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Normal and anomalous nuclear spin-lattice relaxation at high temperatures in Sc-H(D), Y-H, and Lu-H solid solutions

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We report the results of measurements of the proton (^{1}H) spin-lattice relaxation rate R_1 at high temperatures (to $\sim$ 1400 K) in the hcp (α) solid-solution phases of the Sc-H, Y-H, and Lu-H systems, and of $R_1(^{45}\mathrm{Sc})$ in Sc-H and Sc-D solid solutions. The latter measurements show unambiguous evidence of an anomalous increase at $\sim$ 1000 K, whereas $R_1(^1\mathrm{H})$ shows no such increase at any temperature. This behavior of $R_1(^1\mathrm{H})$ contrasts with that in the bcc V-H, etc., solid solutions where anomalous relaxation occurs below $\sim$ 1000 K, and in all investigated metal dihydride phases, MH_{2-x}. The anomalous $R_1(^1\mathrm{H})$ behavior in α-VH_x, α-NbH_x, etc., may be understood in terms of fast spin relaxation in the H_2 gas in equilibrium with the solid, mediated by fast gas-solid exchange of hydrogen. However, in the present systems, α-ScH_x, α-YH_x, etc., the H_2 gas pressure in equilibrium with the hcp systems is extremely low, resulting in negligible H_2 concentration in the gas phase, and consequently a negligible contribution to $R_1(^1\mathrm{H})$. In contrast, some of the present measurements indicate that the $R_1(^{45}\mathrm{Sc})$ anomaly does result from the hydrogen content of the metal, but the mechanism remains unexplained.

I. INTRODUCTION

Anomalous behavior of the proton (^{1}H) and deuteron (^{2}D) spin-lattice relaxation (SLR) rate R_1 at temperatures in the range 700–1300 K has been reported previously in a number of transition metal dihydride and dideuteride phases,[1–3] as well as in the solid-solution phases of the V-H, Nb-H, (Nb-V)-H, and Ta-H systems.[4–7] Similar anomalous behavior of the scandium (^{45}Sc) SLR rate has also been reported for both scandium dihydrides and dideuterides.[8] The anomaly is that, in addition to the usual R_1 maximum that occurs at intermediate temperatures due to hydrogen diffusive motion, R_1 passes through a minimum and increases sharply again at higher temperatures instead of returning to the value R_{1e} determined by the conduction-electron (Korringa) contribution to R_1. Such behavior is also clearly seen to occur for the ^{45}Sc SLR rate in scandium metal containing either 5% hydrogen or 5% deuterium in solid solution [α-$\mathrm{ScH}_{0.05}$ or α-$\mathrm{ScD}_{0.05}$], as shown in Fig. 1.

Considering the number of different metal-hydrogen (M-H) systems in which anomalous high-temperature SLR behavior has been found, it may reasonably be asked if such behavior is indeed a universal characteristic of all M-H systems. To answer this question, Table I lists those systems for which the anomaly has been reported. These are all binary systems (counting the Nb-V alloys as a single metal). No true ternary intermetallic hydride system (e.g., FeTiH_x, $\mathrm{ZrV_2H}_x$, etc.) has yet been studied in this regard. Perhaps more important, continuing the pattern of studying binary systems, only two further classes have remained uninvestigated. These are the hcp solid-solution phases of the group III transition metals Sc, Y, and Lu (studied here), and the fcc solid solutions exemplified by PdH_x.

There are several motives for extending the search for anomalous SLR behavior to other structural types of M-H systems. The first is to determine if the particular structure of the hydrogen sublattice has any bearing on the occurrence of the anomaly. This might be the case,

TABLE I. Metal-hydrogen systems in which anomalous behavior of the nuclear spin-lattice relaxation rate R_1 has been observed at high temperatures.

M-H system	Metal lattice type	NMR nucleus	Examples	Reference
$\alpha - M\mathrm{H}_x$	bcc	^{1}H	M = V, Nb, Ta, Nb-V alloys	4,5,7
$\alpha - M\mathrm{D}_x$	bcc	^{2}D	M = Ta	6
$M\mathrm{H}_{2-x}$	$\mathrm{CaF_2}$	^{1}H	M = Sc, Ti, Y, Zr	1,2,3
$M\mathrm{D}_{2-x}$	$\mathrm{CaF_2}$	^{2}D	M = Y, Sc	1
$M\mathrm{H(D)}_{2-x}$	$\mathrm{CaF_2}$	^{45}Sc	M = Sc	8
$M\mathrm{H}_{2+x}$	$\mathrm{BiI_3}$	^{1}H	M = La	2

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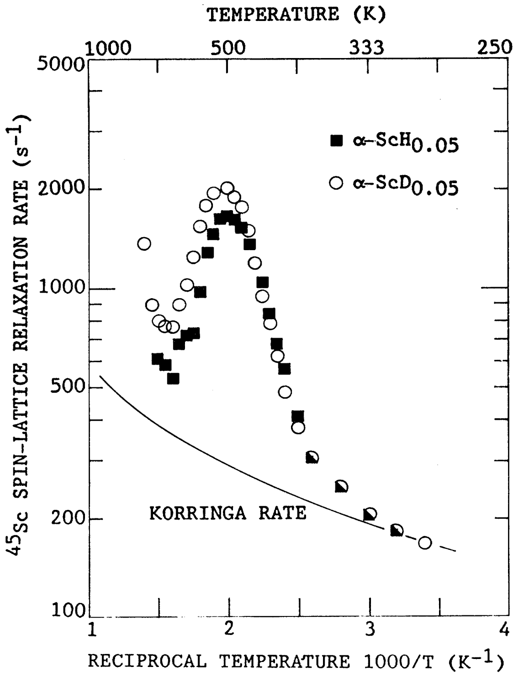

FIG. 1. Temperature dependence of the ^{45}Sc spin-lattice relaxation rate in α-ScD$_{0.05}$ and α-ScH$_{0.05}$ measured at 24 MHz. The solid curve is the conduction-electron contribution R_{1e} extrapolated from low-temperature measurements (Ref. 11). The anomalous relaxation is evident as the increase above 700 K.

for example, if some type of correlated hydrogen motion is involved. Some lattices might more readily support such motion than others. The structure types listed in Table I are those of the host metal lattice. In the bcc lattice, hydrogen occupies tetrahedral (T) interstitial sites, and hydrogen diffusion occurs via direct T-T jumps. In the CaF$_2$ structure hydrogen occupies predominantly T sites, although octahedral (O) site occupancy occurs in YH$_{2+x}$ and LaH$_{2+x}$. But again, hydrogen diffusion occurs via direct T-T jumps in most of these systems. On the other hand, in the hcp metal lattice the T sites occur in isolated close pairs, so that long-range diffusion necessitates a T-O-T jump path.

