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# Anomalous proton spin-lattice relaxation at high temperatures in bcc transition-metal–hydrogen solid-solution systems

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We report anomalous behavior of the proton spin-lattice relaxation time $T_1$ at high temperatures (up to 1000 K) for hydrogen in solution in the bcc metals V, Nb, and Ta and in a Nb-V alloy. Besides the usual $T_1$ minimum at intermediate temperatures ($\sim$225 K) characterized by the mean dwell time for hopping, $\tau_d = \exp(E_a/k_BT)$, $T_1$ again decreases sharply at higher temperatures instead of returning to the value $T_{1e}$ determined by the conduction-electron contribution to $(T_1)^{-1}$. This decrease is well described by an additional contribution to $(T_1)^{-1}$ of the form $\exp(-U/k_BT)$, where $U$ is a phenomenological activation energy. We have also measured the temperature dependence of the hydrogen diffusion coefficient $D$ at high temperatures using an NMR stimulated-echo alternating pulsed-field-gradient technique. Within experimental error $D$ increases with temperature, $D \propto \exp(-E_a/k_BT)$, up to at least 820 K, where $D \gtrsim 10^{-4}$ cm$^2$/s. If a deviation from Arrhenius behavior occurs, it is toward higher $D$ at the highest temperatures. The $T_1$ and $D$ results can be described in terms of a model in which hydrogen motion at high temperatures is controlled by two characteristic times corresponding to mobile and immobile states. Two forms of this model are discussed; however, neither is completely satisfactory. One requires an unusual temperature dependence for the immobile state time, while the other predicts a frequency dependence for $T_1$ that is not observed.

## I. INTRODUCTION

Recent measurements of the proton ($^1$H) spin-lattice relaxation time $T_1$ in the fcc dihydride phases of Sc, Ti, Y, Zr, and La,[1] of the deuteron ($^2$D) $T_1$ in the dideuterides of Sc and Y[1] and of the $^{45}$Sc $T_1$ in scandium dihydrides and dideuterides[2] revealed an anomalous decrease in $T_1$ at high temperatures ($T \gtrsim 800$ K), corresponding to an *apparent* increase in the correlation time $\tau_c$ for hydrogen motion and a decrease in the hydrogen hopping rate $\tau_d^{-1}$. This behavior has been attributed[3] to strong repulsions at the saddle point of the jump path which increase with temperature as vibrational amplitudes increase, making it more difficult for the atom to move through the saddle at elevated temperatures. The model yields reasonable agreement with the $T_1$ measurements and is physically plausible for hydrogen motion in the nearly filled tetrahedral interstitial site sublattice in the fcc metal lattice. However, recent quasielastic neutron scattering experiments[4,5] on YH$_{1.98}$ at high temperatures have shown that hydrogen diffusion continues to increase, following essentially Arrhenius behavior up to 1100 K, making acceptance of the model difficult. Moreover, this model is not applicable in any event at low hydrogen concentrations when the fraction of interstitial sites occupied is small, particularly for hydrogen in the relatively open bcc lattice of the group V metals.

We report measurements of the temperature dependence of the proton ($^1$H) spin-lattice relaxation time $T_1$ in the bcc solid solution ($\alpha$) phases of the V-H, Nb-H, Ta-H, and Nb$_x$V$_{1-x}$-H systems at [H]/[$M$] ratios on the order of 0.2 to 0.3. In addition, the $T_1$ of the vanadium nucleus ($^{51}$V) in VH$_{0.20}$ was also measured over the same temperature range as the proton. The important feature of these measurements is they extend to higher temperature (up to 1000 K) than those reached in previous investigations. Measurements of the temperature dependence of the proton $T_1$ are usually interpreted to reflect, in particular, the temperature dependence of the correlation time $\tau_c$ for fluctuations in the dipolar field at the proton sites. In turn, $\tau_c$ normally reflects the temperature dependence of $\tau_d$, the mean dwell time for hydrogen diffusive hopping between interstitial sites in the host lattice. Thus, one expects $\tau_d$ and $\tau_c$ to decrease with increasing temperature according to the Arrhenius relation,

$$\tau_d = \tau_0 \exp(+E_a/k_BT) ,$$

where $\tau_0^{-1}$ is the jump attempt frequency and $E_a$ is the activation energy for hopping. Normally, at high temperatures, the dipolar $T_1 \propto \tau_d^{-1}$. In contrast to these expectations, the measurements reported here reveal that, in these bcc systems, the proton $T_1$ passes through a maximum value and decreases sharply again at high temperatures as in the dihydride systems.

Measurements of the hydrogen diffusion $D$ were also made on a $Nb_xV_{1-x}H_y$ sample over approximately the same temperature range using a stimulated echo alternating pulsed-field-gradient (SEAPFG) NMR technique.[6] Quasielastic neutron scattering measurements of $D$ have also been made on this sample,[4] and are in good agreement with the SEAPFG measurements. In sharp contrast to the behavior of $T_1$, $D$ increases with increasing temperature to the limit of the measurements (820 K). This finding strongly suggests that the behaviors of $T_1$ and $D$ at high temperatures are determined by different characteristic times. Such different times arise in so-called two-state models of diffusion in which the diffusing particle alternates between a "mobile" state for short periods of time and an "immobile" (or relaxed) state for longer periods during which diffusion does not occur. Fluctuations in the dipolar field at proton sites effective in causing spin-lattice relaxation occur with the characteristic time of the immobile state, whereas diffusion is controlled by the jump rate in the mobile state reduced by the fraction of time spent in the mobile state. The present experimental results along with previous quasielastic neutron scattering (QENS) measurements show the features characteristic of such a two-state model of hydrogen diffusion.

## II. EXPERIMENTAL ASPECTS

Samples were prepared in the Ames Laboratory Materials Preparation Center from highest-purity Ames Laboratory vanadium, niobium, and tantalum. Fine powders suitable for NMR measurements were sealed in quartz tubes under low inert-gas pressure. All handling operations were carried out in an inert-gas atmosphere glove box. The $T_1$ measurements themselves show the paramagnetic impurity content of the samples to be negligible at low temperatures so a paramagnetic contribution to the proton spin relaxation rate at high temperature can be ruled out.[7]

The $T_1$ measurements were made primarily at resonance frequencies of 12.2, 24, and 40 MHz with phase-coherent pulsed NMR spectrometers and associated instrumentation that have been described elsewhere.[7,8] Most of the measurements were made using the inversion recovery sequence, $180°$-$\tau$-$90°$, and sampling the free-induction decay (FID) following the $90°$ pulse. In the high-temperature region of interest, above the $\alpha+\beta$ two-phase region, single-exponential magnetization recoveries were obtained in all cases.

