

## $^{45}\text{Sc}$ NMR and high-resolution quasielastic neutron scattering studies of localized H(D) motion in $\alpha\text{-ScH}_x(\text{D}_x)$

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Nuclear magnetic resonance measurements of the  $^{45}\text{Sc}$  spin-lattice relaxation rates in the solid solutions  $\alpha\text{-ScD}_{0.05}$ ,  $\alpha\text{-ScD}_{0.22}$ , and  $\alpha\text{-ScH}_{0.27}$  have been performed over the temperature range 4.2–299 K and the resonance frequency range 11–86.2 MHz. For all of the samples studied, the  $^{45}\text{Sc}$  relaxation rate shows a peak near 100 K resulting from the electric quadrupole interaction modulated by localized hopping of H(D) atoms. In addition to the strong effect of isotope (H $\leftrightarrow$ D) substitution on the amplitude of this peak, with a larger peak appearing in the deuterides, we have found that in the region of the peak, the frequency dependence of the  $^{45}\text{Sc}$  relaxation rate for  $\alpha\text{-ScH}_{0.27}$  is much weaker than for  $\alpha\text{-ScD}_x$ . These results indicate that the hopping rate distribution for H atoms in scandium is shifted to much higher frequencies from that for D atoms. The results of our high-resolution quasielastic neutron-scattering measurements on  $\alpha\text{-ScH}_{0.27}$  in the temperature range 12–302 K are consistent with this conclusion.

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### I. INTRODUCTION

The behavior of hydrogen in Sc and the related hcp metals Y and Lu shows a number of unusual features. In contrast to most metal-hydrogen systems, hydrogen in  $\text{ScH}_x$ ,  $\text{YH}_x$ , and  $\text{LuH}_x$  is not precipitated into a hydride phase at low temperatures; it remains in the solid-solution ( $\alpha$ ) phase up to  $x = 0.2\text{--}0.3$ . It is believed that the  $\alpha$  phase stabilization is related to the peculiar short-ranged ordering of hydrogen,<sup>1–3</sup> which develops with decreasing temperature. Neutron diffraction<sup>4</sup> and diffuse scattering<sup>1,2</sup> measurements have shown that hydrogen occupies only the tetrahedral interstitial sites in the hcp Sc lattice and tends to form next-nearest-neighbor pairs with a bridging metal atom in the  $c$  axis direction. As the temperature is lowered, these pairs arrange themselves into a longer-range structure, predominantly along the  $c$  direction. However, truly long-range order is not achieved in these systems.

The dynamical properties of hydrogen in Sc are also quite remarkable. Nuclear magnetic resonance (NMR) measurements of the proton spin-lattice relaxation rate  $(T_1^{-1})_{\text{H}}$  in  $\alpha\text{-ScH}_x$  and the related systems<sup>5,6</sup> have revealed a localized H motion with the characteristic hopping rate  $\tau_l^{-1}$  of about  $10^8\text{ s}^{-1}$  at 50 K. This localized motion is evident from an additional frequency-dependent  $(T_1^{-1})_{\text{H}}$  peak 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  $\alpha\text{-ScH}_x$ <sup>7,8</sup> have revealed the existence of a still faster localized H motion with the hopping rate  $\tau_f^{-1}$  passing through an apparent minimum of about  $7 \times 10^{10}\text{ s}^{-1}$  near 100 K and increasing to  $10^{12}\text{ s}^{-1}$  at 10 K. However, because of the

limited energy resolution (70  $\mu\text{eV}$ ), these QENS experiments could not detect the slower H motion found by NMR.<sup>5,6</sup> Since the low-temperature localized hydrogen motion in Sc is likely to be of quantum origin,<sup>7</sup> one may expect pronounced effects of isotope (H $\leftrightarrow$ D) substitution. The first experimental evidence of isotope effects on hydrogen motion in  $\alpha\text{-ScH}_x(\text{D}_x)$  has been obtained from ultrasonic measurements in the 1 MHz range on  $\text{ScH}_{0.25}$  and  $\text{ScD}_{0.18}$ .<sup>9</sup> In these experiments, low-temperature ultrasonic attenuation peaks have been found near 25 K for  $\text{ScH}_{0.25}$  and near 50 K for  $\text{ScD}_{0.18}$ . 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.<sup>9</sup>

Recent NMR measurements of the  $^{45}\text{Sc}$  spin-lattice relaxation rate  $(T_1^{-1})_{\text{Sc}}$  in  $\alpha\text{-ScH}_x(\text{D}_x)$  at 86.2 MHz<sup>10</sup> have revealed dramatic isotope effects on the localized hydrogen motion. The main motional contribution to  $(T_1^{-1})_{\text{Sc}}$  originates from the electric quadrupole interaction modulated by H(D) hopping. This mechanism is expected to lead to a  $(T_1^{-1})_{\text{Sc}}$  peak at the temperature  $T_{\text{max}}$  at which the hydrogen hopping rate  $\tau_l^{-1}$  becomes nearly equal to the  $^{45}\text{Sc}$  resonance frequency  $\omega_{\text{Sc}}$ . 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. However, the measured amplitude of the low-temperature  $(T_1^{-1})_{\text{Sc}}$  peak for  $\alpha\text{-ScD}_x$  samples appears to be much higher than for  $\alpha\text{-ScH}_x$  samples with comparable hydrogen content.<sup>10</sup> This unusual isotope effect indicates that the fraction of D atoms participating in the localized motion on the frequency scale of  $\tau_l^{-1}$  in  $\alpha\text{-ScD}_x$  is approximately six times larger than the corresponding fraction of H atoms in  $\alpha\text{-ScH}_x$ . The results of Ref. 10 show that the picture of the

low-temperature localized motion of H(D) atoms in  $\alpha$ -ScH<sub>x</sub>(D<sub>x</sub>) is more complicated than originally thought. The main unsolved problems may be summarized as follows.

(1) What is the origin of the two frequency scales of the localized H hopping in  $\alpha$ -ScH<sub>x</sub>? It is likely that the faster frequency scale  $\tau_f^{-1}$  corresponds to the hopping of *unpaired* protons.<sup>8</sup> Therefore, it would be natural to ascribe the slower scale  $\tau_l^{-1}$  to the hopping of protons involved in pairing. However, the <sup>1</sup>H NMR data<sup>5</sup> indicate that only a small fraction of protons participate in the slower local motion, while most of hydrogen atoms are believed to be paired at low temperatures.<sup>1-3</sup> This suggests that only a part of paired protons are involved in the slower local motion.

