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Low-temperature ^{3}He NMR studies in aged palladium tritide

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Experimental results from a NMR study of ^{3}He in nanometer-sized microbubbles in aged palladium tritide over the temperature range 4–300 K are presented. A determination of the rigid-lattice–line-shape second moment at 4 K provides a value for the density of ^{3}He that is in good agreement with the value inferred for the same sample from an analysis of ^{3}He spin-lattice relaxation data over the range 50–300 K. This latter analysis is based on the hypothesis of a melting transition for a distribution of densities, and assumes that the bulk helium equation of state applies to helium in the nanometer-sized bubbles. This latter assumption is supported by the agreement between the two independent density determinations. Line-shape analyses reveal narrowing of the ^{3}He spectrum at about 35 K, which agrees with a prediction of motional narrowing based on an extrapolation of ^{3}He diffusivity data determined over the range 100–250 K in an earlier study of aged palladium tritide. The observation of coexisting broad and narrow components in the free-induction decay at 40 K provides direct evidence for a distribution of ^{3}He densities in aged palladium tritide. Because the melting temperature and the rigid-lattice second moment are both strong functions of density, the NMR techniques described here provide a sensitive measure of the density distribution and related properties.

I. INTRODUCTION

This article summarizes nuclear magnetic resonance (NMR) experiments on ^{3}He in aged palladium tritide in the temperature range 4–300 K at the Sandia Tritium Research Laboratory. The aim of these experiments was to obtain a reasonably direct measure of the helium density in the aged material. While the study is primarily motivated by fundamental considerations, it is also driven by the fact that knowledge of density as a function of age allows a prediction of swelling, which is an important parameter in the design of systems (e.g., compressors and separation columns) for tritium process applications using metal tritides. In a previous NMR study,[1] the helium density and pressure (6–11 GPa) were inferred from melting temperature information, which had been obtained from ^{3}He spin-lattice relaxation measurements in the temperature range 80–330 K. A problem with this determination is that it uses the equation of state (EOS) for bulk helium,[2] which may not be a good representation for helium trapped in the highly overpressurized 1–5 nm diameter microbubbles[3] embedded in the host matrix. Measurement of the ^{3}He NMR line shape at sufficiently low temperature provides a direct and reasonably accurate measure of the density (and thus of the swelling), and therefore should give an indication as to the applicability of the bulk EOS to helium in palladium tritide.

The NMR study of ^{3}He in palladium tritide presents certain complications, both in the experiment and in the analysis, which can be ameliorated by the relatively simple process (in Pd) of hydrogen isotopic exchange. NMR studies of ^{3}He in bulk reveal that relaxation is often dominated by interactions at the container walls.[4] Because the ^{3}He in palladium tritide is trapped in nm-scale bubbles,[3] it has a very large surface-to-volume ratio; as many as 20% of the ^{3}He atoms are surface atoms. The potentially complicated set of magnetic interactions in the ternary PdT$_x$He$_y$ system can be simplified by exchanging tritium (T) by deuterium (D) after a sufficient aging period. This latter step serves a dual purpose: (i) it stops the tritium decay clock; and (ii) it replaces a nucleus having the largest magnetic dipole with one having a very weak dipole (the ratio of the relative sensitivity of ^{3}H to that of ^{2}H is 125 versus a ratio of 2.7 for ^{3}H to ^{3}He). Thus, since the palladium nucleus is magnetically unimportant, exchange of D for T should minimize complications due to coupling between unlike spins. (The conduction electrons in palladium or palladium hydride can also influence ^{3}He relaxation at the bubble surface; isotope exchange should not affect this.) An equally important benefit of the exchange is the reduced radiological hazard associated with sample handling.

In this article, we present experimental NMR results which support the idea that the behavior of ^{3}He in palladium tritide is essentially bulklike. At the lowest temperatures, the free induction decay (FID) is consistent with a solid array of spin-$\frac{1}{2}$ nuclei in the rigid-lattice limit, revealing the characteristic beat pattern.[5] Analysis of the FID is complicated by magnetic susceptibility broadening, but a correction allows a determination of the rigid-lattice second moment,[6] from which a value for the mean squared density can be obtained. The resulting density is consistent with a value obtained from the range of melting temperatures deduced from T_1 data at higher temperatures using the bulk helium EOS. In the earlier study,[1] it was assumed that ^{3}He spins relax via modulation of the ^{3}He-^{3}He dipolar interactions by self-diffusion. Dramatic evidence in support of this assumption is provided by the observation of line narrowing in the temperature range predicted by extrapolation of diffusion correlation times obtained via Bloembergen-Purcell-Pound (BPP) analysis of T_1 data from the earlier study. The observation of coexisting broad and narrow components in the free-induction decay within that temperature range provides direct evidence for a distribution of ^{3}He densities in aged palladium tritide.

