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Nuclear magnetic resonance study of the low-temperature localized H(D) motion in α-ScH$_x$(D$_x$): Isotope effects

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Nuclear magnetic resonance measurements of the ^{45}Sc, ^{1}H, and ^{2}D spin-lattice relaxation rates in the solid solutions α-ScH$_x$ ($x=0$, 0.11, and 0.27) and α-ScD$_x$ ($x=0.05$ and 0.22) have been performed over the temperature range 4.2–294 K. For the hydrided and deuterided samples we have found pronounced deviations of the ^{45}Sc relaxation rate measured at 86.2 MHz from the Korringa behavior in the range 30–180 K. The excess ^{45}Sc relaxation rate displays a peak near 100 K in α-ScH$_x$ and near 110–140 K in α-ScD$_x$, resulting from the quadrupole interaction modulated by fast localized hopping of H(D) atoms. The amplitude of the ^{45}Sc relaxation rate peak in the deuterided samples is found to be much higher than in the hydrided samples with comparable hydrogen content. This unusual isotope effect indicates that the fraction of D atoms participating in the fast localized motion in α-ScD$_x$ is approximately six times as large as the corresponding fraction of H atoms in α-ScH$_x$. The results of our measurements of the ^{1}H and ^{2}D relaxation rates are consistent with this conclusion. The strong effect of H↔D substitution on the fraction of atoms involved in the localized hopping should be accounted for in any microscopic model of hydrogen motion in Sc. [S0163-1829(99)15725-4]

I. INTRODUCTION

The unusual low-temperature properties of solid solutions of hydrogen in scandium and the related hcp metals Y and Lu have received much recent attention. The solid-solution (α) phase in these materials is stabilized up to much higher hydrogen concentrations at low temperatures than in other metal-hydrogen systems. In fact, the α phases of these systems are remarkable in that their hydrogen solubility limits $x_{\max}$ do not tend to zero as temperature goes to zero. It is believed that the α phase stabilization is related to the peculiar short-ranged ordering of hydrogen (see, e.g., Ref. 1) that develops with decreasing temperature. Neutron diffraction[2] and diffuse scattering[3,4] measurements have shown that hydrogen occupies only the tetrahedral interstitial sites in the hcp Sc lattice and tends to form next-nearest-neighbor pairs bridging the metal atoms in the *c* axis direction. As the temperature is lowered, these pairs arrange themselves into a longer-range structure, predominantly along the *c* direction. This structure never becomes truly long ranged and thus never develops new Bragg diffraction peaks.

Nuclear magnetic resonance (NMR) measurements of the proton spin-lattice relaxation rate $(T_1^{-1})_{\mathrm{H}}$ in α-ScH$_x$ and related systems[5,6] have revealed a fast localized H motion with characteristic hopping rate τ_l^{-1} of about 10^8 s^{-1} at 50 K. This localized motion gives rise to an additional frequency-dependent maximum of $(T_1^{-1})_{\mathrm{H}}$ at low temperatures (35–80 K). The structure of the sublattice of tetrahedral interstitial sites in a hcp metal suggests that the localized H motion corresponds to hopping between the nearest-neighbor sites, separated by about 1.0 Å in the *c* direction. Quasielastic neutron scattering (QENS) measurements on α-ScH$_x$ (Refs. 7 and 8) have revealed the existence of a still faster localized H motion with hopping rate τ_f^{-1} passing through a *minimum* of about 7×10^{10} s^{-1} near 100 K and increasing to 10^{12} s^{-1} at 10 K. On the other hand, because of the limited energy resolution (70 μeV) these QENS experiments could not detect the slower H motion found by NMR.[5,6] In order to reconcile the NMR and QENS results, it has been suggested[8] that the slower frequency scale τ_l^{-1} corresponds to the hopping of protons involved in pairing, whereas the faster scale τ_f^{-1} corresponds to the hopping of unpaired protons. This interpretation is supported by the observed decrease in the fraction of protons having the hopping rate τ_f^{-1} with decreasing temperature.[8] However, the observed low amplitudes of the low-temperature $(T_1^{-1})_{\mathrm{H}}$ peak in α-ScH$_x$ (Ref. 5) (only about 2% that of the main, higher temperature peak due to diffusive motion) indicate that only a small fraction of protons participate in the slower local motion; this does not support the suggestion[8] that the frequency scale τ_l^{-1} corresponds to the hopping of paired protons, because at low temperatures most of the hydrogen atoms are believed to be paired.[3]