(2) What mechanism is responsible for the strong isotope dependence<sup>10</sup> of the fraction of atoms participating in the localized motion on the frequency scale of  $\tau_l^{-1}$ ? It should be noted that similar effects of isotope (H $\leftrightarrow$ D) substitution on the fraction of atoms participating in the localized motion on the same frequency scale have been observed for the Laves phase hydrides TaV<sub>2</sub>H<sub>x</sub>(D<sub>x</sub>).<sup>11,12</sup> It is plausible that the isotope effects in  $\alpha$ -ScH<sub>x</sub>(D<sub>x</sub>) and TaV<sub>2</sub>H<sub>x</sub>(D<sub>x</sub>) are governed by a common mechanism.

In order to clarify the picture of the localized H(D) motion in  $\alpha$ -ScH<sub>x</sub>(D<sub>x</sub>), it would be helpful to probe this motion by microscopic techniques covering a wide frequency range. In this work we report the results of the <sup>45</sup>Sc spin-lattice relaxation rate measurements in  $\alpha$ -ScD<sub>0.05</sub>,  $\alpha$ -ScD<sub>0.22</sub>, and  $\alpha$ -ScH<sub>0.27</sub> over the temperature range 4.2–299 K and the resonance frequency range 11–86.2 MHz. These results complement our earlier ( $T_1^{-1}$ )<sub>Sc</sub> data<sup>10</sup> at 86.2 MHz. We also report high-resolution quasielastic neutron-scattering measurements in  $\alpha$ -ScH<sub>0.27</sub>. These measurements (sensitive to hydrogen motion on the frequency scale of 10<sup>8</sup>–10<sup>9</sup> s<sup>-1</sup>) form a bridge between the NMR and the intermediate-resolution QENS<sup>7,8</sup> experiments.

## II. EXPERIMENTAL DETAILS

The samples of  $\alpha$ -ScH<sub>x</sub> and  $\alpha$ -ScD<sub>x</sub> 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.<sup>5</sup>

Measurements of the <sup>45</sup>Sc spin-lattice relaxation times  $T_1$  at the frequencies  $\omega/2\pi = 11$  and 21.8 MHz were made using a modernized Bruker SXP spectrometer. The magnetic field was produced by an iron-core electromagnet with NMR field stabilization. The probehead with sample was placed into an Oxford Instruments CF1200 continuous-flow cryostat using helium or nitrogen as a cooling agent. The sample temperature, monitored by a chromel-(Au-Fe) thermocouple, was stable to  $\pm 0.1$  K.

Measurements of the <sup>45</sup>Sc  $T_1$  at  $\omega/2\pi = 86.2$  MHz were made using a Chemagnetics CMX360 spectrometer connected to a 1 kW transmitter. The magnetic field of 8.4 T was produced by a 89-mm-bore superconducting solenoid. Temperatures below 140 K were achieved with a research Dewar built by Kadel Inc. In this range the sample temperature was

stable to  $\pm 0.1$  K, as measured by a thermocouple and a calibrated carbon-glass resistor thermometer. At temperatures above 140 K a thermostated flowing N<sub>2</sub> gas apparatus was used; the sample temperature was measured by a copper-constantan thermocouple and was stable to  $\pm 1$  K.

Spin-lattice relaxation times were determined from the recovery of free-induction decay or echo signals after a saturating train of rf pulses. The typical length of the 90°-pulses was between 1.0 and 1.5  $\mu$ s. At temperature below 250 K the <sup>45</sup>Sc relaxation showed deviations from single-exponential behavior. Such deviations are typical of relaxation of quadrupolar nuclear spins in systems with a strong static quadrupole interaction,<sup>13</sup> where rf pulses cannot cover the entire NMR spectrum. The values of  $T_1$  for <sup>45</sup>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.

QENS measurements were performed on the high-resolution backscattering spectrometer BSS1 in Forschungszentrum Jülich. This spectrometer uses a Si(111) monochromator and analyzers selecting the neutron wavelength  $\lambda = 6.271$  Å. The range of energy transfer  $\hbar\omega$  in our experiments was  $\pm 16$   $\mu$ eV, the energy resolution full width at half maximum being about 1.2  $\mu$ eV. Nine analyzers covered the range of momentum transfer  $\hbar Q$  corresponding to  $Q$  range of 0.16–1.88 Å<sup>-1</sup>. The powdered  $\alpha$ -ScH<sub>0.27</sub> sample was placed into a flat Al container with a depth of 0.8 mm. The plane of the container was oriented along the direction  $2\theta \approx 80^\circ$ . QENS spectra were recorded at eight temperatures between 12 K and 302 K. For normalization of the data we used QENS spectra obtained on a standard vanadium sample at room temperature. The background spectra were measured for the empty container in the same experimental geometry as for the sample.

## III. RESULTS AND DISCUSSION

### A. <sup>45</sup>Sc spin-lattice relaxation

The results of our <sup>45</sup>Sc spin-lattice relaxation rate measurements for  $\alpha$ -ScD<sub>0.05</sub>,  $\alpha$ -ScD<sub>0.22</sub>, and  $\alpha$ -ScH<sub>0.27</sub> are shown in Figs. 1, 2, and 3, respectively. For both deuterided samples the main feature of the data is the frequency-dependent peak of the relaxation rate. For ScH<sub>0.27</sub> such a peak is weaker, and its frequency dependence is also much weaker than for the deuterided samples.