II. EXPERIMENTAL

The material used in this study was from a sample matrix of a previous NMR study.[7] Briefly, aged palladium tritide (T/Pd was maintained near 0.65 atomic ratio for about 8 yr) was evacuated to 10 mTorr at room-temperature, giving palladium with a residual tritium content of $T/Pd \simeq 0.1$. Evacuation from the tritide phase results in an $\sim 10\%$ volume contraction, and releases a small fraction ($< 5\%$) of the ^{3}He. A portion of this material was sieved to give a particle size range of 40–150 μm, and was then mixed with a nearly equal volume of Al_2O_3 powder of comparable particle size. After about 2 yr in a sealed NMR glass tube, the material was removed to a 5-liter stainless-steel container and exposed to successive batches of about 35-Torr D_2 at ambient temperature, until mass spectroscopic analysis (which indicated essentially no release of ^{3}He) showed nearly complete removal of tritium. (The absence of a triton NMR signal confirms that most of the tritium was removed by exchange with the deuterium overgas.) The material, which will be referred to in the following as 8-yr-old PdT_x, was then sealed off in a 7-mm-o.d. evacuated glass tube for the NMR experiments. Presumably, evacuation of the glass tube left the sample in the α phase with a D/Pd atomic ratio of about 0.1. From the earlier study,[7] the ^{3}He concentration is known to be $\simeq 0.3$ (He/Pd atomic ratio).

A pulsed NMR spectrometer used for most of the experiments described here, was designed for tritium resonance at 200 MHz, and thus has a Larmor frequency ($\omega_0/2\pi$) of 142.8 MHz for ^{3}He. It was constructed using commercially available rf gates, phase shifters, filters, mixers, etc., along with a fast-recovery, low-noise receiver.[8] A 125-mm-diameter superconducting magnet provided room-temperature access for a liquid helium Dewar containing a high-Q, series-resonant probe assembly. Pulse sequences were generated using a Nicolet 493B programmable pulser. Phase-sensitive signals were digitized with a dual channel Nicolet Explorer IIIA 20-MHz oscilloscope and quadrature-analyzed with a Nicolet 1180 computer. 90° RF pulse lengths were about 7 μsec using a 100-W linear amplifier. The dead time of the receiver was several μsec. Tests revealed little rf inhomogeneity over the sample in spite of a calculated rf skin depth of 18 μm for Pd metal at 140 MHz, which is considerably smaller than the particle-size range described above. Apparently helium deposition into the lattice from tritium decay has significantly decreased the electrical conductivity of the aged material.

Sample temperatures between 4 and 300 K were obtained by passing helium vapor over the sample and rf coil. A heater at the vapor outlet and a Si-diode sensor on the probehead provided temperature control with 0.5-K stability over most of this range. The sample temperature was measured with a calibrated carbon-glass resistance thermometer adjacent to the sample. It is estimated to have a total uncertainty of 2% after allowing sufficient stabilization time.

T_1 measurements were done using both inversion-recovery and saturation-recovery pulse sequences. Occasionally Hahn echos and solid echos were employed to increase the sensitivity for rapidly decaying FID signals. The low-temperature line was observed using the Fourier-transformed solid-echo technique. Spectral hole-burning experiments were done by adding long, suitably attenuated rf prepulses.