Since the low-temperature localized hydrogen motion in scandium is likely to be of quantum origin,[7] one may expect pronounced effects of isotope (H↔D) substitution. It should be noted that neutron diffraction and diffuse scattering experiments have been performed on deuterided (α-ScD$_x$) samples, whereas the NMR and QENS measurements have been made only on hydrided (α-ScH$_x$) samples. Isotope effects in hydrogen motion in α-ScH$_x$(D$_x$) have been studied by ultrasonic measurements in the 1 MHz range on $ScH_{0.25}$ and $ScD_{0.18}$.[9] These measurements have revealed ultrasonic attenuation peaks near 25 K for $ScH_{0.25}$ and near 50 K for $ScD_{0.18}$. The results have been interpreted in terms of a two-level-system model involving tunneling between asymmetric sites, the model parameters being strongly isotope dependent.[9]

The aim of the present work is to study the effects of H↔D substitution on the parameters of the localized hydrogen motion in α-$ScH_x(D_x)$ using ^{45}Sc, ^{1}H, and ^{2}D spin-lattice relaxation measurements. Relaxation rate measurements on host-metal nuclei with non-zero quadrupole moments serve as an efficient probe of isotope effects in hydrogen motion.[10] For such nuclei the main motional contribution to the relaxation rate originates from the electric quadrupole interaction modulated by H(D) hopping. Since for the quadrupole interaction only *charge* fluctuations are important, H and D atoms are expected to give the same contributions to the host-metal relaxation rate, *if their motional parameters are the same*. We have measured the spin-lattice relaxation rates for ^{45}Sc (with spin $I=7/2$ and quadrupole moment $Q=-0.22\times10^{-24}$ cm^2) in α-ScH_x ($x=0$, 0.11, and 0.27) and α-ScD_x ($x=0.05$ and 0.22) over the temperature range 4.2–294 K. These measurements have revealed that isotope substitution leads to dramatic changes in the amplitude of the relaxation rate anomaly attributed to the localized hydrogen motion. The ^{45}Sc relaxation experiments have been complemented by spin-lattice relaxation rate measurements for protons and deuterons on the same samples.

II. EXPERIMENTAL DETAILS

The samples of α-ScH_x and α-ScD_x were prepared from high-purity Ames Laboratory (Materials Preparation Center) scandium metal having a total rare-earth impurity content of less than 5 ppm and an iron content of less than 13 ppm. The preparation procedures for the powdered samples have been reported previously.[5]

Measurements of the ^{45}Sc, ^{1}H, and ^{2}D spin-lattice relaxation times T_1 were made using a CMX360 Chemagnetics spectrometer connected to a 1 kW transmitter in the magnetic field of 8.4 T produced by a 89 mm-bore superconducting solenoid. The corresponding resonance frequencies were 86.2 MHz for ^{45}Sc, 354.12 MHz for ^{1}H, and 54.36 MHz for ^{2}D. For α-$ScD_{0.22}$ the ^{2}D spin-lattice relaxation times were also measured in a field of 4.7 T (30.7 MHz) produced by a 127 mm-bore superconducting magnet. Temperatures below 140 K were achieved with a research Dewar built by Kadel Inc. In this range the sample temperature was stable to ±0.1 K, as measured by a thermocouple and a calibrated carbon-glass resistor thermometer. At temperatures above 140 K we used a thermostated flowing N_2 gas apparatus; the sample temperature measured by a copper-constantan thermocouple was stable to ±1 K.

Spin-lattice relaxation times were determined from the recovery of free-induction decay or echo signals after a saturating train of rf pulses. For ^{1}H and ^{2}D NMR signals the recovery curves were found to be exponential in the whole temperature range studied. The relaxation of ^{45}Sc showed deviations from the single-exponential behavior. Such deviations are typical of relaxation of quadrupolar nuclear spins in systems with a strong static quadrupole interaction,[11] where rf pulses cannot cover the entire NMR spectrum. The values of T_1 for ^{45}Sc reported here were all defined as the $1/e$ point on the recovery curve. We were careful to measure the recovery curve over a wide range of times, in order to ensure that the nuclear magnetization was allowed to recover fully.

