Detrapping of interstitial helium in metal tritides—NMR studies*

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We present measurements of NMR line shapes and relaxation times for ^{3}H nuclei and their β-decay products ^{3}He in aged samples of titanium tritide (Ti ^{3}H$_x$). Data were obtained on samples aged 1 yr ($x = 1.7$) and 8 yr ($x = 1.4$), where x is the initial concentration. These data indicate that ^{3}He atoms are trapped interstitially in young crystals; whereas, in contrast, the older samples are found to contain helium-gas bubbles. Additionally, the younger sample was found to exhibit considerably more lattice distortion than the older sample. This—to our knowledge—is the first direct evidence for a detrapping mechanism which has been supported by a growing body of indirect evidence. We describe a theory which explains the detrapping by a percolative mechanism: When enough ^{3}He atoms have been created to exceed a relevant critical percolation density, the helium atoms, which are considerably "oversized" for available interstices, are able to cooperatively strain the lattice beyond its elastic limit, hence irreversibly deforming the lattice. The subsequent rapid diffusion of helium would then allow heterogeneous bubble nucleation with release of helium from the crystal by blistering and/or release along grain boundaries.

I. INTRODUCTION

β decay of tritium (^{3}H) nuclei to the light isotope (^{3}He) of helium in transition-metal tritides provides a convenient method of introducing significant quantities of inert-gas atoms into crystals which under normal conditions would dissolve negligible quantities of such gases. Furthermore, the method is unique in that, unlike ion-implantation techniques,[1] the gas is dissolved with negligible damage to the metal lattice.[2] The physical state of the helium in the tritide system is a question of considerable interest. There is strong but indirect evidence that the helium remains trapped in individual interstices for a time period which depends on the composition M ^{3}H$_x$ of the initial metal (M)–tritide sample.[3-6] After the crystals have aged for this period of time, blisters appear quite suddenly on the surface of the crystal.[6] We have taken these results to mean that after this time period, the helium becomes sufficiently detrapped to allow rapid diffusion which could lead to bubble nucleation, with incumbent blister formation.

In this work, we report the first direct microscopic evidence of this detrapping behavior. Namely, we have studied the nuclear-magnetic-resonance line shape and relaxation times for ^{3}H and ^{3}He nuclei in young (~1 yr) and aged (~8 yr) titanium ditritide. [The initial composition of the younger sample was Ti ^{3}H$_{1.7}$; and that of the older sample was Ti ^{3}H$_{1.4}$.] Below we show that the line shape is a sensitive function of the degree of localization of the nuclei. Thus we are able to show that in the younger sample, the ^{3}He atoms are trapped interstitially, while in the older sample, they are much more mobile, evidently in a gase-

ous state. We have developed a theory— involving the percolation of helium-atom clusters—which explains the detrapping as a transition driven by the cooperative straining of the metal-atom lattice by the interstitial helium. We show below that this theory is consistent with a considerable body of experimental and theoretical data bearing on this problem.

II. EXPERIMENT

A. Method and results

Often the physical state of matter is identified by a distinct signature in the NMR of constituent nuclei.[7] For example, protons situated in rigid-lattice positions in hydrides exhibit roughly a 10 G linewidth ($T_2 \approx 4$ μsec) due to H-H dipole interactions; but in H$_2$ gas pockets within the hydride, these interactions are averaged by molecular motion and $\Delta (\propto 1/T_2)$ decreases by roughly three or four orders of magnitude. In addition, a precipitous reduction in Δ for protons in hydrides occurs when the diffusion rate is sufficiently great (i.e., at high enough temperatures). These three situations are easily distinguished in NMR data. For ^{3}He the same general considerations are valid with the added possibility of ^{3}He-^{3}He exchange narrowing[8] of the resonance line. Thus, even at low temperatures where atomic diffusion is frozen out, if sufficiently high ^{3}He densities are present, exchange interactions will narrow the helium resonance.

We present measurements of the ^{3}H and ^{3}He nuclear resonances in two Ti ^{3}H$_x$ samples of ages 1 yr ($x = 1.7$) and 8 yr ($x = 1.4$). There are radical differences between the NMR results in these two samples which we interpret in terms of a detrap-

ping of the helium atoms in the aged crystal.

