Hydrogen Vacancy Diffusion Parameters in ScH_{2-x} and ScD_{2-x} from ^{45}Sc Spin-Lattice Relaxation Time Measurements

M. Jerosch-Herold, L.-T. Lu *, D. R. Torgeson, D. T. Peterson, and R. G. Barnes
Ames Laboratory-USDOE, and Departments of Physics and Materials Science and Engineering, Iowa State University, Ames, Iowa 50011

P. M. Richards
Sandia National Laboratories, Albuquerque, NM 87185

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Dedicated to Professor Dr. A. Weiss on the Occasion of his 60th Birthday

The temperature dependence of the nuclear spin-lattice relaxation rate R_1 of ^{45}Sc has been measured in scandium dihydrides and dideuterides. These data are satisfactorily accounted for by two contributions to R_1, R_{1e} due to conduction electrons, and R_{1Q} due to quadrupole interaction fluctuations resulting from vacancy diffusion on the hydrogen (deuterium) sublattice. Describing these fluctuations by a Lorentzian spectral density and Arrhenius behavior for the vacancy hopping, analysis of the data yields values of the Korringa product $A = T/R_{1e}$ and the activation energy E_a and attempt frequency ν_0 for vacancy-diffusion. In contrast to ν_0 values based on proton R_1 measurements, the ^{45}Sc results agree satisfactorily with the value based on inelastic neutron scattering measurements of hydrogen optic mode vibration frequencies, $\nu_0 \cong 2 \times 10^{14}\,s^{-1}$. We conclude that hydrogen-hydrogen interactions are responsible for the lower ν_0 values derived from proton R_1 measurements.

1. Introduction

We report the first measurements of the temperature dependence of the spin-lattice relaxation rate R_1 of ^{45}Sc in scandium dihydrides and dideuterides. At temperatures on the order of 500 K, R_1 is dominated by quadrupolar relaxation due to the diffusion of hydrogen (deuterium) vacancies in the substoichiometric compounds. These measurements yield values of the activation energy E_a and jump frequency prefactor (attempt frequency) ν_0 for vacancy diffusion.

Measurements of the spin relaxation times of host lattice metal nuclei in hydrides and deuterides can provide an excellent means of studying vacancy diffusion on the hydrogen sublattice when the dominant spin relaxation mechanism is electric quadrupole. The quadrupolar relaxation of a stationary nucleus depends on site occupancy probabilities only. The spin label which distinguishes particles in the magnetic dipolar case (e.g., the diffusing proton) does not influence the electric field gradient (efg) fluctuations which cause the relaxation. In addition, contributions to the relaxation rate of the stationary nucleus from paramagnetic impurities in the lattice is negligible at high temperature. Measurement of the temperature dependence of R_1 of such a stationary metal nucleus should reflect directly the vacancy hopping rate. Unfortunately, almost all metal nuclear species in hydrides of interest require strong magnetic fields (i.e., $B_0 > 2.5\,T$) for effective study of relaxation processes because of large spins and quadrupole moments and/or low abundance. In addition, even when the quadrupole moment is small (e.g., ^{51}V) the conduction electron contribution R_{1e} to the relaxation rate may be too great, making detection of the effect of diffusion very difficult. An exception is ^{45}Sc, and we have measured the temperature dependence of R_1 for this nucleus in both the ScH_{2-x} and ScD_{2-x} phases.

2. Theoretical Background

Both the magnetic dipole and electric quadrupole relaxation rates are functions of power spectra of the randomly varying fields resulting from the atomic diffusive jumps. They depend, respectively,

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* Present address: Watson Laboratory, California Institute of Technology, Pasadena, CA 91125.

Reprint requests to Prof. Dr. R. G. Barnes, Ames Laboratory-USDOE, and Departments of Physics and Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA.

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on the strength of the magnetic dipolar interaction between the diffusing protons and the stationary metal nuclei and on the strength of the quadrupole interaction associated with diffusing hydrogen vacancies in the sub-stoichiometric hydride. In general, both interactions may contribute to the diffusion-controlled relaxation rate. However, our measurements on the scandium hydrides and deuterides show that electric quadrupole relaxation is much stronger than magnetic dipole, so that in the following we neglect the latter for the sake of brevity. Experimental justification is given in the Results section.