III. RESULTS

^{3}He spin-lattice relaxation times (T_1) were measured in the temperature range 7–140 K and at 300 K. Cycling the 8-yr-old PdT_x between 300 and 4 K several times did not affect the 300-K T_1 data. At 300 K and for $T < 43$ K, T_1 appears to be exponential, suggesting that all the helium is in a single phase at these temperatures. However, in the range $43 < T < 140$ K, T_1 is clearly nonexponential suggesting coexistence of solid and fluid phases similar to what has been observed in $PdT_{0.6}$ aged up to 2 yr.[1,9] Analysis of T_1 in terms of an exponential term for the fluid phase and another one for the solid phase provides a determination of the relative amounts of the two phases, and gives values of T_1 for each phase.[9] The physical basis for this analysis is that there is a distribution of helium densities, and thus of melting temperatures, over the ensemble of bubbles. The presumption is that at a given temperature, the range of T_1 values for the set of bubbles containing solid helium is small compared to the difference between the ensemble-averaged solid and fluid T_1's at that temperature. Because of the limited range of recovery times in the T_1 experiments, the analysis is not very reliable when the T_1's for the two phases are comparable. Figures 1 and 2 show the results of this analysis for the 8-yr-old PdT_x. Figure 1 gives T_1 for the fluid and solid phases over the range 40–300 K. The temperature dependence of T_1 in the fluid phase indicates that relaxation in this latter phase is an activated process. Whether a bulk helium mechanism (e.g., diffusional modulation of the dipolar interaction) is dominant in the fluid phase, or whether relaxation occurs primarily at the helium/palladium interface (possibly via a conduction electron mechanism[10]), cannot be ascertained from the present results. Relaxation in the solid phase is qualitatively similar to that observed[1,9] for ^{3}He in $PdT_{0.6}$, with a shallow minimum near 100 K. Figure 2 shows the fraction of helium in the fluid phase as a function of temperature, based on T_1 measurements at 142.8 MHz as well as earlier measurements[7] at 45.7 MHz on the same material.

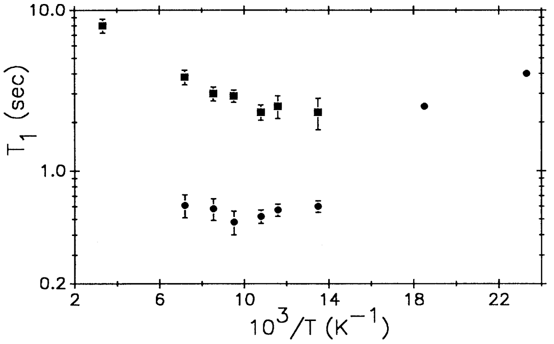

FIG. 1. Temperature dependence of spin-lattice relaxation parameter (T_1) for 8-yr-old PdT_x. Filled squares are for the fluid phase. Filled circles are for the solid phase. The error bars are estimates.

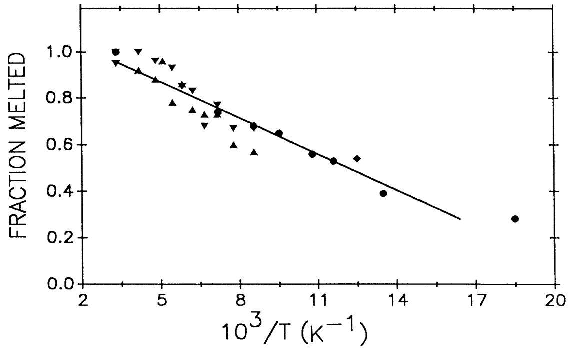

FIG. 2. Fluid phase fraction as a function of temperature from analysis of T_1 data assuming independent exponential relaxation for the two phases. Filled circles are from the present study ($\omega_0/2\pi = 142.8$ MHz), and the remaining symbols refer to analysis of T_1 data taken at 45.7 MHz on different 8-yr-old PdT_x samples (Ref. 7). The solid line is a linear fit to the data.

This figure reveals a wider coexistence range than had been observed for ^3He in the 2-yr-old $PdT_{0.6}$ material.[9] Using the EOS for bulk helium, the density distribution function, $G(\rho)$, can be obtained[9] from the data shown in Fig. 2. Figure 3 compares the resulting distribution function with that which had been earlier determined for the 2-yr-old material.[9] Knowledge of $G(\rho)$ allows calculation of various quantities of interest, such as the mean density $\langle \rho \rangle$. In particular, it allows a determination of swelling, which is just the product of helium concentration with $\langle 1/\rho \rangle$.

