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NMR Studies of Hydrogen Relaxation and Diffusion in TiFeH_x and $\text{TiFe}_{1-y}\text{Mn}_y\text{H}_x$
R. C. Bowman, Jr.*[‡], G. C. Carter[†], Y. Chabre[‡], and A. Attalla*

TiFe and related intermetallic compounds react directly with hydrogen gas to form hydrides which are suitable for energy storage applications. Although some of the characteristics of these materials have been evaluated, many important physical properties such as crystal structures, electronic structures, and hydrogen diffusion behavior are unknown. Since nuclear magnetic resonance (NMR) provides detailed information on the physical states of the hydrogen atoms, various NMR parameters are being measured in the hydride phases produced from TiFe and related alloys. This paper is mainly concerned with hydrides formed from TiFe and $\text{TiFe}_{0.79}\text{Mn}_{0.15}$. At low temperatures interactions with conduction electrons dominate proton spin-lattice relaxation times for both the β and γ phases. Spin echo measurements on β -phase samples showed motional narrowing above 360K and yielded a diffusion activation energy, E_a , of 0.26(2) eV. Hydrogen diffusion in the γ -phase is observed to be slower and an approximate activation energy of 0.80(5) eV is deduced from $T_{1\rho}$ measurements. The present observations for TiFeH_x will be briefly compared with the properties of TiH_x and other Ti-based ternary hydrides.

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[‡]Institute for Materials Research, National Bureau of Standards, Gaithersburg, Maryland, 20760, USA.

[‡]Laboratoire de Spectrométrie Physique, Université Scientifique et Médicale de Grenoble, B.P. 53 - 38041 Grenoble-Cédex, France.

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INTRODUCTION

The intermetallic compound TiFe has been shown by Reilly and Wiswall¹ to absorb large quantities of gaseous hydrogen and form, in succession, three distinct hydride phases: α (solid solution metal), β (tetragonal monohydride) and γ (cubic dihydride). Because the formation and decomposition of the TiFeH_x system are suitable for hydrogen storage applications², there have been several recent publications³⁻⁹ on the chemical, metallurgical, and physical properties of the hydrides formed from TiFe and related alloys. However, many other important physical properties such as crystal structures, electronic structures, and hydrogen diffusion behavior have not been determined for the TiFeH_x phases. The present paper describes the current results from nuclear magnetic resonance (NMR) studies which are being conducted to determine the hydrogen diffusion and electronic properties of the β and γ phases of TiFeH_x and TiFe_{0.79}Mn_{0.15}H_x.

The phase diagram for TiFeH_x as shown in Figure 1 was deduced from the pressure-temperature-composition (P-T-C) measurements of Reilly and Wiswall^{1,10} and Yamanaka et al³. There are two dissimilar sets of P-T-C data available from Reilly and Wiswall. Because (1) the data in Reference 10 were obtained on a high-pressure apparatus with the capability to go to higher temperatures but at lower sensitivity for x, and (2) Yamanaka et al³ data are similar to Reference 1, the data from References 1 and 3 were adopted to establish the absolute phase boundaries near ambient. The disparity between these values (solid lines in Figure 1) and the later data¹⁰ is indicated by the arrows, which point to the x-limits of Reference 10. The lower x-values for the α to $\alpha+\beta$ phase boundary is also preferred from x-ray analyses performed at Brookhaven and observations at NBS. The temperature dependence of the phase limits has been taken from Reference 10 and is represented by the dashed

lines which continue the solid lines to higher temperatures. The most important feature of this revised TiFeH_x diagram is the absence of a critical temperature for the $\beta+\alpha$ two-phase region up to the highest temperature studied, 400K. Our interpretations of the present NMR diffusion measurements, which were performed in this range of x and T , tend to support this new feature of the TiFeH_x phase diagram. Although the $\alpha+\beta$ phase limits can be determined more accurately than the $\beta+\gamma$ limits from the P - T - C curves, there is little doubt that no $\beta+\gamma$ critical temperature exists up to $\sim 400\text{K}$, which was originally suggested¹ to occur near 333K. The diagram in Figure 1 corresponds to equiatomic TiFe . Reilly and Wiswall¹ have shown that increasing the Ti content increases both the solid solubility " α -phase" range and the " $\beta+\gamma$ to γ boundary". This shift in boundaries is less than shown by the arrows in Figure 1, but it can be a major part of the arrows' lengths. Two compositions characterized in the present research by chemical and x-ray analyses, which are not shown in Figure 1 since $\text{Ti}_{1.04}\text{Fe}_{0.96}$ stoichiometry was used, gave an α -phase for $x = 0.36$ and β with some γ phase for $x = 1.2$. It should be noted that Figure 1 rigorously represents a nonequilibrium phase diagram since the hydrides dissociate at one atmosphere pressure (the conventional criteria for defining equilibrium conditions) and TiH_2 is more stable³ than these TiFeH_x phases.