Accordingly, the measured spin-lattice relaxation rate, $R_1 = (T_1)^{-1}$, of a metal nuclear spin in a metal hydride is taken to be the sum of the conduction electron contribution, $R_{1e} = (T_{1e})^{-1}$, and the diffusion controlled quadrupolar relaxation rate R_{1Q}. The conduction electron contribution is insensitive to hydrogen or vacancy diffusion and should dominate the relaxation at low and high temperatures. It is expected to follow the well-known Korringa relation [1] according to which $T_{1e}\,T = \text{constant}$, with $(T_{1e})^{-1/2} \propto N(E_F)$, where $N(E_F)$ is the density-of-states at the Fermi level. Our measurements show that $T_{1e}\,T = 65 \pm 3$ s K for ^{45}Sc in these compounds in the temperature range 77–300 K, close to that reported by Zogal and Idziak [2] for $ScH_{1.98}$. This is a relatively weak interaction, reflecting the rather low value of $N(E_F)$ in the Group III transition metals. For comparison, the corresponding values found for ^{51}V in vanadium hydrides [3] fall in the range 0.8 – 2.8 s K, and for ^{93}Nb in niobium hydrides [4] in the range 0.35 – 2.0 s K. In the latter cases, the short T_{1e} makes it difficult to measure reliably the diffusion controlled quadrupolar rate R_{1Q}.

Therefore, we take the measured relaxation rate to be given by

$$R_1 = R_{1Q} + R_{1e} \tag{1}$$

with $R_{1e} = T/A$ where $A = T_{1e}\,T$ is the Korringa product. Following Wolf [5], the quadrupole relaxation rate is given by

$$R_{1Q} = \tfrac{3}{2}\,\alpha_Q\,c_v\,[J_Q^{(1)}(\omega_0) + J_Q^{(2)}(2\,\omega_0)] \tag{2}$$

where

$$\alpha_Q = \frac{3\,\pi^2}{20}\,\frac{e^2\,Q^2\,(2\,I+3)}{h^2\,I^2\,(2\,I-1)}\,, \tag{3}$$

and c_v is the vacancy concentration. In α_Q, $Q = 0.22 \times 10^{-24}\ \text{cm}^2$ is the ^{45}Sc quadrupole moment [6], $I = 7/2$ the nuclear spin, and h is Planck's constant. If the usual simple exponential correlation function is adopted for the field gradient fluctuations, the spectral density $J_Q^{(1)}(\omega_0)$ is given by

$$J_Q^{(1)}(\omega_0) = \frac{2\,\tau_c}{1+\omega_0^2\,\tau_c^2}\,(e\,q)^2 \tag{4}$$

where ω_0 is the ^{45}Sc Zeeman frequency and τ_c is the correlation time for single vacancy hopping. Here we take the efg to be axially symmetric so that $\partial^2 V/\partial z^2 = e\,q$. This is a good approximation for low vacancy concentrations, $c_v \lesssim 0.1$. For powders, $J_Q^{(2)}(\omega) = 4\,J_Q^{(1)}(\omega)$, and for $I = 7/2$, $\alpha_Q = (\pi\,e\,Q/7\,h)^2$, so that finally

$$R_{1Q} = \frac{3\,\pi^2\,c_v}{49\,\omega_0}\left(\frac{e^2\,q\,Q}{h}\right)^2\left[\frac{y}{1+y^2} + \frac{4\,y}{1+4\,y^2}\right] \tag{5}$$

with $y = \omega_0\,\tau_c$.

We assume that the vacancy jump frequency τ_c^{-1} follows an Arrhenius relationship

$$\tau_c^{-1} = \nu_0 \exp(-\,E_a/k\,T)\,, \tag{6}$$

where E_a is the activation energy for vacancy diffusion, k is Boltzmann's constant, T the absolute temperature, and ν_0 is the jump frequency prefactor or attempt frequency.