Hydrogen diffusion measurements were made on the $Nb_{0.75}V_{0.25}H_{0.23}$ sample over the temperature range from 375 to 825 K using an NMR stimulated spin-echo alternating pulsed-field-gradient technique[6] which significantly reduces the effects of sample-induced magnetic field gradients associated with the granular nature of NMR samples. The SEAPFG technique was tested on $^1H$ in $TaH_{0.73}$ with resulting diffusion coefficients in agreement with published values. In the SEAPFG experiment on H in $Nb_{0.75}V_{0.25}H_{0.23}$, diffusion times, $\delta t$, varied from 34 ms at the lower temperatures to about 5 ms at the highest temperatures with diffusion lengths, $(2D\,\delta t)^{1/2}$, varying between 4 and 10 $\mu$m, thus assuring long-range diffusion.

## III. RESULTS

In giving examples of the $T_1$ behavior, we begin with hydrogen in solution in an alloy, $\alpha$-$Nb_{0.75}V_{0.25}H_{0.23}$. Figure 1 shows the temperature dependence of the proton $T_1$ in the conventional form $\log_{10}T_1$ versus $1000/T$ at two resonance frequencies (12.2 and 40 MHz) for temperatures from 125 to 1000 K. In this alloy the hydride phase formation does not occur with decreasing $T$ until $\sim$215 K, as evidenced by the onset of a second proton resonance with a substantially longer $T_1$ (the 12.2-MHz hydride phase data appear somewhat anomalous because at this frequency the proton $T_1$ is depressed by cross relaxation to the $^{93}Nb$ spins). At this alloy composition and hydrogen concentration, most of the hydrogen remains in solid solution at low temperatures. It is possible to measure the proton $T_1$ in the alloy's $\alpha$ phase throughout the full temperature range from 5 to 1000 K. This is not possible for the unalloyed metals V, Nb, and Ta, as seen in Fig. 2. In $VH_{0.20}$ and $NbH_{0.21}$ the hydride phase precipitates at temperatures of $\sim$420 and 360 K, respectively, withdrawing essentially all of the hydrogen from the $\alpha$ phase. In $TaH_{0.20}$ this transition occurs at the right-hand edge of the figure and is not shown. Accordingly, the temperature dependence of the proton $T_1$ in the $\alpha$ phase can only be determined at temperatures above the hydride precipitation temperature. This presents severe difficulties for analysis of the measurements, as will be seen. In all cases, the strong turndown of the proton $T_1$

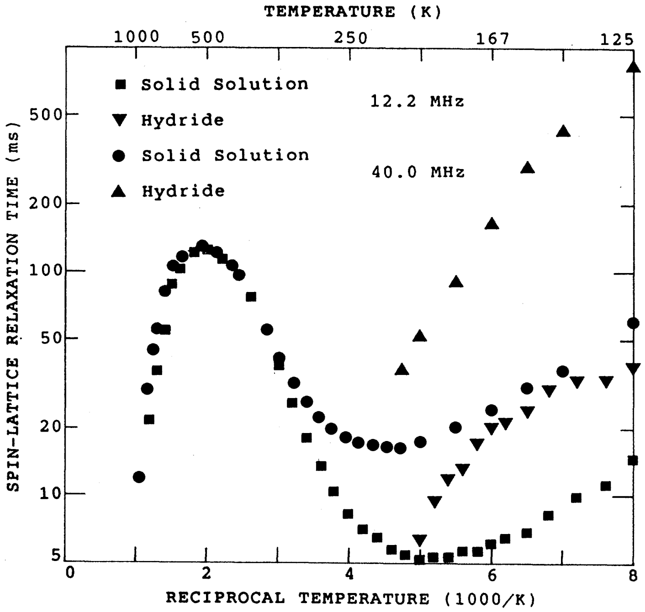

FIG. 1. Temperature dependence of the proton $T_1$ in $Nb_{0.75}V_{0.25}H_{0.23}$ over the temperature range 125–1000 K measured at resonance frequencies of 12.2 and 40 MHz. The hydride phase signal appears at temperatures below 215 K.

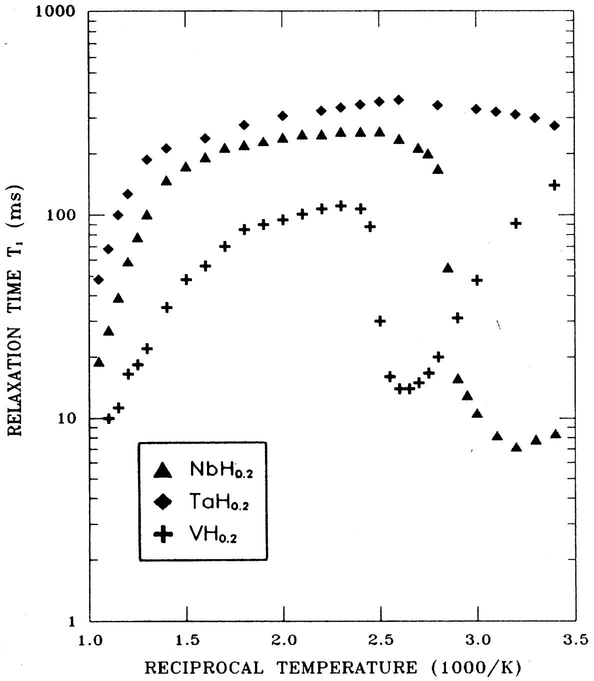

FIG. 2. Temperature dependence of the proton $T_1$ in $VH_{0.20}$, $NbH_{0.21}$, and $TaH_{0.20}$. The sharp changes in $T_1(T)$ in the vicinity of $10^3/K=2.8$ mark the $\alpha$-$\beta$ phase transition in the V-H and Nb-H systems. The same transition in the Ta-H system occurs at a lower temperature just off scale to the right.

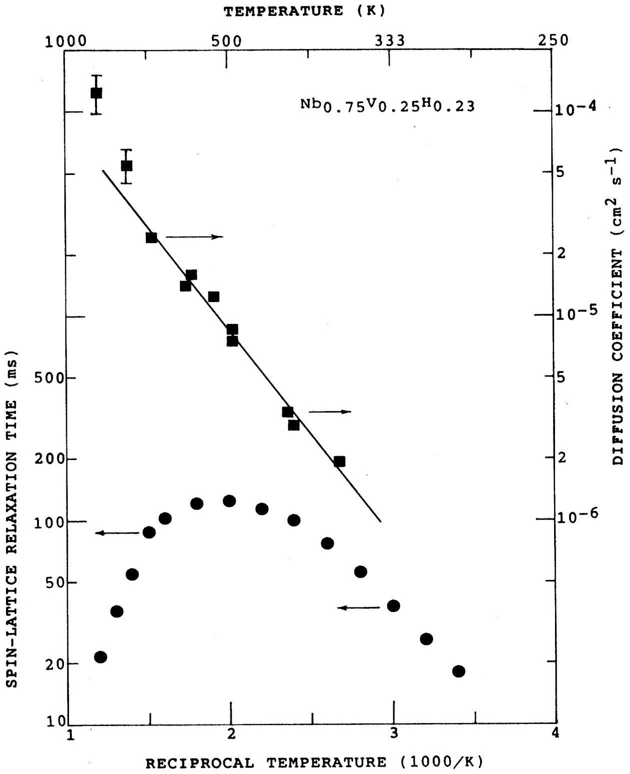

FIG. 3. Temperature dependence of the hydrogen diffusion coefficient $D$ in $Nb_{0.75}V_{0.25}H_{0.23}$ over the temperature range 370–820 K. For comparison and contrast, the $T_1$ data from Fig. 1 are also shown.

at high temperatures is quite evident.