In metal-hydrogen systems the measured spin-lattice relaxation rate 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 ( $T_{1Q}^{-1}$ ); hence

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

The estimated magnetic dipolar contribution to the <sup>45</sup>Sc relaxation rate in  $\alpha$ -ScH<sub>x</sub>(D<sub>x</sub>) appears to be much smaller than the quadrupolar one; therefore, the dipolar contribution can be neglected. The electronic (Korringa) term is typically proportional to temperature,  $T_{1e}^{-1} = R_e T$ , and does not depend on

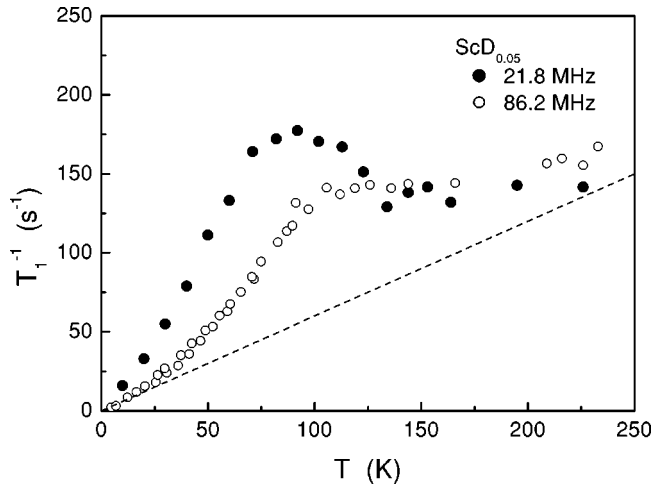


FIG. 1. Temperature dependence of the <sup>45</sup>Sc spin-lattice relaxation rate in  $\alpha$ -ScD<sub>0.05</sub> measured at 21.8 and 86.2 MHz. The dashed line shows the estimated electronic contribution to the relaxation rate.

the resonance frequency. In order to evaluate the electronic contribution, we have used the  $R_e$  values found from the high-temperature <sup>45</sup>Sc relaxation rate measurements<sup>14</sup> for  $\alpha$ -ScH<sub>*x*</sub> ( $x=0.057, 0.11, \text{ and } 0.27$ ). These measurements show that  $R_e$  decreases approximately linearly with increasing hydrogen content, from  $0.60 \text{ s}^{-1} \text{ K}^{-1}$  for  $x=0.057$  to  $0.44 \text{ s}^{-1} \text{ K}^{-1}$  for  $x=0.27$ . We assume that the  $R_e$  values for <sup>45</sup>Sc are equal in ScH<sub>*x*</sub> and ScD<sub>*x*</sub> at equal concentrations,  $x$ , and use the interpolated value for  $x=0.22$ ,  $R_e = 0.48 \text{ s}^{-1} \text{ K}^{-1}$ . The electronic contributions estimated in this way are shown by the dashed lines in Figs. 1–3.

Assuming that the spectral density functions of the local electric-field-gradient (EFG) fluctuations have a simple Lorentzian form, the quadrupolar contribution to the <sup>45</sup>Sc relaxation rate in a powder  $\alpha$ -ScH<sub>*x*</sub>(D<sub>*x*</sub>) sample with low  $x$  can be written as<sup>14</sup>

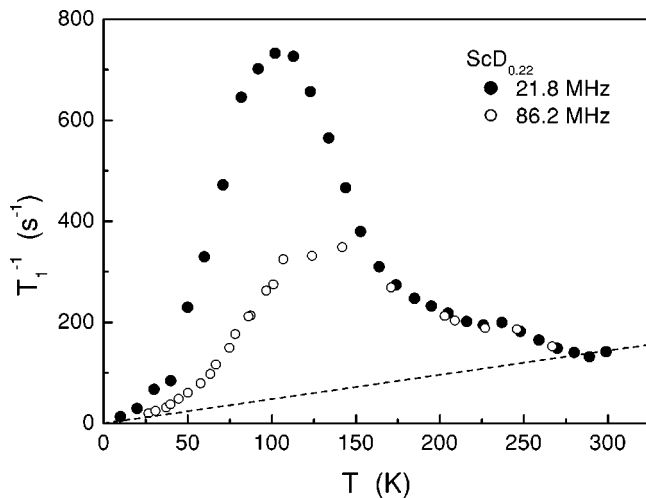


FIG. 2. Temperature dependence of the <sup>45</sup>Sc spin-lattice relaxation rate in  $\alpha$ -ScD<sub>0.22</sub> measured at 21.8 and 86.2 MHz. The dashed line shows the estimated electronic contribution to the relaxation rate.

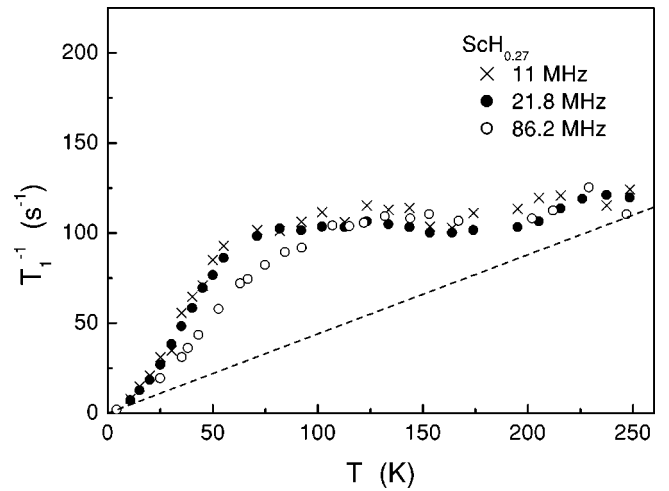


FIG. 3. Temperature dependence of the <sup>45</sup>Sc spin-lattice relaxation rate in  $\alpha$ -ScH<sub>0.27</sub> measured at 11, 21.8, and 86.2 MHz. The dashed line shows the estimated electronic contribution to the relaxation rate.

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

where  $y = \omega_{\text{Sc}}\tau_d$ ,  $\tau_d$  is the relevant mean residence time of a hydrogen atom in an interstitial site, and  $\langle \Gamma_{\text{NN}} \rangle$  is the average quadrupole coupling constant of <sup>45</sup>Sc due to a nearest-neighbor hydrogen. According to Eq. (2), the temperature dependence of  $(T_{1Q}^{-1})_{\text{Sc}}$  is expected to show a maximum at the temperature  $T_{\text{max}}$  at which the condition  $y = \omega_{\text{Sc}}\tau_d \approx 1$  is satisfied. High-temperature measurements of the <sup>45</sup>Sc spin-lattice relaxation rate in  $\alpha$ -ScH<sub>*x*</sub> at  $\omega_{\text{Sc}}/2\pi = 24 \text{ MHz}$ <sup>14</sup> have revealed such a maximum at  $T_{\text{max}} \approx 500 \text{ K}$  (well above the temperature range of the present work). 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  $\tau_l$  being much shorter than  $\tau_d$ , one may expect an additional low-temperature relaxation rate maximum determined by the condition  $\omega_{\text{Sc}}\tau_l \approx 1$ . Such an additional  $(T_{1Q}^{-1})_{\text{Sc}}$  maximum in  $\alpha$ -ScH<sub>*x*</sub>(D<sub>*x*</sub>) has been found in our previous experiments at  $\omega_{\text{Sc}}/2\pi = 86.2 \text{ MHz}$ ,<sup>10</sup> the corresponding  $T_{\text{max}}$  values being in the range 100–130 K (see Figs. 1–3). Equation (2) with  $y = \omega_{\text{Sc}}\tau_l$  predicts the following asymptotic behavior of the relaxation rate:  $(T_{1Q}^{-1})_{\text{Sc}}$  is proportional to  $\tau_l$  (being frequency independent) in the limit of fast motion ( $y \ll 1$ ) and to  $\omega_{\text{Sc}}^{-2}\tau_l^{-1}$  in the limit of slow motion ( $y \gg 1$ ).