3. Experimental Aspects

All of the samples investigated were prepared in the Materials Sciences Division of the Ames Laboratory from high-purity Ames Laboratory scandium containing less than 10 parts-per-million (ppm) total rare-earth impurity according to spark-source mass spectroscopy determinations. The batch numbers of the scandium used for the different samples are included in Tables I and II. All of the hydride samples and one set of deuterides were prepared in the manner which has been previously described for yttrium hydrides [7]. In addition, a second set of deuteride samples was prepared in a modified Sieverts apparatus, as described for the preparation of lanthanum hydrides [8].

The T_1 measurements were made at a resonance frequency of 24 MHz, corresponding to a magnetic field strength of 2.32 T. The phase-coherent pulsed NMR spectrometer and associated instrumentation have been described elsewhere [7]. 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. Some measurements were also made using the saturation recovery sequence with a comb of 10–20 90° pulses (i.e., 90° comb $- \tau -$ 90° sequence). T_1 values so determined were in excellent agreement with those determined by inversion recovery. Single-exponential magnetization recovery was obtained in all cases, showing that the full ^{45}Sc spectrum is inverted (or saturated).

4. Results

An example of the temperature dependence of the measured T_1 is shown in Fig. 1 for $\mathrm{ScH}_{1.87}$. The solid curve is the least squares fit of (1) to the data with $R_{1\mathrm{Q}}$ given by (5) and α_Q an adjustable parameter. To be certain that there is no influence of paramagnetic impurities, measurements were also made on $\mathrm{ScH}_{1.92}$ samples containing controlled levels of Gd of 50 and 100 ppm. These revealed no depression of the Korringa product throughout the low temperature region, showing that the $R_{1\mathrm{p}}$ contribution is not significant.

The proton dipolar contribution $R_{1\mathrm{p}}$ can be estimated from the usual theory [5]. Assuming that the spectral density function for the dipolar interaction has the same form as that for the quadrupole relaxation (and which is the case if an exponential correlation function is adopted), then the maximum relaxation rate $R_{1\mathrm{d,\,max}}$ occurs when $y = 0.616$. For $\mathrm{ScH}_{1.87}$ for example, $R_{1\mathrm{d,\,max}} = 5.4\ \mathrm{s}^{-1}$, whereas the measured $R_{1\mathrm{Q,\,max}}$ inferred from the data of Fig. 1 is $139\ \mathrm{s}^{-1}$, that is, 26 times greater, so that we are well justified in ignoring $R_{1\mathrm{d}}$. In the deuterides, because the deuteron moment is roughly 7 times smaller than that of the proton, the dipolar contribution is substantially weaker than this estimate.

Fitting (1) to the measurements yields values of the Korringa product A, activation energy E_a, attempt frequency ν_0, and the maximum relaxation rate $R_{1\mathrm{Q,\,max}}$. The latter quantity can be calculated from $R_{1\mathrm{Q,\,max}} = R_{1,\,\mathrm{max}} - (A/T_\mathrm{min})^{-1}$ where T_min is the temperature at which the minimum in T_1 occurs. The values of A, E_a, ν_0, and $R_{1\mathrm{Q,\,max}}$ so determined are summarized in Tables I and II for the hydrides and deuterides, respectively.

The average quadrupole coupling responsible for spin-lattice relaxation can be obtained from the

Table 1. Vacancy concentration c_v, Korringa product A, vacancy diffusion activation energy E_a, attempt frequency ν_0, and maximum quadrupolar relaxation rate $R_{1\mathrm{Q,\,max}}$ for scandium hydrides ScH_{2-x} determined from ^{45}Sc T_1 measurements at 24 MHz.