The hydrogen diffusion coefficient $D$ results in the alloy sample are shown in Fig. 3. For comparison, the values of $T_1$ in the same temperature range are also shown. $D$ follows Arrhenius behavior closely up to 650 K and appears to increase more rapidly above that. The straight-line fit of $D=D_0\exp(-E_a/k_BT)$ to the data points between 370 and 650 K shown in Fig. 3 yields $E_a=0.20$ eV/atom and $D_0=8.6\times10^{-4}$ cm²/s. These values may be compared with the results of bulk diffusion measurements, over a temperature range 230–475 K for the same alloy composition,[9] which are $E_a=0.227$ eV/atom and $D_0=13\times10^{-4}$ cm²/s, extrapolated to zero hydrogen concentration.

The vanadium $^{51}V$ spin-lattice relaxation time temperature dependence in the $VH_{0.20}$ sample has also been measured, and the results are shown in Fig. 4. In this case, no anomalous behavior is seen. The data are fit satisfactorily by the conduction electron contribution to the relaxation only (see further below), as shown by the solid curve in the figure. This behavior contrasts sharply with $^{45}Sc$ in the scandium dihydrides and dideuterides, in which $T_1$ of $^{45}Sc$ also decreases at high temperatures. The marked difference in $T_1$ behavior in the two cases is a consequence of the much weaker conduction electron and stronger quadrupole (motional) contributions to the $^{45}Sc$ relaxation rate vis a vis that of $^{51}V$ (see Sec. VI).

## IV. THEORETICAL BACKGROUND

In the absence of paramagnetic impurity effects, the temperature dependence of the spin-lattice relaxation time $T_1$ of protons ($^1H$) in a metallic host lattice is expected to be accounted for by the sum of the conduction electron and diffusion modulated dipolar contributions $(T_{1e})^{-1}$ and $(T_{1d})^{-1}$, respectively, to the total relaxation rate

$$(T_1)^{-1}=(T_{1e})^{-1}+(T_{1d})^{-1} . \tag{1}$$

Here, $T_{1e}$ is expected to depend inversely on temperature according to the Korringa relation, $T_{1e}T=\text{constant}$, with the value of the constant depending on the electronic density of states at the Fermi level, $N(E_F)$.

For V, Nb, and their alloys, the diffusion modulated dipolar contribution is given by

$$(T_{1d})^{-1}=\frac{\gamma_I^2M_2^{\text{H-}M}}{2\omega_{\text{H}}}\left[\left[\frac{y}{1+fy^2}+\frac{3y}{1+y^2}+\frac{6y}{1+gy^2}\right]+\frac{8M_2^{\text{H-}M}}{3M_2^{\text{H-}M}}\left[\frac{y}{4+y^2}\frac{+y}{1+y^2}\right]\right] , \tag{2}$$

where $\gamma_{\text{H}}$ is the proton gyromagnetic ratio, $M_2^{\text{H-}M}$ and $M_2^{\text{H-H}}$ are the dipolar second moments (in magnetic field units) at the proton sites due to the metal nuclei ($^{51}V$ and

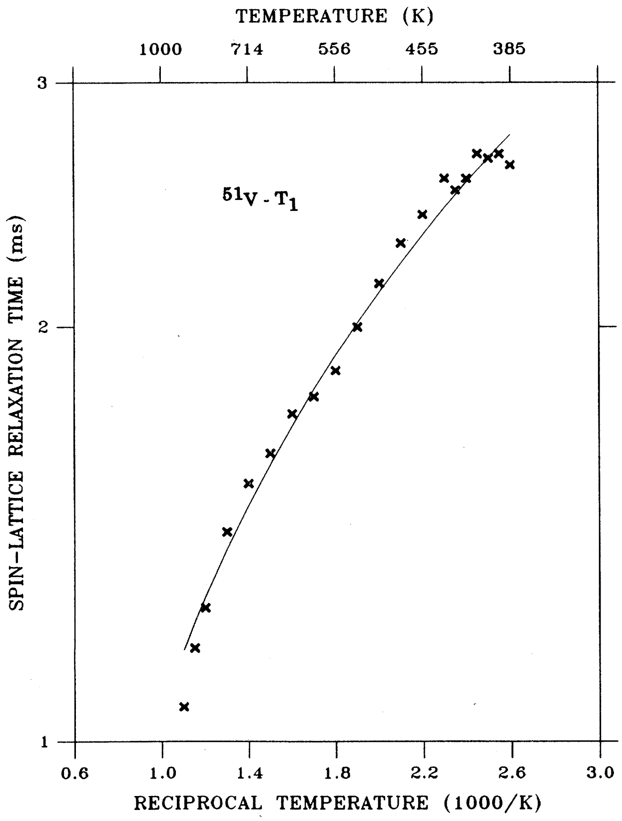

FIG. 4. Temperature dependence of the $^{51}$V$T_1$ in VH$_{0.20}$ measured at a resonance frequency of 24 MHz. The curve conforms to $T_1T = 1.06$ s K behavior.

$^{93}$Nb) and $^1$H, respectively, and $\omega_M$ and $\omega_{\rm H}$ are the respective Zeeman frequencies. A Lorentzian form has been assumed for the spectral density functions. The correlation time $\tau_c = \tau_d$ in the terms associated with the $^{51}$V and $^{93}$Nb moment fluctuations, $\tau_c = \tau_d/2$ in those associated with $^1$H moment fluctuations, and $y = \omega_{\rm H}\tau_d$. The factors $g$ and $f$ result from the spectral densities at $\omega_{\rm H} \pm \omega_M$, respectively (i.e., $f = [1-(\omega_M/\omega_{\rm H})]^2$, etc.). By far the major contribution to $(T_{1d})^{-1}$ results from the modulation of the $^{51}$V and $^{93}$Nb dipolar fields by the hopping motion of the hydrogen, so the second set of terms in Eq. (2) makes only a small contribution.