Reilly and Johnson⁵ have shown the pressure-composition behavior of TiFeH_x can be modified in a controlled manner by a partial substitution with other first row transition metals. In particular, the $\text{TiFe}_{1-y}\text{Mn}_y$ system has improved characteristics for hydrogen storage. Although Sandrock et al^{6,7} have evaluated some of the metallurgical factors that influence the hydriding behavior of $\text{TiFe}_{1-y}\text{Mn}_y$, the fundamental physical properties of $\text{TiFe}_{1-y}\text{Mn}_y\text{H}_x$ are mostly unknown. NMR techniques can provide information on these hydrides as well as the TiFeH_x phases.

Initial results of our proton NMR studies of TiFeH_x were recently reported¹¹. These measurements were somewhat limited by the quality of the available TiFeH_x samples, whose compositions were not generally single phase. However, some significant observations on the properties of β and γ phase TiFeH_x were made. Various magnetic impurities produced substantial inhomogeneous broadening of the proton linewidths. Measurements of the low temperature spin-lattice relaxation times (T_1) implied differences in the electronic structures of the β and γ phases. In a predominantly β -phase sample the onset of proton diffusion above $\sim 340\text{K}$ is manifested from both the T_1 and spin-spin relaxation times. At 433K this sample experienced a sudden loss of hydrogen leading to a single α -phase, as verified by subsequent x-ray diffraction measurements.

This paper describes further NMR measurements performed on additional β and γ TiFeH_x samples as well as γ -phase $\text{TiFe}_{0.79}\text{Mn}_{0.15}\text{H}_2$. In addition to verifying our previous observations, these studies have provided more accurate values for the diffusion and electronic parameters and new data on the γ -phase. In this paper the available NMR results are presented and discussed in relation to the phase diagram of Figure 1 and the properties of hydrides formed from titanium alloys.

EXPERIMENTAL DETAILS

The three TiFe alloys used for the preparation of the hydride samples are summarized in Table I. TiFe possesses a CsCl -type crystal structure with a published¹² lattice constant of $a_0 = 2.976 \text{ \AA}$. Thermochemical studies^{1,7} indicate the hydriding properties to be rather dependent on the exact Ti-Fe stoichiometry. Fe contents in excess of $\sim 50.5 \text{ at. \%}$ causes magnetic TiFe_2 to form and TiFe_2 apparently does not hydride, which drastically reduces

hydrogen storage capacity. Magnetic inclusions are also very undesirable since they drastically reduce NMR sensitivity. Ti in excess of ~52 at. % causes a solid solution Ti-phase to form which can react with hydrogen readily yielding⁷ the stable TiH_2 phase. The TiFe prepared at the National Bureau of Standards (NBS) from 99.9% pure iodide Ti and Ferrovac Iron (vacuum remelted Fe) was Ti-rich to avoid formation of magnetic TiFe_2 , which is expected to be present in the TiFe batch from Alfa-Ventron*. The Mn-doped TiFe alloy was kindly provided by Dr. J. Reilly (Brookhaven National Laboratory). The measured alloy composition of this batch was $\text{TiFe}_{0.79}\text{Mn}_{0.15}$ and is Ti-rich to enhance⁷ single phase formation, which was verified by x-ray diffraction analysis. The oxygen contents given in Table I were obtained by neutron activation analyses performed at Mound prior to initiating the hydride synthesis procedures.

