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ISOTOPE EFFECTS AND HELIUM RETENTION BEHAVIOR IN VANADIUM TRITIDE

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ABSTRACT

The relaxation times of the H, T, and  $^3\text{He}$  nuclei have been measured in vanadium hydride and tritide samples. Substantial isotope effects in both the phase transition temperatures and diffusion parameters have been found. When compared to hydrides, the tritide samples have lower transition temperatures and faster mobilities. The differences in the occupancies of the interstitial sites are largely responsible for these isotope effects. Most of the helium atoms generated by tritium decay remain trapped in microscopic bubbles formed within the  $\text{VT}_x$  lattice. Evidence is presented for the gradual growth of the helium bubbles over periods of hundreds of days.

INTRODUCTION

The vanadium-hydrogen phases exhibit unusually large isotope effects with respect to phase compositions, crystal structures, and diffusion properties. Although most previous studies have been on the vanadium hydrides and deuterides,<sup>1-3</sup> some results for the tritide phases are now available.<sup>4-7</sup> The present paper summarizes extensive nuclear magnetic resonance (NMR) measurements on the two tritide compositions  $\text{VT}_{0.50}$  and  $\text{VT}_{0.75}$  as well as the corresponding hydrides  $\text{VH}_{0.50}$  and  $\text{VH}_{0.76}$ . Isotope effects in the phase transitions and diffusion properties were

obtained from the temperature dependences of the proton and triton relaxation times. Furthermore, the relaxation times of the tritium decay product (i.e.,  $^3\text{He}$  -- the light helium isotope) have been monitored for several years in both  $\text{VT}_{0.50}$  and  $\text{VT}_{0.75}$ . The age dependences of the  $^3\text{He}$  relaxation times are very similar to the behavior previously observed in several other metal tritides.<sup>8-10</sup> The rather substantial quantities of helium that are retained in the  $\text{VT}_x$  samples are believed to be in the form of very high pressure microscopic gas bubbles.<sup>8-10</sup> This conclusion is consistent with recent transmission electron microscopy (TEM) studies<sup>11</sup> in  $\text{VT}_x$ . The  $^3\text{He}$  relaxation times have also indicated that the mean radius of the helium bubbles in  $\text{VT}_x$  has increased by a factor of about three between 100 and 1600 days.

EXPERIMENTAL SECTION

All of the  $\text{V(H,T)}_x$  samples had been prepared from the same rod of zone-refined vanadium metal that was purchased from Materials Research Corporation, Orangeburg, New York. Synthesis details as well as summaries of various properties of the  $\text{VH}_x$  and  $\text{VT}_x$  samples have been published.<sup>4</sup> The powders were sealed in 7-mm and 9-mm o.d. evacuated glass tubes for the NMR measurements. The pulsed NMR techniques and spectrometer that were used to measure the

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spin-lattice ( $T_1$ ) and spin-spin ( $T_{2m}$ ) relaxation times have also been previously described.<sup>4,5,8</sup> Although some  $T_1$  values were determined at several resonance frequencies,<sup>4,5</sup> most of the proton and triton relaxation time data were obtained at 34.5 MHz. In order to minimize deleterious effects from helium generation, all of the triton data were collected within a few weeks after synthesis. All of the  $^3\text{He}$  NMR experiments were performed at a resonance frequency of 45.7 MHz and  $^3\text{He}$  data were obtained only at room temperature. After the completion of the NMR studies, each  $\text{VT}_x$  sample was analyzed for its final composition. Portions of the powders were thermally decomposed by induction heating to a nominal maximum temperature of about 1000°C in a calibrated volumetric system based upon an all metal Töpler pump. The compositions of the evolved gases were determined by mass spectrographic analysis.