A second motive is to determine the relevance of the mechanism of fast gas-solid exchange of hydrogen, combined with fast spin relaxation in the gas phase, to M-H systems in general. This mechanism has recently been established[7] as the source of the anomalous high-temperature proton relaxation rate in the solid-solution phase of Nb$_{0.5}$V$_{0.5}$H$_x$. It is a mechanism that may be anticipated to apply whenever the hydrogen pressure in equilibrium with the solid phase approaches ~ 1 atm. However, it is not evident how this process could account for the anomalous relaxation of metal nuclei, e.g., ^{45}Sc.

An additional motive for investigating the hcp solid-solution phases is that in the case of α-ScH$_x$ it is also possible to measure the ^{45}Sc SLR rate as well as that of the protons. ^{45}Sc is unique among metal nuclei in M-H systems in manifesting relatively weak SLR due to conduction electrons, so that quadrupolar SLR resulting from hydrogen motion is readily apparent. This is not true for other metal nuclei. This favorable property has already been noted in the Sc dihydride and dideuteride phases.[8]

And, finally, a further motive related to the last is to address the question, do the anomalous ^{45}Sc and ^{1}H SLR rates have the same origin or not?

Experimentally, the objective of the work reported here has been to search for anomalous proton SLR behavior in the hcp solid-solution phases of the Sc-H, Y-H, and Lu-H systems. Also, as noted above, R_1(Sc) behaves anomalously at high temperatures in the Sc dihydride and dideuteride phases. Hence, α-ScH$_x$(D$_x$) presents a good candidate solid-solution phase in which to search for anomalous metal nuclear R_1 behavior. On the other hand, the unusually strong electric quadrupole interaction of ^{175}Lu in α-LuH$_x$, inferred from the ^{1}H-^{175}Lu cross-relaxation rate,[9] has prevented measurements of R_1(^{175}Lu) and of the resonance spectrum itself. Since ^{89}Y has spin 1/2 and no quadrupole moment, it would in principle be an excellent metal nucleus for monitoring both hydrogen diffusion and anomalous R_1 behavior in α-YH$_x$. However, the very small ^{89}Y magnetogyric ratio (0.05 that of ^{1}H) means that magnetic dipolar relaxation is extremely weak. In addition, the fairly strong relaxation contribution R_{1e} by conduction electrons ($T/R_{1e} = 15\,\mathrm{s\,K}$) (Ref. 10) overwhelms the weak dipolar relaxation, especially at high temperatures. The net result is that ^{45}Sc remains the only practicable metal nuclear probe in these solid-solution systems.

II. EXPERIMENT

All samples were prepared in a modified Sieverts apparatus from high-purity Ames Laboratory metals, with purity established by spark-source mass spectroscopy. Samples were then crushed in a mortar in a He-filled glove box, filtered through a 200-mesh sieve, and sealed in quartz tubes under low inert-gas pressure. Compositions were initially determined from the weight gain and final hydrogen pressure, and finally by hot vacuum extraction analysis.

The samples studied in this investigation were subjects of previous measurements at low to moderate temperatures, so that the parameters of "normal" R_1 behavior, i.e., the conduction-electron contribution R_{1e} and the motional contribution R_{1d} or R_{1Q}, were established. Both the localized motion of hydrogen at low temperatures[11] and long-range diffusion at intermediate temperatures[12] had been investigated in the α-ScH$_x$ samples utilizing both R_1(^{1}H) and R_1(^{45}Sc) measurements. Similarly, the temperature dependences of R_{1e} and R_{1d} of the ^{1}H resonance in both α-YH$_x$ and α-LuH$_x$ had been determined.[9,13]

Measurements at Ames were made using a phase-coherent pulsed NMR spectrometer and associated instrumentation.[14] Values of R_1 were obtained from fitting magnetization recovery curves resulting from measurements of the free-induction-decay (FID) signal following either a 180° inversion pulse or a saturation comb of 90° pulses (see below). For the high-temperature measurements, a home-built, water-cooled furnace probe was used, and temperatures were measured with a Pt-Pt/10% Rh thermocouple.

Experiments at Washington University used a superheterodyne pulsed NMR spectrometer. The 82.76 MHz ^{45}Sc measurements were performed in an 8.0 T superconducting solenoid, and the 21 MHz ^{1}H experiments in a water cooled electromagnet with ^{19}F field stabilization. Relaxation rate data were obtained using a saturation-recovery pulse sequence. Saturation was usually achieved with a single 90° pulse (protons) or a comb of fifty 90° pulses (^{45}Sc). Some of the ^{45}Sc measurements used a single long ($\sim$ 500 μs) saturation pulse. The high-temperature furnaces were water cooled with either molybdenum wire (low field) or type-E sheathed thermocouple wire (high field) used for the heater windings. Temperatures were monitored with a stainless-steel-jacketed type-K thermocouple.

III. RESULTS

A. R_1(Sc) measurements

The measured spin-lattice relaxation rate R_1(Sc) of ^{45}Sc is expected to result from the sum of the conduction-electron contribution R_{1e}(Sc) and the quadrupolar relaxation rate R_{1Q} resulting from hydrogen diffusive hopping:

$$R_1(\mathrm{Sc}) = R_{1e}(\mathrm{Sc}) + R_{1Q} \quad . \tag{1}$$

The contribution R_{1e}(Sc) is believed to be insensitive to hydrogen diffusion, but depends on hydrogen concentration since $(R_{1e}/\mathrm{T})^{1/2} \propto N(E_F)$, the electronic density of states at the Fermi level. R_{1e}/T decreases with increasing x in the α-ScH$_x$ system.[12] Previous measurements had shown that for hydrogen in solution in Sc metal, electric quadrupole relaxation of ^{45}Sc due to hydrogen hopping is much stronger than magnetic dipolar, so that the latter may be neglected. For small hydrogen concentrations, $c_H = x \ll 1$, and adopting the simple Lorentzian form for the spectral density functions of the electric field gradient (EFG) fluctuations, R_{1Q} in a powder sample is given by[8]

$$R_{1Q} = \frac{15\pi^2 c_{\mathrm{H}}}{49\omega_{\mathrm{Sc}}} \langle e^2 Q q_{\mathrm{NN}}/h \rangle^2 \left[\frac{y}{1+y^2} + \frac{4y}{1+4y^2} \right] \tag{2}$$