Samples were prepared using Sievert's method and subsequently stored in glass vials. Very little of the older material was available so that the filling factor was reduced in this case. The sample holders were sufficient to absorb the β rays.

Standard single-coil phase coherent NMR techniques were employed to measure the spin-lattice (T_1) and spin-spin (T_2) relaxation times. A Varian spectrometer was used for the wide-line work. The transient experiments were carried out at 25 MHz and the cw experiments at 16 MHz. Low temperatures were obtained by pumping on liquid helium in which the samples were immersed.

The nature of the NMR signals was such that wide-line cw data were obtained at room temperature for ^3H in both samples and ^3He in only the younger sample, whereas transient signals were only found for ^3He at low temperature in the older materials. The absence of transient signals for ^3H in both, and ^3He in the younger sample, is consistent with the observed broad cw lines. A homogeneous broadening mechanism is thus indicated; undoubtedly resulting from dipole-dipole interactions as in metal hydrides.[9] Table I lists the experimental second moments of the various NMR lines.

The absence of a cw signal for ^3He in the older sample is probably caused by saturation since both T_1 and T_2 are fairly long. However, the reduced filling factor, due to the small sample size, also influences this measurement. Our relaxation-time data for ^3He in the older sample are summarized in Fig. 1.

B. Discussion

Consider first the ^3He resonance from the 8-yr sample (Fig. 1), since the NMR furnishes a more detailed description of the atomic environment in this case. Note that T_2 is in the sec range for $T \geqslant 77$ K, suggesting line narrowing due to atomic motion. Since the narrowing (i.e., long T_2) persists down to 77 K, the motion is unlikely to be

simple interstitial diffusion; instead, atomic motion in helium gas is indicated. At 4 K and below, the lines were Lorentzian, which is characteristic of both solid and liquid helium.[10] The magnitudes and temperature dependence of spin-lattice relaxation times indicate the presence of solid He. In fact, for $T = 1.2$ K, nonexponential magnetization was observed, which is also observed in the solid.[10] The nonexponential magnetization recovery and the temperature independence of T_1 for $1.2 \leqslant T < 4$ K also provide strong evidence that exchange modulation of the dipole-dipole interactions in ^3He is the principal relaxation mechanism. Assuming this, a calculation of the exchange constant using T_1 and T_2 is presented from which the atomic volume or pressure can be inferred.

An estimate of the exchange constant can be obtained following the work of Garwin and Landesman.[11] For an assumed isotropic system,[7]

$$T_1^{-1} = J_1(\omega) + 4J_1(2\omega), \qquad (1)$$

$$T_2^{-1} = \tfrac{3}{2}J_1(0) + \tfrac{5}{2}J_1(\omega) + J_1(2\omega), \qquad (2)$$

where $J_1(\omega)$ is the spectral density function. If the exchange frequency is much larger than the atomic-jump rate,[11] the exchange modulation dominates the relaxation mechanism and

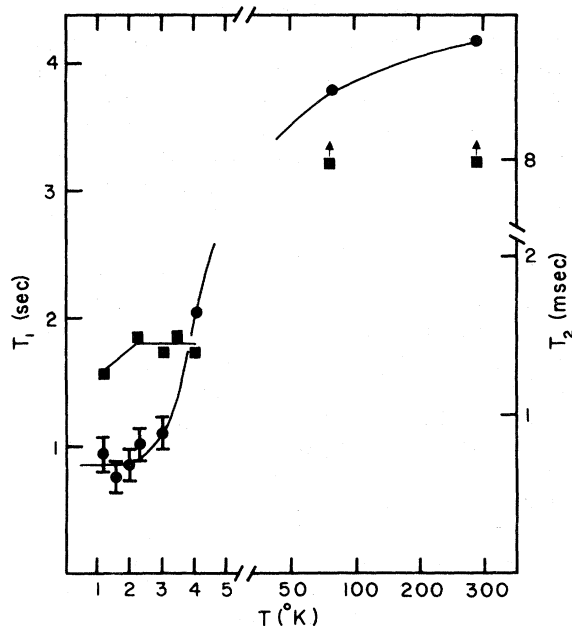$$J(\omega) \approx \frac{\alpha}{\omega_e} \exp(-\omega^2/2\omega_e^2), \qquad (3)$$

TABLE I. Summary of resonance-line second moments in units of G^2. The ^3H second moment in an unaged tritide is determined by scaling the value for protons in $TiH_{1.6}$(Ref. 9) with the square of the gyromagnetic ratio.