H/Sc	c_v	A (s · K)	E_a (ev/atom)	ν_0 ($10^{14}\,\mathrm{s}^{-1}$)	$R_{1\mathrm{Q,\,max}}$ (s^{-1})
2.00[a]		68	0.53	2.0	80
1.87[b]	0.065	62	0.64	2.1	140
1.83[b]	0.085	62	0.74	10.8	
1.79[b]	0.105	63	0.74	6.7	660

[a] Scandium metal used: Sc-91278.
[b] Scandium metal used: Sc-12681.
Estimated uncertainties: in c_v, ± 0.01; in A, ± 3 s · K; in E_a, ± 0.03 eV/atom; in ν_0, ± 50%; and in $R_{1\mathrm{Q,\,max}}$, ± 5%.

Table 2. Vacancy concentration c_v, Korringa product A, vacancy diffusion activation energy E_a, attempt frequency ν_0, and maximum quadrupolar relaxation rate $R_{1\mathrm{Q,\,max}}$ for scandium deuterides ScD_{2-x} determined from ^{45}Sc T_1 measurements at 24 MHz. All samples were prepared from Ames Laboratory scandium No. Sc-11465.

D/Sc	c_v	A (s · K)	E_a (eV/atom)	ν_0 ($10^{14}\,\mathrm{s}^{-1}$)	$R_{1\mathrm{Q,\,max}}$ (s^{-1})
1.99	0.005	66	0.59	5.8	31.4
1.98[a]	0.01	64	0.63	1.0	50
1.91[a]	0.045	64	0.67	0.9	690
1.88[a]	0.06	66	0.74	4.4	
1.88	0.06	71	0.71	2.0	900
1.82[a]	0.09	62	0.80	30	825
1.82	0.09	63	0.76	10	900

[a] Series B samples; others are series A.
Estimated uncertainties same as in Table 1.

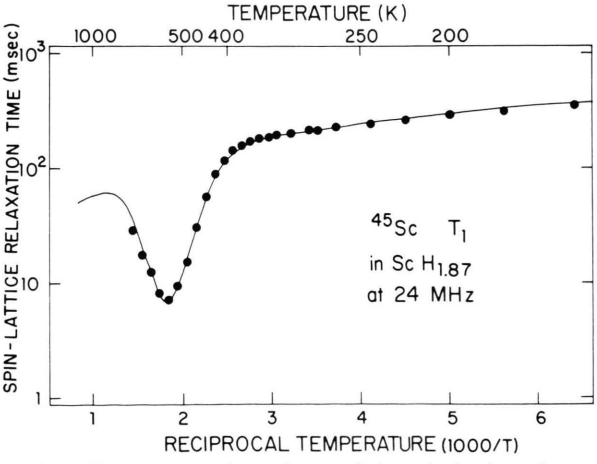

Fig. 1. Temperature dependence of the spin-lattice relaxation time T_1 in $\mathrm{ScH}_{1.87}$. The solid curve is the least squares fit of (1) to the data points with $R_{1\mathrm{Q}}$ given by (5) and α_Q an adjustable parameter.

maximum relaxation rate $R_{1Q,\max}$. From (5) we have

$$\langle (e^2 q Q/h)^2 \rangle = \frac{49\,\omega_0}{3\,\pi^2 c_v} \frac{R_{1Q,\max}}{1.425},$$

where 1.425 is the maximum value of the spectral density function in square brackets, which occurs when $\omega_0 \tau_c = 0.616$. Then, for example, for $ScD_{1.98}$ for which $c_v = 0.01$, $R_{1Q,\max} = 74.4\ s^{-1}$, and with $\omega_0 = 48\,\pi \times 10^6\ s^{-1}$, we obtain $\langle (e^2 q Q/h) \rangle = 1.14$ MHz. Similarly, using the values in Table II we have for $ScD_{1.88}$ that $\langle (e^2 q Q/h) \rangle = 1.62$ MHz.