A more accurate form of the spectral density functions in Eq. (2) need not be adopted because in the high-temperature regime in which the $T_1$ anomalies are found, the short-correlation-time approximation applies. In this limit, $\omega_{\rm H}\tau_d \ll 1$, and for this mechanism $(T_{1d})^{-1}$ is determined by long-range diffusion. In addition, the spectral densities become independent of frequency, $\omega_{\rm H}$, and Eq. (2) becomes

$$(T_{1d})^{-1} = 5\gamma_I^2\tau_d(M_2^{\text{H-}M} + \tfrac{1}{3}M_2^{\text{H-H}}) \tag{3}$$

in which $M_2^{\text{H-H}} \ll M_2^{\text{H-}M}$ and can be neglected in this case (but see further, below). With this, the high-temperature form of Eq. (1) becomes

$$(T_1)^{-1} = T/C_e + A\exp(E_a/k_BT) , \tag{4}$$

where $C_e = T_{1e}T$ is the Korringa product, $A = 5\gamma_I^2M_2^{\text{H-}M}\tau_0$, and we have assumed $\tau_d$ follows Arrhenius behavior in these systems, i.e., $\tau_d = \tau_0\exp(E_a/k_BT)$.

## V. DATA ANALYSIS

An attempt to fit Eq. (4) to the high-temperature proton data of Fig. 1 is shown in Fig. 5(a). This attempt clearly fails. Application of Eq. (4) to the data for hydrogen in V, Nb, and Ta, shown in Figs. 2(a) and 2(b), cannot be made because the transition from the hydride phase to the disordered $\alpha$ phase eliminates almost entirely the low-temperature side of the $\alpha$ phase $T_1$ minimum. Consequently, a reliable estimate of $E_a$ cannot be obtained from Eq. (4).

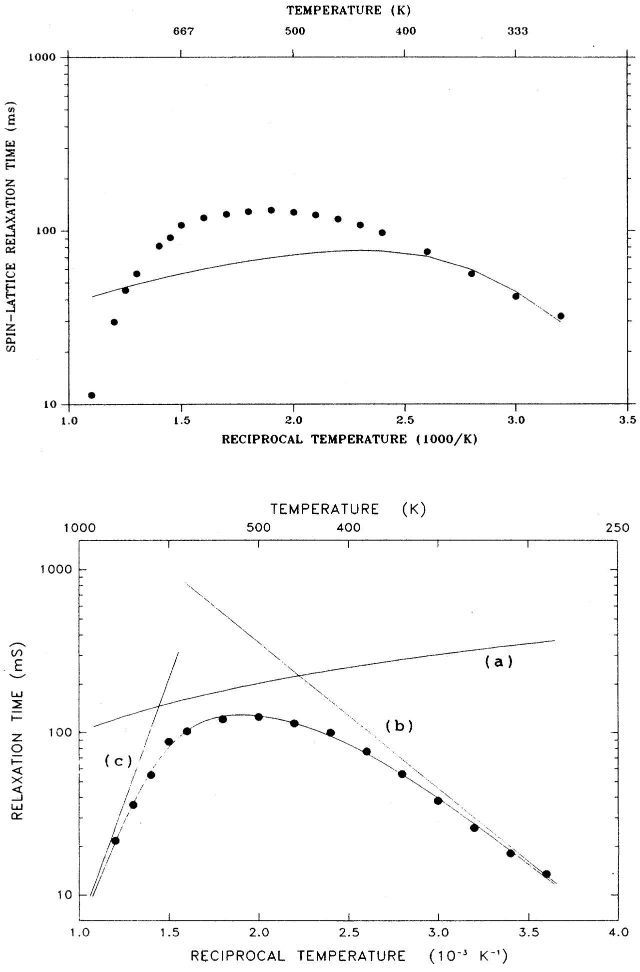

FIG. 5. (a) Attempt to fit the $T_1$ data of Fig. 1 using only the conduction electron contribution $C_e/T$ and the expected activated (Arrhenius) decrease of $\tau_d$ with increasing temperature [Eq. (4) in the text]. (b) Fit to the data of Fig. 1 using an additional relaxation contribution corresponding to excitation to a state in which ultrafast relaxation occurs [Eq. (5) of the text]. The resulting fit parameters are given in the text.

On the other hand, the data, of Fig. 1 for the Nb-V alloy are fit by a simple phenomenological extension of Eq. (4) which assumes the decrease in $T_1$ results from an additional contribution of the form $A' \exp(-U/k_B T)$. The possible significance of this contribution is discussed further below. With this addition, Eq. (4) becomes

$$(T_1)^{-1} = T/C_e + A \exp(E_a/k_B T) + A' \exp(-U/k_B T) \ . \tag{5}$$

The excellent fit of Eq. (5) to the $Nb_{0.75}V_{0.25}H_{0.23}$ data at 12.2 MHz is shown in Fig. 5(b) where the solid curve shows the fitted function of Eq. (5). The data at this frequency provide a longer linear region on the high-temperature side of the normal minimum than at 40 MHz, therefore yielding more reliable estimates of $E_a$ and $A$. For the values of the five parameters determined by the fit we obtain $C_e = 101$ s K, $A = 4.48 \times 10^{-2}$ s$^{-1}$, $E_a = 0.18$ eV/atom, $A' = 1.7 \times 10^5$ s$^{-1}$, and $U = 0.60$ eV/atom. The other three solid lines in Fig. 5(b) show the temperature dependence of the three terms in Eq. (6), curve (*a*) being the conduction electron contribution, (*b*) the "normal" motional or dipolar contribution, and (*c*) the added high-temperature term described above. The 40-MHz data were also fit in this manner using the $E_a$ value found from the 12.2-MHz fit. The remaining parameters were $C_e = 93 \pm 3$ s K, $A = 3.87 \times 10^{-2}$ s$^{-1}$, $A' = 3.84 \times 10^5$, and $U = 0.71 \pm 0.03$ eV/atom.

In contrast to the proton data, the temperature dependence of $T_1$ of $^{51}$V closely follows relaxation expected solely from the conduction electron contribution, i.e., $T_1 = C_e/T$. The solid curve shown in Fig. 4 corresponds to $C_e = 1.06$ s K. In view of the negligible solubility of H in V at low temperatures, a measurement of $C_e$ at such temperatures is not possible. However, the present result can be compared with Ce obtained by Gunther and Kanert[10] for V metal at high temperatures. In that case, $C_e = 0.85$ s K at 500 K, increasing to 0.97 s K at 1000 K. Our data do not appear to reflect such a strong increase. However, the decrease in $C_e$ from V metal to the V-H solid solution is consistent with the reduction in the density of states with the addition of hydrogen.

## VI. DISCUSSION

As in the case of the group III dihydrides,[1,2] it is natural to suspect initially the anomalous relaxation behavior originates from some interaction having little real significance for the study of hydrogen motion in metal-hydrogen systems. The following brief listing of such interactions includes, in each case, a fundamental objection to the mechanism.

(1) *Metal atom self-diffusion* cannot affect the proton $T_1$ because the superposition of such relatively fast hydrogen motion can make very little difference in the overall dipolar fluctuations.

(2) *Oxygen, nitrogen, etc., atom diffusion* cannot affect the proton $T_1$ for the same reason given in (1).