	Unaged	1 yr	8 yr
^3H	25	73	20
^3He	$\cdots$	17	$\sim 10^{-4}$

FIG. 1. Summary of ^3He $^3H_1$ (●) and T_2(■) in Ti $^3H_{1.4}$ (8 yr) as a function of temperature. Note that the scale for T_2 is broken and in msecs.

where ω_e is the exchange frequency and α is a constant involving rigid-lattice parameters. Combining (1), (2), and (3) and using $\omega \gg \omega_e$ yields

$$(\omega/\omega_e)^2 = 2\ln(2T_1/3T_2) . \qquad (4)$$

Direct substitution of the low-temperature relaxation times and $\omega = 25$ MHz into (4) yields $\omega_e = 7$ MHz. Comparing this value to the experimental work on solid helium[10] yields a molar volume[12] of 21.4 cm^3. In turn, thermodynamic data for ^{3}He yield a pressure at the melting point of about 60 atm for this volume.[12]

One of the problems with the application of Eq. (4) is that the small confines for the ^{3}He introduce appreciable wall effects on the relaxation times.[13] Usually this affects T_2 more seriously than T_1. If the measured T_2 in the range $1.2 < T \leq 4$ K is assumed to be entirely due to wall relaxation and the value of T_2^{-1} at 1.2 K is the sum of T_2^{-1} (exchange) and T_2^{-1} (wall), the exchange spin-spin relaxation time can be estimated to be ≈ 5.5 msec. However, due to the insensitivity of ω_e in Eq. (4) to the value to T_2, the helium pressure is, under this condition, estimated to be about 40 atm. Interestingly, if the observed change from nonexponential to exponential spin-echo decay (i.e., T_2 plot) between 4 and 3.5 K is assumed to be the effect of freezing ^{3}He, a pressure of about 100 atm is implied.[12] Even in view of the uncertainties involved here, a pressure of around 50 atm appears to be implied.

In contrast to the results for the aged samples, the 1-yr tritide exhibited a homogeneously broadened ^{3}He line of about 5 G($M_2^{\exp} = 17$ G^2), which is qualitatively expected for ^{3}He-^{3}H dipole-dipole broadening and is approximately two orders of magnitude larger than for the aged samples. However, in order to quantitatively calculate the ^{3}He linewidth, the position of the tritons as well as ^{3}He must be specified.

Hydrogen positions in hydrides are determined by comparing the Van Vleck second moment,[14] calculated for various assumed atomic configurations, with experiment. Briefly, the second moment of the resonance line for a powdered crystal with spins located at N different point-symmetry sites in a unit cell is given by a weighted average of the Van Vleck contribution[15] for each type of symmetry site, i.e.,

$$M_2(y) = \frac{C_y \hbar^2 I(I+1)}{x} \sum_{i,j}^{N} w_i \alpha_i \alpha_j S_{ij} , \qquad (5)$$

where x is the tritium-to-metal ratio, w_i is the number of i-type sites in the unit cell, α_i is the probability of occupation of an i site, and S_{ij} is the sum $\sum_i r_i^{-6}$ with an origin at an i-type site

which runs over all j-type sites. The letter y refers to either triton (t) or helium, where $C_t = \frac{3}{5}\gamma_t^2$ and $C_{He} = \frac{4}{15}\gamma_h^2$; γ_y is the gyromagnetic ratio of a y spin. Equation (5) neglects helium-helium, helium-metal, and tritium-metal interactions, which are easily shown to produce small contributions.