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

The R_1(Sc) measurements were made at frequencies of 24 MHz, corresponding to a magnetic field strength of 2.32 T, and 82.76 MHz, corresponding to 8.0 T. Because the ^{45}Sc resonance in hcp scandium experiences a moderately strong static electric quadrupole interaction (quadrupole coupling constant $e^2Qq/h = 2.02$ MHz), [15] so that the powder spectrum consists of the central $(+1/2 \leftrightarrow -1/2)$ transition plus symmetrically placed satellite transitions, all of the R_1(Sc) measurements were made using a saturation-recovery pulse sequence employing a saturation comb of fifty to one hundred 90° pulses lasting altogether about 2 ms to ensure complete saturation and exponential magnetization recovery. The comb was 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. In one exception to this procedure, a single long saturating pulse was used instead of the comb to test whether the method of achieving saturation affected the measurement. Figure 2 shows that R_1 measurements on α-ScH$_{0.11}$ using these different methods yielded entirely similar results. It also demonstrates the consistency of

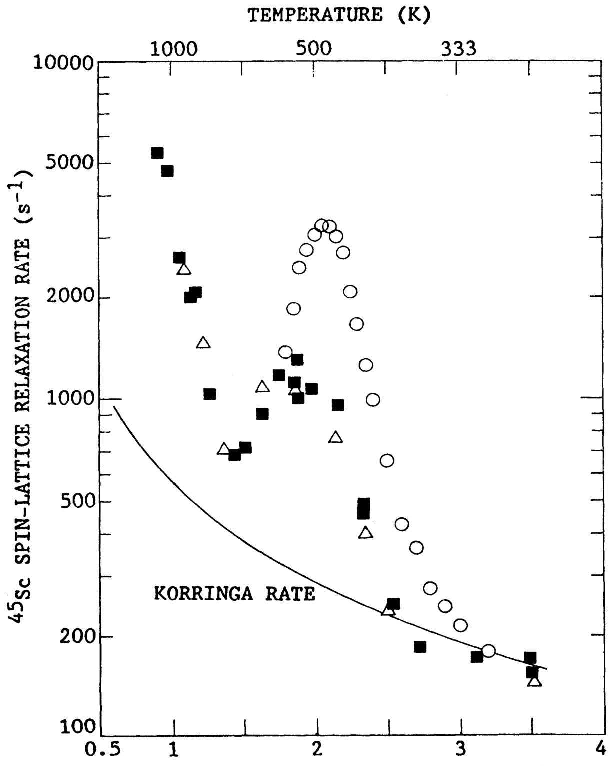

FIG. 2. Temperature dependence of the ^{45}Sc spin-lattice relaxation rate in α-ScH$_{0.11}$, testing different pulse sequences for measuring R_1, as follows: ○, 100 of 8 μs saturation pulses at 24 MHz; ■, a single long saturation pulse at 82.76 MHz; △, 40 of 20 μs saturation pulses at 82.76 MHz. Anomalous relaxation is evident above 700 K.

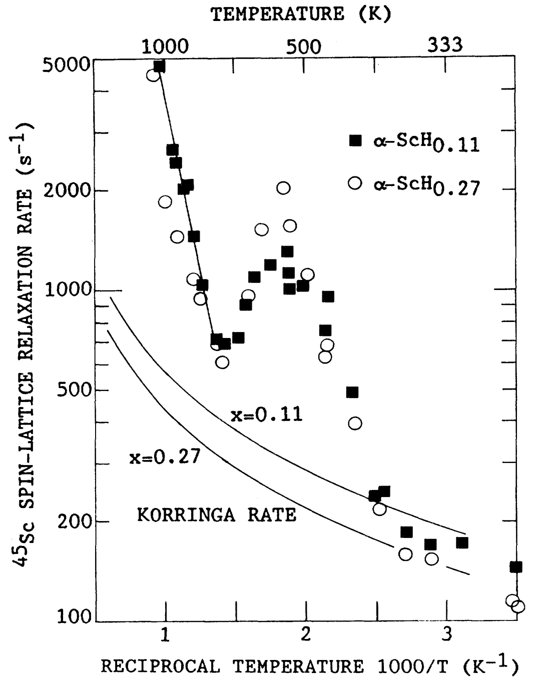

FIG. 3. Temperature dependence of the ^{45}Sc spin-lattice relaxation rate in α-ScH$_{0.11}$ and α-ScH$_{0.27}$ measured at 82.76 MHz. The solid curves show the conduction-electron contribution R_{1e} for the two hydrogen concentrations. The straight line through the steeply rising high-temperature points corresponds to an activation energy of 0.47 eV/atom.

the measurements made at 24 and 82.76 MHz.

The R_1(Sc) measurements show anomalous relaxation behavior above ~ 700 K. Such measurements in α-ScH$_{0.05}$ and α-ScD$_{0.05}$ at 24 MHz are compared in Fig. 1. The solid curve shows the temperature dependence of R_{1e} extrapolated from measurements made below 300 K. Although the data at this relatively low hydrogen concentration and low resonance frequency are not of extremely high quality, it is clear that anomalous behavior occurs in both the Sc-H and Sc-D solid solutions.

Figure 3 compares R_1 measurements at 82.76 MHz in two α-ScH$_x$ compositions $x = 0.11$ and 0.27. Again, the solid curves show the temperature dependence of R_{1e} extrapolated from low temperatures. The straight line drawn through the steeply rising data points for $x = 0.11$ above ~ 700 K corresponds to an apparent activation energy of 0.47 eV/atom.