(3) *Paramagnetic impurities* have been eliminated as a possible cause of the anomaly in the dihydrides by numerous measurements made on samples containing controlled levels of such impurities. The mass spectrographic analyses show the metals used in the present study contain insignificant levels of such impurities.

(4) *Octahedral site occupancy* by hydrogen would decrease $T_{1d}$ slightly, but not nearly enough to account for the observed change.

(5) *Chemical exchange with H in the gas phase* is unlikely because the time required for hydrogen to diffuse across a grain at high temperatures is longer than the observed relaxation times. The gas-solid exchange rate and the gas phase $T_1$ could reduce the effectiveness of this relaxation mechanism.

(6) *Interaction with ortho-$H_2$ molecules on grain surfaces* suffers from the same drawback as (5). It is also noted that diffusion of H to grain surfaces could not possibly affect $T_1$ of the host metal nuclei which, for example $^{45}$Sc in $ScH_x$, has the same anomaly as does the proton $T_1$.

Three other possible mechanisms which might be responsible for the anomalous behavior have significance for understanding diffusion and electronic structure of hydrogen in metals and merit more detailed consideration.

(1) *An electronic structure transition* would affect all nuclei (metal and $^1$H) at the same temperature. It also seems extremely improbable that all these systems would undergo such hitherto unnoticed transitions.

(2) *Temperature dependence of the Korringa product* leads to relaxation rate behavior of the form $(T_1)^{-1} = (T/C_e)(1 + bT^2)$, where the parameter $b$ is proportional to the curvature of the density of states at the Fermi level with respect to energy, and $C_e$ is the normal temperature-independent Korringa product.[11] This effect is not strong enough to match the exponential behavior of the $T_1$ downturn of Eq. (5) seen in Fig. 5(b).

(3) *Lengthening of $\tau_d$ caused by large-amplitude vibrations* of hydrogen in $T$ sites towards empty $O$ sites, proposed by Richards[3] to account for the anomalous $T_1$ behavior in the dihydrides, implies that diffusion becomes slower at high temperatures. However, both pulsed-field-gradient NMR and quasielastic neutron scattering measurements[4,5] on $YH_{1.98}$ as well as on the NbV-H solid solution system show that diffusion does not decrease at high temperatures.

We return now to the dipolar interaction of Eqs. (2) and (3). At high temperatures we expect $(T_{1d})^{-1} \propto (\Delta\omega)^2 \tau_d$ [Eq. (3)], where $\Delta\omega$ is an interaction frequency (necessarily of dipolar origin in the case of protons). The decrease of $T_{1d}$ can, in principle, result from an increasing $\Delta\omega$, an increasing $\tau_d$, or possibly both. An increase in $\tau_d$ would be incompatible with the increase in $D$. Assuming diffusion continues to increase normally at high temperatures (meaning $\tau_d$ decreases in an Arrhenius manner), we can estimate from the measured $D$ at 800 K in the case of the Nb-V-H system, $\tau_d \simeq 4 \times 10^{-13}$ s, with the result $\Delta\omega \simeq 1.3 \times 10^7$ s$^{-1}$. For protons, this corresponds to an effective dipolar field $\Delta H \simeq 500$ Oe, almost 2 orders of magnitude above normal.

The largest possible increase in dipolar $\Delta H$, of about 10–30 Oe, could result from a strongly increasing tendency for protons to occupy *nearest-neighbor* $T$ sites with increasing temperature. Such behavior would necessitate a rather violent contradiction of the well-established Switendick-Westlake rule[12,13] that hydrogens do not occupy sites separated by less than approximately 2.1 Å. We do not consider this to be a strong possibility, but see the calculations of Rao and Jena[14] and the molecular-dynamics simulations of Richards[15] which consider the occurrence of unusually close approaches, i.e., ~1 Å. Alternatively, a $\Delta$H of the necessary magnitude might result from a hyperfine interaction of electronic origin. If so, we are unable to suggest a plausible mechanism by which this might occur.

Finally, we consider the possibility that hydrogen motion at high temperatures is controlled by two characteristic times. This might occur in two ways. First, the motion of a group of ions might be highly correlated with the relative positions of ions within the moving group, assuming the relative ion position might not change while a succession of jumps takes place.[1] Then $\tau_c$ for dipolar interactions within the group would become significantly longer than $\tau_d$; since the former governs $T_{1d}$ and the latter $D$, an increasingly correlated motion with increasing temperature could explain qualitatively their differing behaviors. However, the very large ratio $\tau_c:\tau_d$ required seems physically unrealistic. The second way in which two characteristic times might arise is in a *two-state model of hydrogen diffusion* introduced by Lottner and coworkers[16,17] in their analysis of QENS spectra of hydrogen diffusion in single crystal $\alpha$-VH$_x$, etc., at high temperatures (to 500° C). In this model hydrogen alternates between a "mobile" state in which it moves rapidly over $T$ sites for a total time $\tau_m$, and a "rest" state in which it remains immobile for a longer time $\tau_r$. The number of jumps while in the mobile state is $n_m=4p_1\tau_m$, where the jump rate $p_1=(4\tau_j)^{-1}$. Here $\tau_j$ is the time per individual jump while in the mobile state. The diffusion is then given by[17] $D=(a^2/12)p_1\tau_m/(\tau_m+\tau_r)$, where $a$ is the lattice parameter.

In this model

$$(T_{1d})^{-1}=\omega_r^2\tau_r(1-f_m)+\omega_m^2\tau_j f_m ,$$

where $f_m$ is the fraction of time in the mobile state, $\omega_r^2$ and $\omega_m^2$ are effective mean-squared dipolar interaction (frequencies) in the rest and mobile states, and $f_m=\tau_m/(\tau_m+\tau_r)$. This partitioning of the contributions to $(T_{1d})^{-1}$ is similar to one used by Boyce *et al.*[18] for different kinds of states in an ionic conductor, and is based on the assumption that the exchange between the two states is fast enough for use of the weighted average of rest and mobile state relaxation rates.