There are two high-symmetry interstitial sites (tetrahedral and octahedral) in the Ti ^{3}H$_x$ lattice (CaF$_2$ structure). The sites are distributed so that there are eight tetrahedral and four octahedral sites in a unit cell containing four metal atoms. If all of the tritons are placed in tetrahedral sites, as is the case for protons[15] in TiH$_x$, $M_2 = 24$ G^2 for $x = 1.7$. For $x < 1.4$ a two-phase dihydride-metal solid solution exists so that the experimental line is characteristic of an $x \approx 1.4$ hydride or $M_2 \approx 21$ G^2. This value compares favorably with the 8-yr tritide line, but is much smaller than the observed $M_2^{\exp}$ (= 73 G^2) for the 1-yr sample (see Table I). The triton resonance lines from the two samples are shown in Fig. 2. Note the larger width for the younger sample.

The calculated M_2 increases when some of the tritons are placed on octahedral positions, but the maximum M_2 from Eq. (5) for $x = 1.7$ is 43 G^2. Since the ^{3}He recoil energy (1–5 eV) is much smaller than energies required for metal-atom displacements (~20 eV), it is unlikely that tritium (or helium) atoms reside appreciably on the metal sites. Probably the larger helium atoms (compared to ^{3}H) strain the lattice so that on the average a substantial fraction of the tritons are closer together than the rigid-lattice sum in Eq. (5) specifies. At first, this appears improbable in view of the large difference in the observed and calculated M_2. However, a 20% reduction in the tritium separation accounts for this discrepancy. This is
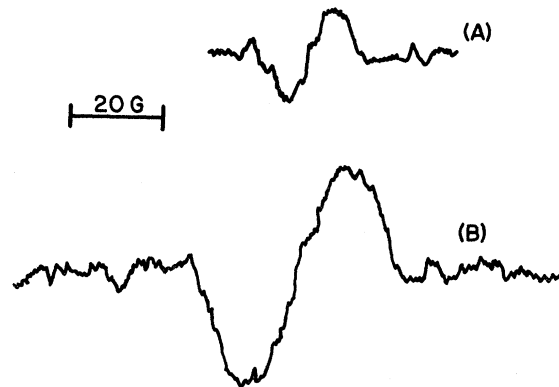

FIG. 2. Triton resonance line for ^{3}He contained in an 8 (A) and 1 (B) yr titanium-tritide sample. Note that the width for B is larger than A.

at least plausible since the volume available at an octahedral site is about 25% smaller than the ^{3}He atomic volume.[16] Thus, the lattice must be distorted an amount comparable to that needed for the large linewidth.

Although this lattice distortion prevents a quantitative calculation of the ^{3}He second moment leading to location of the helium, there is evidence that the octahedral position is favored. This follows from the rigid-lattice ^{3}He second moments for octahedral and tetrahedral occupancy. The main contribution to the ^{3}He second moment arises from ^{3}He-^{3}H dipole-dipole interactions which yield $M_2 = 24$ G^2 for octahedral and 11 G^2 for tetrahedral occupancy. However, the large He atom tends to push at least near neighbors away so that the observed second moment would be reduced from the rigid-lattice value. Our experimental value $M_2 = 17$ G^2, therefore, strongly suggests octahedral occupancy for the He. In this regard the neutron-diffraction work of Masland[17] on young tritides also indicates that the He reside at the octahedral sites.

Table I also lists the measured M_2 for an unaged tritide, as determined from hydride work, and for the 8-yr sample. In both these cases, the second moments are close to the calculated values of 24 and 21 G^2 for 0 and 8 yr, respectively, assuming that tritons are located in tetrahedral sites. This contrasts strongly with the 1-yr sample discussed above, for which $M_2 \simeq 73$ G^2, indicative of a highly strained environment. Apparently, the formation of bubbles or pockets of ^{3}He, some time after 1 yr, is accompanied by a relaxation of the lattice.