B. R_1(H) measurements

For protons, the spin-lattice relaxation rate is normally given by

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

where R_{1e}(H) also depends on hydrogen concentration. The dipolar relaxation rate due to hydrogen motion, R_{1d}, depends in general on both the metal nuclear dipolar field and that of the protons.[12] However, in α-ScH$_x$ R_{1d} results primarily from modulation of the ^{45}Sc dipolar field by the hopping motion of the hydrogen, the ^{1}H-^{1}H dipolar interaction being essentially negligible at low hydrogen concentrations.[12] On the other hand, in α-YH$_x$ the dipolar field of ^{89}Y is so weak that it contributes negligibly to R_{1d}. Consequently, the maximum R_{1d} value in α-YH$_x$ is more than an order of magnitude weaker than in α-ScH$_x$ at the same resonance frequency (see below). In α-LuH$_x$, the two contributions are comparable, and the maximum rate is roughly half that in α-ScH$_x$.

Proton R_1 measurements were made using the inversion-recovery sequence, 180°-τ-90°-FID, or by using the saturation-recovery sequence (as for ^{45}Sc) with a short saturation comb of four or five closely spaced 90° pulses.

1. α-ScH$_x$

The temperature dependence of R_1(H) was measured in two samples with hydrogen concentrations $x = 0.11$ and 0.27 at resonance frequencies of 21, 24, and 40 MHz. The 21 MHz results are shown in Fig. 4. The highest tem-

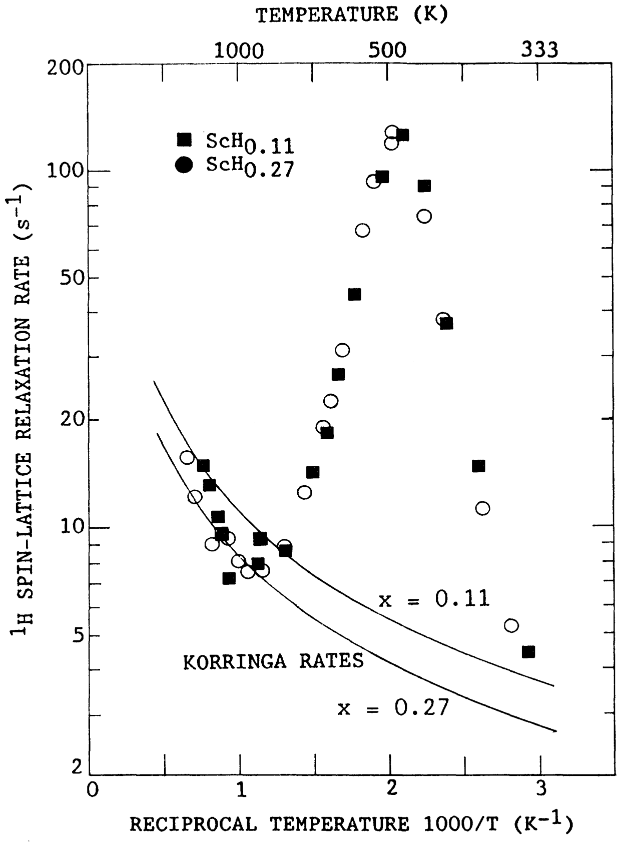

FIG. 4. Temperature dependence of the ^{1}H spin-lattice relaxation rate in α-ScH$_{0.11}$ and α-ScH$_{0.27}$ measured at 21 MHz. The solid curves show the conduction-electron contribution R_{1e} for the two hydrogen concentrations. No high-temperature anomalous relaxation is evident, even at 1384 K.

peratures reached were 1313 K for $x = 0.11$ and 1384 K for $x = 0.27$. No convincing evidence of anomalous behavior was found in any of the measurements despite the fact that these extend to temperatures well above that at which $R_1(\mathrm{H})$ returns to $R_{1e}(\mathrm{H})$.

2. α-YH$_x$

Measurements of $R_1(\mathrm{H})$ were made on two samples having hydrogen concentrations $x = 0.18$ and 0.21. Figure 5 shows the temperature dependence of $R_1(\mathrm{H})$ for $x = 0.21$ over the range 77–850 K measured at 40 MHz. The electronic structure transition that accompanies the hydrogen pairing phenomenon[16] is clearly evident as an increase in the Korringa parameter R_{1e}/T with increasing temperature. The weak peak in R_{1d} due to hydrogen diffusion is also evident at ~ 550 K. However, the measurements show no indication of an anomalous increase in $R_1(\mathrm{H})$ in the temperature range above the R_{1d} peak, i.e., 600–850 K. Measurements at higher temperatures, 600–1300 K, were made on the $x = 0.18$ sample at 21 MHz, and the results are shown in Fig. 6. The greater scatter in the data points reflects the inherent difficulties involved at these high temperatures; the error bars shown are ±5%. A least-squares fit to the data yields the straight line shown in the figure, having slope $R_{1e}/T = 8.24 \times 10^{-3}\ (\mathrm{s\,K})^{-1}$ and intercept of 0.25 s^{-1}. The slope is in good agreement with the value $8.00 \times 10^{-3}\ (\mathrm{s\,K})^{-1}$ obtained previously on this sample at 400 MHz,[13] and the small nonzero intercept may be attributed to the residual Gd impurity content of the yttrium metal.[16] Again, no indication of an anomalous increase in $R_1(\mathrm{H})$ is seen even at these very high temperatures.

3. α-LuH$_x$

Proton spin-lattice relaxation in α-LuH$_x$ differs from that in the other two systems studied in that strong ^{1}H-^{175}Lu cross relaxation R_{1c} occurs at low and interme-

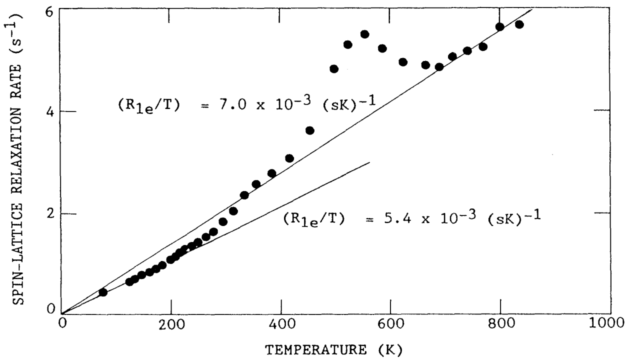

FIG. 5. Temperature dependence of the ^{1}H spin-lattice relaxation rate in α-YH$_{0.21}$ measured at 40 MHz. The solid lines show the conduction-electron contribution R_{1e} at low and high temperatures (Ref. 13).