III. RESULTS AND DISCUSSION

A. ^{45}Sc relaxation

In metal-hydrogen systems the measured spin-lattice relaxation rate T_1^{-1} for host-metal nuclei with nonzero quadrupole moment usually results from a sum of contributions due to conduction electrons (T_{1e}^{-1}) and due to the electric quadrupole interaction modulated by H(D) hopping (T_{1Q}^{-1}). Our estimates and the results of high-temperature relaxation rate measurements[12] show that for ^{45}Sc in α-$ScH_x(D_x)$ the magnetic dipolar contribution to T_1^{-1} can be neglected, since it is much lower than the quadrupolar one; hence

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

The electronic (Korringa) term is typically proportional to temperature, $T_{1e}^{-1}=R_eT$, and does not depend on the resonance frequency. Assuming that the spectral density functions of the electric field gradient (EFG) fluctuations have a simple Lorentzian form, the quadrupolar contribution in a powder α-ScH_x sample can be written as[12]

$$(T_{1Q}^{-1})_{Sc}=\frac{15\pi^2x}{49\omega_{Sc}}\langle\Gamma_{NN}\rangle^2\left[\frac{y}{1+y^2}+\frac{4y}{1+4y^2}\right]. \tag{2}$$

Here ω_{Sc} is the ^{45}Sc resonance frequency and $y=\omega_{Sc}\tau_d$, where τ_d is the relevant mean residence time of a hydrogen atom in an interstitial site. $\langle\Gamma_{NN}\rangle$ is the average quadrupole coupling constant of ^{45}Sc due to a nearest-neighbor hydrogen. The relaxation rate is due only to Sc having nearest-neighbor protons, so that at low H contents it is proportional to hydrogen concentration x. The temperature dependence of $(T_{1Q}^{-1})_{Sc}$ is expected to show a maximum at the temperature T_{max} at which the condition $y=\omega_{Sc}\tau_d\approx1$ is satisfied. High-temperature measurements of the ^{45}Sc spin-lattice relaxation rate in α-ScH_x at $\omega_{Sc}/2\pi=24$ MHz (Ref. 12) have revealed such a maximum at $T_{max}\approx500$ K. This maximum results from H jumps leading to long-range hydrogen diffusion. However, if long-range H diffusion coexists with localized H hopping with the characteristic time τ_l (or τ_f) being much shorter than τ_d, one may expect an additional low-temperature relaxation rate maximum determined by the condition $\omega_{Sc}\tau_l\approx1$ (or $\omega_{Sc}\tau_f\approx1$). Such an additional low-temperature maximum was observed for the ^{51}V spin-lattice relaxation rate in the Laves phase hydrides $TaV_2H_x(D_x)$, which also shows fast localized H(D) motion.[13,14]

The results of our ^{45}Sc spin-lattice relaxation rate measurements for α-$ScH_x(D_x)$ at $\omega_{Sc}/2\pi=86.2$ MHz are shown in Fig. 1. As expected, for the hydrogen-free Sc the measured relaxation rate is approximately proportional to temperature at $T<100$ K with $R_e=(T_{1e}T)^{-1}=0.80\pm0.01$ s^{-1} K^{-1}. This result is in general agreement with the low-temperature R_e values for polycrystalline Sc found

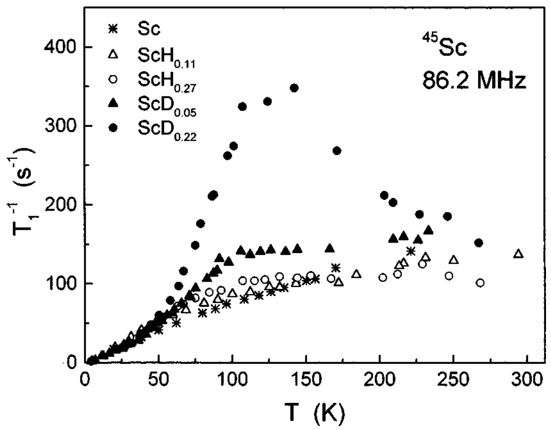

FIG. 1. Temperature dependence of the ^{45}Sc spin-lattice relaxation rate in Sc, α-ScH$_x$, and α-ScD$_x$ measured at 86.2 MHz.