The temperature dependence of  $(T_{1Q}^{-1})_{\text{Sc}}$  obtained by subtracting the electronic contributions  $(T_{1e}^{-1})_{\text{Sc}}$  from the experimental relaxation rates is shown in Fig. 4. The main features of the behavior of  $(T_{1Q}^{-1})_{\text{Sc}}$  are as follows.

(i) The amplitude of the  $(T_{1Q}^{-1})_{\text{Sc}}$  peak in  $\alpha$ -ScD<sub>*x*</sub> increases with increasing D content. In agreement with Eq. (2), this amplitude appears to be nearly proportional to  $x$ .

(ii) The amplitude of the  $(T_{1Q}^{-1})_{\text{Sc}}$  peak in ScH<sub>0.27</sub> is much lower than in ScD<sub>0.22</sub> (see Fig. 4), despite the somewhat higher hydrogen concentration in the hydride. This dramatic

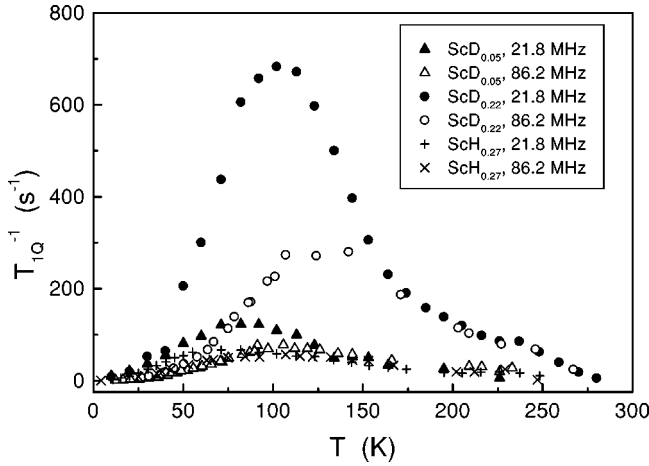


FIG. 4. Temperature dependence of the motional contribution to the  $^{45}\text{Sc}$  spin-lattice relaxation rate in  $\alpha\text{-ScD}_{0.05}$ ,  $\alpha\text{-ScD}_{0.22}$ , and  $\alpha\text{-ScH}_{0.27}$  at 21.8 and 86.2 MHz. This is the data of Figs. 1, 2, and 3 after subtraction of the electronic contributions to the relaxation rates.

isotope effect first reported in Ref. 10 implies that the mean-square amplitude of EFG fluctuations (in the frequency range around  $\omega_{\text{Sc}}$ ) at Sc sites in  $\text{ScH}_{0.27}$  is much smaller than in  $\text{ScD}_{0.22}$ . Since H and D atoms are believed to occupy the same interstitial sites, the value of  $\langle \Gamma_{\text{NN}} \rangle$  should be the same for  $\alpha\text{-ScH}_x$  and  $\alpha\text{-ScD}_x$ . Therefore, in order to account for the strong difference in the mean-square amplitudes of EFG fluctuations in terms of Eq. (2), we have to assume that only a fraction  $p_l$  of H(D) atoms participates in the localized motion on the frequency scale of  $\omega_{\text{Sc}}$ , and that this fraction in  $\alpha\text{-ScH}_x$  is considerably smaller than in  $\alpha\text{-ScD}_x$ , as discussed in Ref. 10.

(iii) For  $\alpha\text{-ScD}_x$ , the observed changes in  $(T_{1Q}^{-1})_{\text{Sc}}$  with the resonance frequency  $\omega_{\text{Sc}}$  are in qualitative agreement with Eq. (2): on the low-temperature slope of the  $(T_{1Q}^{-1})_{\text{Sc}}$  peak the relaxation rate increases with decreasing  $\omega_{\text{Sc}}$ , and on the high-temperature slope of the peak this frequency dependence disappears. However, the observed frequency dependence of  $(T_{1Q}^{-1})_{\text{Sc}}$  is considerably weaker than that predicted by Eq. (2). For example, the peak amplitude is expected to be proportional to  $\omega_{\text{Sc}}^{-1}$ . Thus, the expected ratio of the maximum  $(T_{1Q}^{-1})_{\text{Sc}}$  values at 21.8 and 86.2 MHz is  $86.2/21.8 = 3.95$ , whereas the corresponding experimental ratios are 1.6 for  $\text{ScD}_{0.05}$  and 2.4 for  $\text{ScD}_{0.22}$ . The observed frequency dependence of  $(T_{1Q}^{-1})_{\text{Sc}}$  on the low-temperature slope of the peak is also considerably weaker than the  $\omega_{\text{Sc}}^{-2}$  dependence expected in this range, being approximately  $\omega^{-1.25}$ .

(iv) For  $\text{ScH}_{0.27}$ , the frequency dependence of  $(T_{1Q}^{-1})_{\text{Sc}}$  is much weaker than for  $\text{ScD}_{0.22}$ . In fact, the ratio of the maximum  $(T_{1Q}^{-1})_{\text{Sc}}$  values at 21.8 and 86.2 MHz in  $\text{ScH}_{0.27}$  is only 1.17, and the measured relaxation rates at 11 MHz are very close to those at 21.8 MHz (see Fig. 3).

