Composition-Dependent Hydrogen Motion in a Random Alloy, $V_xNb_{1-x}H_{0.2}$: From Localized Motion at V Atoms to Long-Range Hydrogen Diffusion

L. Lichty, J. Shinar, R. G. Barnes, D. R. Torgeson, and D. T. Peterson
Ames Laboratory–U.S. Department of Energy, and Departments of Physics and Materials Science and Engineering, Iowa State University, Ames, Iowa 50011

(Received 15 July 1985)

Proton spin-lattice relaxation times (T_1) measured for the first time across a random transition-metal alloy system, $V_xNb_{1-x}H_{0.2}$, from 100 to 700 K reveal (a) a suppression of hydride phase precipitation at low temperatures accompanied by enhanced retention of hydrogen in the solid-solution (α) phase compared to pure V or Nb, (b) hydrogen motion in the α phase at intermediate compositions governed by a distribution of activation energies, and (c) a transition to short, almost temperature-independent, T_1 behavior in α-$V_{0.1}Nb_{0.9}H_{0.2}$ consistent with localized hydrogen motion around attracting V atoms.

PACS numbers: 66.30.Jt, 71.20.+c, 76.60.Es

Several experimental and theoretical studies have addressed the structural and dynamical aspects of hydrogen associated with dilute interstitial (e.g., N and O) or substitutional (e.g., V and Mo) impurities in Nb.[1-3] Yet little is known about the dynamical behavior of hydrogen in the Nb lattice containing a *dense* concentration of V atoms. In particular, no measurements of the low-temperature proton NMR relaxation time, a powerful microscopic probe of structural and dynamical properties, have yet been reported on *any* concentration x of V in $V_xNb_{1-x}H_y$. This Letter describes the results and interpretation of such measurements in $V_xNb_{1-x}H_y$, $x=0.1$, 0.25, 0.5, 0.75, and 0.9, $y \approx 0.2$.

The V-Nb alloys were prepared by arc melting of pure metals from Wah Chang Corporation. The total interstitial concentration in V was 0.06 at.% and in Nb was 0.11 at.% with oxygen being the principal interstitial. A single portion of each alloy was charged with a measured amount of H_2 from the gas phase at 500 °C. The charged massive alloys were ground in a diamond mortar to 200-mesh powder.

The proton T_1 measurements at 12.2 and 40.0 MHz were made by use of the inversion-recovery sequence and digital signal averaging with a phase-coherent pulsed NMR spectrometer constructed at the Ames Laboratory. T_1 values were determined from least-squares fits to the complete magnetization recovery curves. In those temperature ranges in which proton signals arise from both solid-solution and hydride phases, the T_1 values were extracted with the aid of measurements on different portions of the free induction decay.

The results of the T_1 measurements are shown in Figs. 1(a) and 2. Not shown are T_1 data for $x=0.9$ (which are similar to those for $x=0.1$) and for $x=0.75$ (similar to $x=0.25$). Whereas the precipitation of the hydride phase below about 220 K for $x=0.25$ and 0.75, and below about 300 K for $x=0.1$ and 0.9, could clearly be detected by the appearance of a second relaxation time, no precipitated hydride phase could be detected in $V_{0.5}Nb_{0.5}H_{0.2}$ down to 100 K. The unambiguous detection of the α-phase proton NMR in all the samples down to at least 110 K clearly confirms the enhanced retention of hydrogen at low temperatures in the α phase of all these alloys as compared to