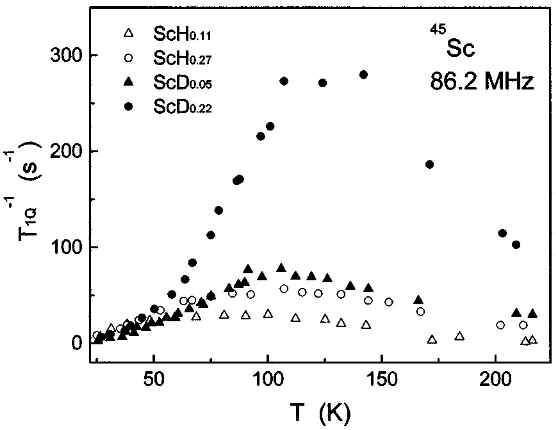

FIG. 2. Temperature dependence of the motional contribution to the ^{45}Sc spin-lattice relaxation rate in α-ScH$_x$ and α-ScD$_x$ at 86.2 MHz.

by Narath (0.77 $\mathrm{s}^{-1}\ \mathrm{K}^{-1}$)[15] and Umemura and Masuda (0.63 $\mathrm{s}^{-1}\ \mathrm{K}^{-1}$).[16] Ross *et al.*[17] have measured the ^{45}Sc spin-lattice relaxation rate in single-crystal Sc and found a dependence of T_{1e}^{-1} on the angle θ between the c axis and the direction of the static magnetic field. Their experimental R_e values at 77 K are 0.67 $\mathrm{s}^{-1}\ \mathrm{K}^{-1}$ for $\theta = 90°$ and 0.86 $\mathrm{s}^{-1}\ \mathrm{K}^{-1}$ for $\theta \approx 55°$ (''magic angle''). It should be noted that above 100 K the measured relaxation rate in Sc shows a downward deviation from linear behavior (Fig. 1). A similar deviation was reported by Umemura and Masuda;[16] it may be attributed to the peak in the density of electron states near the Fermi level in Sc.[18]

As can be seen from Fig. 1, the behavior of $(T_1^{-1})_{\mathrm{Sc}}$ in the H- and D-doped samples differs considerably from that in hydrogen-free Sc. The electronic contribution $(T_{1e}^{-1})_{\mathrm{Sc}}$ is known to *decrease* with increasing hydrogen content, the R_e values estimated from high-temperature ^{45}Sc relaxation rate measurements in α-ScH$_x$ (Ref. 12) being 0.57 $\mathrm{s}^{-1}\ \mathrm{K}^{-1}$ for $x = 0.11$ and 0.44 $\mathrm{s}^{-1}\ \mathrm{K}^{-1}$ for $x = 0.27$. This means that the *enhancement* of $(T_1^{-1})_{\mathrm{Sc}}$ revealed in our measurements for the H- and D-doped samples in the range ~40–200 K should be ascribed to the quadrupolar contribution. The main qualitative features of the behavior of $(T_1^{-1})_{\mathrm{Sc}}$ in this range are as follows.

(1) For both H- and D-doped samples the amplitude of the relaxation rate anomaly increases with increasing H(D) concentration. Qualitatively, such concentration dependence is consistent with the x dependence of Eq. (2).

(2) The amplitude of the ^{45}Sc relaxation rate anomaly in D-doped samples is much higher than in H-doped samples of comparable concentration. This unusual isotope effect implies that the mean-square amplitude of EFG fluctuations [caused by H(D) hopping] at Sc sites in α-ScD$_x$ is much higher than in α-ScH$_x$. The value of $\langle \Gamma_{\mathrm{NN}} \rangle$ is expected to be the same in H- and D-doped samples if H and D atoms occupy the same interstitial sites, as is believed to be the case. Here we recall that H and D have the same charge and produce the same quadrupole interaction. Therefore, in order to account for the strong difference in the mean-square amplitude of EFG fluctuations at Sc sites, we are forced to the conclusion that only a fraction p of H(D) atoms participates in the fast localized motion, and that this fraction in α-ScD$_x$ is considerably higher than in α-ScH$_x$. One may estimate the relative fractions p of H and D atoms involved in the fast localized motion by comparing the maximum ^{45}Sc relaxation rates of ScH$_x$ and ScD$_x$. Hydrided and deuterided samples with the same concentrations x are not available, so the nearly linear dependence of the maximum relaxation rate upon x is used to normalize the rates to equal concentrations. From the data of Fig. 2 one finds that the fraction of D atoms participating in the fast localized motion is approximately six times as large as the fraction of H atoms.

Similar effects of isotope (H↔D) substitution on the amplitude of the low-temperature relaxation rate maximum were observed for ^{51}V in TaV$_2$H$_x$(D$_x$).[13,14] The maximum motional contribution to the low-temperature ^{51}V relaxation rate in the deuterides was found to be approximately three times higher than in the hydrides with nearly the same x values. These results were also interpreted[19] in terms of different fractions of atoms participating in the localized motion, the value of p for D being higher than that for H.