#### RESULTS AND DISCUSSIONS

Summaries of the phase transitions for  $\text{V}(\text{H,D,T})_{0.50}$  and  $\text{V}(\text{H,D,T})_{0.75}$  are presented in Table I where the phase compositions and transition temperatures are based upon previous resistivity, thermal analysis, x-ray and neutron diffraction, microscopy, and NMR measurements.<sup>1-4</sup> Detailed descriptions of the various phases are available in Refs. 1-4. The  $\alpha$ -phases are body-centered cubic where the hydrogen isotopes predominantly occupy the tetrahedral interstitial sites in a statistically random fashion.<sup>1</sup> All of the other  $\text{V}(\text{H,D,T})_x$  phases result from at least partial ordering on either octahedral sites (i.e.,  $\beta_{\text{H}}$ ,  $\beta_{\text{D}}$ ,  $\beta_{\text{T}}$ ,  $\delta_{\text{H}}$ , and  $\epsilon_{\text{H}}$ ) or tetrahedral sites (i.e.,  $\gamma_{\text{D}}$ ,  $\delta_{\text{D}}$ ,  $\zeta_{\text{D}}$ , and presumably analogous phases for  $\text{VT}_{0.75}$ ) which generate tetragonal or orthorhombic distortions of the vanadium lattice.<sup>1,4</sup> The low-temperature phase compositions of  $\text{VT}_{0.50}$  and  $\text{VT}_{0.75}$  have not been definitely established but are based<sup>4</sup> upon the character of the triton relaxation times and expected analogies to the  $\text{VD}_x$  phases. Further work is needed to complete the  $\text{VT}_x$  phase diagram.

Table I. Summary of phase transitions for several isotopic vanadium-hydrogen compositions. Transition temperatures correspond to a heating sequence. Descriptions of various phases are given in References 1-4.

$\beta_{\text{H-VH}}_{0.50}$	$\xrightarrow{446 \text{ K}}$	$\epsilon_{\text{H-VH}}_{0.50}$	$\xrightarrow{470 \text{ K}}$	$\alpha_{\text{H-VH}}_{0.50}$
$\beta_{\text{D-VD}}_{0.50}$	$\xrightarrow{407 \text{ K}}$	$\alpha_{\text{D-VD}}_{0.50}$		
$\beta_{\text{T-VT}}_{0.50}$	$\xrightarrow{372 \text{ K}}$	$\alpha_{\text{T-VT}}_{0.50}$		
$\delta_{\text{H-VH}}_{0.75}$	$\xrightarrow{210 \text{ K}}$	$\epsilon_{\text{H-VH}}_{0.75}$	$\xrightarrow{455 \text{ K}}$	$\alpha_{\text{H-VH}}_{0.75}$
$\alpha_{\text{D-VD}}_{0.75}$	$\xrightarrow{151 \text{ K}}$	$\delta_{\text{D-VD}}_{0.75}$	$\xrightarrow{211 \text{ K}}$	$\zeta_{\text{D-VD}}_{0.75}$
	$\xrightarrow{217 \text{ K}}$	$\alpha_{\text{D-VD}}_{0.75}$		
$\delta_{\text{T-VT}}_{0.75}$	$\xrightarrow{?}$	$\zeta_{\text{T-VT}}_{0.75}$	$\xrightarrow{225 \text{ K}}$	$\alpha_{\text{T-VT}}_{0.75}$

Since the NMR relaxation times for  $\text{VH}_{0.50}$  and  $\text{VT}_{0.50}$  have been previously compared in some detail, the temperature dependent behavior of the relaxation times for  $\text{VH}_{0.76}$  and  $\text{VT}_{0.75}$  is emphasized in the present paper. Figures 1 and 2 present the  $T_1$  and  $T_{2m}$  data for these samples. Within experimental accuracy all the  $T_1$  magnetization recoveries were exponential throughout the measured temperature ranges for both samples in contrast to the regions of nonexponential  $T_1$  behavior previously found<sup>4,5</sup> for  $\text{VT}_{0.50}$ . The frequency dependent  $T_1$  minima indicate<sup>12</sup> that diffusion is the primary spin relaxation process for both systems. The temperature behavior of the  $T_{2m}$  parameters is also consistent<sup>12</sup> with substantial proton and triton mobilities for temperatures above 150 K. However, the temperatures of the  $T_1$  minima are significantly different (i.e., 282 K for  $\text{VH}_{0.76}$  and 217 K for  $\text{VT}_{0.75}$  at 34.5 MHz) which implies isotopic differences in the proton and triton diffusion parameters. This view is supported by the activation energies ( $E_a$ ) obtained from conventional analyses<sup>5,12</sup> of the proton and triton relaxation times. The available  $E_a$  values for several  $\text{V}(\text{H,D,T})_x$  compositions are compared in Table II along with the expected phase and interstitial site occupancy. The results for  $\text{V}(\text{H,D,T})_0$  are