Two forms of the two-state model will be discussed. In one $f_m \ll 1$, in the other the rest state is defined to be a trap for one or more H atoms. If $f_m \ll 1$ we have $(T_{1d})^{-1}\propto\tau_r$, and the equation for $D$ becomes $D=(a^2/48)(n_m/\tau_r)$. An estimate of $\tau_r\approx\tau_d$ can be obtained from $(T_{1d})^{-1}$ using Eq. (3) and $n_m$ can be estimated from $D$. At 800 K, we have $(T_{1d})^{-1}=60$ s$^{-1}$, $D=5\times10^{-5}$ cm$^2$/s, yielding $\tau_r\sim3\times10^{-10}$ s and $n_m\approx800$. At 800 K, $(T_{1d})^{-1}$ is almost entirely due to the high-temperature mechanism $A'\exp(-U/k_BT)$, from which $\tau_r\propto\exp(-U/k_BT)$. In this model it also follows that the product

$$\tau_r D\propto\exp[-(U+E_a)/k_BT] .$$

With $E_a=0.18$ eV and $n_m=800$ at 800 K, we then have $n_M=11$ at 580 K which compares favorably with the result of Lottner *et al.*[17] who found for NbH$_{0.02}$ $n_m=6$. The extrapolation is sensitive to the value of $U$; if $U=0.71$ eV/atom obtained from the 40-MHz data is used, we find $n_m=6$, in agreement with the QENS result. The unusual conclusions from this analysis are that the immobile state dwell time $\tau_r$ increases as $T$ increases, and furthermore (unless $\tau_m$ increases even more rapidly with $T$) the fraction of time spent in the immobile state also increase as $T$ increases, identifying the immobile state as the excited state of the system. No mechanism for such a state of affairs has been conclusively identified; there has been no confirmation of the suggestion,[1] taken from the behavior of some fast ion conductors, that when a sufficient density of hydrogen ions has been excited from their interstitial sites, they may form temporary, relatively immobile clusters (which break up, of course, at yet higher temperatures).

Since Eq. (5) indicates a thermal excitation is associated with the high-temperature mechanism, we also consider a model in which the rest state is a trap for an H atom. Dislocations, point defects, and impurity atoms are known to be effective traps for H atoms. At high temperature, H atoms will encounter traps frequently but cannot interact, or become trapped, unless the trap is vacant. A trap vacancy is created by thermal excitation, and therefore the appropriate excitation factor would appear in the added term in $(T_{1d})^{-1}$. If the rest state is in a region of high-spin lattice relaxation rate, it could contribute to a faster $(T_{1d})^{-1}$ for the entire H spin system.

Simple numerical estimates of the strength of this mechanism indicate a relatively high, but possible, density of imperfections would be needed to account for the anomaly in $(T_{1d})^{-1}$, but the additional relaxation mechanism would depend on the NMR frequency $\omega_{\rm H}$, an effect which was not observed. Details and discussion of this mechanism are given in the Appendix. Since $D\propto f_m$, $D$ would be affected little with $\tau_m$ being greater than $\tau_r$.

In the trapping model

$$\begin{aligned} n_m &= (\tau_m/\tau_j) \\ &= (\tau_j^{-1}/\tau_m^{-1}) \\ &= (4\pi r_t c_t D\tau_{j0})^{-1}\exp[(U_t+E_a-E_j)/k_BT] , \end{aligned}$$

where we assume $\tau_j$ has the form $\tau_{j0}\exp(E_j/k_BT)$ and $\tau_m^{-1}$ is given by Eq. (A2) in the Appendix. $E_j$ is the activation energy for H atom jumps in a defect-free host, and assuming $E_j\approx E_a$, $n_m\propto\exp(U_t/k_BT)$. In the trapping model $n_m$ decreases as $T$ increases. Physically, the number of uninterrupted jumps decreases as trap vacancies become more available at high temperatures.

The two-state model with $f_m\ll1$ also offers a plausible interpretation of the anomalous $^1$H and $^{45}$Sc $T_1$ behavior in the scandium dihydrides $ScH_{2-x}$. There, the $T$-site sublattice is essentially filled since $x$ is small, and relaxation of the $^{45}$Sc spins results from the fluctuating electric field gradient (EFG) at Sc sites due to vacancy motion. At all hydrogen concentrations $n_H = 1 - x/2$, the hydrogen and vacancy hopping rates $\tau_H^{-1}$ and $\tau_v^{-1}$, respectively, are related by $n_H \tau_H^{-1} = n_v \tau_v^{-1}$, with the result

$$\tau_v = (n_v / n_H)\tau_H = [x/(2-x)]\tau_H \simeq (x/2)\tau_H$$

since $x$ is small. This accounts for the observation that the normal proton $T_1$ minimum occurs at a substantially higher temperature than does the $^{45}$Sc $T_1$ minimum. We need only extend the above relation between hydrogen and vacancy hopping rates to the two-state high-temperature regime in the form $\tau_{vr} = (x/2)\tau_{Hr}$, where $\tau_{vr}$ and $\tau_{Hr}$ are the respective vacancy and hydrogen rest state times, to account for the similar observation that the high-temperature turn down of the $^{45}$Sc $T_1$ occurs at a lower temperature than the proton $T_1$ in $ScH_{2-x}$. Therefore, the $T_1$ behavior would be associated with the increase of $\tau_{vr}$ and $\tau_{Hr}$ at high temperatures. Although $D$ has not been measured in the scandium dihydrides, results for yttrium dihydrides[4,5] show, in this closely similar system, that $D$ increases in an essentially Arrhenius manner at high temperatures. The two-state trapping model would not account for the anomalous $T_1$ behavior of the host nucleus as observed in $^{45}$Sc NMR in $ScH_{2-x}$. To first approximation the trapping kinetics would not affect the vacancy motion in trap-free regions of the sample

In $ScH_{\sim 2}$ (and $ScD_{\sim 2}$) the anomalous decrease of $T_1$ of the scandium nucleus $^{45}$Sc at high temperatures is also observed,[2] in contrast to the present case in which $T_1$ of $^{51}$V shows no departure from purely Korringa-type behavior. The anomalous relaxation of $^{45}$Sc in $ScH_{\sim 2}$ is due to the fluctuating electric quadrupole interaction caused by diffusing vacancies on the hydrogen sublattice.[2] Correspondingly, one might anticipate the quadrupole interaction of $^{51}$V with diffusing hydrogen in $\alpha$-$VH_x$ would yield a similar contribution to $T_1$, causing it to decrease at high temperatures. However, two factors combine to make detection of this effect unlikely.

First, and most importantly, the Korringa product $T_{1e}T$ characterizing the conduction electron relaxation rate of $^{51}$V in $\alpha$-$VH_x$ is only 1.06 s K, whereas $T_{1e}\,T$ for $^{45}$Sc in the dihydrides is 65 s K.[8,19] Hence, conduction-electron relaxation of $^{51}$V in $\alpha$-$VH_x$ is 60 times stronger than for $^{45}$Sc in $ScH_{\sim 2}$. Second, the quadrupole moment of $^{45}$Sc is $0.22 \times 10^{-24}$ cm$^2$ whereas that of $^{51}$V is only $0.05 \times 10^{-24}$ cm$^2$.[20] All other factors (e.g., the Sternheimer antishielding factor[21] and the effective electric charge on the moving hydrogen) being equal, the $^{45}$Sc quadrupole interaction is then about 4.5 times stronger than that of $^{51}$V. Taken together with the disparity in Korringa products, this means that relative to conduction-electron relaxation, quadrupolar relaxation of $^{51}$V is about $4.5 \times 60 = 270$ times weaker than for $^{45}$Sc. The anomalous high-temperature relaxation of $^{45}$Sc in $ScH_{\sim 2}$ has a maximum rate of about 300 s$^{-1}$.[2] We expect the corresponding maximum rate for $^{51}$V in $\alpha$-$VH_x$ will be about $\frac{300}{270} = 1.1$ s$^{-1}$. This is entirely negligible in comparison to the measured Korringa rate of 500–1000 s$^{-1}$ at high temperatures (Fig. 4). We conclude that quadrupolar relaxation of $^{51}$V, due to the diffusing hydrogen, cannot be detected in $\alpha$-$VH_x$.