The results of QENS measurements in α-ScH$_x$ (Ref. 8) are consistent with a temperature-dependent fraction p (growing with increasing T). The existence of ''static'' protons (on the relevant frequency scale of the experiment) is expected to arise from the H–H interaction leading to the formation of hydrogen pairs, as discussed in the Introduction. Only unpaired protons are likely to participate in the fast localized motion.[8] Because of the thermal activation, the hydrogen pairs tend to disappear at high temperatures; this results in the growth of p with increasing T. The temperature dependence of p can be rationalized by assuming the existence of a certain energy gap ΔE between ''static'' and ''mobile'' hydrogen states.[8] In terms of this approach, the isotope effect observed in our $(T_1^{-1})_{\mathrm{Sc}}$ measurements implies that the value of ΔE for D is lower than for H. One may assume that H(D) atoms become ''mobile'' when they are in the excited vibrational states; in this case the inequality $\Delta E^{\mathrm{D}} < \Delta E^{\mathrm{H}}$ would be quite natural.

The temperature dependence of $(T_{1Q}^{-1})_{\mathrm{Sc}}$ obtained by subtracting the electronic contribution $(T_{1e}^{-1})_{\mathrm{Sc}}$ from the experimental relaxation rate is shown in Fig. 2. At each temperature the electronic contribution has been determined using the high-temperature R_e values found by Han *et al.*[12] for α-ScH$_x$ ($x = 0.057$, 0.11, and 0.27) or the interpolated R_e

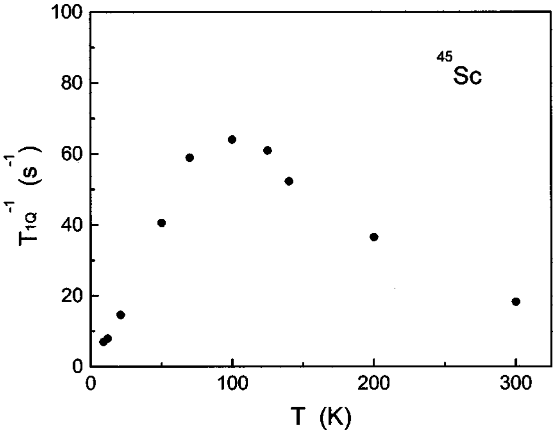

FIG. 3. The motional contribution to the ^{45}Sc spin-lattice relaxation rate in α-ScH$_{0.27}$ calculated using the hydrogen hopping rates $\tau_f^{-1}(T)$ found from the QENS experiments (Refs. 7 and 8). See the text for details.

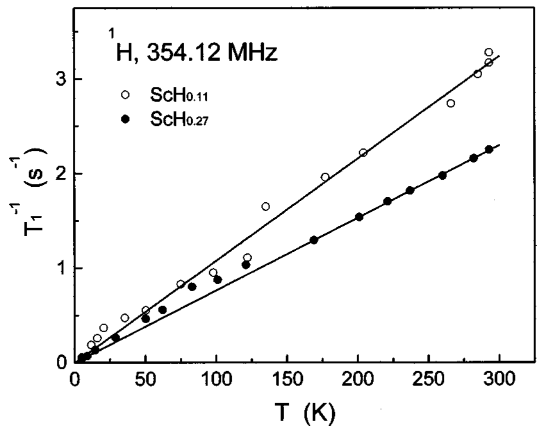

FIG. 4. Temperature dependence of the proton spin-lattice relaxation rate in α-ScH$_{0.11}$ and α-ScH$_{0.27}$ measured at 354.12 MHz. The solid lines represent the linear fits to the data points at $T > 150$ K.

values for other x. We assume that the R_e values for ^{45}Sc are equal in ScH$_x$ and ScD$_x$ at equal concentrations, x. As can be seen from Fig. 2, for all of the studied H- and D-doped samples, the temperature dependence of $(T_{1Q}^{-1})_{\mathrm{Sc}}$ shows a maximum below 150 K. The temperature of the maximum in the deuterided samples is higher than in the hydrided samples with comparable x, and for both isotopes this temperature slightly increases with increasing H(D) content.