The hydrides were prepared at Mound Laboratory and NBS by reacting crushed (~100 mesh) TiFe powders with 900-1000 psi high purity hydrogen gas following the general procedures described by Reilly and Wiswall¹. Several hydriding-dehydriding cycles were performed until constant absorbed hydrogen contents were obtained. The offgassing of hydrogen from the TiFeH_x samples was inhibited by exposing the samples, cooled in a liquid nitrogen bath, to air and allowing the air-exposed sample to warm to room temperature. This procedure was initially suggested by Reilly and Wiswall¹ and produces an uncharacterized surface film of magnetic oxides which prevents the rapid release of hydrogen up to ~400K, depending on the sample. However, present measurements as well as the observations of Swartendruber et al⁴ indicate air-stabilized TiFeH_x will gradually lose hydrogen over periods of months at

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room temperature. This decomposition is often inhomogeneous resulting in the simultaneous presence of the α , β , and γ hydride phases in the samples. Prior to commencing the NMR studies, room temperature x-ray diffraction powder patterns were obtained to determine the phase compositions of the samples. Although the lattice parameters were not evaluated in every case, typical values for the tetragonal β -phase [$a_0 = 3.17(1)$ and $c_0 = 8.76(2)$] and cubic γ -phase [$a_0 = 6.61(2)$] were obtained and are in excellent agreement with the lattice parameters of Reilly and Wiswall¹. A lattice parameter of $a_0 = 6.63(3)$ was found for the γ -phase $\text{TiFe}_{0.79}\text{Mn}_{0.15}\text{H}_2$ sample. The properties of the TiFeH_x samples used in the present NMR studies are given in Table II, which also contains several of the parameters determined by the NMR measurements. Although these samples are nominally single phase, evidence for the other TiFeH_x phases were found in some samples. This behavior probably reflects the character of the hydriding reaction and the relative instabilities¹ of the TiFeH_x phases.

Two pulse NMR spectrometer systems were used to study the proton resonance in TiFeH_x . Measurements at Mound were performed primarily at 34.5 MHz on a Bruker variable frequency spectrometer. Proton resonance was observed exclusively at 15 MHz on the spectrometer at the University of Grenoble. Since the electronic recovery times of the spectrometers are typically $\geq 10\mu\text{s}$ and the proton resonance in TiFeH_x often experiences large linewidth broadening^{11,13}, detection of the free induction decays (FIDs) is generally very difficult. Consequently, the majority of the NMR measurements were performed using spin-echo techniques¹⁴. The linewidth relaxation time (T_2^*) is defined as the time required for the proton signal to decay to $1/e$ of its value at the echo maximum or initial FID value. The spin-spin relaxation time (T_2) is obtained from the decay of echo maxima as a function of spacing between

$\pi/2$ -pulses. The laboratory spin-lattice relaxation time (T_1) was measured by several standard¹⁴ techniques. The Jeener¹⁵ 3-pulse technique was used to determine the dipolar spin-lattice relaxation time (T_{1D}) in γ -phase $\text{TiFe}_{0.79}\text{Mn}_{0.15}\text{H}_2$. At Mound the samples were sealed in small glass tubes during NMR measurements between 130-435K. During the measurements at Grenoble the samples were in open tubes under helium atmospheres for temperatures between 280-433K.

RESULTS

As reported previously^{11,13}, the proton linewidths for TiFeH_x are inhomogeneously broadened with $T_2^* < 10\mu\text{s}$ being observed for all samples at 34.5 MHz. T_2^* varies with the alloy composition, hydride phase composition, temperature, and resonance frequency. The shortest T_2^* (i.e., 3-5 μs at room temperature) occurs for samples A and B, which were prepared from $\text{Ti}_{0.98}\text{Fe}_{1.02}$ alloy. Since this iron-rich alloy probably contains TiFe_2 as well as titanium-iron oxides^{7,8} and surface oxide films, extensive magnetic impurity effects are expected for the $\text{Ti}_{0.98}\text{Fe}_{1.02}\text{H}_x$ samples. However, the Ti-rich samples also have short T_2^* of $\sim 5\text{-}7\mu\text{s}$ and this suggests surface oxides and intrinsic bulk magnetic susceptibility¹⁶ are important contributors to proton linewidths in TiFeH_x . Unhydrided TiFe is rather strongly paramagnetic¹⁷ and the corresponding hydrides are probably also paramagnetic.