These values may be compared with that expected for a single hydrogen vacancy with effective charge $Z' e$. The coupling constant will be $QCC = (Z' e^2 q Q/h)(1 - \gamma_\infty)$ where $\gamma_\infty = -7$ is the Sternheimer antishielding factor [9] for Sc^{3+}, and $q = 2\,r^{-3}$ whre r is the metal-hydrogen separation. For nearest-neighbor (nn) vacancies, $r = 2.05$ Å, and $(QCC)_{nn} = 14.2\,Z'$ MHz, and for next-nearest-neighbor (nnn) vacancies, $r = 3.93$ Å, and $(QCC)_{nnn} = 2.0\,Z'$ MHz. Thus, for nn vacancies we have good agreement with the experimental value if $Z' \cong 0.1$, whereas agreement for nnn vacancies would require $Z' \cong 0.5$. Self-consistent band structure calculations for ScH_2 [10] have concluded that the additional electronic charge within the hydrogen muffin-tin sphere is 0.15 e. Thus, the present measurements are consistent with the source of the relaxation being efg fluctuations due to vacancies moving in and out of the nearest-neighbor hydrogen shell around the scandium.

5. Discussion

The results summarized in Tables 1 and 2 give rise to several interesting and important conclusions concerning the activation energy and attempt frequency of hydrogen vacancy diffusion in scandium dihydride in particular, and in f.c.c. structure hydrides in general. We consider these factors in the following subsections.

Activation Energy

Figure 2 shows how the activation energies listed in Tables 1 and 2 depend on the vacancy concentration c_v. The activation energy decreases with decreasing vacancy concentration (increasing hydrogen concentration) over the entire composition range of the dihydride phase. The decrease is substantial, from $E_a \cong 0.8$ eV at $c_v = 0.05$ to $E_a \cong 0.60$ eV at $c_v = 0.005$ in the deuterides, and from $E_a \cong 0.75$ eV to $E_a \cong 0.52$ eV over the same range of c_v in the hydrides. The isotope difference is in reasonable accord with the expected difference in zero-point energies, 0.055 eV, based on the proton vibrational frequency [11]. The same trend of E_a values is also found in the results [12] of measurements of the proton T_1 in the same samples, which are also shown in Figure 2. However, the activation energies based on the proton measurements consistently fall about 0.1 eV below those based on the ^{45}Sc measurements.

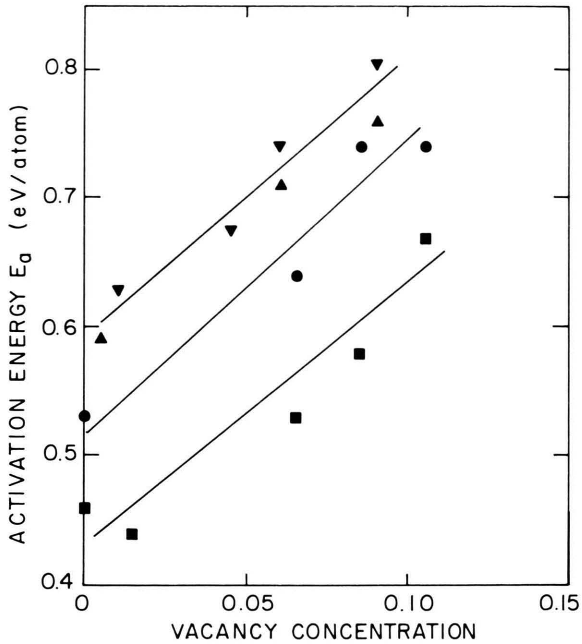

Fig. 2. Activation energies for vacancy diffusion determined from ^{45}Sc T_1 measurements. (●: ScH_{2-x}; ▲: ScD_{2-x} series A samples: ▼: ScD_{2-x} series B samples). Activation energies for hydrogen diffusion determined from proton T_1 measurements (■: ScH_{2-x}). The solid lines are guides to the eye only.

