

Proton and ^{45}Sc nuclear-magnetic-resonance study of hydrogen diffusive hopping in hcp scandium

J-W. Han, C-T. Chang, D. R. Torgeson, E. F. W. Seymour, and R. G. Barnes

Ames Laboratory, Iowa State University, Ames, Iowa 50011

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The activation energy E_a (0.54 ± 0.01 eV) and attempt frequency ν_0 (1×10^{14} Hz $\pm 50\%$) of hydrogen diffusive hopping in dilute solid solution in hcp Sc metal ($\alpha\text{-ScH}_x$) have been determined from NMR measurements of the temperature dependence of the spin-lattice relaxation rates of both proton and ^{45}Sc . For low hydrogen concentrations ($x \leq 0.11$), the results are in excellent agreement with expectations based on inelastic neutron scattering measurements on the closely similar Y-H system. The absence of a prefactor anomaly, in particular in the proton results, is consistent with repulsive particle-particle interactions at the saddle point being responsible for such anomalies.

We report the determination of the diffusion parameters of interstitial hydrogen in solid solution in a hexagonal-close-packed (hcp) metal (Sc) based on measurements of the spin-lattice relaxation rates (R_1) of both the diffusing hydrogen (^1H) and stationary metal (^{45}Sc) nuclei. At temperatures on the order of 500 K, R_1 of both species is dominated by relaxation processes due to the diffusing hydrogen, dipolar in the case of ^1H and quadrupolar in the case of ^{45}Sc , thereby yielding values of the activation energy E_a and attempt frequency ν_0 for hydrogen diffusive hopping. A primary objective of these measurements has been to determine if the jump attempt frequency of a dilute concentration of hydrogen in a close-packed metal lattice exhibits a prefactor anomaly¹ when compared with the value expected on the basis of the optic-mode vibration frequency derived from inelastic neutron scattering experiments.

Neutron diffraction measurements² on $\alpha\text{-ScD}_{0.33}$ have shown that, within the limits of the experimental precision, deuterium atoms occupy only the tetrahedral (T) interstitial sites of the hcp Sc lattice. As shown in Figs. 1(a) and 1(b), the T sites occur in close pairs (T_1 and T_2) along the c axis. At temperatures below ~ 170 K, neutron diffraction³ has shown that in the similar lutetium-hydrogen solid-solution phase hydrogen tends to order in pairs of T sites separated by an intervening metal atom [T_1 and T_3 in Figs. 1(a) and 1(b)], but at higher temperatures the extent of ordering decreases. Both members of the close pairs of T sites, which are spaced only ~ 1.35 Å apart in these metals, are probably never occupied, since this distance is regarded as too close for simultaneous occupancy.⁴ This conclusion is supported by recent NMR measurements on $\alpha\text{-YH}_{0.18}$.⁵ Quasielastic neutron scattering measurements on $\alpha\text{-YH}_{0.2}$ indicate that at high temperatures hydrogen diffusion occurs via T - O - T jump paths (O is an octahedral site),⁶ and similar behavior is expected in $\alpha\text{-ScH}_x$.

Solid-solution (α) phase ScH_x samples were prepared from high-purity Ames Laboratory (Materials Preparation Center) scandium metal having a total rare-earth impurity content of less than 5 parts per million (ppm) and an iron content of less than 13 ppm as determined by

mass-spectrographic analysis. Preparation involved reacting the bulk metal with hydrogen gas to obtain the dihydride ScH_2 which was crushed in an inert atmosphere to fine powder (< 74 μm). Sufficient hydrogen was then extracted under vacuum at high temperature to bring the composition into the solid-solution range, the final composition being determined by high-temperature vacuum extraction. Samples were sealed in quartz tubes under low inert-gas pressure.