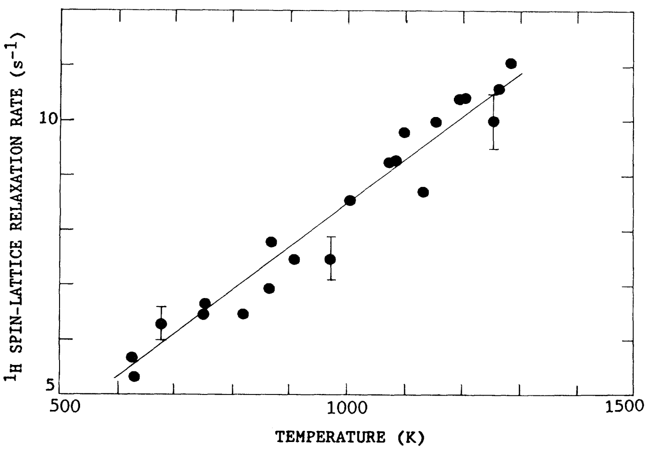

FIG. 6. Temperature dependence of the ^{1}H spin-lattice relaxation rate in α-YH$_{0.18}$ in the range 600–1300 K, measured at 21 MHz. The solid line is a least-squares fit to the data points (see text). Error bars shown are ±5%. The good fit demonstrates the absence of additional (anomalous) relaxation at high temperatures.

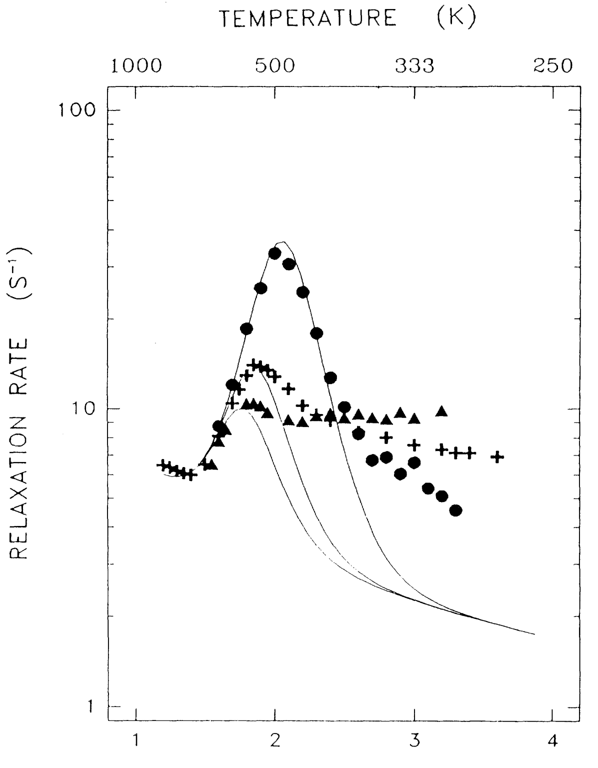

FIG. 7. Temperature dependence of the ^{1}H spin-lattice relaxation rate in α-LuH$_{0.15}$ measured at 12.2, 40, and 65 MHz. The solid curve for 12.2 MHz is a least-squares fit; the 40 and 65 MHz curves use the same fit parameters. At low temperatures, ^{1}H-^{175}Lu cross relaxation increases the proton relaxation rate above the conduction-electron contribution.

diate temperatures.[9] However, this relaxation channel, which effectively short-circuits the conduction-electron rate R_{1e}, becomes ineffective in the temperature regime of fast hydrogen diffusion. It then becomes possible to measure $R_{1e} + R_{1d}$ without interference from R_{1c}. R_1(H) measurements in α-LuH$_{0.15}$ to 833 K at 40 MHz are shown in Fig. 7, together with measurements at 12.2 and 65 MHz to somewhat lower temperatures. The solid curve through the 12.2 MHz data is a least-squares fit using $R_{1e}/\mathrm{T} = 6.76 \times 10^{-3}$ (s K)$^{-1}$ from 400 MHz measurements,[9] yielding an activation energy of 0.52 eV/atom for hydrogen diffusion from the motionally modulated dipolar contribution R_{1d}.[9] The solid curves through the 40 and 65 MHz points are drawn with the same parameters determined from the fit to the 12.2 MHz data. At temperatures below the R_{1d} peak, ^{1}H-^{175}Lu cross relaxation increases the measured proton relaxation rate above the electronic contribution R_{1e}.[9] Higher-temperature measurements were not attempted due to concern over exploding the sample. Nevertheless, the data show no indication of anomalous behavior up to ~ 100 K above the dipolar maximum.

IV. DISCUSSION

In the Sc dihydrides and dideuterides, anomalous high-temperature behavior of both the ^{1}H (and ^{2}D) and ^{45}Sc SLR rates has been observed.[1,8] In these phases the fluctuations in the ^{45}Sc quadrupole interaction result from vacancy hopping on the hydrogen sublattice. At all vacancy concentrations c_v, $c_v\tau_v^{-1} = c_{\mathrm{H}}\tau_d^{-1}$ where c_{H} is the hydrogen concentration and τ_v^{-1} and τ_d^{-1} are the vacancy and hydrogen hopping rates, respectively.[12] For $c_v \ll 1$, $\tau_v^{-1} \gg \tau_d^{-1}$ since a hydrogen cannot jump unless it has an adjacent vacancy, with the result that the temperature dependence of R_{1Q}(^{45}Sc) is shifted to lower temperatures relative to that of R_{1d}(^{1}H). Thus, the usual R_{1Q}(Sc) maximum at intermediate temperatures is found experimentally at a lower temperature than the R_{1d}(H) maximum in the same sample. Likewise, the anomalous relaxation at high temperatures is first apparent in R_1(Sc) at a lower temperature than in R_1(H); this *suggests* that hydrogen vacancy motion may be responsible for the anomalous relaxation rates in ScH$_2$ and ScD$_2$.