Table I summarizes the major results inferred from ^3He T_1 measurements in aged palladium materials. The 8-yr-old material reveals a significantly lower mean density than the 2-yr-old material; however, the two materials were treated differently, in that the older sample was detritided prior to NMR analysis while the younger sample was not. Due to the relatively large lattice contraction ($\simeq 12\%$ by volume) upon hydrogen removal,[11] the ensemble of bubbles is subjected to a substantial perturbation by this process, which could influence the results. Thus the large decrease in ^3He density could be either a consequence of this perturbation, or a systematic aging effect. From BPP theory,[12] the quantity in the last column ideally should be independent of $\langle \rho \rangle$ and of the Larmor frequency (ω_0) if the same solid phase bulk mechanism is operative for the two materials. Existence of a distribution is expected to cause some deviation from this relationship; nonetheless the agreement of this quantity between the two samples is strong evidence for a common bulk relaxation mechanism.

The obvious candidate for such a mechanism is relaxation via modulation of the helium-helium dipolar interaction due to helium diffusion in the solid precipitate. This mechanism was proposed in the earlier study,[1] with significant support provided by a comparison of the diffusion activation energy (W) for ^3He in $PdT_{0.6}$ (obtained from the BPP analysis) with activation energies obtained from NMR studies of bulk ^3He at much lower densities. Based on that comparison, one can obtain a dependence of W on density, and thus an estimate of $\langle W \rangle$ [we use $\langle W \rangle \simeq W(\langle \rho \rangle)$] for the 8-yr-old palladium material. This procedure gives $\langle W \rangle / k = 270$ K (k is Boltzmann's constant), which can be compared to $\langle W \rangle / k = 370$ K determined[1] for ^3He in 1-yr-old $PdT_{0.6}$. The solid phase T_1 data shown in Fig. 1 is consistent with $200 < \langle W \rangle / k < 300$ K. If we assume that the preexponential factor is independent of density, then the BPP correlation time (τ_c) obtained in the earlier study[1] can be scaled by the appropriate value of $W(\rho)$, using $\tau_c \propto \exp(W/kT)$, to provide an estimate of $\tau_c(\rho)$ as a function of temperature for helium of a given density in the 8-yr-old material.

An important consequence of diffusive motion is that at sufficiently high temperature, the NMR linewidth is relatively narrow due to motional averaging of the dipolar interaction (referred to as "motional narrowing").[14,16] At low enough temperatures, the motion is too slow to average the dipolar interaction and the linewidth [referred to in this limit as the "rigid lattice (RL) linewidth"] is considerably broader. A good example of motional narrowing is provided by NMR studies of hy-

TABLE I. Summary of NMR results for ^3He in aged PdT_x.

Sample	Age (yr)	$\langle \rho \rangle$ (mole/cm^3)	$\omega_0/2\pi$ (MHz)	$(T_1)_{min}$ (sec)	$(T_1)_{min}\langle \rho \rangle^2/\omega_0$
$PdT_{0.6}$	2	0.20	25	0.050	8.0×10^{-5}
PdT_x	8	0.15	143	0.5	8×10^{-5}

drogen in metals,[10] where it is known that as the temperature increases beyond the rigid-lattice limit, the NMR line narrows abruptly. The condition for motional narrowing[10] is that the time between diffusive hops ($\tau_d = 2\tau_c$) must be less than the inverse of the rigid-lattice linewidth (ω_{RL}), *viz*,

$$\tau_d < (2\omega_{\mathrm{RL}})^{-1} . \qquad (1)$$

The quantity ω_{RL} in Eq. (1) is essentially determined by ρ. Therefore, because $\tau_d \propto \exp(W/kT)$, Eq. (1) allows a prediction of the narrowing temperature (T_n) for a given value of ρ. Note that T_n depends linearly on W but only logarithmically on the preexponential factor, so that the uncertainty in the latter quantity is relatively unimportant for the determination of T_n. Using the range of densities observed for the 8-yr-old material (Fig. 3) and the procedure described above to obtain $\tau_c(\rho)$, line narrowing is predicted to occur in the range 22–40 K. Figure 4 shows the measured linewidth as a function of temperature. Abrupt narrowing is observed to occur in the range 30–45 K, in good agreement with the prediction.

Figure 5 shows the FID observed at 41 K and reveals coexisting rapidly and slowly decaying ^{3}He spins. The 300-K FID is shown for comparison. This result is consistent with an ensemble of bubbles characterized by a range of densities and thus, from Eq. (1) and the discussion below Eq. (1), a range for T_n. Presumably, this type of data can provide additional information characterizing the ensemble. Figure 6 shows the rigid-lattice solid-echo FID (taken at 4 K), which exhibits a beat pattern characteristic of a solid array of spin-$\frac{1}{2}$ nuclei,[5] in spite of the nearly 40% spread in ^{3}He density (see Fig. 3). A simulation of the effect of a range of densities, based on an analytic representation[13] of the dipolar FID and using the fact that the second moment (S_2) scales with ρ^2, is consistent with the observed beat pattern shown in Fig. 6.