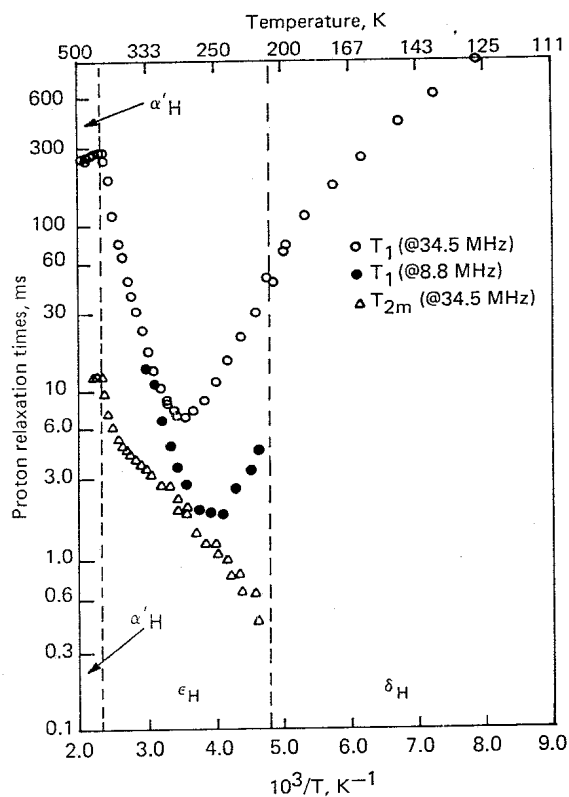


Fig. 1. Proton relaxation times for  $VH_{0.76}$  that were obtained during cooling sequences. The vertical dashed lines indicate the transitions between the hydride phases from References 1-3.

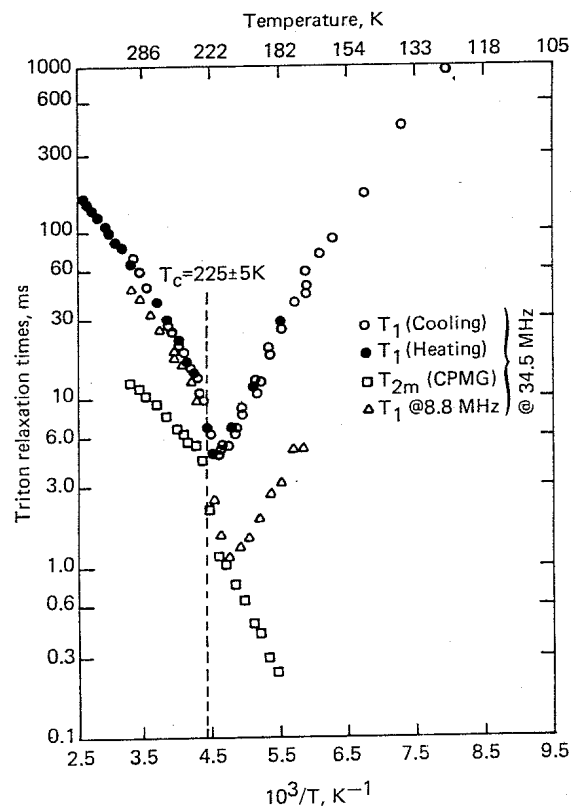


Fig. 2. Triton relaxation times for  $VT_{0.75}$  obtained during heating and cooling cycles. A phase transition from the high temperature  $\alpha_T$  phase is indicated at  $225 \pm 5$  K; however, no significant changes in the  $T_1$  and  $T_{2m}$  data are observed at the expected  $\gamma_T \rightarrow \delta_T \rightleftharpoons \epsilon_T$  phase transitions that would be analogous to  $VD_{0.75}$  behavior.