This behavior of the activation energy may be compared with that in the similar dihydrides of Ti, Zr, Y, and La. In making this comparison, we focus attention on the possible significance of hydrogen 0-site occupancy in determining the composition dependence of E_a. In this regard, ScH_{2-x} lies intermediate between TiH_{2-x} and ZrH_{2-x} for which there is no evidence that 0-sites are occupied [13], and YH_{2-x} and LaH_{2+x} for which there is clear evidence that 0-sites are occupied [14, 15]. The lattice parameter of ScH_2 (4.738 Å) also falls between those of TiH_2 and ZrH_2 (4.447 Å and 4.603 Å, respectively) and of YH_2 and LaH_2 (5.204 Å and 5.663 Å, respectively). However, like Ti and Zr, Sc does not form a trihydride phase [16], whereas Y and La do [16]. These observations suggest that 0-site occupancy is unlikely to be significant in ScH_2. This conclusion is supported by electron spin resonance (ESR) studies [17] of dilute Er^{3+} in ScH_2 which indicate that the fraction of 0-sites occupied in ScH_2 is less than 0.5% and by the absence of any 0-site contribution in inelastic neutron scattering [11].

Various proton T_1 and $T_{1\varrho}$ (T_1 in the rotating frame) measurements in TiH_{2-x} have found $E_a \cong 0.50$ eV/atom essentially independent of hydrogen concentration [18, 19]. However, recent proton $T_{1\varrho}$ measurements [20] in ZrH_{2-x} show a small decrease ($\sim 10\%$) of E_a with decreasing vacancy concentration in the range $0.1 > c_v > 0.5$ in which the lattice experiences a small tetragonal distortion. For both of these systems the argument has been advanced that E_a could be expected to increase as the limiting dihydride composition is approached due to the additional energy required to create a vacancy on the hydrogen sublattice [20]. This effect would presumably only be noticeable for compositions very close to the dihydride limit. And indeed, such an increase in E_a was recently reported for $ZrH_{1.997}$ on the basis of proton $T_{1\varrho}$ measurements [20].

In contrast to these results, proton spin relaxation time measurements on both yttrium and lanthanum dihydrides yield activation energies that decrease significantly with increasing hydrogen content [21, 22]. For the lanthanum hydrides, this trend was already evident in the pioneering work of Schreiber and Cotts [15]. All these pieces of information, taken together, strongly suggest that the ability of hydrogen to occupy the octahedral interstitial sites may be the principal factor responsible for the activation energy decreasing with increasing hydrogen concentration in f.c.c. structure hydrides. In the case of ScH_{2-x}, the observed behavior of E_a may indicate that 0-site occupancy, or at least the ability to sample 0-sites, is non-negligible at high temperatures.

Attempt Frequency

The most striking feature of the present results are the attempt frequency values. In sharp contrast to such parameters based on proton T_1 measurements, the present results based on the ^{45}Sc T_1 measurements show little dependence on vacancy concentration and agree satisfactorily with the value anticipated from inelastic neutron scattering measurements of hydrogen optic mode vibration frequencies. For single particle hopping on an empty lattice, the attempt frequency ν_0 is given by

$$\nu_0 = z\,\nu_0^0\,, \tag{7}$$

where ν_0^0 is the optic mode frequency and $z = 6$ is the number of neighbor sites on the simple cubic T-site sublattice of hydrogen in the f.c.c. hydrides. Unpublished neutron measurements [11] give a mean value of $h\,\nu_0^0 = 126$ meV which follows the trend of published data [23] for f.c.c. hydrides. With this we have $\nu_0 = 1.80 \times 10^{14}\ s^{-1}$ in very good agreement with the experimental values, particularly at the lower vacancy concentrations. There does appear to be a trend toward somewhat greater ν_0 values at the higher vacancy concentrations.

For comparison, values of the vacancy attempt frequency $\nu_0 = z\,\nu_0^0$ derived from proton T_1 data are displayed in Figure 3. For TiH_{2-x} and ScH_{2-x} the points are derived from T_1 measurements ([18] and [12], respectively), and for ZrH_{2-x} from $T_{1\varrho}$ measurements (see [20]). It's evident that the proton-derived values of ν_0 fall 1 to 2 orders of magnitude below the anticipated value of $2 \times 10^{14}\ s^{-1}$ based on the neutron measurements and also found from the ^{45}Sc T_1 results. Note that the values for ScH_{2-x} decrease more rapidly with increasing hydrogen concentration than do those for TiH_{2-x} and ZrH_{2-x}. This difference between the Group III and IV metal hydrides is further born out by similar data for YH_{2-x} [21, 22].