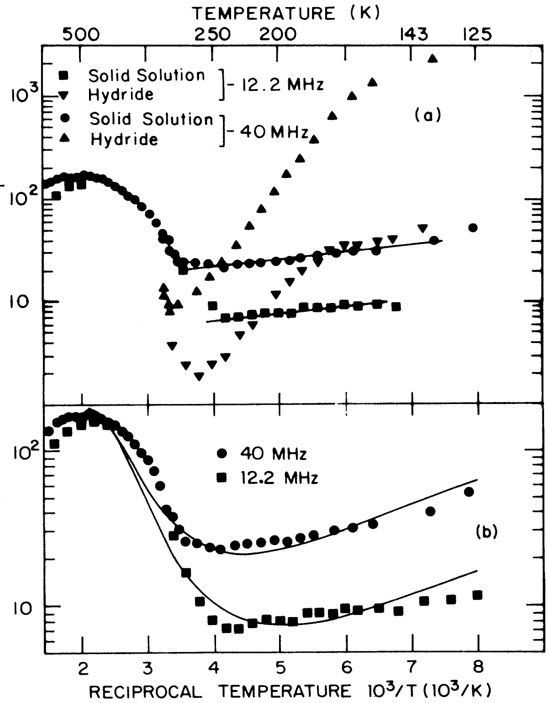

FIG. 1. (a) Proton spin-lattice relaxation time T_1 in $V_{0.1}Nb_{0.9}H_{0.19}$ at 40 and 12.2 MHz. Note the equal, very low slopes of $\log T_1$ vs $1/T$ at the two frequencies for $T \lesssim 250$ K in the solid-solution phase. (b) Solid-solution phase data as in (a) with best fit (solid lines) of activation-energy distribution model [Eq. (1) of text].

pure Nb or V.[3,4] A quantitative determination of the $V_xNb_{1-x}H_{0.2}$ phase diagram by means of the ^{51}V and ^{93}Nb NMR is presently under way. Since the structure of the alloy hydrides is not known, the analysis of the T_1 measurements in these phases will be deferred to a later work. In the following, we focus attention on the solid-solution (α) phase results.

In these alloys containing a low hydrogen concentration and metal nuclei (^{51}V and ^{93}Nb) with substantial nuclear moments, the proton spin-lattice relaxation rate $(T_{1d})^{-1}$, in a powder sample, due to the fluctuating dipolar fields resulting from the hydrogen motion is given by[5]

$$T_{1d}^{-1}=\tfrac{3}{2}\gamma_I^2C_I[J(\omega_I)+4J(2\omega_I)]+\tfrac{1}{2}\gamma_I^2C_S[J(\omega_I-\omega_S)+3J(\omega_I)+6J(\omega_I+\omega_S)], \tag{1}$$

with

$$J(\omega)=\frac{4}{15}\frac{\tau_c}{1+\omega^2\tau_c^2}\sum_i r_i^{-6}, \tag{2}$$

where I refers to the proton, S refers to the metal nucleus, $C_I=\gamma_I^2\hbar^2I(I+1)$, and $C_S=\gamma_S^2\hbar^2S(S+1)$, ω is the resonance (Larmor) frequency, and γ the nuclear magnetogyric ratio. The first two terms in Eq. (1) give the proton-proton (II) contribution and the last three terms the proton-metal (IS) contribution to the rate. The sum in Eq. (2) extends over all occupied H lattice sites from a generic H site in the II terms and over all metal lattice sites in the IS terms. The Lorentzian spectral density $J(\omega)$ is the Fourier transform of the correlation function of the fluctuating dipolar fields, assumed to decay as a simple exponential.[6] The correlation time τ_c for the dipolar fluctuations is related to the hydrogen hopping rate ν by $\nu=(2\tau_c)^{-1}$ in the proton-proton terms and by $\nu=\tau_c^{-1}$ in the proton-metal terms. Equations (1) and (2) predict a symmetric minimum in a plot of $\log T_{1d}$ vs $1/T$ with T_{1d} independent of ω_I on the high-temperature side of the minimum and $\propto\omega_I^2$ on the low-temperature side. In metallic hydrides proton spins are also weakly relaxed at a rate $(T_{1e})^{-1}$ by their interaction with the conduction electrons so that the measured rate is $(T_1)^{-1}=(T_{1e})^{-1}+(T_{1d})^{-1}$.[5] This contribution has been taken into account in the following analyses of experimental data.

As shown in Figs. 1(a) and 2 for three of the samples studied, the $\log T_1$ vs $1/T$ plots are *not* symmetric about the T_1 minimum, the slope on the low-temperature side being always substantially weaker than that on the high-temperature side. Also, in the intermediate compositions shown in Fig. 2 there occurs a pronounced frequency dependence of T_1 at temperatures well above the T_1 minimum. However, this behavior is not seen in the $V_{0.1}Nb_{0.9}$ alloy [Fig. 1(a)] where the T_1 values at the two frequencies coincide above the T_1 minimum (most of the 12.2-MHz data points in this region are omitted for clarity).