Summarizing the main features of the behavior of the  $^{45}\text{Sc}$  relaxation rate, we can conclude that in  $\alpha\text{-ScD}_x$  the relaxation rate peak results from the usual mechanism. Thus, the deuterium local hopping rate  $\tau_l^{-1}$  increases with  $T$  and, at

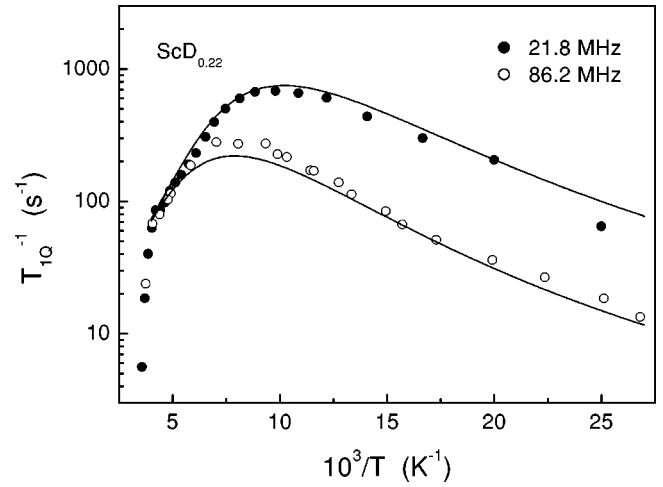


FIG. 5. Motional contributions to the  $^{45}\text{Sc}$  spin-lattice relaxation rate in  $\alpha\text{-ScD}_{0.22}$  at 21.8 and 86.2 MHz as functions of reciprocal temperature. The solid lines represent the simultaneous fit of the model with a Gaussian distribution of activation energies to the data (see text for details).

the temperature of the relaxation rate maximum, becomes approximately equal to the resonance frequency  $\omega_{\text{Sc}}$ . This conclusion is supported by the results of  $^2\text{D}$  spin-lattice relaxation rate measurements<sup>10</sup> showing that for  $\alpha\text{-ScD}_x$  samples with the same  $x$  the maxima of  $(T_1^{-1})_{\text{D}}$  and  $(T_1^{-1})_{\text{Sc}}$  at comparable frequencies occur in the same temperature range. If  $\tau_l^{-1}$  follows the Arrhenius relation,

$$\tau_l^{-1} = \tau_{l0}^{-1} \exp(-E_a^l/k_B T), \quad (3)$$

where  $E_a^l$  is the activation energy for the localized motion, then Eq. (2) predicts that the plot of  $\log(T_{1Q}^{-1})_{\text{Sc}}$  vs  $T^{-1}$  is linear both in the limit of fast motion ( $y \ll 1$ ) and in the limit of slow motion ( $y \gg 1$ ) with the slopes  $E_a^l/k_B$  and  $-E_a^l/k_B$ , respectively.

The experimental  $\log(T_{1Q}^{-1})_{\text{Sc}}$  vs  $T^{-1}$  plot for  $\text{ScD}_{0.22}$  is shown in Fig. 5. It can be seen that for both resonance frequencies the low-temperature slope of this plot is much less steep than the high-temperature slope. Such an asymmetry as well as the weak frequency dependence of the relaxation rate [feature (iii) of the data] can be accounted for by a model employing a distribution of  $\tau_l^{-1}$  (or  $E_a^l$ ) values.<sup>15,16</sup> In this model the motional contribution to the relaxation rate is calculated as

$$T_{1Q}^{-1} = \int T_{1Q}^{-1}(E_a^l) G(E_a^l) dE_a^l, \quad (4)$$

where  $G(E_a^l)$  is the normalized distribution of  $E_a^l$  values, and  $T_{1Q}^{-1}(E_a^l)$  is defined by Eqs. (2) and (3). For parametrization of the data near the relaxation rate peak we have used a Gaussian distribution function  $G(E_a^l)$ . The model parameters are  $\langle \Gamma_{\text{NN}} \rangle^2$ , the preexponential factor  $\tau_{l0}^{-1}$ , the average activation energy  $\bar{E}_a^l$  and the distribution width  $\Delta E_a^l$  (full width at half maximum). These parameters are varied to find the best fit to the  $T_{1Q}^{-1}(T)$  data at two frequencies simultaneously.

Since such a model cannot describe the break in the slope of the  $\log T_{1Q}^{-1}$  vs  $T^{-1}$  plots near 230 K (see Fig. 5), the data for  $T > 230$  K have been excluded from the fitting. The results of the simultaneous fit are shown as solid lines in Fig. 5, the fit parameters being  $\tau_{10}^{-1} = 10^{11} \text{ s}^{-1}$ ,  $\overline{E}_a^T = 47 \text{ meV}$ , and  $\Delta E_a^T = 15 \text{ meV}$ . As can be seen from Fig. 5, although the model describes the main qualitative features of the data in the range 37–230 K, the observed frequency dependence of  $T_{1Q}^{-1}$  is still somewhat weaker than that suggested by the fit. It is interesting to compare our data on the deuterium hopping rate with the results of ultrasonic measurements in the 1 MHz range,<sup>9</sup> which have revealed the attenuation peak in ScD<sub>0.18</sub> near 50 K. Using our fitted values of  $\tau_{10}^{-1}$  and  $\overline{E}_a^T$  for ScD<sub>0.22</sub> we find that the most probable value of  $\tau_l^{-1}$  at 50 K is  $1.8 \times 10^6 \text{ s}^{-1}$ , i.e., just in the 1 MHz range. Therefore, both the <sup>45</sup>Sc relaxation rate peak and the ultrasonic attenuation peak<sup>9</sup> in  $\alpha$ -ScD<sub>x</sub> are likely to result from the same motional process.

The break in the slope of the  $\log T_{1Q}^{-1}$  vs  $T^{-1}$  plot near 230 K is probably related to deuterium ordering (pairing) in this temperature range. A similar feature has been found for the proton spin-lattice relaxation rate in  $\alpha$ -ScH<sub>x</sub><sup>5</sup> in the region 180–210 K; it has been attributed to the change in the electronic contribution  $T_{1e}^{-1}$  due to hydrogen ordering.