The ^{45}Sc R_1 measurements were made at a resonance frequency of 24 MHz, corresponding to a magnetic field strength of 2.32 T, and those of the proton R_1 were made at both 24 and 40 MHz (0.564 and 0.939 T, respectively). The phase-coherent pulsed NMR spectrometer and associated instrumentation have been described previously.⁷ Because the ^{45}Sc resonance in hcp scandium experiences a moderately strong static quadrupole interaction (quadrupole coupling constant $\Gamma = 2.02$ MHz)⁸ so that the powder spectrum consists of the central ($+\frac{1}{2} \leftrightarrow -\frac{1}{2}$) transition plus symmetrically placed satellite transitions, all of the ^{45}Sc R_1 measurements were made using a saturation-recovery sequence employing a saturation comb of typically 100 90° pulses lasting about 2 ms altogether to insure complete saturation and exponential recovery, followed by another 90° pulse after τ seconds which sampled the recovered magnetization, observing the free-induction decay (FID) signal (i.e., 90° comb- τ - 90° -FID). The proton R_1 measurements were made using the inversion-recovery sequence, 180° - τ - 90° -FID, as previously described.⁷

The temperature dependence of the ^{45}Sc R_1 is shown in Fig. 2(a) for the three compositions of $\alpha\text{-ScH}_x$ studied. The dashed lines are least-squares fits to the data points (see further below). Qualitatively, it is evident that the maximum rate $R_{1Q,\text{max}}$ increases with increasing hydrogen concentration, $c_H = x$, but that the increase is not linear, and that the $x = 0.27$ data are not fit nearly as well by the relatively simple theory (see below) compared to the other two compositions. A similar set of proton measurements made at a resonance frequency of 40 MHz is shown in Fig. 2(b). These data show no evidence of paramagnetic-impurity-induced relaxation,⁷ consistent

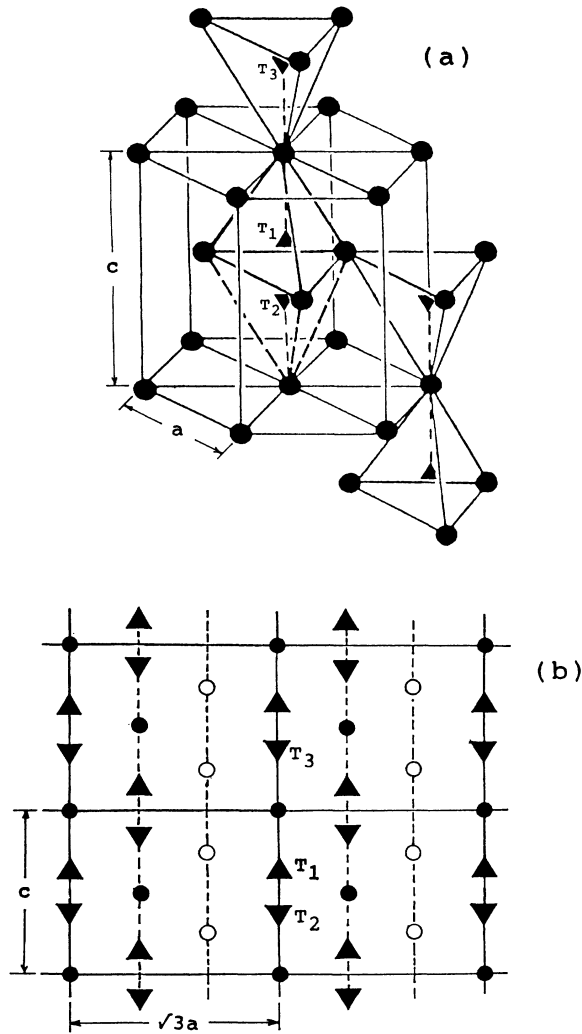


FIG. 1. (a) Hexagonal close-packed metal lattice (filled circles) showing the location of the tetrahedral interstitial sites (filled triangles). Sites T_1 and T_2 form a close pair separated by $\sim 0.25c$. (b) Cross section in the cb plane in the hcp lattice showing the location of both tetrahedral (filled triangles) and octahedral (open circles) sites. As in (a), sites T_1 and T_2 form a close pair.

with the high purity of the Sc metal used in preparing the hydrides. The data taken at 24 MHz are entirely consistent with those at 40 MHz, being independent of frequency at temperatures above that of the R_1 maximum, following the expected frequency dependence at lower temperatures, and showing the expected shift in temperature of the maximum [Eq. (4) below]. The near coincidence of the data for different compositions indicates that relaxation results predominantly from fluctuations in the ^{45}Sc dipolar field caused by proton hopping—the proton-proton contribution to the relaxation is virtually negligible.