The T_1 relaxation times have been measured at 34.5 MHz and have been found to obey the Korringa relation^{18,19}

$$T_1 T = \text{constant} \quad (1)$$

at low temperatures as shown in Figures 2 and 3. The experimental constants, which reflect interactions with the conduction electrons, for these samples are listed in Table II. The break observed near 260K in the β -phase sample A is probably not due to hydrogen diffusion because T_1 is essentially

independent of resonance frequency at 300K as expected for a conduction electron dominated relaxation mechanism. Furthermore, since the conduction electron interaction for the β -phase is quite large (i.e., $T_1T = 3 \text{ sK}$), motional narrowing (i.e., T_2' increases) is expected¹⁸ to become observable before the diffusion contribution is apparent in the proton T_1 values. Increases in the proton T_2' are not found for β -phase TiFeH_x until $\sim 350\text{K}$, as will be described in more detail later in this paper. Hence, the change in T_1 for sample A suggests the β -phase $\text{TiFeH}_{1.0}$ may undergo a change in its electronic structure near 260K rather than having hydrogen diffusion processes contributing to proton T_1 relaxation. Similar T_1 behavior at low temperatures was also found for predominantly β -phase sample D. The compositions of samples B and E are not very different, and the low temperature T_1 data indicate their electronic structures are apparently identical and correspond to γ -phase TiFeH_2 . The low hydrogen composition for sample B occurs for two reasons: (1) the presence of some nonhydriding TiFe_2 because of excess Fe in the alloy, and (2) a relatively large oxygen impurity concentration as indicated in Table I. Oxygen in TiFe alloys can form⁸ an impurity phase characterized^{6,7} as $\text{Ti}_{10}\text{Fe}_7\text{O}_3$, which apparently does not react with hydrogen. Hence, 0.3 wt. % oxygen as $\text{Ti}_{10}\text{Fe}_7\text{O}_3$ can reduce⁶ the maximum composition to only $\text{TiFeH}_{1.70}$ while the hydride consists of pure γ -phase. Thus, both samples B and E should contain the γ -phase and yield similar T_1T values, which are observed in Table II.

At temperatures where diffusion starts to contribute to proton T_1 relaxation in metal hydrides¹⁸, T_1 generally obeys the relation

$$T_1^{-1} = T_{1e}^{-1} + T_{1d}^{-1} \quad (2)$$

where T_{1e} is the electronic contact term from equation 1 and T_{1d} is the diffusion term. The proton T_1 has been measured in β -phase TiFeH_x to temperatures near $\sim 420\text{K}$. T_1 data obtained at 15 MHz on sample C is presented in

Figure 4 and $\ln T_1$ is linearly dependent on T^{-1} as expected¹⁸ for hydrogen diffusion being a major relaxation mechanism above room temperature. However, for reasons presented in our previous work¹¹ the slope of $\ln T_1^{-1}$ versus T^{-1} does not correctly reflect the hydrogen diffusion activation energy (E_a), even after subtracting the electron term from the low temperature T_1 data. Magnetic contributions to T_1 could be a major factor for the observed¹¹ low E_a values from the T_1 measurements since the hydrogen diffusion rate is still rather slow at the highest temperatures investigated before irreversible decomposition occurs. Consequently, little emphasis has been placed on the study of T_1 above room temperature.

It was possible to measure at 15 MHz the dipolar spin-lattice relaxation time T_{1D} in the γ -phase sample F of $\text{TiFe}_{0.79}\text{Mn}_{0.15}\text{H}_{2.0}$. The T_{1D} data could be obtained up to $\sim 380\text{K}$. Upon reaching 406K a dramatic increase in T_2' and apparent hydrogen loss was observed. During this experiment sample F was contained in a large reservoir under one atmosphere of helium. Hence, some hydrogen began escaping at $\sim 380\text{K}$ causing a phase change to the β -phase. Room temperature x-ray analysis performed a few days after completion of NMR measurements on this sample verified the presence of both β and γ phases in roughly equal amounts. The experimental T_{1D} and T_1 results for γ -phase sample F are shown in Figure 5. An extrapolation of the T_{1D} data towards higher temperatures, which should have been observable if hydrogen loss had not occurred above $\sim 380\text{K}$, approaches a straight line corresponding to an E_a of $0.80(5)$ eV. This same E_a value is obtained if the T_{1D}^{-1} data in Figure 5 is corrected with the temperature variation of the corresponding T_1 data (i.e., the nonlinearity of $\ln T_1^{-1}$ is assumed to be present in $\ln T_{1D}$). The large ratio of T_{1D}^{-1} to T_1^{-1} near room temperature is not understood at present, but it may reflect some additional paramagnetic contributions to relaxation processes. Diffusion is not expected to be observed from T_2'