The behavior of the <sup>45</sup>Sc relaxation rate for ScH<sub>0.27</sub> can hardly be described in terms of the same mechanism as for  $\alpha$ -ScD<sub>x</sub>. The unusually weak frequency dependence of  $(T_{1Q}^{-1})_{\text{Sc}}$  for ScH<sub>0.27</sub> in the range 40–120 K (Figs. 3 and 4) suggests that the relaxation rate in this region is dominated by some *frequency-independent* contribution. One possible  $\omega_{\text{Sc}}$ -independent contribution to  $(T_{1Q}^{-1})_{\text{Sc}}$  has been proposed in our previous work.<sup>10</sup> It is related to the very fast localized H motion with the characteristic hopping rate  $\tau_f^{-1}$ , much higher than  $\omega_{\text{Sc}}$ , as observed by quasielastic neutron scattering.<sup>7,8</sup> Although such a motion with  $\tau_f^{-1} \gg \omega_{\text{Sc}}$  is usually assumed to give a negligible contribution to the relaxation rate, this may not be true if the amplitude of fluctuating interaction is sufficiently large. The estimates<sup>10</sup> based on Eq. (2) and the experimental  $\tau_f^{-1}(T)$  data for ScH<sub>0.16</sub><sup>7,8</sup> show that this contribution can account both for the position and the amplitude of the observed  $(T_{1Q}^{-1})_{\text{Sc}}$  peak in ScH<sub>0.27</sub> (see Fig. 3 of Ref. 10). It should be noted that, for this contribution, the  $(T_{1Q}^{-1})_{\text{Sc}}$  maximum results from the  $\tau_f^{-1}(T)$  *minimum*<sup>7,8</sup> near 100 K; we recall that this minimum jump rate was found to be of order of  $10^{11} \text{ s}^{-1}$ , greatly exceeding  $\omega_{\text{Sc}}$ . Thus, the low-temperature <sup>45</sup>Sc relaxation rate peaks in the D-doped and H-doped samples are evidently of different nature. We cannot exclude the possibility that a certain fraction of H atoms also participates in the motion on the slower frequency scale  $\tau_l^{-1}$  (being close to  $\omega_{\text{Sc}}$  near 100 K); however, the weak frequency dependence of  $(T_{1Q}^{-1})_{\text{Sc}}$  indicates that such a fraction must be quite small. This is consistent with the small amplitude of the <sup>1</sup>H spin-lattice relaxation rate peak in  $\alpha$ -ScH<sub>x</sub>.<sup>5</sup> The frequency dependence of the proton relaxation rate peak in  $\alpha$ -ScH<sub>x</sub> in the region of the peak was also found to be rather weak, and the attempts to de-

scribe it in terms of a Gaussian distribution of activation energies resulted in distribution widths comparable to the average activation energies.<sup>5</sup>

Another possible scenario that may lead to a relaxation rate maximum with weak frequency dependence is related to H motion between unequal potential wells. Such motion may be relevant to hydrogen in Sc,<sup>5,9</sup> especially if we consider the case of a hydrogen atom jumping out of the *paired* configuration. In this case, the expression for the relaxation rate contains the reduction factor  $\text{sech}^2(\Delta/2k_B T)$ ,<sup>17,18</sup> where  $\Delta$  is the difference between H site energies in the two wells. Since the reduction factor decreases rapidly with decreasing temperature, the relaxation rate peak may occur in the temperature range where  $\tau_l^{-1} > \omega_{\text{Sc}}$  if this decrease becomes faster than the increase in  $T_{1Q}^{-1}$  due to the slowing of H motion. In most cases these conditions are difficult to meet;<sup>18</sup> however, in the case of localized H motion in  $\alpha$ -ScH<sub>x</sub>, two factors make this scenario reasonable. First, the effective value of  $\Delta$  is expected to increase with decreasing  $T$ , as typical of an ordering transition. This leads to a faster decrease in the  $\text{sech}^2(\Delta/2k_B T)$  factor, as compared to the case of temperature-independent  $\Delta$ . Second, the decrease in  $\tau_l^{-1}$  with decreasing temperature may be slower than that described by the Arrhenius relation. Such a behavior is expected if the localized motion of protons is dominated by quantum effects.

Our results suggest a strong difference between the frequency distributions for the localized hopping of H and D atoms in scandium. For D atoms at 100 K the distribution maximum is close to  $10^8 \text{ s}^{-1}$ , whereas for H atoms the distribution maximum appears to be shifted to much higher frequencies, so that only the low-frequency tail of this distribution can be probed by NMR measurements. A strong difference between the parameters of the localized hopping of H and D atoms has also been found in recent measurements of the ultrasonic attenuation in Laves-phase TaV<sub>2</sub>H<sub>0.18</sub> and TaV<sub>2</sub>D<sub>0.17</sub><sup>19</sup> in the frequency range of 1 MHz. For TaV<sub>2</sub>D<sub>0.17</sub> the ultrasonic attenuation exhibits a peak near 25 K, which can be attributed to the localized motion of D with the hopping rate nearly equal to the ultrasonic frequency. However, for TaV<sub>2</sub>H<sub>0.18</sub> no evidence of a low-temperature attenuation peak has been found down to 3 K.<sup>19</sup> The results of these experiments suggest that the rate of local hopping of H atoms remains well above 1 MHz down to the lowest temperature of the measurements.

## B. Quasielastic neutron scattering

For the case of spatially confined (localized) atomic motion within pairs of sites, the incoherent neutron-scattering function can be written in the form<sup>20</sup>

$$S_{\text{inc}}(Q, \omega) = e^{-2W} \{A_0(Q) \delta(\omega) + [1 - A_0(Q)]L(\omega, \Gamma)\}, \quad (5)$$

where  $e^{-2W}$  is the Debye-Waller factor,  $\delta(\omega)$  is the elastic  $\delta$  function,  $L(\omega, \Gamma)$  is a quasielastic Lorentzian of half-width  $\Gamma$ , and  $A_0(Q)$  is the elastic incoherent structure factor (EISF). The value of  $\Gamma$  is proportional to the atomic hopping rate, and  $A_0(Q)$  contains information on the geometry of the