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

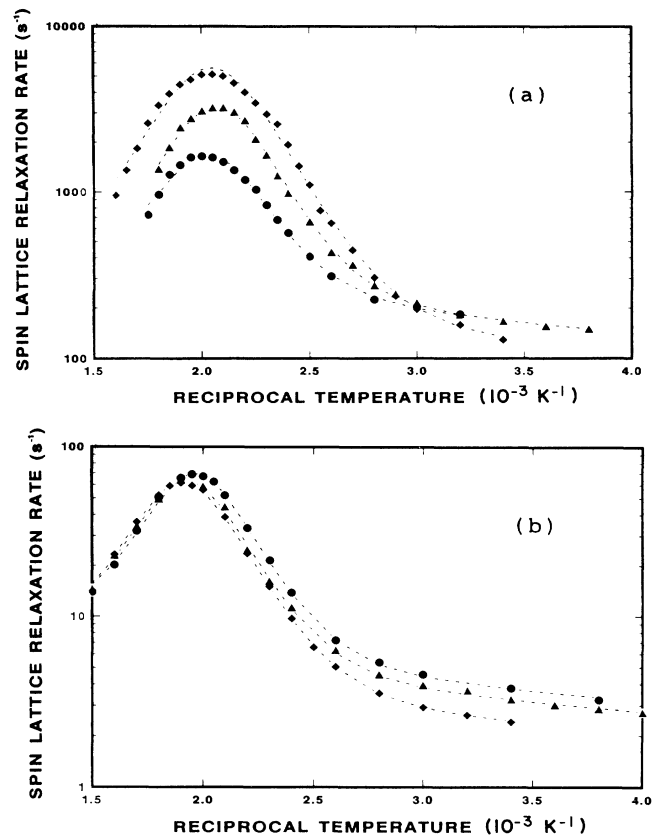


FIG. 2. Temperature dependence of the spin-lattice relaxation rate of (a) ^{45}Sc and (b) ^1H for three concentrations of hydrogen in $\alpha\text{-ScH}_x$ (filled circles, triangles, and diamonds for $x=0.057$, 0.11 , and 0.27 , respectively). The dashed lines are the least-squares fits of Eqs. (3) and (4) in the text to the data points.

strength of the magnetic dipolar interaction between the diffusing protons themselves and with the metal nuclei, and on the strength of the metal nuclear quadrupole coupling resulting from the presence of the interstitial hydrogen. Our measurements show that for hydrogen in solid solution in Sc metal the electric quadrupolar relaxation of ^{45}Sc is much stronger than the magnetic dipolar which is readily estimated from $R_{1d}(\text{H})$, and in the following we neglect the latter for the sake of brevity.

Accordingly, the measured spin-lattice relaxation rate $R_1(\text{Sc})$ of ^{45}Sc , taken to be the sum of the conduction-electron contribution, $R_{1e}(\text{Sc})$, and the quadrupolar relaxation rate, R_{1Q} , resulting from hydrogen diffusion, is

$$R_1(\text{Sc}) = R_{1Q} + R_{1e}(\text{Sc}) \quad (1)$$

The contribution $R_{1e}(\text{Sc})$ is insensitive to hydrogen diffusion, but depends on hydrogen concentration since $(R_{1e}/T)^{1/2} \propto N(E_F)$,⁹ where $N(E_F)$ is the density of states at the Fermi level. $N(E_F)$ is known to decrease with increasing hydrogen content in lutetium,¹⁰ and we find that $R_{1e}(\text{Sc})$ does also. For small hydrogen concentrations, $c_H \ll 1$, and adopting the simple Lorentzian form for the spectral density functions of the electric field gradient (EFG) fluctuations (since more exact lattice-specific

functions are not yet available for this case), R_{1Q} in a powder sample is given by¹¹

$$R_{1Q} = \frac{15\pi^2 c_H}{49\omega_{\text{Sc}}} \langle \Gamma_{\text{NN}} \rangle^2 \left(\frac{y}{1+y^2} + \frac{4y}{1+4y^2} \right) \quad (2)$$