measurements until the extrapolated T_{10}^{-1} reaches $\sim 10^5 s^{-1}$ or less (i.e., near 433K or above where most of the hydrogen is suddenly lost¹¹). Indeed, the FID and spin echo ($\pi/2-\tau-\pi$ pulse sequence) measurements at 15 MHz indicate the proton linewidths of sample F are homogeneously broadened (i.e., $T_2^* \approx T_2 \approx 10-15 \mu s$) and nearly temperature independent prior to heating above $\sim 380K$. A constant T_2 of $40(1) \mu s$ was also obtained between 150K and 383K during spin echo ($\pi/2-\tau-\pi/2$ pulse sequence) measurements at 34.5 MHz on a second unheated sample F, which verifies the absence of motional narrowing in γ -phase $TiFe_{0.79}Mn_{0.15}H_2$ below $\sim 380K$. However, the T_2 values obtained at 15 MHz and 34.5 MHz are seen to be in poor agreement. Although experimental differences (i.e., two spectrometers with different electronic recovery times, different pulse sequences and analysis techniques, etc.) can account for some of this discrepancy, such a large disagreement is surprising. Since x-ray measurements on sample F before and after the 34.5 MHz spin echo measurements indicated only the γ -phase was present, the T_2 value of $40(1) \mu s$ obtained at 34.5 MHz is believed to correspond to γ -phase $TiFe_{0.79}Mn_{0.15}H_2$. The NMR techniques are not sufficiently sensitive to produce signals as large as were detected at 34.5 MHz for sample F from a β -phase component whose presence cannot be observed by x-ray diffraction. Although the discrepancy for the T_2 values has not been resolved, we believe that it is primarily caused by experimental limitations.

Spin echo measurements of T_2 have been performed on most of the available $TiFeH_x$ samples. The results obtained at 34.5 MHz and 15 MHz are shown in Figures 6 and 7, respectively. The T_2 values are observed to be essentially constant below the temperature (T_{MN}) where motional narrowing begins and the hydrogen diffusion rate becomes sufficient to start reducing the rigid-lattice dipolar spin interactions¹⁸. If the echo decays below T_{MN} exhibit gaussian time dependence, the dipolar second moment (M_{2D}) can be obtained from the T_2

values by the relation

$$M_{2D} = 2/(\gamma_H T_2^2)^2 \quad (3)$$

where γ_H is the proton gyromagnetic ratio. Experimental T_{MN} and M_{2D} values for β and γ phase $TiFeH_x$ are summarized in Table II. When the locations of the metal atoms have been determined for the $TiFeH_x$ phases, it should be possible to deduce¹⁸ the interstitial sites occupied by the hydrogen atoms from these proton M_{2D} values. However, the M_{2D} data can only be regarded as empirical parameters, at the present, until the $TiFeH_x$ crystal structures are known. Nevertheless, a significant difference in M_{2D} is observed for the β -phase samples A and D and the γ -phase samples B and E, which is consistent with different arrangements of the hydrogen atoms in these two phases. The rather small M_{2D} value for sample F is unexpected since the x-ray studies described previously indicated only the γ -phase is present in this sample. Although this may be a manifestation of the experimental problems in the spin echo techniques, which was discussed above, assessments of the M_{2D} values must await future evaluation of the crystal structures. When the β -phase is predominant, T_{MN} is about 350(10)K and is independent of resonance frequency or exact composition. However, the T_{MN} for the γ -phase samples E and F actually correspond to transformations to β -phase diffusion behavior, as described in more detail later in this paper.

The spin echo measurements provide insight into the hydrogen diffusion behavior of the $TiFeH_x$ phases. The T_2^{-1} data above T_{MN} can be represented by an Arrhenius equation to deduce the diffusion activation energy E_a . The experimental E_a values are presented in Table II. The T_2^2 data in Figure 6 were obtained by heating sealed sample tubes. Shortly after completing the T_2^2 measurements at 434K sample E violently decomposed. A similar sudden hydrogen loss has been observed¹¹ at 433K on a predominantly β -phase sample. A rapid release of hydrogen gas at an elevated temperature (T_{loss}) is not