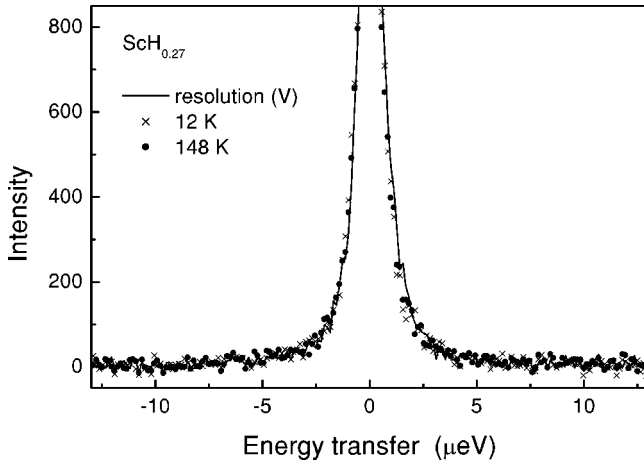


FIG. 6. Quasielastic neutron-scattering spectra measured at  $Q = 1.88 \text{ \AA}^{-1}$  for vanadium reference sample ( $T=300 \text{ K}$ ) and for  $\alpha\text{-ScH}_{0.27}$  ( $T=12$  and  $148 \text{ K}$ ). The spectra are normalized to the same maximum intensity. There is no discernible broadening of the  $\text{ScH}_{0.27}$  spectra.

localized motion.<sup>20</sup> To be compared to the experimental QENS spectra  $S_{exp}(Q, \omega)$ , the model scattering function  $S_{inc}(Q, \omega)$  defined by Eq. (5) should be convoluted with the instrumental resolution function  $R(Q, \omega)$ .

We have not found any signs of quasielastic line broadening for  $\alpha\text{-ScH}_{0.27}$  in the studied temperature range 12–302 K. The shape of the observed QENS spectra in this range is well described by the instrumental resolution function  $R(Q, \omega)$ . As an example of the data, Fig. 6 shows the QENS spectra at  $Q = 1.88 \text{ \AA}^{-1}$  for vanadium and for  $\alpha\text{-ScH}_{0.27}$  at 12 K and 148 K. These spectra are normalized to the same maximum intensity. As can be seen from Fig. 6, even for the highest  $Q$  value the shapes of the QENS spectra for  $\alpha\text{-ScH}_{0.27}$  at  $T=12 \text{ K}$  and  $148 \text{ K}$  do not differ from the shape of the spectrum for vanadium that represents the resolution function. These results indicate that the majority of H atoms do not show any motion in the frequency range limited by about one third of the resolution half-width ( $0.2 \text{ \mu eV}$ , i.e.,  $1.5 \times 10^8 \text{ s}^{-1}$  in frequency units) from below and by about one half of the maximum energy transfer ( $8 \text{ \mu eV}$ , i.e.,  $6 \times 10^9 \text{ s}^{-1}$ ) from above. Taking experimental uncertainties into account, the upper limit of the fraction of H atoms participating in localized motion in this frequency range at  $T \leq 302 \text{ K}$  can be estimated as 7%.

However, our high-resolution QENS results appear to be consistent with the existence of a localized H motion on a faster frequency scale ( $\tau_f^{-1}$ ).<sup>7,8</sup> If the characteristic frequency of a localized motion exceeds the width of the instrumental frequency “window” ( $\pm 16 \text{ \mu eV}$  in our case), this motion gives rise to a flat background (instead of a quasielastic line) in the observed spectrum. Therefore, such a motion cannot be detected from the shape of a QENS spectrum which contains only the elastic line. However, the presence of the high-frequency motion affects the *intensity* of the elastic line, leading to the loss of intensity at high  $Q$ . In fact, as can be seen from Eq. (5), the behavior of the elastic line intensity is determined by the EISF,  $A_0(Q)$ . Figure 7 shows

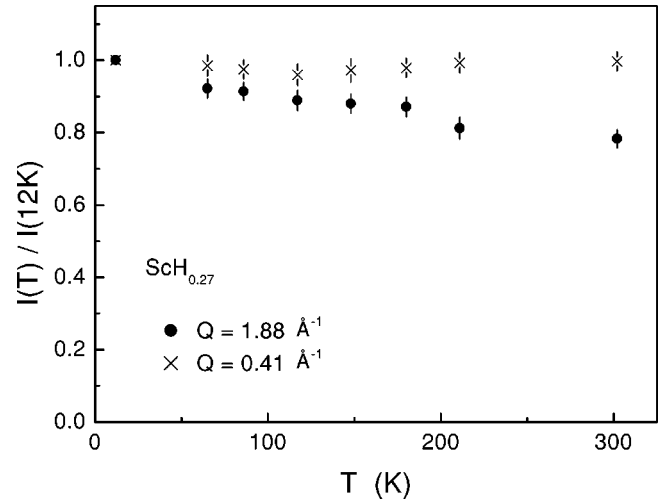


FIG. 7. Temperature dependence of the integrated elastic line intensities at  $Q = 1.88$  and  $0.41 \text{ \AA}^{-1}$ . The intensities are normalized to their corresponding values at  $12 \text{ K}$ .

the temperature dependence of the elastic line intensity for  $Q = 1.88 \text{ \AA}^{-1}$  and  $0.41 \text{ \AA}^{-1}$ . It can be seen that at low  $Q$  the intensity is nearly temperature independent, whereas at high  $Q$  the intensity decreases substantially with increasing temperature. Note that the decrease in the intensity at  $Q = 1.88 \text{ \AA}^{-1}$  is considerably greater than that resulting from the Debye-Waller factor. Using the inelastic neutron-scattering data on the hydrogen vibration frequencies in  $\alpha\text{-ScH}_x$ <sup>21</sup> we have estimated the Debye-Waller factor at  $Q = 1.88 \text{ \AA}^{-1}$  to be 0.945. Similar temperature dependence of the EISF has been found in the intermediate-resolution QENS experiments on  $\alpha\text{-ScH}_x$ .<sup>7,8</sup> In order to account for the observed temperature dependence of the EISF, we have to assume that only a fraction  $p_f$  of H atoms participates in the localized motion on the frequency scale of  $\tau_f^{-1}$ , and this fraction increases with temperature. The fraction  $1 - p_f$  of “static” protons can be identified as the fraction of protons involved in pairing.<sup>7,8</sup>