Figure 7 shows the results of hole-burning experiments[14] at 300 and 4.2 K. These experiments demonstrate that the broadening at 4 K is primarily homogeneous (consistent with dipolar broadening), however, the asymmetry introduced by the hole-burning prepulse indicates an inhomogeneous contribution as well. At 300 K, where dipolar broadening is negligible because of motional narrowing, the linewidth ($\Delta\nu$) is about 5 kHz and is probably determined by magnetic susceptibility effects in the powdered sample.[15] The susceptibility should be approximately that of palladium metal, which is fairly substantial. The temperature dependence of the palladium susceptibility has been determined[16] down to about 4 K, and shows a maximum at about 70 K with a slight falloff at lower temperatures. Thus, in order to obtain the dipolar contribution to the rigid-lattice FID shown in Fig. 6, a correction has been made based on the observed FID at 95 K, where dipolar broadening is unimportant due to the motional narrowing. The 95 K FID falls off as

$$F_s(t) = 1 - 0.0086t \qquad (2)$$

(t is in μsec) out to about 35 μsec. The subscript in Eq. (2) signifies that the FID is determined by susceptibility broadening. In Eq. (2) and in what follows, $F(t)$ (with or without a subscript) signifies the normalized FID; *viz*, $F(t) = \mathrm{FID}(t)/\mathrm{FID}(0)$. The rigid lattice FID of Fig. (6) can be written as

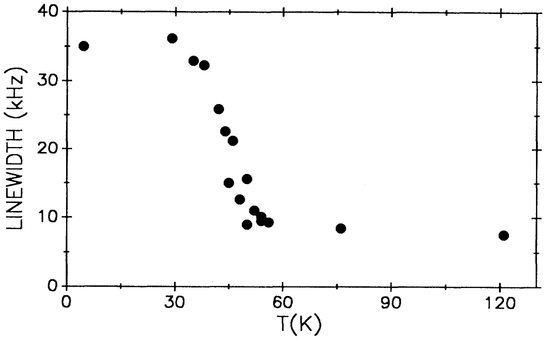

FIG. 4. Spectral linewidth of ^{3}He in 8-yr-old PdT$_x$ as a function of temperature ($\omega_0/2\pi = 142.8$ MHz).

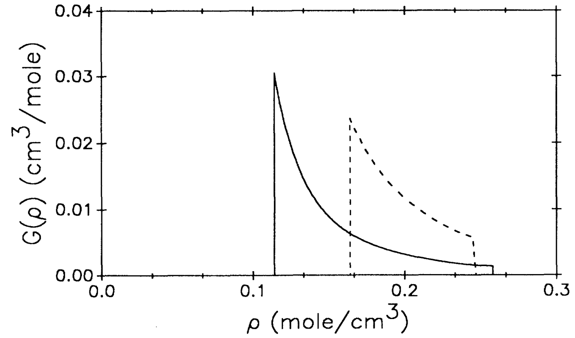

FIG. 3. The solid curve shows the density distribution for ^{3}He in 8-yr-old PdT$_x$ derived from the fit to the data shown in Fig. 2, using the bulk helium EOS. The dashed curve shows the density distribution obtained for 2-yr-old PdT$_x$ (Ref. 9).

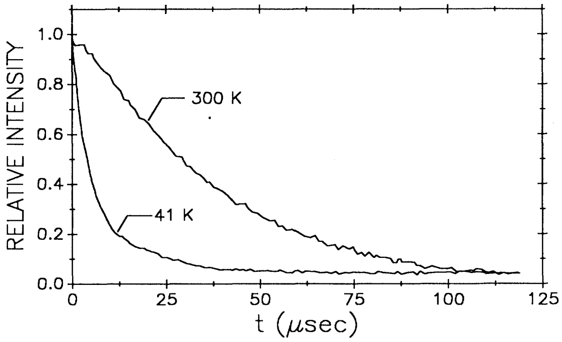

FIG. 5. ^{3}He FID at 300 and 41 K in 8-yr-old PdT$_x$ ($\omega_0/2\pi = 142.8$ MHz). The 41 K FID is consistent with coexisting rigid-lattice (the rapidly decaying component) and motionally narrowed (the slowly decaying component) ^{3}He spins.