Table II - Comparison of isotope effects in diffusion activation energy ( $E_a$ ) for vanadium-hydrogen phases.

Sample Composition	Phase	Hydrogen Site Occupancy	$E_a$ (meV)	Temperature Range	Method
$VH_{\sim 0}$	$\alpha H$	Tetrahedral	$45 \pm 3$	140 K-570 K	Gorsky <sup>a</sup>
$VD_{\sim 0}$	$\alpha D$	Tetrahedral	$73 \pm 3$	175 K-570 K	Gorsky <sup>a</sup>
$VT_{\sim 0}$	$\alpha T$	Tetrahedral	$94 \pm 7$	133 K-373 K	Gorsky <sup>a</sup>
$VH_{0.50}$	$\beta H$	Octahedral	$410 \pm 20$	320 K-400 K	NMR( $T_1$ )
$VT_{0.50}$	$\beta T$	Octahedral	$310 \pm 30$	290 K-345 K	NMR( $T_1$ )
$VH_{0.76}$	$\epsilon H$	Octahedral	$260 \pm 15$	280 K-450 K	NMR( $T_1$ )
$VH_{0.76}$	$\epsilon H$	Octahedral	$180 \pm 10$	210 K-280 K	NMR( $T_1$ )
$VT_{0.75}$	$\alpha T$	Tetrahedral	$160 \pm 10$	230 K-380 K	NMR( $T_1$ )
$VT_{0.75}$	$\delta T(?)$	Tetrahedral	$185 \pm 15$	150 K-210 K	NMR( $T_1$ )

<sup>a</sup>Reference 6.

from Grosky effect measurements<sup>6</sup> while the  $E_a$  values for  $VH_{0.50}$  and  $VT_{0.50}$  are from the previous NMR studies.<sup>5</sup>

Several interesting isotope effects for the diffusion activation energies are apparent in Table II. First,  $E_a$  increases rapidly with isotope mass in the low limit concentrations, whereas the opposite trend is observed for  $x = 0.50$  and  $x \approx 0.75$ . Neither semi-classical nor current quantum theories can provide a satisfactory and quantitative description of the hydrogen diffusion processes in the bcc metals V, Nb, or Ta although polaron models<sup>13</sup> do give qualitative understanding for much of the experimental results.<sup>6</sup> For  $x = 0.50$ , the smaller  $E_a$  for the tritide has been attributed<sup>5</sup> to increased disorder of the tritons among the interstitial sites of the  $\beta_T$ -phase which is reflected in more rapid mobilities and lower effective diffusion activation energies than are observed in the more highly ordered  $\beta_H$ -phase of  $VH_{0.50}$ . The smaller  $E_a$  for  $\epsilon_H$ - $VH_{0.76}$  is also consistent with a direct correlation between more rapid motion (i.e., smaller  $E_a$  values) and increased disorder since the protons in the  $\epsilon_H$ -phase are randomly distributed over all the  $Oz$  octahedral sites but the protons are ordered<sup>1</sup> on a subset of octahedral sites (i.e.,  $Oz_1$ ) in  $\beta_H$ - $VH_{0.50}$ . From the phase boundaries given in Figure 1, it is clear that  $E_a$  values for the  $VH_{0.76}$  sample correspond to the diffusion behavior in the  $\epsilon_H$ -phase. The different  $E_a$  values obtained above and below the  $T_1$  minima for  $\epsilon_H$ - $VH_{0.76}$  are believed to reflect complications that arise from the simultaneous presence of short-range and long-range jump processes with differing activation energies.<sup>14</sup> However, the  $E_a$  values for  $VT_{0.75}$  correspond to diffusion in the disordered  $\alpha$ -phase above 225 K and one or more of the ordered phases for temperatures below 210 K. The relatively small  $E_a$  values and rapid triton mobilities observed for the  $VT_{0.75}$  phases are probably consequences of preferred triton occupancies on tetrahedral sites. Similar diffusion parameters have been