III. THEORETICAL DISCUSSION

In the γ phase of titanium tritide, the metal atoms occupy a face-centered lattice with the (nominally) two tritium atoms per metal atom occupying a simple-cubic lattice of tetrahedral interstices (CaF$_2$ structure).[18] The ^{3}He atom created by β decay of the tritium nucleus is much different from the tritium parent atom. In particular, it is a closed-shell atom unlike the tritium which is open shelled. Thus the hydrogen-metal bonds which favor the tetrahedral sites are absent. Furthermore, the Pauling atomic radius of ^{3}He is about $2\frac{1}{2}$ times that of the tritium atoms.[19] Indeed, Farnum[20] has done a semiclassical[19,20] calculation in which he shows that the tetrahedral interstix of the unstrained lattice is a factor of 8 too small in volume for the helium atom. On the other hand, Farnum shows that the octahedral interstices are only about 30% too small in the volume for helium atoms. (These octahedrals form an fcc lattice

whose union with the metal-atom lattice is a sodium-chloride-like lattice.) The β-decay process imparts an average recoil energy of about 1–5 eV to the daughter helium atom. This energy is probably sufficient to "knock" the helium atom from its tetrahedral site. Of course, once the helium atom is in an octahedral site, size considerations alone show that its return to a tetrahedral site is overwhelmingly improbable.

Thus our picture of a young crystal is one in which helium atoms are randomly distributed on octahedral interstices throughout the lattice. Wilson and Johnson[21] have calculated the energy barrier for octahedral-octahedral helium diffusion in isomorphous CaF$_2$ and found it to be 1.4 eV. From the data of Rodin and Surenyants,[3] we deduce an effective activation energy for ^{3}He diffusion in Ti^{3}H$_x$, at and near room temperature, well in excess of 1 eV.[22] With such high barriers, the ^{3}He atoms may be considered to be frozen in the lattice— in agreement with experimental results presented above for the young crystal.

As the random β-decay process continues, the number of helium atoms grows. At any given time the helium-to-metal ratio of a crystal with initial composition Ti ^{3}H$_{2x}$ will be given by $n = 2x(1 - 3^{-0.054t})$, where t is the age of the crystal in years. (This neglects the loss of an infinitesimal fraction of the ^{3}He, due to early release of ^{3}He generated in the surface layers.) Recall that the octahedral interstices form an fcc lattice. According to percolation theory,[23] there will appear a macroscopic connected (via first-neighbor bonds) island of helium atoms on this lattice when n becomes equal to or greater than 0.195. Furthermore, by the time n becomes equal to 0.32, virtually every helium β-decay product formed will find itself in this connected island.[24]

The picture we propose is that the helium atoms cooperatively strain the crystal in such a manner that helium diffusion becomes greatly enhanced in the helium clusters or islands. This is not unreasonable given the size of the strains induced by individual helium atoms [the lattice-constant distortion is about (10–20)%]. Now as long as the helium are in isolated finite clusters, they cannot diffuse throughout the crystal. However, in a macroscopic island the helium atoms may cooperatively inhomogeneously strain the lattice beyond its local elastic limit— hence irreversibly creating channels of high diffusivity throughout the crystal. This "bond-breaking" mechanism effectively removes nearly all the stress on the crystal. This release of stress is evidently the cause of the pronounced narrowing of the linewidth of the triton resonance in the 8-yr sample (as compared to the young sample). Thus, according

to the percolative picture, after completion of percolation ($n \simeq 0.32$), every ^{3}He atom created would be free to diffuse to defect sites and form bubbles.

Rodin and Surenyants[5] have studied the rate of evolution of ^{3}He from a Ti^{3}H$_x$ crystal (with x initially about 1.5) as a function of crystal age. Their results indicate that extremely little ^{3}He is released until the crystal is about $3\frac{1}{2}$ to 4 yr, at which time the fraction of octahedral sites occupied by ^{3}He atoms has increased to ~25%.[5] Thereafter, rapid evolution of ^{3}He from the crystal was found to occur. They conclude that Ti^{3}H$_{1.5}$ will not retain helium when the fractional occupancy of octahedral sites exceeds 30%. In Fig. 3 we plot their release data as a function of crystal age. The vertical axis is the rate of release of ^{3}He, normalized to the release rate at 7.5 yr. At 7.5 yr the release rate (~4×10^{10}atoms/sec) is comparable to the rate of formation of ^{3}He by β decay. From the figure we see that in a young crystal, virtually no ^{3}He is released, and that a sharp break upward occurs at about 4 yr. The cross-hatched band corresponds to the interval between incipient percolation— after which the percolated fraction of ^{3}He becomes nonzero— and complete percolation— after which virtually every ^{3}He atom is "born" in a percolated island.