surprising since the equilibrium dissociation pressures for the TiFeH_x phases^{1,3} are above one atmosphere at room temperature. The oxygen stabilization technique¹ is only effective as long as the surface oxide film can impede the hydrogen escape. As the temperature is raised, the permeation rate through the surface film increases until rapid hydrogen release occurs. Since T_{loss} is apparently less than $\sim 435\text{K}$ for TiFeH_x and motional narrowing does not begin until at least $\sim 350\text{K}$, only a small temperature range is available to determine E_a from the T_2 spin echo measurements. Thus, the accuracy of the E_a values can be rather limited. Furthermore, slow release of hydrogen was observed for samples C and G during measurements at 15 MHz. Motional narrowing began near $\sim 340\text{K}$ when these β -phase samples were initially heated in an open system; however, above $\sim 410\text{K}$ the T_2 values deviated from the Arrhenius curve as shown in Figure 7. This change is believed to be caused by a partial hydrogen loss. The subsequent T_2 data for sample C (i.e., mixed $\alpha+\beta$ phases) were shifted to lower temperatures (see Figure 7). Hydrogen loss was later confirmed by x-ray analysis of this sample when some α -phase TiFe was detected. However, identical E_a values were obtained for sample C before and after the hydrogen loss indicating the spin echo measurements were monitoring β -phase diffusion in both cases. Figure 7 includes the earlier¹¹ preliminary T_2 data on a mixed-phase (but mainly β -monohydride) TiFeH_x sample. As previously reported¹¹, this data yields an E_a of $\sim 0.3\text{ eV}$ in good agreement with the results in Table II for the β -phase samples. Results on the mixed β - γ phase sample G (i.e., the initially γ -phase $\text{TiFe}_{0.79}\text{Mn}_{0.15}\text{H}_2$ sample F which experienced some hydrogen loss above 400K as described previously in this paper) are also included in Figure 7. The T_2 data for this sample is consistent with the other β -phase data as shown in Figure 7 and Table II.

DISCUSSION

A comprehensive evaluation of the TiFeH_x system from NMR measurements has been hampered by the lack of important physical properties such as crystal structures for the β and γ phases and phase compositions at elevated temperatures for $x > 1.5$. Nevertheless, some insight into the electronic structures and hydrogen diffusion behavior has been obtained. The most reliable parameters obtained during the present NMR studies are summarized in Table III. During the present discussions the partial substitution of Mn for Fe will be assumed to have little influence on the composition of the β and γ TiFeH_x phases. This view is supported by previous hydride formation and metallurgical studies⁵⁻⁷ as well as the x-ray measurements conducted in conjunction with the present NMR investigations.

The proton $T_{1\rho}$ can be approximately related^{19,20} to the density of electronic states at the Fermi surface $N_e(E_f)$ through the relation

$$(T_{1\rho}T)^{-1} = C_e N_e(E_f)^2 \quad (4)$$

where C_e is constant within a nuclear enhancement factor. The $T_{1\rho}T$ values in Table III for β and γ phase TiFeH_x are a factor of 10-30 times smaller than $T_{1\rho}T$ for the TiH_x ^{20,21} and $\text{Ti}_{1-y}\text{Nb}_y\text{H}_x$ ²² systems. This implies a significantly higher density of states at the Fermi surface in TiFeH_x , as sampled at the hydrogen site. Furthermore, $T_{1\rho}T$ differs by nearly a factor of two between the β and γ TiFeH_x phases indicating a difference in electronic structure. The change in $T_{1\rho}T$ observed near 260K for the β -phase samples serve to increase this difference and may reflect those contributions suggested by Korn²⁰ for TiH_x . Since the crystal structures^{21,22} of TiH_x and $\text{Ti}_{1-y}\text{Nb}_y\text{H}_x$ are not equivalent to the TiFeH_x phases¹, detailed comparisons of electronic structures are not possible. Nevertheless, such large differences in $T_{1\rho}T$ may be related to hydride stability and chemical bond

formation. Within the TiFeH_x system, the increase of T_1T for the γ -phase may correlate with a higher dissociation pressure at constant temperature. This idea is supported by the T_1T data for γ -phase $\text{TiFe}_{0.79}\text{Mn}_{0.15}\text{H}_2$ (sample F) where its T_1T value is $\sim 75\%$ of the T_1T value for the γ -phase TiFeH_x samples. Reilly and Johnson⁵ have found that Mn substitution significantly reduces the equilibrium pressures. However, further investigations on TiFeH_x related systems are required to evaluate this correlation between decreasing hydride phase stability and reduction in $N_e(E_f)$.