reported<sup>6,15</sup> for hydrogen isotopes in  $NbH_x$  and  $TaH_x$  where tetrahedral interstitial site occupancy is also dominant.<sup>1</sup> From the  $E_a$  values in Table II, we conclude that disorder among the tetrahedral sites in  $VT_{0.75}$  has only minor influence on diffusion activation energies in contrast to the large effects found for diffusion among the octahedral interstitial sites of the  $\beta$  and  $\epsilon_H$  phases. The effect of hydrogen isotope concentration can be ascertained only for  $\alpha$ -phase  $VT_x$  where  $E_a$  increases by a factor of 1.7 between  $x = 0$  and  $x = 0.75$ . Similar comparisons of the published data<sup>6,15</sup> for  $\alpha$ - $NbH_x$  and  $\alpha$ - $TaH_x$  yield increases of 1.6 and 1.3, respectively. These larger values of  $E_a$  are probably related to the contributions of hydrogen-hydrogen repulsive interactions to the diffusion process.<sup>15</sup> Consequently, the systematic reduction of this effect with the increased mass of the host metal is particularly intriguing and warrants further detailed study for all the hydrogen isotopes in these three metals.

The room temperature  $^3He$  relaxation times  $T_1$  and  $T_{2m}$  for the two  $VT_x$  samples are summarized in Figure 3. Although both parameters increase with age (i.e., helium content),  $T_{2m}$  increases roughly twice as fast as  $T_1$  while both parameters are essentially constant after about 1800 days. Similar behavior for the  $^3He$  relaxation times has been previously observed<sup>8,10</sup> in the tritides of Ti, Li, and U and has been related<sup>8</sup> to the formation and growth of microscopic (i.e., mean diameters  $\leq 10$  nm) bubbles of very high pressure helium gas. The present  $^3He$  relaxation times in  $VT_x$  are completely consistent with this model. In fact, recent high-resolution TEM measurements<sup>11</sup> on  $\beta$ - $VT_x$  have detected large concentrations of 1-2 nm diameter helium bubbles after only 100 days of tritium decay. From the increases in the  $^3He$  relaxation times, it is estimated that the mean bubble diameters in both  $VT_x$  samples increase by approximately a factor of three

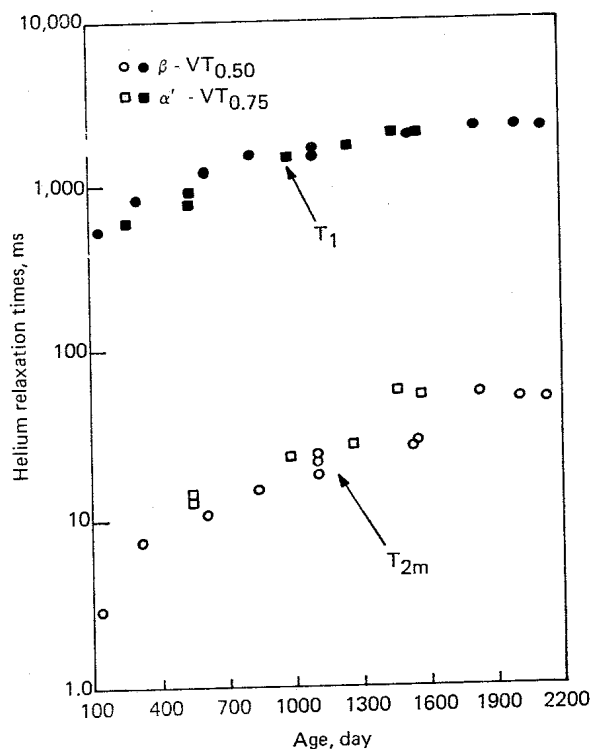


Fig. 3. Room temperature  $^3\text{He}$  relaxation times  $T_1$  (closed symbols) and  $T_{2m}$  (open symbols) for the  $\text{VT}_x$  samples.

between 100 and 1500 days but remain essentially constant at about 5-6 nm after 1800 days for  $\text{VT}_{0.50}$ . This latter behavior probably reflects the irreversible rupture of the largest bubbles to release the helium from the solid as was originally proposed<sup>8</sup> for helium retention in  $\text{UT}_3$ .