The situation is different in the α solid-solution phase in which the fluctuations in the ^{45}Sc quadrupole interaction result from hydrogen hopping on an essentially empty sublattice. Accordingly, one expects the normal R_{1Q}(Sc) and R_{1d}(H) maxima resulting from long-range hydrogen diffusion to occur at the same temperature for measurements made at the same resonance frequency. That they indeed do is seen by comparing the 24 MHz ^{45}Sc data for α-ScH$_{0.11}$ in Fig. 2 with that for ^{1}H at 21 MHz in the same sample, shown in Fig. 4. (The small difference in resonance frequencies, 24 MHz for ^{45}Sc versus 21 MHz for ^{1}H, is not significant.) The same cannot be said for the high-temperature behavior. At 1000 K, R_1(Sc) is already nearly an order of magnitude greater than R_{1e}(Sc) (Fig. 2), whereas R_1(H) remains at the value of R_{1e}(H) even at 1300 K (Fig. 4). Moreover, the minimum reached by R_1(Sc) between the normal diffusion maximum and the anomalous regime occurs at ~ 700 K, whereas R_1(H) has not yet returned to its R_{1e} value at that temperature.

As in other systems investigated, the anomalous rate may be represented by a phenomenological term of the form

$$R_{1A} = A' \exp(-U/k_BT) \tag{4}$$

added to the right-hand side of Eq. (1). As already noted, for ^{45}Sc in α-ScH$_{0.11}$, U = 0.47 eV/atom; also from Fig. 3, one has $A' = 9.3 \times 10^5$ s^{-1}. The value of U is essentially the same as found for ^{45}Sc in ScH$_{1.83}$ (0.46 eV/atom);[8] however, the value of A' is more than an order of magnitude greater than that in ScH$_{1.83}$ (3.3×10^4 s^{-1}). On the other hand, when compared with anomalous relaxation of protons, this value of A' is two orders of magnitude stronger than that found for ^{1}H in ZrH$_{1.98}$,[3] but comparable to that of ^{1}H in Nb$_{0.75}$V$_{0.25}$H$_{0.23}$.[4]

A. ^{1}H relaxation

Recent calculations[17] have focused on the possibility that the origin of the anomalous rate may involve the formation of close pairs of H atoms ("molecules") at high temperatures. This would presumably be an excited state in which a strong proton spin-spin interaction could occur. It is not unreasonable to expect that the presence of a transient H$_2$ molecular entity would give rise to a substantial electric field gradient (EFG) at neighboring Sc sites, resulting in anomalous relaxation of ^{45}Sc, as observed in the present measurements. But if this is the origin of the ^{45}Sc anomalous rate, it is then difficult to understand the absence of anomalous proton relaxation. Furthermore, formation of pairs would be extremely sensitive to hydrogen concentration, although the ^{45}Sc relaxation anomaly is not very different in the present dilute solid solutions (Fig. 3) and previously studied ScH$_x$ (x ~ 2) hydrides.

On the other hand, extensive new measurements[7] on the solid-solution system Nb$_{0.5}$V$_{0.5}$H$_{0.36}$ found that the anomalous proton SLR, R_{1A}(H), resulted from spin relaxation in molecular hydrogen in the gas phase in equilibrium with the solid metal-hydrogen system. The extremely fast exchange of hydrogen between the solid and gas phases facilitates the transfer of relaxation from gas to solid. Under such conditions the overall ^{1}H relaxation rate R_1 for the gas-solid system is the weighted average of the rates in the two phases (M = metal, G = gas):[7]

$$R_1 = R_{1M}\frac{C_M}{C_M + C_G} + R_{1G}\frac{C_G}{C_M + C_G} \quad . \tag{5}$$

The spin heat capacities C_M and C_G are the numbers of protons in each phase (at these high temperatures H$_2$ molecules have reached the 3:1 ortho-para composition ratio equivalent to uncorrelated ^{1}H spins). The first term in Eq. (5) is the direct relaxation in the solid (metal) phase, i.e., the Korringa rate plus the motionally modulated dipolar rate. The anomalous rate is given by the second term,

$$R_{1A} = R_{1G}\frac{C_G}{C_M} \quad , \tag{6}$$

since $C_G \ll C_M$ because most of the protons are in the metallic phase.

In the case of $Nb_{0.5}V_{0.5}H_{0.36}$ at 860 K,[18] the H_2 vapor over the metal has a pressure of 7 atm and a density of 2.2 amagats (assuming ideal gas behavior). Thus 1 proton in 180 is in the gas phase, assuming the interstitial volume between the metal particles equals that of the particles themselves. For these conditions, gas-phase measurements[7] yielded $R_{1G} = 4.8 \times 10^3$ s^{-1}, in agreement with previous work.[19] Therefore, Eq. (6) predicts $R_{1A} = 27$ s^{-1}, in reasonable accordance with the experimental value $R_{1A} = 39$ s^{-1}. A similar explanation may be anticipated for the V-H, Nb-H, and Ta-H solid-solution phases in which anomalous ^{1}H SLR has also been observed.[4–6] For example, at a hydrogen/metal ratio of 0.2 at $T \simeq 900$ K, the equilibrium hydrogen vapor pressure in the V-H system is approximately 10 atm.

In marked contrast to the bcc, metal-hydrogen solid-solution phases, the equilibrium H_2 vapor pressure over the Sc-H, Y-H, and Lu-H solid phases remains extremely low at high temperatures. This means there is very little hydrogen present in the gas phase even at $T \simeq 1000$ K and higher. For example, for α-$ScH_{0.2}$ at $T = 875$ K, $p \simeq 1.3 \times 10^{-6}$ atm.[20] For α-$YH_{0.2}$ at 875 K, $p \simeq 10^{-7}$ atm,[21] and for α-LuH_x similar low pressures occur.[22]

Such low pressures imply correspondingly low H_2 densities. A pressure of 10^{-7} atm at 875 K implies a gas density of 3.2×10^{-8} amagat and an H_2 gas concentration of 0.79×10^{-12} mol in the NMR sample volume (6 mm i.d. × 2 cm long). A typical sample of 2 g of $YH_{0.2}$ contains 4.5×10^{-3} mol H (2.25×10^{-3} mol H_2 equivalent), so that there is one H_2 molecule in the gas phase for $\sim 3 \times 10^9$ in the solid phase. Hence, the ratio of the spin heat capacities in Eq. (6) has the value $C_G/C_M \simeq 3.3 \times 10^{-10}$.