for nuclear spin $I = \frac{7}{2}$. Here ω_{Sc} is the ^{45}Sc Zeeman frequency, and $y = \omega_{\text{Sc}}\tau_d$ where τ_d is the correlation time which in this case equals the mean dwell time for hydrogen diffusive jumps. $\langle \Gamma_{\text{NN}} \rangle$ is the average quadrupole coupling constant of ^{45}Sc due to a nearest-neighbor hydrogen. The numerical prefactor includes a factor of 5 for the number of nearest-neighbor T sites, assuming that only one member of each of the close pairs of T sites is ever occupied.⁵ This result assumes that a spin temperature is maintained among the Sc spins; this is consistent with the fact that the magnetization recoveries were exponential within experimental uncertainty at all temperatures. It also assumes that, at the temperatures of measurement, the occupation of T sites is random apart from the restriction on close-pair occupancy.

Similarly, the spin-lattice relaxation rate of the protons $R_1(\text{H})$ is given by

$$R_1(\text{H}) = R_{1d} + R_{1e}(\text{H}) , \quad (3)$$

where $R_{1e}(\text{H})$ also depends on hydrogen concentration. The dipolar relaxation of the ^1H spins results primarily from the modulation of the ^{45}Sc dipolar field by the hopping motion of the hydrogen. However, in fitting the ^1H data, we have used the full expression for R_{1d} , including both ^{45}Sc and ^1H contributions,¹² even though the maximum ^1H contribution to R_{1d} is just 7% (for $x = 0.27$):

$$R_{1d} = \frac{\gamma_I^2 M_2^{I-\text{Sc}}}{2\omega_I} \left[\left(\frac{y}{1+fy^2} + \frac{3y}{1+y^2} + \frac{6y}{1+gy^2} \right) + \frac{8M_2^{I-I}}{3M_2^{I-\text{Sc}}} \left(\frac{y}{4+y^2} + \frac{y}{1+y^2} \right) \right] . \quad (4)$$

Here, γ_I is the proton gyromagnetic ratio, $M_2^{I-\text{Sc}}$ and M_2^{I-I} are the dipolar second moments (in magnetic field units) at the proton sites due to ^{45}Sc and ^1H , respectively, and ω_{Sc} and ω_I are the respective Zeeman frequencies. A Lorentzian form has again been assumed for the spectral density functions. The correlation time $\tau_c = \tau_d$ in the

terms associated with the ^{45}Sc moment fluctuations, $\tau_c = \tau_d/2$ in those associated with ^1H moment fluctuations, and $y = \omega_I\tau_d$. The factors g and f result from the spectral densities at $\omega_I \pm \omega_{\text{Sc}}$, respectively {i.e., $f = [1 - (\omega_{\text{Sc}}/\omega_I)]^2$, etc.}.

We assume that the hopping time follows thermally activated behavior, so that

$$\tau_d = \tau_0 \exp(E_a/kT) , \quad (5)$$

where $\tau_0^{-1} (= \nu_0)$ and E_a are the jump attempt frequency and activation energy for hydrogen diffusion, respectively, and k is Boltzmann's constant. In making least-squares fits of Eqs. (1) and (2) to the ^{45}Sc data, and of Eqs. (3) and (4) to the ^1H data, the fitting parameters were taken to be E_a , τ_0 , $R_{1Q,\text{max}}$, M_2^{I-I} , and the ratio $M_2^{I-\text{Sc}}/M_2^{I-I}$. The Korringa product A , defined by $R_{1e} = T/A$, was obtained from fitting the data for temperatures below 300 K [not shown in Figs. 2(a) and 2(b)]. The ratio of the values of A for ^{45}Sc and ^1H is the same for all concentrations, as expected. The resulting fit parameter values are listed in Table I.

The E_a and ν_0 values derived from the ^{45}Sc measurements on the $x = 0.057$ and 0.11 samples are virtually identical, and the $R_{1Q,\text{max}}$ values scale with c_H (within the uncertainties in c_H and $R_{1Q,\text{max}}$). Both behaviors indicate that the assumptions underlying Eq. (2) are appropriate. However, $R_{1Q,\text{max}}$ for the 0.27 sample is less than expected compared to the results for the smaller c_H values (the fitted curve in Fig. 1 exceeds the data in the vicinity of the maximum, but both the experimental and fitted values of $R_{1Q,\text{max}}$ are smaller than expected). This trend is consistent with the increased probability of occurrence of two hydrogen nearest neighbors as c_H increases beyond 0.1 because the majority of configurations in which there occur two nearest neighbors cause less than a doubling of the EFG at the Sc site due to a single neighbor. Increased hydrogen concentration results in "saturation" of $R_{1Q,\text{max}}$ as has also been found in the scandium dihydride phase.¹³ It also appears that the simple Lorentzian spectral density function fails to provide a good fit over the entire relevant temperature range. For these reasons, we do not rely strongly on the E_a and ν_0 values listed in Table I for this sample.