Two plausible explanations of this low-temperature maximum may be suggested. The first possibility has been already mentioned above; it implies that the frequency of the localized H(D) hopping, τ_l^{-1}, increases with T and at a certain temperature becomes approximately equal to the resonance frequency ω_{Sc}. According to Eq. (2), at this temperature the value of $(T_{1Q}^{-1})_{\mathrm{Sc}}$ is expected to show a maximum. In this case the observed temperatures of the peaks indicate that the hopping rate of D atoms is lower than that of H atoms (at a given temperature), and for both isotopes τ_l^{-1} decreases weakly with increasing x. The second possibility is related to the very fast localized H(D) motion with the characteristic hopping rate τ_f^{-1}, much higher than ω_{Sc}. It is usually assumed that such a motion gives a negligible contribution to the relaxation rate. However, this is not the case if the amplitude of the fluctuating interaction is sufficiently large. In order to illustrate this point, we have calculated the behavior of $(T_{1Q}^{-1})_{\mathrm{Sc}}$ using τ_f^{-1} values obtained from the QENS measurements for α-ScH$_{0.16}$.[7,8] For such tentative calculations we have used Eq. (2) assuming that all H atoms participate in the motion and that the localized motion modulates one third of the interaction modulated by the long-range diffusion in α-ScH$_{0.27}$.[12] Thus, the value of $\langle \Gamma_{\mathrm{NN}} \rangle^2$ is taken as 1/3 of that describing the peak in $(T_1^{-1})_{\mathrm{Sc}}$ at 500 K. The results of these calculations are shown in Fig. 3. Note that in this case the relaxation rate does not depend on ω_{Sc}, and its maximum results from the $\tau_f^{-1}(T)$ minimum[7,8] discussed in the Introduction. Comparison of Figs. 2 and 3 shows that the mechanism related to the $\tau_f^{-1}(T)$ minimum can, in principle, be responsible for the observed $(T_{1Q}^{-1})_{\mathrm{Sc}}$ maximum in H-doped samples. However, this mechanism appears to be too weak to describe the larger observed relaxation rate maximum in D-doped samples. Therefore the low-temperature $(T_{1Q}^{-1})_{\mathrm{Sc}}$ maximum in α-ScD$_x$ should be determined by the usual condition $\omega_{\mathrm{Sc}}\tau_l \approx 1$. This conclusion is supported by the results of ^{2}D spin-lattice relaxation measurements discussed in the next section.

B. ^{1}H and ^{2}D relaxation

The results of our high-field measurements of ^{1}H and ^{2}D spin-lattice relaxation rates in α-ScH$_x$(D$_x$) are shown in Figs. 4 and 5. The proton spin-lattice relaxation rate $(T_1^{-1})_{\mathrm{H}}$ in metal-hydrogen systems can usually be described as a sum of contributions due to conduction electrons, $(T_{1e}^{-1})_{\mathrm{H}}$, and due to internuclear dipole-dipole interaction modulated by H hopping, $(T_{1d}^{-1})_{\mathrm{H}}$. It has been suggested[5] that if only a fraction of H atoms participates in the localized motion, a single value of the observed proton relaxation rate in α-ScH$_x$ may result from the rapid equalization of spin polarization (*spin diffusion*), so that $(T_{1d}^{-1})_{\mathrm{H}}$ is proportional to this fraction. In some metal-hydrogen systems an additional contribution from cross relaxation between proton and quadrupolar nuclear spins[20] is known to be important at low temperatures. However, for proton spin-lattice relaxation rate in α-ScH$_x$

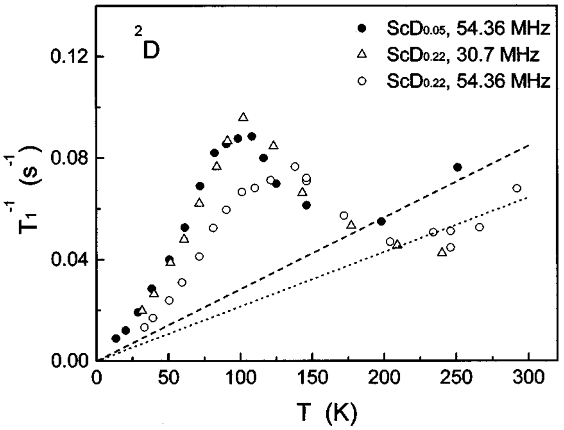

FIG. 5. Temperature dependence of the ^{2}D spin-lattice relaxation rate in α-ScD$_x$. The dashed and the dotted lines represent the electronic (Korringa) contributions for α-ScD$_{0.05}$ and α-ScD$_{0.22}$, respectively.