Strictly speaking, to estimate the anomalous rate R_{1A} from Eq. (6), the rate R_{1G} in the gas at low densities and high temperatures is required. As a function of gas density ρ, R_{1G} attains its maximum value $(R_{1G})_{\max}$ when $\omega_0\tau_c \approx 1$, where ω_0 is the proton Larmor frequency and τ_c the correlation time for collisions between molecules and/or with the particle surfaces that reorient the molecular angular momentum. For $Nb_{0.5}V_{0.5}H_{0.36}$ the relatively high gas pressures and densities ensured that the condition $\omega_0\tau_c \ll 1$ was always satisfied, i.e., that the system was in the fast-fluctuation (short-correlation-time) regime.[7] In the present case, the low pressures and densities mean that $\omega_0\tau_c \gg 1$; i.e., the system is in the slow-fluctuation regime. However, lacking measurements of R_{1G} at low densities (Hardy's measurements[19] extend only to H_2 densities of ~ 0.1 amagat at 77.5 K), and with an unknown rate of H_2 collisions with the metal particles, we base our estimate of R_{1A} on the *maximum relaxation rate* $(R_{1G})_{\max}$. Because of the very low vapor pressure and small spin heat capacity ratio, R_{1A} will nevertheless be entirely negligible.

The maximum rate is given by[19]

$$(R_{1G})_{\max} \simeq M_2/\omega_0 \quad , \tag{7}$$

where M_2 is the second moment describing the intramolecular dipole-dipole and spin-rotation interactions. In Hardy's work at $\omega_0/2\pi = 30$ MHz,[19] a maximum rate of 5.2×10^3 s^{-1} was found, in excellent agreement with spin-relaxation theory. The second moment M_2 will increase slightly with temperature: the dipole-dipole interaction in the $J = 1$ manifold is 0.4 that of the classical value, so that the dipolar contribution to M_2 can increase by at most a factor of $(1/0.4)^2 = 6.25$.[23] The spin-rotation contribution to M_2 in a *classical* system varies linearly with temperature (from the equipartition theorem); because of the quantum nature of rotation in cold H_2, the spin-rotation part of M_2 will increase by a factor of ~ 5 at 1000 K.[24] Thus a conservative upper limit on the maximum H_2 relaxation rate R_{1G} at 21 MHz is 50×10^3 s^{-1} [see Eq. (7) above].

The *maximum* anomalous rate R_{1A} may be obtained from Eq. (6) using the above estimate of $(R_{1G})_{\max}$ and the spin heat capacity ratio C_G/C_M. The result is 1.6×10^{-5} s^{-1}, completely negligible in comparison with the 8 s^{-1} rate measured in $YH_{0.18}$ at 875 K (Fig. 6). Even at the highest temperature attained, 1283 K, the vapor pressure of $\sim 10^{-3}$ atm (Ref. 20) corresponds to a H_2 gas density of 2.1×10^{-4} amagat and a spin heat capacity ratio of 2.4×10^{-6}. Thus, again assuming R_{1G} has its maximum possible value of 5×10^4 s^{-1}, the anomalous relaxation rate from Eq. (6) is 0.12 s^{-1}, a factor of 100 smaller than the observed 11 s^{-1} (Fig. 6).

As noted above, the equilibrium H_2 gas pressures in the α-ScH_x and α-LuH_x systems are very small, similar to those in α-YH_x. Consequently, the estimated values of R_{1A} are also similar to those estimated above for α-YH_x. We conclude that our inability to detect an anomalous, high-temperature contribution to the ^{1}H relaxation rate is consistent with the fast gas-solid exchange mechanism for the origin of $R_{1A}(^1\mathrm{H})$: The H_2 vapor pressures of the hcp solutions are many orders of magnitude too small.

B. ^{45}Sc relaxation

In contrast to the absence of $R_{1A}(^1\mathrm{H})$, anomalous behavior of $R_1(^{45}\mathrm{Sc})$ is clearly evident in Figs. 1–3. This dichotomy appears to indicate that the anomalous rates $R_{1A}(^1\mathrm{H})$ and $R_{1A}(^{45}\mathrm{Sc})$ have *different origins.* As detailed above, the nonoccurrence of $R_{1A}(^1\mathrm{H})$ is consistent with the mechanism of relaxation in the gas phase mediated by fast gas-solid exchange. It is extremely unlikely that $R_{1A}(^{45}\mathrm{Sc})$ can result from this mechanism because the Sc spins are stationary in the lattice. Also, the normal $R_{1Q}(^{45}\mathrm{Sc})$ peak is due to hydrogen diffusion, and at higher temperatures hydrogen motion is too fast to be effective in relaxing ^{45}Sc spins, i.e., $\omega_{\mathrm{Sc}}\tau_c \ll 1$. Furthermore, as seen in Figs. 2 and 3, the maximum rate reached at the highest temperature in the anomalous regime exceeds $(R_{1Q})_{\max}$ due to hydrogen diffusion by factors of 2–3. More striking, $R_{1A}(^{45}\mathrm{Sc})$ appears to increase indefinitely. The latter observation stands in contrast to that in the Sc dihydrides where $R_{1A}(^{45}\mathrm{Sc})$ appears to reach a maximum value.[8] As noted above, the presence of transient H_2 molecular entities within the metal lattice could certainly result in strong ^{45}Sc spin relaxation, but the failure to detect the accompanying $R_{1A}(^{1}\mathrm{H})$ rules out this mechanism, which is in any event unlikely on theoretical grounds.

Since ^{45}Sc is the only metal nucleus for which anomalous relaxation has been found in M-H systems [a search for $R_{1A}(^{51}\mathrm{V})$ in α-$\mathrm{VH}_{0.2}$ was unsuccessful[4]], it may be that Sc is a pathological case, the anomaly being due to some as-yet unidentified impurity present in the metal, for example. The impurity would need to be effective in both the hcp lattice of the α phase and the fcc lattice of the dihydride. Two primary candidate impurities are oxygen and iron, both of which are initially present in the nominal high-purity Sc metal used in this work, oxygen at a level of 100–300 parts per million atomic (ppma) and iron at 30–100 ppma. Additional oxygen may be introduced during hydride preparation and sample handling. Oxygen-induced quadrupolar relaxation of ^{51}V spins was found in high-temperature measurements on vanadium metal.[25] In that case the relaxation strength increased steadily with time at high temperature and with cyclic heating and cooling, behavior never observed in the present work on Sc-H.