The  $^3\text{He}$  contents in  $\text{VT}_x$ , obtained from non-destructive NMR spin counts<sup>8</sup> as well as thermal desorption experiments, are compared in Figure 4 to the predicted amount of  $^3\text{He}$  generated by tritium decay. Both techniques yielded  $^3\text{He}$  contents below the predictions although the uncertainty of the spin counts is about 10 to 20%. Because the  $^3\text{He}$  relaxation times had been constant for the previous several hundred days (i.e., corresponding to the continual rupture of the largest helium bubbles), the substantial release of  $^3\text{He}$  gas observed after 2000 days at

room temperature is not particularly surprising. However, the absence of significant  $^3\text{He}$  contents in the gases evolved from 600-day old  $\text{VT}_{0.50}$ , and the very low quantity of  $^3\text{He}$  obtained from the  $\text{VT}_{0.75}$  after 1320 days is inconsistent with the essentially normal NMR signal amplitudes observed during the  $^3\text{He}$  relaxation time experiments performed over this time period. Consequently, it is strongly suspected that not all of the helium is being released at the highest temperatures (i.e., approximately 1000°C) of the thermal desorption experiments on the younger samples. Because helium should be much more deeply trapped in isolated defects (e.g., vacancies) or very small clusters (i.e., bubble precursors), the presence of larger bubbles would facilitate helium release at lower temperatures for the older samples. This explanation qualitatively reconciles the NMR spin count and thermal desorption results in Figure 4, and it is consistent with the increasing bubble size implied by the  $^3\text{He}$  relaxation times in Figure 3. However, it is

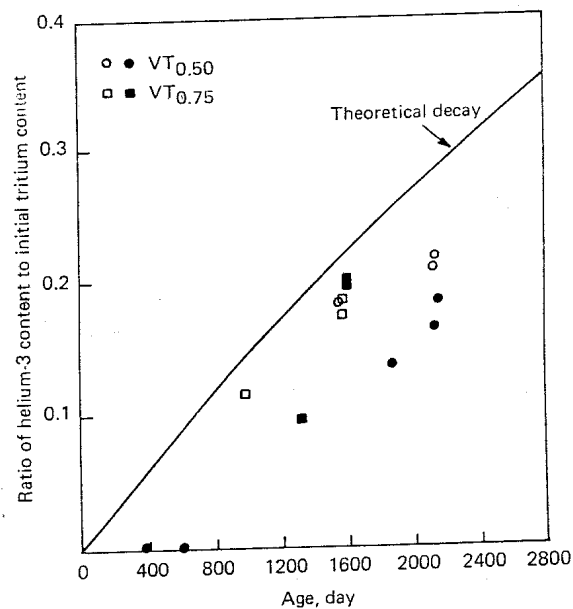


Fig. 4. Normalized helium-3 contents in  $\text{VT}_x$  samples from  $^3\text{He}$  NMR spin-counts (open symbols) and thermal desorption measurements (closed symbols). The solid curve represents helium generated in  $\text{VT}_x$  from tritium radioactive decay.

presently impossible to estimate quantitatively how much of the helium not detected by the thermal desorption experiments was actually deeply trapped. From comparisons of the spin count and thermal desorption data in Figure 4, it appears that the VT<sub>0.75</sub> sample had released some (i.e., about 10 to 15%) of its helium content after 1600 days at room temperature, and subsequently released essentially all of its helium when heated to 1000°C. On the other hand, 2100-day old VT<sub>0.50</sub> has apparently released about 25% of its helium at room temperature, but it had also retained more helium (i.e., roughly 10%) during the 1000°C desorption. Because VT<sub>0.75</sub> generates helium at a rate about 1.5 times faster than VT<sub>0.50</sub> (where the small differences<sup>4</sup> in lattice volumes are ignored), nominally identical quantities of helium had been formed and the above differences cannot be readily attributed to any major variation in total helium concentration. Furthermore, the <sup>3</sup>He relaxation times from Figure 3 indicate the mean bubble radii are also comparable. Hence, other factors, which currently remain unidentified, can also influence the specific mechanisms for helium release. More information on the effects of stoichiometry, phase composition, etc., on the distribution of helium bubbles and other defects will be required to resolve this issue.

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