At the same time, since quadrupolar relaxation contributes negligibly to the $^{51}$V relaxation rate, the close conformity of the $^{51}$V relaxation rate to normal Korringa behavior supports the conclusion the anomalous proton $T_1$ behavior does not result from an interaction related to electronic structure.

## VII. CONCLUSIONS

The temperature dependence of the proton spin-lattice relaxation time $T_1(T)$ at high temperatures for hydrogen in solid solution in the bcc metals V, Nb, and Ta (and in Nb-V alloys) is anomalous because it is incompatible with the hydrogen diffusion $D(T)$ in the same temperature range. A variety of possible causes have been shown to be inapplicable or incapable of accounting for the anomaly. Some success in reconciling $T_1(T)$ and $D(T)$ behaviors is found by invoking either of the two-state models of hydrogen diffusion involving a relaxed (rest) state and a mobile state during which random diffusive jumps occur in very rapid succession. In one model the number of jumps $n_m$ made while in the mobile state increases exponentially with increasing temperature, and $n_m$ determined from these measurements is consistent with $n_m$ determined at lower temperatures in $NbH_x$ on the basis of neutron scattering measurements. This interpretation of the anomaly also affords an explanation of the similar anomalous behavior of $T_1(T)$ previously reported for protons, deuterons, and $^{45}$Sc in the fcc dihydride phases of the Sc-H, Y-H, etc., systems. However, in this model the rest-state lifetime must increase as $T$ increases, raising the question whether one anomaly replaces another. The other model is based on the trapping model of Richter and Springer,[22] and assumes trapping due to lattice imperfections and impurities. This model relies on fast spin-lattice relaxation for trapped H atoms, and it can account for the anomaly of $^1$H $T_1$ in metal hydrides. However, it cannot explain the anomaly in $T_1$ observed in the host metal NMR, such as $^{45}$Sc in $ScH_x$. A flaw in the trapping model is that the $(T_1)^{-1}$ anomaly occurs on the low-temperature (long correlation time) side of a second $(T_1)^{-1}$ maximum where $(T_1)^{-1}$ should depend upon the Larmor frequency $\omega_H$. No frequency dependence was observed. The two-state models nearly explain the anomalies observed in $T_1(T)$, but the shortcomings of the models indicate there are still open questions on these issues.

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## APPENDIX

In the trapping model, the rest state results from the presence of deep traps for hydrogen (H) atoms. These might be host metal atom vacancies, dislocation lines, or oxygen impurities, for example. Each trap could hold a fixed number of H atoms. An H atom passing near a trap could not be trapped unless that trap were empty of at least one H atom at the time of passage. Because of an assumed large trap binding energy, the H atom lifetime in the trap would be long compared to the mean residence time when in its mobile state. There might be local motion in the trap, and this local motion might extend over large enough displacements to effectively modulate the H nuclear dipolar interactions which are still thought to be dominated by H-*M* interactions in the trap. We call the NMR correlation time for this local motion $\tau_l$, with $\tau_l = \tau_{l_0} \exp(U_l/k_B T)$.

Then, neglecting H-H interactions for the moment, the dipolar relaxation rate in the trap will be, from Eq. (2),

$$R_{1dt} = (T_{1dt})^{-1} = \frac{\gamma^2 M_2^{\text{H-}M}}{2\omega_\text{H}} F(y_l) , \tag{A1}$$

where $y_l = \omega_\text{H} \tau_l$. The mean time spent in the trap is $\tau_r = \tau_{ro} \exp(U_r/k_B T)$, and the concentration of unoccupied traps is $c_{t*}$ given by [23] (assuming the bulk of H atoms are in the mobile state)

$$c_{t*} = c_{t0}\{[c_\text{H}/(c_\text{mo} - c_\text{H})] \exp[(E_m - E_t)/k_B T] + 1\}^{-1} , \tag{A2}$$

where $c_{t0}$ is the trap site concentration, $c_\text{H}$ is the H atom concentration, $c_\text{mo}$ is the concentration of available normal interstitial sites that would be occupied by H atoms in their mobile state. These sites have energy $E_m$, and $E_t$ is the trap site energy.

In a bcc host lattice there are six *T* sites/metal atom. Assuming each H atom in a normal site blocks the four neighboring *T* sites, $c_\text{mo} = 6c_M/4$, where $c_M$ is the metal atom concentration. For $[\text{H}]/[M] = x$, $c_\text{H} = xc_M$, meaning $c_\text{H}/(c_\text{mo} - c_\text{H}) = x/(1.5 - x)$. For deep traps,

$$[x/(1.5 - x)] \exp[(E_m - E_t)/k_B T] \gg 1 \tag{A3}$$

at even the highest temperatures, so that $c_{t*}$ becomes

$$c_{t*} = c_{t0}[(1.5 - x)/x] \exp(-U_t/k_B T) , \tag{A4}$$

where $U_t = (E_m - E_t)$. For our sample, $(1.5 - x)/x = 5.5$ with $x = 0.23$. $U_t$ and $U_r$ may be nearly equal in magnitude.

The probability of a proton spin flip occurring in one visit or encounter between an H atom and an unoccupied trap site (during the time the H atom is trapped) would be $P_r = R_{1dt}\tau_r$. Call the rate at which H atoms encounter unoccupied traps $R_\text{enc}$. If these traps are the primary cause of interruption of H atom motion in their normal course of diffusive motion, then $R_\text{enc} = 1/\tau_m$, where $\tau_m$ is the mean time in the mobile state. For point defects,[22]

$$\tau_m^{-1} = 4\pi r_t D c_{t*} , \tag{A5}$$

where $r_t$ is the effective trap radius and $D$ is the H atom diffusion coefficient. Combining these expressions, we have for the unknown, additional contribution to the proton relaxation rate, $R_{1x}$,

$$\begin{aligned} R_{1x} &= R_\text{enc} P_r \\ &= 4\pi r_t D_0 \exp(-E_a/k_b T) 5.5 c_{t0} \exp(-U_t/k_B T) \\ &\quad \times \frac{\gamma^2 M_2^{\text{H-}M}}{2\omega_\text{H}} F(\omega_\text{H}\tau_l) \tau_{r0} \exp(U_r/k_B T) . \end{aligned} \tag{A6}$$

$R_{1x}$ is clearly temperature dependent.