Asymmetry of the kind seen in Fig. 2 has been observed in many, usually disordered, metal-hydrogen systems[7,8] and solid electrolytes[9] and interpreted in two different ways. One model[7] assumes that the H motion is characterized by a single correlation time τ_c at every temperature so that Eqs. (1) and (2) may be applied directly. If we fix the lattice constants of the alloys so that the calculated lattice sums in Eq. (2) cause Eq. (1) to yield the observed values of the minimum T_{1d}, $T_{1d,\min}$ (assuming that the closest proton-proton approach is the third-nearest neighbor position in the tetrahedral interstitial site sublattice[10]), the value of the hydrogen hopping rate ν at each temperature can be obtained. However, the values of $\nu(T)$ extracted from T_1 measured at different ω_I's should coincide. Yet the results of this procedure yield ω_I-dependent hopping rates as illustrated in Fig. 3 for the $V_{0.5}Nb_{0.5}H_{0.21}$ sample (although the hopping

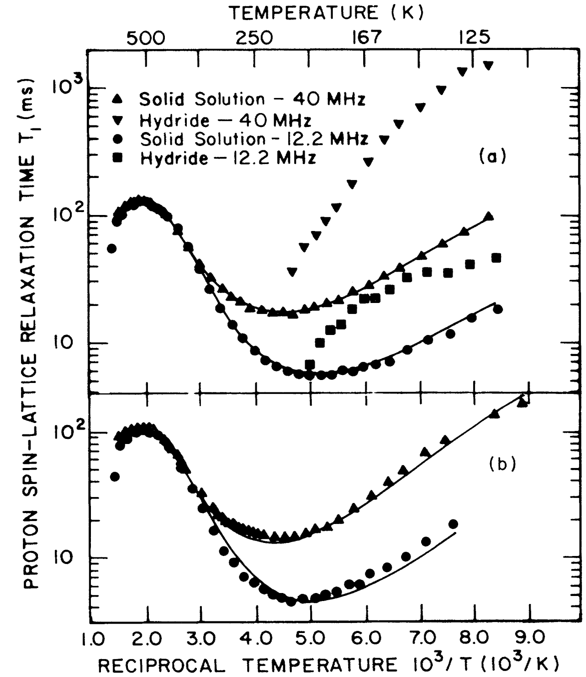

FIG. 2. Proton spin-lattice relaxation times T_1 in (a) $V_{0.25}Nb_{0.75}H_{0.231}$ and (b) $V_{0.5}Nb_{0.5}H_{0.21}$. Note the similar behavior of T_1 in the α phase in all compositions and the undetected precipitation of the hydride phase in $V_{0.5}Nb_{0.5}H_{0.21}$. The solid lines are the best fits of the activation-energy distribution model [Eq. (1) of text] to the data.

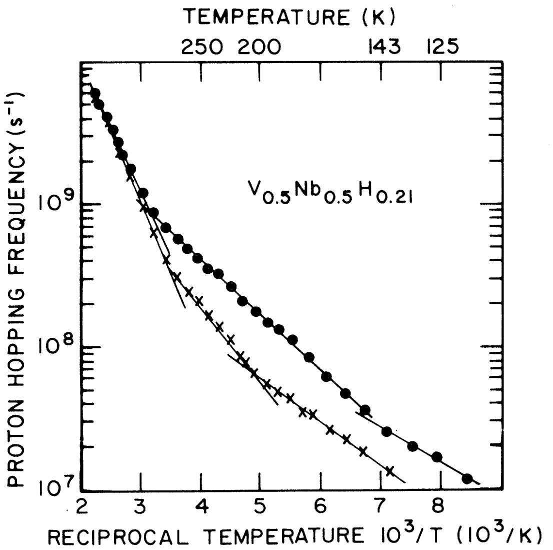

FIG. 3. The values of the hopping rates in $V_{0.5}Nb_{0.5}H_{0.21}$ as extracted from the Bloembergen-Purcell-Pound equations. Note the agreement of the values extracted from the two Larmor frequencies at high temperature and the large difference in values at lower temperatures.

rates coincide at high temperatures, as expected). Similar ω_I-dependent hopping rates were obtained for $x = 0.25$ and 0.75, through use of this analysis. In addition, the observed value of $T_{1\,\mathrm{min}}$ in the intermediate-composition samples could only be reproduced by our setting the lattice constant $a_0 = 4.10$, 3.96, and 4.0 Å for $x = 0.25$, 0.5, and 0.75, respectively. These values are much larger than the measured values for the hydrogen-free alloys, 3.24, 3.177, and 3.106 Å, respectively.[11] Since the strain field created by a hydrogen atom in the pure V (Nb) lattice enlarges the tetrahedral site nearest-neighbor metal distance by only 12.5% (8.5%) (see Behr *et al.*,[12] and references therein) this discrepancy is large. It therefore appears that this model is not applicable to α-phase $V_xNb_{1-x}H_y$.