The average quadrupole coupling responsible for the ^{45}Sc relaxation rate follows from the maximum rate,

TABLE I. Values of E_a , ν_0 , $R_{1Q,\text{max}}$, A , $M_2^{I-\text{Sc}}$, and M_2^{I-I} resulting from least-squares fits to the ^1H and ^{45}Sc data for $\alpha\text{-ScH}_x$ for different values of x shown in Figs. 2(a) and 2(b). The ^1H measurements were made at 40 MHz and the ^{45}Sc at 24 MHz.

x	E_a (eV/atom)	ν_0 (10^{14} Hz)	$R_{1Q,\text{max}}$ (s^{-1})	A (sK)	$M_2^{I-\text{Sc}}$ (Oe^2)	M_2^{I-I} (Oe^2)
^{45}Sc						
0.057	0.55	1.0	1400	1.67		
0.11	0.545	1.2	3020	1.76		
0.27	0.49	0.30	5000	2.28		
^1H						
0.057	0.53	2.1		86	9.8	0.21
0.11	0.54	0.45		91	9.0	0.36
0.27	0.52	0.30		121	8.8	0.72

$R_{1Q,\max}$. From Eq. (2) we have

$$\langle \Gamma_{\text{NN}} \rangle^2 = \frac{49\omega_{\text{Sc}}}{15\pi^2 c_{\text{H}}} \frac{R_{1Q,\max}}{1.425}, \quad (6)$$

where 1.425 is the maximum value of the spectral density function in the square brackets in Eq. (2) which occurs when $\omega_{\text{Sc}}\tau_d = 0.615$. Using $R_{1Q,\max}$ for the $x = 0.057$ α -ScH_x sample (Table I), yields $\langle \Gamma_{\text{NN}} \rangle = 0.93$ MHz. This result may be compared with that expected for a single hydrogen with effective charge $Z'e$, $\Gamma_{\text{NN}} = (Z'e^2 q_{\text{NN}} Q / h)(1 - \gamma_{\infty})$, where $\gamma_{\infty} = -7$ is the Sternheimer antishielding factor for Sc³⁺,¹⁴ $q_{\text{NN}} = 2r^{-3}$, where $r = 1.985$ Å is the nearest-neighbor metal-hydrogen separation, $Q = 0.22 \times 10^{-24}$ cm² is the ⁴⁵Sc quadrupole moment,¹⁵ and h is Planck's constant. With these values, $\Gamma_{\text{NN}} = 15.6Z'$ MHz. Good agreement with experiment is obtained with $Z' = 0.06$, which is essentially the same value found for hydrogen vacancies in nonstoichiometric ScH₂.¹³ Some difference could be expected since conduction electron screening will be different in the two cases.

Despite the approximations used in analyzing both ¹H and ⁴⁵Sc data, the E_a and ν_0 values deduced from the two sets of data agree remarkably well. All of the E_a values (¹H and ⁴⁵Sc) are in good agreement with Weaver's result¹² ($E_a = 0.54$ eV) based on motional narrowing of the ¹H resonance in an $x = 0.37$ sample, but not with his value 0.44 eV determined from proton R_1 measurements. The latter probably suffers from neglect of relaxation by paramagnetic impurities almost surely present in Sc metal at that time. The values of the second-moment contributions $M_2^{I-\text{Sc}}$ and M_2^{I-T} found from fitting Eq. (4) to the ¹H data (Table I) are substantially smaller than expected on the basis of the rigid-lattice Van Vleck formula.¹⁶ The latter yields for the ⁴⁵Sc contribution at a T site, $M_2^{I-\text{Sc}} = 12.78, 12.63,$ and 12.19 Oe², for $x = 0.057, 0.11,$ and 0.27 , respectively, as the lattice parameters increase with increasing c_{H} .¹⁷ The proton contribution, $M_2^{I-T} = 0.94$ Oe², for $x = 0.27$, for example (again assuming that only one member of a close pair of T sites is ever occupied). The smaller values found experimentally indicate that $\sim 25\%$ of the rigid-lattice M_2 has already been averaged out at a lower temperature by fast localized motion of the hydrogen and therefore cannot contribute to spin-lattice relaxation in the temperature range of interest here. Measurements at temperatures below 180 K confirm that this is the case.¹⁸