Taking into account the fraction of “static” protons, the orientationally averaged form of the EISF for the hopping within pairs of sites separated by a distance  $d$ <sup>20</sup> is given by

$$A_0(Q) = 1 - p_f + \frac{p_f}{2} [1 + j_0(Qd)], \quad (6)$$

where  $j_0(x)$  is the spherical Bessel function of zeroth order. The experimental  $Q$  dependence of the EISF for  $\alpha\text{-ScH}_{0.27}$  has been found from the elastic line intensities normalized with respect to the corresponding intensities for vanadium. The data have been corrected for the host-metal (Sc) contribution which is responsible for about 17% of the incoherent scattering cross section of  $\alpha\text{-ScH}_{0.27}$ . Figure 8 shows the  $Q$  dependence of the EISF at  $T=302 \text{ K}$ . The fit of Eq. (6) to these data yields  $p_f = 0.95 \pm 0.05$  and  $d = 1.02 \pm 0.04 \text{ \AA}$ ; the result of the fit is shown by the solid line in Fig. 8. Note that the fitted value of  $d$  is in excellent agreement both with the structural data<sup>4</sup> (giving  $1.03 \pm 0.03 \text{ \AA}$  for the distance between the nearest-neighbor tetrahedral sites in  $\alpha\text{-ScD}_{0.33}$ )

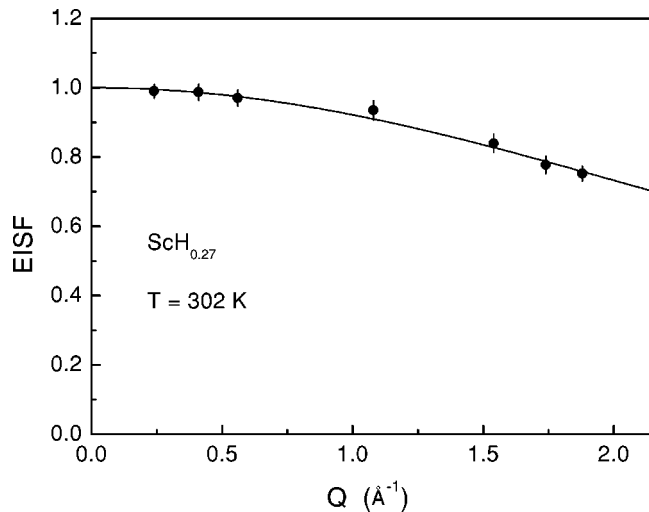


FIG. 8. The elastic incoherent structure factor for  $\alpha$ -ScH<sub>0.27</sub> as a function of  $Q$  at  $T=302$  K. The solid line represents the fit of the two-site model [Eq. (6)] to the data.

and with the results of the intermediate-resolution QENS measurements<sup>8</sup> ( $d=1.02\pm 0.02$  Å for  $\alpha$ -ScH<sub>0.16</sub>). The fitted value of  $p_f$  indicates that at  $T=302$  K nearly all protons participate in the localized motion on the frequency scale of  $\tau_f^{-1}$ . It should be noted that the available experimental  $Q$  range (with the maximum  $Q$  value of  $1.88$  Å<sup>-1</sup>) is not sufficient to trace the EISF described by Eq. (6) to the first minimum of the Bessel function. Therefore, the fit presented in Fig. 8 may not seem impressive. However, for fixed  $d$  values considerably exceeding  $1$  Å the fits become definitely worse, since the fitting curves start to show the inflection point and leveling off at  $Q>1.6$  Å<sup>-1</sup>, whereas no such features are seen in the experimental data. For fixed  $d$  values being less than  $1$  Å the fits result in  $p_f$  values exceeding  $1$ , which is unphysical.

Thus, the results of our high-resolution QENS measurements support the conclusion that only a small fraction of H atoms in  $\alpha$ -ScH<sub>0.27</sub> participate in the localized motion on the frequency scale of  $\tau_f^{-1}\sim 10^8$ – $10^9$  s<sup>-1</sup> at low temperatures. However, the observed behavior of the elastic line intensity as a function of  $T$  and  $Q$  is consistent with the existence of a localized H motion on the faster frequency scale ( $\tau_f^{-1}>7\times 10^{10}$  s<sup>-1</sup>), involving a large fraction of H atoms (at 300 K).

#### IV. CONCLUSIONS

Measurements of the <sup>45</sup>Sc spin-lattice relaxation rates in  $\alpha$ -ScD<sub>*x*</sub> ( $x=0.05$  and  $0.22$ ) and  $\alpha$ -ScH<sub>0.27</sub> have revealed

strong deviations from the Korringa behavior of the relaxation rate in the temperature range 25–230 K. The excess relaxation rate  $T_{1Q}^{-1}$  showing a peak near 100 K can be attributed to the electric quadrupole interaction modulated by a localized motion of H(D) atoms. In addition to the strong effect of isotope (H $\leftrightarrow$ D) substitution on the amplitude of the  $T_{1Q}^{-1}$  peak, with a much stronger peak in the deuteride, we have found that in the region of the peak, the frequency dependence of  $T_{1Q}^{-1}$  for  $\alpha$ -ScH<sub>0.27</sub> is much weaker than for  $\alpha$ -ScD<sub>*x*</sub>. The behavior of the <sup>45</sup>Sc relaxation rate in  $\alpha$ -ScD<sub>*x*</sub> can be described by a model employing a distribution of D hopping rates  $\tau_i^{-1}$ , with the most probable  $\tau_i^{-1}$  value increasing with temperature and passing through the <sup>45</sup>Sc resonance frequency near 100 K. However, such a description is not applicable to the <sup>45</sup>Sc relaxation rate data for  $\alpha$ -ScH<sub>0.27</sub>. Our results suggest that the maximum of the hopping rate distribution for H atoms is shifted to much higher frequencies from that for D atoms. Hence, only a tail of this distribution can be probed by NMR measurements on the H-doped samples. A large difference between the characteristic hopping rates of H and D atoms is consistent with a quantum origin of the localized hydrogen motion in scandium.

High-resolution quasielastic neutron-scattering measurements on  $\alpha$ -ScH<sub>0.27</sub> in the temperature range 12–302 K have not revealed any additional line broadening on the energy transfer scale of 0.2–8  $\mu$ eV. In agreement with the <sup>45</sup>Sc relaxation rate data, these results show that most H atoms in  $\alpha$ -ScH<sub>0.27</sub> do not participate in the motion on the frequency scale of  $10^8$ – $10^9$  s<sup>-1</sup> at low temperatures. However, the behavior of the elastic line intensity for this sample as a function of  $T$  and  $Q$  indicates the presence of localized H motion on a faster frequency scale.

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