The second model[8,9] assumes that the motion of hydrogen atoms in a substitutional alloy or structurally disordered lattice is governed by a *distribution* of activation energies, E_a. The spin-lattice relaxation rate $(T_{1d})^{-1}$ of protons undergoing such motion has been derived previously,[8,9] and is given by

$$T_{1d}^{-1} = \int dE_a\, G(E_a)\, T_{10}^{-1}(E_a, \nu_0), \tag{3}$$

where T_{10}^{-1} is given by Eqs. (1) and (2), $G(E_a)$ is a distribution function, and ν_0 is the prefactor in the Arrhenius relation. In the fitting of this model to the measured values of T_1 a Gaussian distribution function was chosen and the Zener relation[13] $\nu_0 = \nu_{00}\exp(\beta E_a)$ between ν_0 and E_a was adopted. This relation is observed in many disordered systems[13,14] and is expected when lattice strain fields are dominant in determining E_a. The value of β $(=5\times10^{-4}\ \mathrm{K}^{-1})$ used in all cases is of the same order as observed in cases of chemical diffusion of C, N, and O in transition metals.[13] This value is so small as to render the resulting prefactor ν_0 almost independent of E_a.

The results of this fitting procedure yield the solid lines in Fig. 2. The values of the fitting parameters were closely similar in all cases; the average $E_{a_0} = 140 \pm 5$ meV, the distribution width $\Delta E_a = 33 \pm 3$ meV, and $\nu_{00} = (2.4 \pm 0.1)\times10^{11}\ \mathrm{s}^{-1}$. The Korringa product $T_{1e}T = 125$, 110, and 85 s·K, and $a_0 = 3.73$, 3.6, and 3.70 Å, for $x = 0.25$, 0.50, 0.75, respectively. Note the excellent agreement between this model and the experimental results, in contrast to the disagreement with the previous model (Fig. 3). The values of a_0 are also significantly lower than those employed in the latter case. These values are, however, 15% larger than those observed in the hydrogen-free alloys, and therefore still somewhat larger than expected from the lattice dilatation effects of H in pure V or Nb.[12]

In contrast to the proton relaxation rates in the mid-range compositions, the results in the 10% V and 10% Nb compositions cannot be modeled by a distribution of activation energies. The large asymmetry between the high- and low-temperature $\log T_1$ behavior requires a broad distribution of activation energies. As a consequence, the frequency dependence of T_1 will persist to relatively high temperatures, considerably above the T_1 minimum, whereas this is not the case for the experimental data. These features are clearly evident in Fig. 1(b) which shows the best-fit distribution of activation energies to the α-phase $V_{0.1}Nb_{0.9}H_{0.19}$ data with $E_{a_0} = 172$ meV, $\Delta E_a = 60$ meV, $\nu_{00} = 2.0\times10^{12}\ \mathrm{s}^{-1}$, $\beta = 5\times10^{-4}\ \mathrm{K}^{-1}$, $T_{1e}T = 125$ s·K, and $a_0 = 3.68$ Å. (The data points for the hydride phase have been omitted for clarity.) In sharp contrast, this persistence of the frequency dependence of both the measured and calculated points to high temperatures is obvious in the mid-range compositions (Fig. 2).

We conclude that the high- and low-temperature branches of T_1 in $V_{0.1}Nb_{0.9}H_{0.19}$ reflect different kinds of proton motion. Although it is now known that low concentrations of V do not totally suppress precipitation of the hydride phase in Nb,[2] previous results do indicate that V centers are attractive potentials for H in Nb.[2,3] The present T_1 data for α-phase $V_{0.1}Nb_{0.9}H_{0.19}$ therefore suggest a transition from lattice motion at high temperatures ($\gtrsim 290$ K) to "localized" motion about the V atoms at low temperatures ($\lesssim 270$ K), concurrent with precipitation of the hydride phase. Since even at 10% V concentration, the probability of one V atom having another V as nearest neighbor is 55%, such localized motion might well involve several lattice sites.