The results of Rodin and Surenyants[5] are seen to be in good agreement with our hypothesis that no ^{3}He is released from the bulk of the crystal prior to percolation, and that ^{3}He is released as formed after completion of percolation. Finally, we note that the arrows in Fig. 3 indicate the ages of the young and old samples studied herein. Even when the age of the young sample is adjusted to allow for its higher initial tritium concentration,[25] it is clearly below the threshold age for incipient percolation. In contrast, the old sample corresponds to a completed percolated crystal.

The release data of Rodin and Surenyants[5] is complemented by the studies of Beavis and Miglionico[6] who— as noted above— made electron-microscopy studies of several metal-tritide films and found pockets, assumed to be helium bubbles, to appear after a year or two. Spalling of the films occurred between 2–5 yr of life, indicating a fracturing of the lattice by pressure buildup in the bubble. Thus, the picture of initially trapped helium followed by the occurrence of bubbles, which we use to interpret NMR data, appears applicable to these aging studies. The percolative theory predicts the time to detrapping, and not, directly, the age to accelerated release, since there is a time lag between detrapping and release
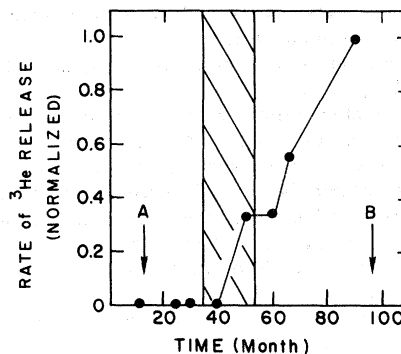

FIG. 3. Rate of release of ^{3}He from titanium ditride with an initial tritium-to-metal ratio of 1.5. The rate of release is normalized to that at 90 mo (4×10^{10} atoms/sec). The crosshatched band indicates the timespan between incipient and complete percolation; and the two arrows indicate the ages of the two crystals studied by NMR. The release data are taken from Ref. 5.

due to the mechanics of bubble blowing and fracture. However, we expect this time lag to be very short on a scale determined by the age to percolation. The consistency of the NMR studies with the release studies[3-6] confirms this viewpoint.

IV. CONCLUSION

The character of the NMR signal from ^{3}He contained in titanium tritide drastically changes with sample age from a homogeneously broad to a motionally narrowed line at room temperature. We interpret this as a detrapping of the originally isolated helium atoms by a collective distortion of the lattice when macroscopic clusters of near neighbor ^{3}He occur. Percolation theory is applied to determine the time required for infinite clusters to form. These clusters are physically realized as ^{3}He gas bubbles in the solid. The change from the trapped or rigid-lattice configuration to bubbles is exhibited in the NMR as a change from a homogeneously broadened line to a motional or exchange-narrowed line. The detrapping mechanism provides an explanation for the threshold effects found in previous studies of ^{3}He release from tritides.[2-6]

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[22] There are difficulties in interpreting these results since the very high temperatures involved in the experiments could lead to diffusion rates characteristic of the high-temperature lattice, rather than the highly strained low-temperature lattice. Additionally, the experiments were performed on crystals of about 3 yr. This is very close to the age at which percolative detrapping would occur. Nevertheless, their lower-temperature ($T \sim 600\,°C$) results indicate at least a 1-eV barrier.

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[24] Above this density, the number of helium atoms in the percolated cluster becomes virtually equal to the number of helium atoms present.

[25] Since the initial tritium concentration of the young sample was 1.7 rather than 1.5, the threshold for percolation is lowered to ~ 2.4 yr, and the age to complete percolation drops to ~ 3.6 yr.