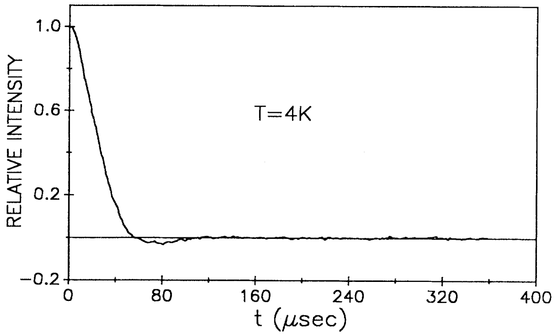

FIG. 6. Solid-echo FID for ^{3}He in 8-yr-old PdT$_x$ at 4 K ($\omega_0/2\pi = 142.8$ MHz). The solid line represents the base line for the acquisition.

$$F(t)=F_s(t)F_d(t)\ , \tag{3}$$

where F_s and F_d are, respectively, the susceptibility and dipolar contributions to F. The observed line shape, obtained by Fourier transformation[13] of the FID, is a convolution of the susceptibility and dipolar line shapes. Equation (3), together with Eq. (2) allows a determination of the rigid-lattice dipolar term $F_d(t)$ for small values of t.

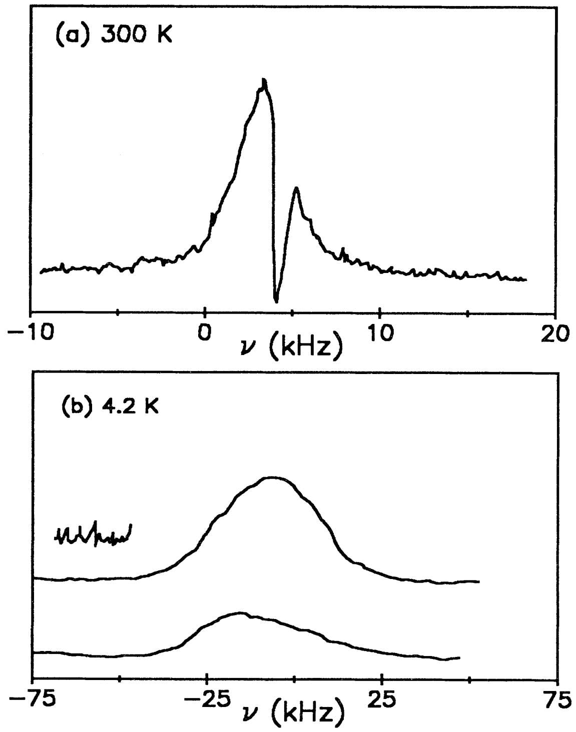

FIG. 7. Effect of hole burning on (a) 300-K line shape, and (b) 4.2-K line shape in 8-yr-old PdT$_x$. The zero on the frequency scale corresponds to $\simeq 143$ MHz. The bottom trace in (b) is with the hole-burning prepulse, while the trace immediately above it is with no prepulse. Since the spectra in (b) have been smoothed, the partial trace between −75 and −25 kHz is shown to indicate signal-to-noise ratio.

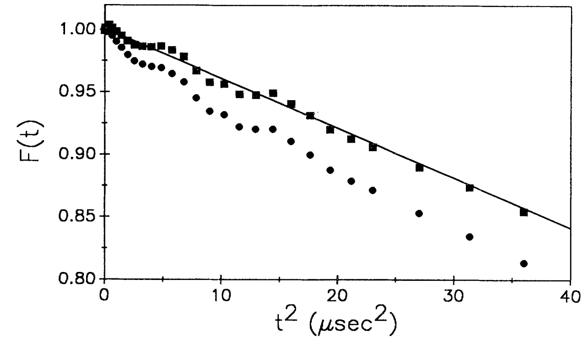

FIG. 8. ^{3}He solid-echo FID at 4 K in 8-yr-old PdT$_x$, shown as a function of t^2 for small values of t. Filled circles represent the uncorrected FID and filled squares represent the FID corrected for susceptibility broadening. The solid line is a least-squares fit ($t < 7$ μsec) to the corrected FID.