In the short- and long-correlation-time limits, the spectral density function $F(y_l)$ [given by Eq. (2)] becomes, for $y_l \ll 1$,

$$F(y_l) \approx 10 y_l \approx 10 \omega_\text{H} \tau_{l0} \exp(U_l/k_B T) \tag{A7}$$

and for $y_l \gg 1$,

$$F(y_l) \approx 10/y_l \approx 10(\omega_\text{H}\tau_{l0})^{-1} \exp(-U_l/k_B T) . \tag{A8}$$

Hence, for $y_l \ll 1$, $R_{1x}$ is independent of $\omega_\text{H}$, and

$$R_{1x} \propto \exp[-(E_a + U_t - U_l - U_r)/k_B T] ,$$

for $y_l \gg 1$,

$$R_{1x} \propto \omega_\text{H}^{-2} \exp[-(E_a + U_t + U_l - U_r)/k_B T] ,$$

and for $y_l \approx 1$,

$$R_{1x} \propto \omega_\text{H}^{-1} \exp[-(E_a + U_t - U_r)/k_B T] ,$$

over a limited temperature range.

We can now estimate the trap concentration $c_t$ needed to yield the measured $R_{1x}$ in the two cases: (I) $y_l \ll 1$, and (II) $y_l \gg 1$. We take the trap radius $r_t \approx 10$ Å, $D_0 = 8.6 \times 10^{-4}\ \text{cm}^2\,\text{s}^{-1}$ from the fit to the data in Fig. 5, $\gamma^2 M_2^{\text{H-}M} \approx 350 \times 10^8$ for $M_2^{\text{H-}M} \approx 50\ \text{Oe}^2$, and $\omega_\text{H} \approx 10^8\ \text{s}^{-2}$.

*Case I:* From Eqs. (A6) and (A7), we have

$$\begin{aligned} R_{1x} &\approx 1.02 \times 10^3 c_{t0} \tau_{l0} \tau_{r0} \\ &\quad \times \exp[-(E_a + U_t - U_r - U_l)/k_B T] \end{aligned}$$

and comparing this with the third term in Eq. (5) we identify $U$ with $(E_a + U_t - U_r - U_l)$ so that

$$\overline{A'} \approx 1.02 \times 10^3 c_{t0} \tau_{l0} \tau_{r0} .$$

For $\overline{A'} \approx 2.5 \times 10^5\ \text{s}^{-1}$ (an average of the two experimental values), and estimating $\tau_{l0}\tau_{r0} \sim 10^{-26}\ \text{s}^2$, this yields an impossible point defect density

$$c_{t0} \approx 2.5 \times 10^{28}\ \text{cm}^{-3} .$$

*Case II:* From Eqs. (A6) and (A8),

$$R_{1x} \propto 1.02\times10^{-13} c_{t0} \exp[-(E_a+U_t+U_l-U_r)/k_BT] ,$$

where we have assumed $\tau_{l0}\approx\tau_{r0}$, leading to $\overline{A'}=1.02\times10^{-13}c_{t0}$, which yields

$$c_{t0}\approx2.4\times10^{18}\ \text{cm}^{-3} .$$

Thus, assuming the traps are point defects, we see that for case I a trap concentration on the order of $10^6$ times greater than the metal atom density is required. On the other hand, for case II, the required trap concentration amounts to about one defect for every $2\times10^4$ metal atoms [50 parts per million (ppm)]. Case II is feasible, but requires a moderately high defect density. It must be noted that for case II the relaxation rate increases as $T$ increases, but an $\omega_H^{-2}$ dependence is predicted for unique activation energies. A distribution of $U_l$ or $U_t$ (or both) would wash out the frequency dependence to some extent. It is also unlikely $\tau_{l0}=\tau_{r0}$, as assumed. A more careful consideration might change the conclusion on the required $c_{t0}$ in this case.

We now consider the possibility that the traps are dislocation lines. In a plane normal to the lines their density is $c_{ta}$ cm$^{-2}$. The encounter rate, determined by two-dimensional diffusion, is given by[24]

$$R_{\text{enc}}=2\pi c_{ta^*}D/\ln(r_1/r_0) , \tag{A9}$$

where $c_{ta^*}$ is the density of unoccupied dislocation lines, $D$ is the diffusion coefficient, $r_0$ the radius of the dislocation for trapping, and $r_1$ the radius of a circle bounding the average area of one dislocation [i.e., $\pi r_1^2=1/c_{ta}$], and $r_1 \gg r_0$. As for point defects, $R_{1x}=R_{\text{enc}}P_r$, so

$$(R_{1x})=\frac{2\pi D_0 5.5 c_{ta}}{\ln(r_1/r_0)}\frac{\gamma^2 M_2^{\text{H-}M}}{2\omega_{\text{H}}}\tau_{r0}F(\omega_{\text{H}}\tau_l) \times \exp[-(E_a+U_t-U_r)/k_BT] . \tag{A10}$$

To proceed further, we assume first that $\ln(r_1/r_0)$ is of order unity. Then,

$$R_{1x}\approx5.1c_{ta}\tau_{r0}F(\omega_{\text{H}}\tau_l)\exp[-(E_a+U_t-U_r)/k_BT] .$$

Finally, the dislocation density $c_{ta}$ can now be estimated for cases I and II, as was done for point defects, with the results for *case I*,

$$c_{ta}\approx4.7\times10^{21}\ \text{cm}^{-2} ,$$

and for *case II*,

$$c_{ca}\approx4.9\times10^{11}\ \text{cm}^{-2} .$$

The last result is feasible, although high. Since there are about $2\times10^{15}$ atoms cm$^{-2}$ in a lattice plane, this result corresponds to about one dislocation line for every 4000 metal atoms in a plane.

We see again that case II is feasible with $5\times10^{11}$ cm$^{-2}$ dislocations required, not an unreasonable number. Case I is impossible since it requires a greater dislocation density than there are metal atoms. Again, in case II, $R_{1x}\propto\omega_{\text{H}}^{-2}$ so a strong frequency dependence should be observed, perhaps partially obscured by distributions of activation energies. As in the case of point defects, the assumption $\tau_0=\tau_{r0}$ should be questioned.

To summarize, we have considered a particular mechanism for the anomalous relaxation rate $R_{1x}$ which would fit into the two-state model of Lottner *et al.* A specific description for H atoms in their immobile state is trapping near a point defect or dislocation line for a time $\tau_r$. In this trapped state there may be some local motion with characteristic time $\tau_l$. This local motion causes a nuclear dipolar relaxation rate given by Eq. (6); with no local motion $\tau_l=\tau_r$. By comparing calculated and measured values of $R_{1x}$, we find that this mechanism would work for relatively large trap densities and with $U=(E_a+U_l+U_t-U_r)\approx0.6$ eV/atom. Since $E_a\approx0.2$ eV/atom, $(U_t+U_l-U_r)\approx0.4$ eV/atom. The principal difficulty with this two-state model picture is its prediction of a stronger frequency dependence of $R_{1x}$ than is seen experimentally.

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