The values of T_1 in the α phase of $V_{0.1}Nb_{0.9}H_{0.19}$ [Fig. 1(a)] below 250 K are short, almost temperature independent, but frequency dependent. In view of the failure of the activation-energy distribution model, we conclude that the slope of the low-temperature data [solid lines in Fig. 1(a)] represents an apparent activation energy $E_a^x = 14 \pm 1.5$ meV. Although the values of the slope at $\omega_I = 40$ and 12.2 MHz are equal, the frequency dependence is weaker ($\propto \omega_I$) than expected ($\propto \omega_I^2$) on the basis of Eq. (1). In any case, this value of E_a^x is about one-fifth the low-temperature (<220 K) diffusional activation energy of H in pure Nb (68 meV).[15] Moreover, it compares favorably with an estimated value, $E_a^x = 26$ meV, based in part on the strength of the elastic interaction of the proton with the metal lattice.[16] Therefore, we conclude that the observed relaxation is due to localized hydrogen motion (presumably activated tunneling) among sites adjacent to V impurities.

In summary, the behavior of the proton spin-lattice relaxation time T_1 in the intermediate composition range, $0.25 \leq x \leq 0.75$, of α-phase $V_xNb_{1-x}H_{0.2}$ alloys differs significantly from that in either the vanadium-rich or niobium-rich compositions. In this composition range, wherein both V and Nb atoms form a (albeit random) macroscopic network, trapping effects are not evident, and the data are well represented by a distribution of activation energies. In contrast, the behavior of T_1 in $V_{0.1}Nb_{0.9}H_{0.19}$ cannot be represented by an activation-energy distribution, and we conclude that a transition occurs from long-range lattice motion ($T \gtrsim 290$ K) to localized motion (activated tunneling) of hydrogen between states adjacent to V atoms ($T \lesssim 270$ K) with an activation energy of 14 meV, significantly lower than that in pure Nb.

The authors are indebted to A. Johnson for careful preparation of the alloy samples. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences.

[1] H. Wipf and K. Neumaier, in *Electronic Structure and Properties of Hydrogen in Metals,* Proceedings of the NATO Symposium, Richmond, Virginia, 1982, edited by P. Jena and C. B. Satterthwaite (Plenum, New York, 1983), Vol. 6, p. 485, and references therein.

[2] A. Magerl *et al.,* Phys. Rev. B **27**, 927 (1983), and references therein.

[3] T. Matsumoto, Y. Sasaki, and M. Hihara, J. Phys. Chem. Solids **36**, 215 (1975); T. Matsumoto, J. Phys. Soc. Jpn. **42**, 1583 (1977).

[4] T. Schober and H. Wenzl, in *Hydrogen in Metals II,* edited by G. Alefeld and J. Völkl (Springer-Verlag, New York, 1978), p. 15.

[5] R. M. Cotts, Ber. Bunsenges. Phys. Chem. **76**, 760 (1972).

[6] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948); A. Abragam, *Principles of Nuclear Magnetism* (Oxford Univ. Press, Oxford, England, 1961).

[7] R. C. Bowman *et al.,* Phys. Rev. B **26**, 6362 (1982), and Solid State Commun. **47**, 779 (1983).

[8] J. Shinar, D. Davidov, and D. Shaltiel, Phys. Rev. B **30**, 6331 (1984).

[9] R. E. Walstedt *et al.,* Phys. Rev. B **15**, 3442 (1977).

[10] If the protons are allowed to approach one another closer than third-nearest neighbors, the value of a_0 required to reproduce $T_{1\,\mathrm{min}}$ becomes unreasonably large. In addition, empirical models indicate that proton-proton distances do not fall below 2.1 Å in a metal lattice [see, e.g., A. C. Switendick, in *Hydrogen Energy, Part B,* edited by T. N. Veziroglu (Plenum, New York, 1978), p. 1029], which would exclude simultaneous occupation of first- and second-nearest neighbor tetrahedral sites.

[11] S. O. Nelson, Ph.D. thesis, Iowa State University, Ames, Iowa, 1982 (unpublished).

[12] H. Behr *et al.,* J. Phys. F **13**, L29 (1983).

[13] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949); C. Zener, J. Appl. Phys. **22**, 372 (1951); C. P. Flynn and A. M. Stoneham, Phys. Rev. B **1**, 3966 (1970).

[14] J. Shinar *et al.,* Solid State Commun. **37**, 175 (1981), and **40**, 645 (1981).

[15] J. Völkl and G. Alefeld, in *Hydrogen in Metals I,* edited by G. Alefeld and J. Völkl (Springer-Verlag, New York, 1978), p. 329.

[16] K. W. Kehr, Kernforschungsanlage, Jülich, Report No. JÜL-1211, 1975 (unpublished).