In the case of iron, recent experimental[26] and theoretical[27] investigations have shown that an iron impurity in Sc carries a nonzero magnetic moment. Moreover, Fe is a fast-diffusing interstitial in Sc, having an activation energy of 0.56 eV/atom.[28] The rapid motion of such a paramagnetic entity could provide an effective relaxation mechanism for the stationary ^{45}Sc spins, whereas it would probably have little effect on the already rapidly moving protons.

As an initial step to investigate relaxation by impurities, the temperature dependence of $R_1(^{45}\mathrm{Sc})$ was measured in a sample of Sc metal powder. The data are shown in Fig. 8. Measurements were first made on the metal powder itself, without any material added to separate the grains. After heating to approximately 750 K inspection of the sample revealed some light sintering and adhesion of the metal particles to the walls of the quartz tube. A second sample of the same metal was then mixed with carefully baked MgO powder and sealed in a new container. The R_1 measurements were repeated and extended to higher temperatures, as shown in Fig. 8. It is clear that $R_1(^{45}\mathrm{Sc})$ follows essentially the same behavior at high temperatures as in the solid-solution samples, showing a weak R_{1Q} peak at about 650 K and an anomalous increase above $\sim$ 750 K. The weak R_{1Q} peak indicates that this sample still contains some hydrogen (see below).

The Sc metal powder was prepared by extracting the hydrogen from one of the α-ScH_x samples at a high temperature. Unfortunately, the temperature required to extract all of the hydrogen results in sintering of the metal grains, rendering the material unfit for NMR work. In the present case, sintering was avoided by not raising the temperature too high, but the resulting metal powder was subsequently found to have the composition $\mathrm{ScH}_{0.027}$. Interestingly, when $R_{1A}(^{45}\mathrm{Sc})$ for this sample is compared with that for α-$\mathrm{ScH}_{0.11}$ (Fig. 3), the values scale with hydrogen concentration. Thus, at 1000 K, $R_{1A} = R_{1Q} - R_{1e} \simeq 1000\ \mathrm{s}^{-1}$ for $x = 0.027$, and $R_{1A} \simeq 4000\ \mathrm{s}^{-1}$ for $x = 0.11$, consistent with $0.11/0.027 \simeq 4$, and suggesting that $R_{1A}(^{45}\mathrm{Sc})$ is a consequence of the hydrogen content of the metal. Nevertheless, this result should be regarded with caution until measurements have been made on Sc metal of demonstrably higher purity and freedom from hydrogen than in the present work, as well as on samples prepared from Sc containing controlled levels of oxygen and/or iron.

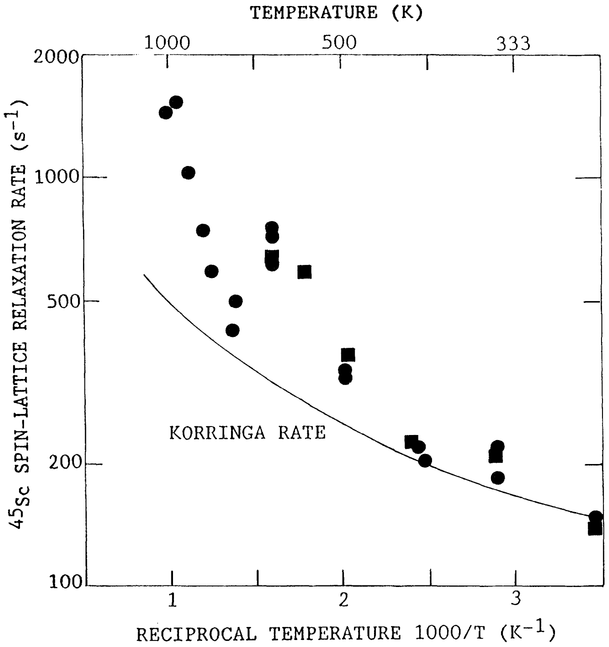

FIG. 8. Temperature dependence of the ^{45}Sc spin-lattice relaxation rate in a sample of Sc metal powder prepared by extracting the hydrogen from a Sc-H sample at high temperature. Subsequent analysis showed the sample composition to be $\mathrm{ScH}_{0.027}$. ■, metal powder only; ●, metal powder mixed with outgassed MgO powder. The solid curve is the conduction-electron rate R_{1e} extrapolated from low temperatures.

V. SUMMARY AND CONCLUSIONS

The spin-lattice relaxation rates $R_1(^{1}\mathrm{H})$ and $R_1(^{45}\mathrm{Sc})$ have been measured to temperatures as high as 1384 K in the solid-solution M-H systems α-ScH_x, α-YH_x, and α-LuH_x. For $R_1(^{45}\mathrm{Sc})$, a strong anomalous contribution $R_{1A}(^{45}\mathrm{Sc})$ occurs at $T \gtrsim 800$ K in all Sc-H solid solutions studied ($x = 0.05$, 0.11, and 0.27) as well as in α-$\mathrm{ScD}_{0.05}$ and in nominally pure Sc metal itself. On the other hand, no indication of a corresponding contribution $R_{1A}(^{1}\mathrm{H})$ could be detected for $R_1(^{1}\mathrm{H})$. These behaviors contrast with that found in the dihydride phase, ScH_{2-x}, in which strong anomalous rates are found for both nuclei at high temperatures.[1,8]

The results for ^1H relaxation, i.e., the absence of $R_{1A}(^1H)$, support the fast gas-solid exchange mechanism for $R_{1A}(^1H)$ at high temperatures.[7] The extremely low H_2 gas pressure and density in equilibrium with the solid M-H phase lead to this conclusion. In contrast, the anomalous ^{45}Sc relaxation remains unexplained, although $R_1(^{45}Sc)$ measurements on a sample of α-$ScH_{0.027}$, compared to $R_1(^{45}Sc)$ in α-$ScH_{0.11}$, showed that $R_{1A}(^{45}Sc)$ scales with the hydrogen concentration x, suggesting that the anomalous rate is indeed somehow a consequence of the hydrogen content and not an intrinsic property of Sc metal. However, the possibility that $R_{1A}(^{45}Sc)$ results from the motion of an unidentified impurity in the metal, e.g., oxygen or iron, cannot yet be unambiguously determined.

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