The proton spin echo measurements have clearly established the hydrogen diffusion behavior in the β -monohydride phase. Motional narrowing begins at 350(10)K with an E_a of 0.26(2) eV. It is possible to obtain an order of magnitude estimate of the hydrogen diffusion constant D in β -phase TiFeH_1 using the equation¹⁸

$$D = \frac{\langle \lambda^2 \rangle}{6\tau_c} \quad (5)$$

where $\langle \lambda^2 \rangle$ is the mean-squared jump distance (i.e., λ is assumed to be the proton separation distance r_{HH}) and τ_c is the diffusion correlation time. In the limit $\tau_c < M_{2d}^{1/2}$, τ_c obeys¹⁸

$$\tau_c^{-1} = \gamma_H^2 M_{2d} T^2. \quad (6)$$

Because the crystal structure of the β -monohydride has not been determined, r_{HH} (hence, λ) are unknown. An estimate of r_{HH} is possible using the van Vleck moment analysis²³

$$M_{2D} = C_I \sum_i r_i^{-6} \simeq \frac{8.402 C_I}{r_{HH}^6} \quad (7)$$

where C_I is a constant, the summation is over all protons, and the protons in $\beta\text{-TiFeH}_{1.0}$ are assumed to form a simple cubic unit cell of length r_{HH} . Although the M_{2D} is sensitive to actual arrangements of protons in the crystal lattice, the approximation in equation 7 is valid within a factor of two or

three for any reasonable structure. Using $T_2 = 114 \mu\text{s}$ at 413K for sample A and a calculated r_{HH} of 3.5×10^{-8} cm from equation 7 and the β -phase M_2D in Table I, a value of $D(413\text{K}) = 3 \times 10^{-11}$ cm^2/s is obtained. Assuming Arrhenius behavior, $D = D_0 \exp(-E_a/kT)$, with $E_a = 0.26$ eV, the hydrogen diffusion constant for $\text{TiFeH}_{1.0}$ at 300K is $\sim 10^{-13}$ cm^2/s . This value should be reliable within an order of magnitude and compares well with 300K diffusion constants between 2.2×10^{-12} cm^2/s and 2.7×10^{-13} cm^2/s for TiH_x compositions¹⁹ with x between 1.6 and 1.95. The diffusion behavior in β -phase TiFeH_x is also consistent with recent NMR studies on other titanium-based ternary hydrides^{22,24}. The observed kinetics of the charging-discharging of TiFe hydrogen storage systems and inelastic neutron scattering by Lebsanft, et al⁹ gives an upper limit of $D \lesssim 10^{-8}$ cm^2/s at 343K, which is $\sim 10^4$ times larger than the D implied by the present NMR studies. Although our values are an order of magnitude estimate, they are believed to center on a better magnitude than the Lebsanft, et al upper limit. Extensive microcracking of the TiFe particles occurs^{6,7,9} during the activation process with grain sizes down to $\sim 1 \mu\text{m}$. In addition, high dislocation densities can also be expected and these can also provide surfaces for reaction with hydrogen gas. Hence, accurate estimates of the sizes of activated TiFe particles, needed to derive D from the charging-discharging times, can be difficult. Also, one deals with the α , β , and γ phases simultaneously in such an analysis. The neutron scattering data give strictly a lower limit of diffusion required for line-width broadening to be observable and do not point to an actual order of magnitude. With a sufficient effective surface area, a D of $\sim 10^{-12}$ cm^2/s would be adequate for the observed^{2,9} charging-discharging time constants, on the order of a few minutes.

Slower hydrogen diffusion is indicated for the γ -phase E and F samples by the absence of motional narrowing before reaching the change to β -phase

behavior at $\sim 390\text{K}$. This is confirmed by the $T_{1\rho}$ data for sample F which yields an activation energy of $0.80(5)$ eV below $\sim 380\text{K}$. A T_2 increase was observed above 390K for sample E (see Figure 6); however, the $E_a = 0.25(1)$ from T_2 measurements above 400K is suspiciously close to the β -phase E_a value. As noted previously in this paper, spin echo measurements on sample F after heating above $\sim 380\text{K}$ are also consistent with the β -phase diffusion characteristics (see sample G in Table II). There are two possible explanations for these observations: (1) the γ -phase dihydride goes through a phase transition to the β -phase near $\sim 390\text{K}$, which is perhaps a critical temperature that would close the $\beta+\gamma$ phase region in Figure 1; and (2) some hydrogen is released from the γ -phase sample above $\sim 390\text{K}$ which results in the formation of a β - γ phase mixture. Both factors may be partially responsible for the motional narrowing of T_2 for the γ -phase samples. Certainly, evidence for some hydrogen loss exists for both γ -phase samples. The violent decomposition of sample E at 434K must have been caused by hydrogen gas pressure in the sealed sample tube. Without a better understanding of the high composition phase diagram above $\sim 350\text{K}$, a reliable assessment of the hydrogen diffusion behavior in these TiFeH_x samples is not possible. Future NMR experiments on γ -phase TiFeH_x samples should be performed on apparatus with the capability of maintaining high pressure hydrogen gas to inhibit decomposition.