Figure 8 shows the corrected and uncorrected FID, plotted versus t^2 out to about 7 μsec. For sufficiently short solid-echo delay, twice the slope of the dipolar FID near the time origin in such a plot gives the second moment (S_2) of the NMR line shape.[14,16] However, if the echo delay is not short enough, spin-diffusion effects become important and must be accounted for. The phases of exchanging spins (spin diffusion occurs by exchange between neighboring spins) are randomized and their contribution to the solid echo is lost. This part decays as $\exp[-(2\tau_e/T_{2\mathrm{SD}})^2]$, where $2\tau_e$ is the echo delay and $T_{2\mathrm{SD}}$ is the spin-diffusion time constant. Figure 9 is a plot of S_2 values, corrected for susceptibility broadening, as a function of $(2\tau_e)^2$. The second moment of the dipolar line shape in the absence of spin diffusion is then given by the $\tau_e = 0$ intercept in Fig. 9. This limiting value is simply related to the density; i.e., $S_2 = 544.5\rho^2$ for ^{3}He in an hcp lattice (S_2 has nearly the same relationship to ρ for a bcc lattice),[6] with S_2 in G^2 and ρ in mol/cm^3. For a

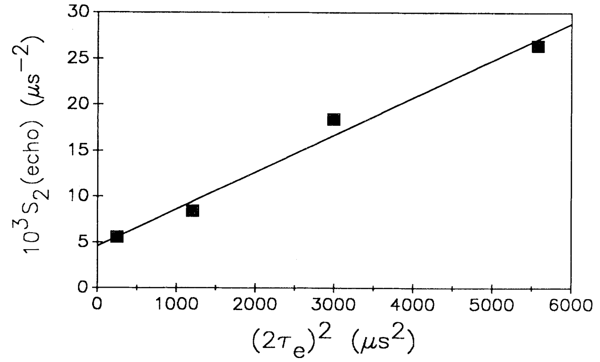

FIG. 9. Second moment as a function of the square of the echo delay. The intercept at zero delay gives the second moment in the absence of spin-diffusion effects.

distribution of densities, the rigid solid line shape can be approximated by a sum of Gaussians with linewidths in accord with the distribution. The FID corresponding to this distribution is the product of $\exp(-S_2t^2/2)$ terms, which for small t falls off as t^2 with a proportionality constant given by $\langle S_2\rangle/2$, where

$$\langle S_2\rangle = 544.5\langle\rho^2\rangle \tag{4}$$

is related to the root-mean-squared (rms) density. With this analysis, the data in Fig. 9 gives for the rms density $\sqrt{\langle\rho^2\rangle} = 0.14$ mole/cm^3. This result can be compared with a value of 0.15 mole/cm^3 obtained directly from the density distribution function shown in Fig. 3 using

$$\langle\rho^2\rangle = \int_0^\infty \rho^2 G(\rho)d\rho \; . \tag{5}$$

[Note that the value of $\sqrt{\langle\rho^2\rangle}$ obtained from Eq. (5) is approximately equal to the value of $\langle\rho\rangle$ given in Table I. This reflects the fact that $G(\rho)$ is reasonably narrow—see Fig. 3.] Considering the uncertainty in the second moment determination introduced by the susceptibility correction procedure, the two values for the rms density are in good agreement. The susceptibility correction could presumably be minimized by studying ^{3}He in the hydride phase (i.e., PdD$_{0.6}$) for which χ is greatly reduced relative to palladium metal.[17]

IV. DISCUSSION

The experimental results described above, together with the results reported earlier,[1,9] lend confidence to the hypothesis[1] that the strongly nonexponential spin-lattice relaxation observed over a range of temperatures for ^{3}He in aged palladium tritide materials is a consequence of coexisting solid and fluid helium precipitates described by a distribution of densities. This hypothesis is consistent with the observation that this nonexponential relaxation can be fitted by a sum of two distinct exponentials whose weights and characteristic time constants (i.e., T_1 values) evolve smoothly to values observed in temperature regions (both above and below the region of nonexponential relaxation) that show exponential relaxation, characteristic of a single phase.