measured at high frequency (354 MHz), the cross-relaxation term should be negligible. The electronic (Korringa) contribution $(T_{1e}^{-1})_{\rm H}$ is expected to be proportional to temperature. As can be seen from Fig. 4, the experimental $(T_1^{-1})_{\rm H}$ data for α-ScH$_x$ are roughly described by linear functions over the whole temperature range of our measurements. Solid lines in Fig. 4 represent the results of linear fits to the data at $T > 150$ K. The values of $(T_1T)_{\rm H}^{-1}$ resulting from these fits are equal to 11×10^{-3} and 7.7×10^{-3} s^{-1} K^{-1} for $x = 0.11$ and 0.27, respectively. They are in good agreement with the $(T_{1e}T)_{\rm H}^{-1}$ values derived from the high-temperature relaxation rate measurements[12] in α-ScH$_x$ at 24 MHz (11×10^{-3} and 8.3×10^{-3} s^{-1} K^{-1} for $x=0.11$ and 0.27, respectively). Therefore we can conclude that the proton relaxation rates measured at 354 MHz are dominated by the electronic contribution.

Small systematic deviation of the data from the linear fit (evident for ScH$_{0.27}$ in the range 30–120 K) may be ascribed to the motional contribution $(T_{1d}^{-1})_{\rm H}$. Such a small motional contribution at 354 MHz could be expected on the basis of the low-frequency proton relaxation rate measurements in α-ScH$_x$.[5] In fact, the maximum $(T_{1d}^{-1})_{\rm H}$ value should be inversely proportional to the resonance frequency, if the maximum is determined by the condition $\omega_{\rm H}\tau_l \approx 1$ [this is the same inverse proportionality evident in Eq. (2)]. On the other hand, one may expect that the relaxation rate measurements at 354 MHz are sensitive to the very fast H motion with the characteristic hopping rate τ_f^{-1}. However, our results indicate that the contribution of this motion to the measured proton relaxation rate is also very small. This is consistent with the results of QENS experiments[7,8] showing that the fraction of H atoms participating in the localized motion on the frequency scale of τ_f^{-1} is less than 20% near 100 K.

The electronic contribution to the ^{2}D spin-lattice relaxation rate, $(T_{1e}^{-1})_{\rm D}$, for ScD$_x$ can be obtained by multiplying the $(T_{1e}^{-1})_{\rm H}$ value for ScH$_x$ with the same x by the factor $(\gamma_{\rm D}/\gamma_{\rm H})^2$, where $\gamma_{\rm D}$ and $\gamma_{\rm H}$ are the gyromagnetic ratios of ^{2}D and ^{1}H. The behavior of $(T_{1e}^{-1})_{\rm D}$ calculated in this way using the $(T_{1e}T)_{\rm H}^{-1}$ values for ScH$_x$ (Ref. 12) is shown by lines in Fig. 5. As can be seen from this figure, in the temperature range 30–180 K the experimental $(T_1^{-1})_{\rm D}$ values for ScD$_{0.05}$ and ScD$_{0.22}$ are considerably higher than the corresponding electronic contributions. The excess relaxation rate shows a maximum near 100 K, as is expected to result from the localized motion of deuterium. In addition to the dipole-dipole contribution $(T_{1d}^{-1})_{\rm D}$, the motional relaxation rate of ^{2}D should also contain a quadrupole contribution $(T_{1Q}^{-1})_{\rm D}$. The amplitude of the peak in the ^{2}D relaxation rate in α-ScD$_x$ is not strongly dependent on deuterium concentration (Fig. 5). This feature is common for those metal-deuterium systems in which both the dipolar fields and electric field gradients at D sites originate mainly from the metal sublattice.[21] Solid solutions α-ScD$_x$ are expected to belong to such systems. In connection with this, we contrast the x dependence of the motional contributions to T_1^{-1} of ^{45}Sc and ^{2}D: for ^{45}Sc, the spin heat capacity is independent of x, while for ^{2}D the spin heat capacity is directly proportional to the D-atom content, x. Thus, if the fraction of D atoms participating in the localized motion is constant, the T_1^{-1} of ^{2}D will be independent of x and the T_1^{-1} of ^{45}Sc will vary linearly with x. Both of these predictions are in approximate accord with the data, indicating that the fraction of D atoms involved in the local motion is nearly independent of x.