The relation between the jump attempt frequency ν_0 and the optic-mode frequency ν_{opt} is expected to be

$$\nu_0 = z'(1-x)\nu_{\text{opt}}, \quad (7)$$

where $z = 6$ is the number of adjacent sites to which hydrogen can jump, and $(1-x)$ is the probability that such a site is vacant. We estimate ν_{opt} from the recent inelastic neutron scattering data of Anderson, Rush, Udovic, and Rowe,¹⁹ for α -YH_x using the "Ross formula,"²⁰ $h\nu_{\text{opt}} \propto R^{-3/2}$, where R is the metal-hydrogen separation. For the T - O - T jump path identified as the probable one for long-range diffusion the relevant vibration frequency in α -YH_x is that in the basal plane $\nu_a = 33$ THz. With this we obtain $\nu_a = 38$ THz in α -ScH_x, and Eq. (7) then yields $\nu_0 = 2.0 \times 10^{14}$ s⁻¹ for $x = 0.11$, for example. This

may be compared with the experimental result $\nu_0 = 1.2 \times 10^{14}$ s⁻¹ based on the ⁴⁵Sc measurements and 0.45×10^{14} s⁻¹ derived from the proton data. The comparison must certainly be regarded as satisfactory for both sets of measurements. On the other hand, for the $x = 0.27$ sample, Eq. (7) yields $\nu_0 = 1.7 \times 10^{14}$ s⁻¹, to be compared with 0.3×10^{14} s⁻¹ found from both the ⁴⁵Sc and ¹H measurements (Table I). However, as already remarked above, the poor fits of Eqs. (2) and (4) to the measured R_1 values indicate that at this relatively high hydrogen concentration the simple spectral densities used are evidently no longer appropriate.

Very much larger discrepancies than are found here occur in the dihydride phase of the Sc-H system, between values of ν_0 derived from ¹H R_{1d} on the one hand and those from ⁴⁵Sc R_{1Q} and ν_{opt} on the other,²¹ the former being smaller by a large factor. Richards¹ has worked out the consequences for these derived values of ν_0 if strong repulsions at the saddle point make the hopping of hydrogen to a vacant site unfavorable unless there is another vacant site nearby. Although this model does not explain this prefactor anomaly in the dihydride quantitatively, it predicts such a difference. Clearly, this type of consideration is more important at high hydrogen concentrations, and the near absence of the effect in the α -phase, as found here, provides support for the general thesis that the anomaly is caused by short-range hydrogen-hydrogen repulsions. For instance, taking the simplest form of the theory in which a T - O - T jump can only occur if at least one of the four nearest-neighbor T sites of that O site is vacant (i.e., T sites other than those from and to which the jump occurs), the additional factor $(1-x^4)$, which is involved in Eq. (7) for the value of ν_0 derived from the proton R_{1d} , lies between 0.99 and 1.00 for all α -phase concentrations, and so is of no consequence. In the present case we can also discount another suggestion that nonallowance for the effect of paramagnetic impurities may result in an incorrect analysis of the data in determining ν_0 , since any such effect would have to occur for all the present samples, two of which show in fact no anomaly whatsoever.

In summary, our best estimate of E_a is (0.54 ± 0.01) eV for $x = 0.057$ and 0.11 ; the value of ν_0 is somewhat more model dependent but is believed to be 1.0×10^{14} Hz to within a factor of 2. The evidence appears to point to slightly smaller values of both quantities in ScH_{0.27} but a firm decision on this point must await more accurate theoretical spectral density functions appropriate to this higher hydrogen concentration, and clarification of the influence of hydrogen-hydrogen interactions.

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