The hypothesis is also supported by the result that the mean density inferred from the melting temperature information for 2-yr-old palladium tritide is in good agreement with theory[18] and with independent determinations[19] in the related TaT$_x$ and NbT$_x$ systems. Further substantiation is provided by the observation of a characteristic T_1 minimum in the low-temperature region.[1] Although the magnitude of this minimum is larger than the BPP prediction for a homogeneous system at the mean density, it is in fact consistent with a distribution of densities. The result that the magnitude of T_1 at the minimum scales with $\omega_0/\langle\rho\rangle^2$ (see Table I) in a comparison between two very different samples (2 vs 8 yr aging) provides evidence for a common bulk ^{3}He relaxation mechanism, *viz.* modulation of the ^{3}He-^{3}He dipolar interaction by ^{3}He self-diffusion. The earlier studies[1,9] revealed this scaling behavior in a comparison between T_1 measurements taken on the same sample at different Larmor frequencies (25 and 45.7 MHz). The very large magnetic susceptibility of Pd, which plays a role in the line shape, is not expected to influence T_1.

One can be sure that at 4 K, the helium in the 8-yr-old palladium material is in the solid phase. The observation of motional narrowing above 30 K and of a homogeneously broadened FID below this temperature provides very strong evidence for a bulklike dipolar interaction modulated by the hopping motion of helium in a solid lattice. With a reasonable assumption about the fluid phase viscosity, it is only in the solid phase that the helium diffusivity could satisfy the motional narrowing condition given by Eq. (1). The successful prediction of the temperature range for motional narrowing, using information about diffusivity obtained from a BPP analysis of T_1 data in the vicinity of the minimum, supports the notion that in the temperature range of the minimum the helium is in the same phase (and thus has the same diffusion characteristics) as at 30 K.

The fact that the T_1 minimum falls in a temperature range just below the hypothesized solid/fluid mixed phase region is therefore consistent with the notion that in this latter region the helium fraction characterized by the shorter T_1 is in the solid phase. The fraction characterized by the slower relaxation process (longer T_1) most likely corresponds to ^{3}He spins having a much greater diffusivity than the solid fraction, consistent with $\omega_0\tau_c \ll 1$ (the temperature of the T_1 minimum is determined by $\omega_0\tau_c \simeq 1$) and therefore with T_1 values much larger than $(T_1)_{\rm min}$. The most plausible interpretation is that of a melting transition, especially given that qualitatively similar behavior for T_1 is observed in studies, through the known melting transition at much lower densities, of bulk helium[6,20] and of helium in porous glasses.[21]

However, the most direct support for the hypothesis is the agreement, for the 8-yr-old palladium material, of the mean-squared density obtained from the 4-K second moment analysis with that obtained from the density distribution function. Because the distribution function is derived from an analysis—based on the bulk helium EOS—of the nonexponential spin-lattice relaxation in terms of coexisting solid and fluid components, the good agreement strongly supports the hypothesis referred to at the beginning of this section. It also provides some justification for use of the bulk EOS for helium in palladium.

The existence of a distribution of helium densities, suggested primarily by the range of temperatures over which strongly nonexponential T_1's are observed, is consistent with the microscopic evidence[3] for an ensemble of 1–5 nm bubbles (referred to here as helium precipitates) in palladium tritide. An alternative explanation might be that all the precipitates have about the same density and that the observed range of melting temperatures corresponds to the coexistence range of solid and fluid helium within each bubble. The fact that the coexistence range is much larger than for bulk helium of comparable density[2] might just be a consequence of surface interactions. The problem with this interpretation is that in such a small system (each bubble has $\simeq 10^3$ helium atoms) a given helium spin would sample both phases many times before relaxation could occur. This would give an exponential relaxation, with a characteristic time constant corresponding to the weighted average of the two components, rather than the observed nonexponential relaxation. Moreover, the observation of coexisting broad and narrow lines at 41 K (implied by the 41-K FID shown in Fig. 5) is consistent with a range of densities, but is difficult to explain if all bubbles have the same density (and therefore the same helium diffusivity). Thus, on both of these counts, this alternative explanation can be ruled out.

In conclusion, the experimental results of the present low-temperature NMR study are consistent with essentially bulklike behavior of ^{3}He in nanometer-sized microbubbles in aged palladium tritide. The results provide strong support for the hypothesis of a distribution of ^{3}He melting transitions over a temperature range where the magnetization recovery is strongly nonexponential. Because the melting temperature and the rigid-lattice second moment are both strong functions of density, the NMR techniques described here provide a sensitive measure of the density distribution and thus of any related property, such as swelling of the host material.

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