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Table I - Properties of starting alloys used in preparing hydrides

Alloy Composition	Source	Oxygen Content (w ppm)	Lattice Constant a(A)
$\text{Ti}_{0.98}\text{Fe}_{1.02}$	Alfa-Ventron	2710	2.975
$\text{Ti}_{1.04}\text{Fe}_{0.96}$	N.B.S.	----	2.980
$\text{Ti}_{1.0}\text{Fe}_{0.79}\text{Mn}_{0.15}$	International Nickel	830	2.979

Table II - Summary of TiFeH_x and $\text{TiFe}_{0.79}\text{Mn}_{0.15}\text{H}_x$ samples including parameters derived from proton NMR measurements

Sample	Alloy	Hydrogen content(x)	Predominant phase	M_{2D}^e (gauss ²)	$T_1 \cdot T$ (s K)	T_{MN} (K)	E_a (eV)
A	$\text{Ti}_{0.98}\text{Fe}_{1.02}$	1.03	β	1.60	3.0(3)	360	0.26(1)
B	$\text{Ti}_{0.98}\text{Fe}_{1.02}$	1.70	γ	2.16	5.6(4)	---	---
C	$\text{Ti}_{1.04}\text{Fe}_{0.96}$	$\sim 1^a$	β (pure)	----	---	340	0.26(1)
D	$\text{Ti}_{1.04}\text{Fe}_{0.96}$	1.15	β	1.63	3.0(2)	360	---
E	$\text{Ti}_{1.04}\text{Fe}_{0.96}$	1.98	γ (pure)	2.19	5.5(3)	390 ^d	0.25(1) ^d
F	$\text{TiFe}_{0.79}\text{Mn}_{0.15}$	2.01	γ (pure)	1.76	4.2(5)	not observed	0.80(5) ^c
G	$\text{TiFe}_{0.79}\text{Mn}_{0.15}$	unknown ^b	$\beta + \gamma$	----	---	350	0.32(2) ^d

^aInitially, $x \approx 2$ and x-ray diffraction indicated single γ -phase ($a_0 = 6.61 \text{ \AA}$); however, at time of NMR measurements (approximately one year after synthesis) x-ray indicated pure β -phase.

^bAfter sample F had been heated above $\sim 390\text{K}$ and release of some hydrogen gas observed.

^cDetermined from T_{1D} data corrected as described in text.

^dAttributed to β -phase as explained in text.

^eFrom spin echo measurements at 34.5 MHz.

Table III - Most reliable NMR parameters for TiFeH_x and TiFe_{1-y}Mn_yH_x phases

Alloy	Phase	$T_1 \cdot T$ (s K)	E_a (eV)	T_{MN} (K)
TiFe	β	3.0(3)	0.26(2)	350(10)
TiFe	γ	5.5(4)	---	---
TiFe _{0.79} Mn _{0.15}	β	---	0.32(4)	350(10)
TiFe _{0.79} Mn _{0.15}	γ	4.2(5)	0.80(5)	$\sim 430^a$

^aDeduced by extrapolating $\ln T_1 D^{-1}$ (Figure 5) to $\sim 10\mu s$, where diffusion is expected to commence.

LIST OF FIGURES

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- Figure 6 Temperature dependence of the proton T_2 relaxation time (34.5 MHz) for β and γ phase TiFeH_x samples A, and E.

Figure 7. Inverse T_2^{-1} relaxation times versus T^{-1} obtained at 15 MHz for β -phase TiFeH_x . (Δ) sample C during initial heating cycle; upon heating this sample to 414K, the datum point in the shaded area was observed, which does not lie on the Arrhenius plot. This was interpreted in terms of loss of some hydrogen between this and the previous point. Returning to lower temperatures, the triangles with point down (∇) were obtained varying temperatures both up and down. Room temperature x-ray analysis (a few days later) showed that indeed hydrogen had been lost with roughly equal amounts of α and β present. Yet the slope, E_A , had not changed. ($\bullet$) sample G after hydrogen loss above $\sim 390\text{K}$, determined to be $\beta+\gamma$ phase mixture by subsequent room temperature x-ray diffraction; ($\circ$) ($\beta+\gamma$) mixed-phase sample from Ref. 11.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7