For ScD$_{0.22}$ the ^{2}D relaxation rates have been measured at two frequencies, 30.7 and 54.36 MHz. The observed changes of the relaxation peak with the resonance frequency $\omega_{\rm D}$ are typical of cases in which the motional relaxation peak is determined by the condition $\omega_{\rm D}\tau_l \approx 1$: with decreasing $\omega_{\rm D}$ the peak shifts to lower temperature and its amplitude increases. It should be noted, however, that the observed frequency dependence of the motional relaxation rate on the low-temperature slope of the peak is weaker than the expected $\omega_{\rm D}^{-2}$ dependence. This may indicate the existence of a distribution of hopping rates[22] and/or the presence of additional relaxation mechanisms contributing to the peak and having weaker frequency dependences. Comparison of the positions of ^{2}D and ^{45}Sc relaxation rate maxima for the same samples supports the idea that both the ^{2}D and ^{45}Sc peaks in α-ScD$_x$ are determined by the same motional process. In fact, the temperatures of the maxima in the motional relaxation rates of ^{2}D at 54.36 MHz are 98 and 138 K for ScD$_{0.05}$ and ScD$_{0.22}$, respectively; the corresponding temperatures of the ^{45}Sc maxima at 86.2 MHz are 106 and 142 K. Taking into account the different resonance frequencies and the uncertainty of experimental determination of the peak position, we may conclude that both the ^{2}D and ^{45}Sc relaxation rate peaks in α-ScD$_x$ originate from the localized motion of D atoms with the hopping rate τ_l^{-1}, which passes through the spin precession frequency ($\omega_{\rm D}$ of order of 3×10^8 s^{-1}) near $T\approx100$ K.

IV. CONCLUSIONS

Measurements of the temperature dependence of the ^{45}Sc spin-lattice relaxation rate in α-ScH$_x$(D$_x$) have revealed pronounced deviations from the Korringa behavior of the relaxation rate in the range 30–200 K. The excess relaxation rate shows a peak near 100 K in α-ScH$_x$ and near 110–140 K in α-ScD$_x$ and can be attributed to fast localized motion of H(D) atoms. The most intriguing feature of our data is the strong effect of isotope (H$\leftrightarrow$D) substitution on the amplitude of the ^{45}Sc relaxation rate peak: the peak amplitude in α-ScD$_x$ is found to be much higher than in α-ScH$_x$ with comparable x value. These results indicate that the fraction of D atoms participating in the fast localized motion in α-ScD$_x$ is considerably higher than the corresponding fraction of H atoms in α-ScH$_x$. Based on a comparison of the maximum ^{45}Sc relaxation rates normalized to the same concentration x, it is estimated that six times as many D atoms are involved as H atoms.

The temperature dependence of the ^{2}D spin-lattice relaxation rate in α-ScD$_x$ also shows a peak near 100 K. Our results suggest that both the ^{2}D and ^{45}Sc relaxation rate peaks in α-ScD$_x$ are determined by the same motional process, with characteristic frequency τ_l^{-1} increasing with temperature and passing through 3×10^8 s^{-1} near 100 K. For α-ScH$_x$ the situation is more complicated since the motional contributions to the ^{1}H and ^{45}Sc relaxation rates are found to be small both at 354 MHz (^{1}H) and 86.2 MHz (^{45}Sc). In particular, the high-frequency measurements of the proton relaxation rate have not revealed any significant contribution from the very fast H motion with hopping rate τ_f^{-1}, as found in the QENS experiments.[7,8] This is consistent with a small fraction of H atoms participating in the localized motion on the frequency scale of $\tau_f^{-1} > 7 \times 10^{10}\ \mathrm{s}^{-1}$ at low temperatures. The fraction of H atoms participating in the motion on the frequency scale of $\tau_l^{-1} \sim 10^8\ \mathrm{s}^{-1}$ also appears to be small.

The observation of a large H–D isotope effect has a substantial impact on the interpretation of neutron scattering data in this system. All of the neutron diffraction and diffuse scattering data that reveal the structural nature of the pairing and further short-range ordering have been from deuterided material. The quasielastic neutron scattering data that monitor the hydrogen dynamics all refer to the hydrided material. The large isotope effect in the NMR relaxation data reported here indicates that the neutron data refer to *different physical systems*.

Our results show that the picture of the low-temperature localized motion of H(D) atoms in α-ScH$_x$(D$_x$) is more complicated than originally thought. Any microscopic model of the localized hydrogen motion in this system should account for the strong effect of isotope (H↔D) substitution on the fraction of atoms involved in the motion. In order to clarify the picture of the localized H(D) motion in α-ScH$_x$(D$_x$), it would be helpful to study the frequency dependence of the ^{45}Sc relaxation rate and to perform high-resolution quasielastic neutron scattering measurements sensitive to a motion on the frequency scale of 10^8–$10^9\ \mathrm{s}^{-1}$. Such experiments are in progress now.

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