helium bubble expansion with lattice rehydriding. Although the room temperature T_1 analysis used to provide this test has not been proven to be quantitative, it clearly demonstrates that bubble expansion will be reflected in the T_1 relaxation. These observations have the following implications for swelling measurements made on samples allowed to dehydride after aging.

- 1) Measurements made in the β -phase will be erroneously high.
- 2) Measurements in the α -phase should give values appropriate for non-disturbed, β -phase samples. (NMR measurements in the α -phase can be used directly, but physical expansion measurements must be corrected for the $\beta \rightarrow \alpha$ dehydriding contraction.)

Although other NMR techniques have been found useful for determining the absolute swelling, they require considerable statistics for resolving small changes. The room-temperature T_1 analysis approach presented here appears highly sensitive to small changes in swelling. It should also be useful for characterizing changes to the bubble pressure or bubble-metal interface resulting from other effects. For example, these techniques should be useful for measuring relaxation of the lattice around bubbles occurring with a re-hydride expansion or for examining the small bubble growth resulting from a temperature rise transient.

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