One can show that the average labeled particle (ν_p) and vacancy (ν_v) hopping rates are in the ratio $c_v/(1 - c_v)$ even if proton-proton interactions strongly affect the rates. The proton and ^{45}Sc data, which should measure the former and latter rates, respectively, are in clear disagreement with this. A possible explanation concerns the effect of interactions when, for $c_v \ll 1$, vacancies move much faster than labeled particles. Suppose the rate to hop from site i to j depends on the distribution of vacancies in

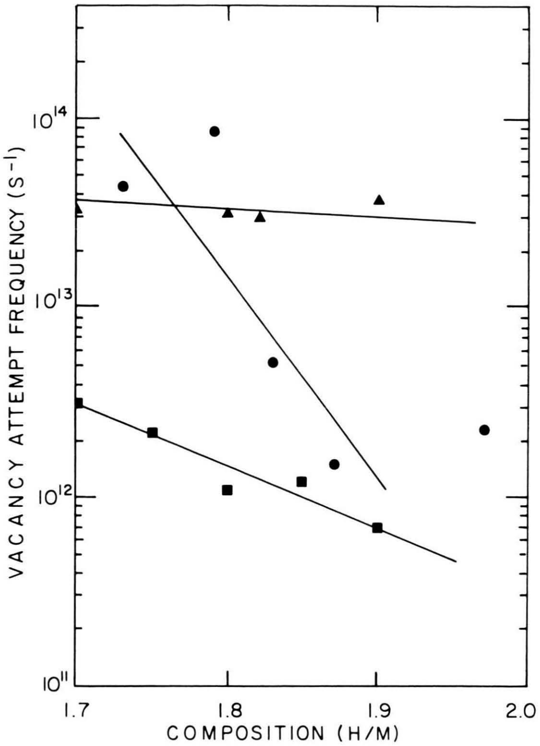

Fig. 3. Hydrogen concentration dependence of the vacancy attempt frequency ν_0 derived from proton T_1 measurements in the dihydride phases of Sc, Ti, and Zr. (▲: TiH_{2-x} from Ref. 20; ●: ScH_{2-x} from [13]; and ■: ZrH_{2-x} from [22]. The solid lines are guides to the eye only.

other neighboring sites k because of interactions. For a labeled-particle hop it is proper to compute the rate by taking an average over this distribution because of the rapid vacancy fluctuations. (That is, a mean-field description of labeled particle hopping is exact [24] for $c_v \to 0$.) Such is not the case, however, if the $i \to j$ hop is a vacancy one, since then the distribution of k fluctuates on the same time scale. The vacancy rate can therefore be non-mean-field and weighted toward the value corresponding to the most probable distribution (all surrounding sites occupied) rather than to the average rate. There can be considerable difference between these for small c_v if, owing to strong repulsions at the saddle point, the rate increases strongly as the instantaneous number of vacancies in the surrounding sites k increases. This model will be treated in detail elsewhere. A further point to consider might be that in proton NMR where R_{1d} dominates, one is dealing with 2-particle interactions which may be affected by 2 or more-particle correlated hopping processes.

6. Conclusions

The measurements reported here show that the ^{45}Sc spin-lattice relaxation rate R_1 in ScH_{2-x} and ScD_{2-x} at intermediate temperatures is predominantly quadrupolar in origin, resulting from vacancy diffusive jumps on the hydrogen (deuterium) sublattice. The conduction electron contribution to the relaxation rate is relatively weak, consistent with a low density-of-states at the Fermi level. The jump frequency prefactor (attempt frequency) for hydrogen vacancy diffusion derived from the temperature dependence of R_1 agrees well with the value expected on the basis of neutron scattering measurements of the hydrogen optic mode frequency. In contrast, attempt frequency values based on proton spin-lattice relaxation rate data are 1 to 2 orders of magnitude less than this, indicating possible effects of hydrogen-hydrogen interactions and/or 2 or more-particle correlated hopping processes.

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