Light hydrogen isotope μ^+ in Sc and α -ScH_x solid solutions

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The response of Sc and α -ScH_x systems ($0 \leq x \leq 0.25$) to the implantation of positive muons, i.e., light H isotopes, has been studied by μ^+ SR spectroscopy in high and low transverse magnetic field, and in zero field (ZF). The investigation covered a temperature range from 300 K down to 2 K, for various orientations of the single-crystal samples with respect to the field or initial μ^+ polarization. Below 30 K the positive muons occupy, in pure Sc, a localized “fast-tunneling” state, extending over two adjacent, interstitial-tetrahedral (*T*) sites above and below the *ab*-atomic plane of the hcp lattice. In α -ScH_x, a fraction of the muons stays in this tunneling state, while for the other part, the muons pair with a H atom, to form the analog of the *T*-pair state H-Sc-H aligned along the *c* axis, specific to the α^* phase. The electric-field gradients, of muonic as well as intrinsic-crystalline origin, acting on the nuclei near the μ^+ influence the results at low and zero magnetic fields. Their characteristics and the H-concentration dependences are evaluated. For the ZF-data analysis a newly developed uniaxial version of the Kubo-Toyabe formula was applied. Above 30 K the long-range diffusion of positive muons becomes noticeable; a two-state model explains very well the data. It assumes the μ^+ to be, alternatively, in a state of free diffusion between localized-tunneling states or in a μ^+ -Sc-H trap. The model describes the repeated μ^+ -capture and release processes with three characteristic correlation times, which follow Arrhenius laws. The parameters, e.g., activation energies and preexponential factors, are compared to the parameters of the H and D dynamics in α -ScH(D)_x. From μ SR measurements in a deuterated sample (α -ScD_{0.10}) one infers very similar behaviors of the μ^+ in D and H solid solutions in the Sc host.

I. INTRODUCTION

This work, in which we use positive muons to study metal-hydrogen interstitial-solution systems, was motivated by the observation of quantum effects in the proton dynamics of these systems. The positive muon, as a rule, mimics the properties of hydrogen (proton) dissolved in metallic lattices, but, since the muon mass is approximately 1/9 that of the proton, the muon dynamics provides a more sensitive probe of quantum behavior. In addition, the μ^+ allows us to deduce the behavior of a H isotope in matter at the limit of infinite dilution, a goal unattainable for the conventional techniques dealing with H or D.

In a first step we present results concerning the localization and motion of the μ^+ in the scandium-hydrogen (or deuterium) system. In a second step, the results enable us to discuss the metal-hydrogen system itself.

We have performed μ^+ -spin rotation/relaxation (μ SR) studies¹ on single-crystal samples of scandium and α -ScH_x with $x = 0.05, 0.10, 0.25$, and α -ScD_{0.10}. The relaxation rate of the μ^+ precession was measured at various temperatures

as a function of the strength and direction of the magnetic field $\mathbf{B}_{\text{ext}}$ for the “transverse” geometry (TF). The relaxation rate was also measured at various temperatures for $\mathbf{B}_{\text{ext}} = 0$ (ZF), as a function of the angle between muon polarization and the hexagonal *c* axis.

In nonmagnetic metals like Sc and the α -ScH(D)_x systems the total magnetic field at the μ^+ position is composed of $\mathbf{B}_{\text{ext}}$ and the dipolar fields from the nuclear magnetic moments of the surrounding atoms. Averaging over all muons observed in a measurement one obtains, because of the random direction of the nuclear spins, a characteristic field distribution around $\mathbf{B}_{\text{ext}}$ (around zero in the case of a ZF experiment). The atomic and μ^+ dynamics affect the time-averaged field distribution, and the spin-orientation randomness is modified in case of nonzero nuclear quadrupolar moments, due to the interaction of these moments with the electric-field gradient (EFG) at the nuclear positions. The field distribution seen by the muons is reflected in the distribution of the μ^+ Larmor precession frequency, the basic observable in a μ SR experiment. A continuous field distribution is observed via the decay (relaxation) of the muon-

FIG. 1. (a) The hcp lattice of ScH_x. In the α^* phase two H-H pairs can occupy sites T1, T5, and T3, T4, straddling a metal atom, on adjacent c axes shifted along the a' direction (a' is perpendicular to the bc plane). T1–T2 and T1–T5 are, respectively, first- and second-nearest-neighbor tetrahedral sites along the c axis (from Ref. 9). Location of μ^+ : the μ^+ -tunneling state in adjacent- T sites (T1, T2), and the trapped static μ^+ in the μ^+ -Sc-H T -pair configuration (e.g., T3, T4) across a Sc atom in the c direction. The μ^+ or H position (z_0) in the T -interstice is indicated. Above 50 K the muons perform long range diffusion by T - O - T jumps, e.g., the T1–O1–T6 transition. (b) and (c). Two possible two-chain arrangements made of H-H pairs on adjacent c axes along the a' direction in α^* -ScH_x (from Ref. 10).

spin polarization, due to the phase spread in precession, increasing with the time.

The paper is organized as follows: Section II recapitulates the present knowledge on rare-earth metal–hydrogen interstitial solutions. Section III is a compilation of formulas used in the following—besides commonly used relations the new “uniaxial-Gaussian” approximation for ZF measurements is presented. Section IV comprises the experimental procedure, whereas in Sec. V the results of the low-temperature measurements are analyzed and the locations of the nondiffusing muons are discussed. Section VI deals with the modeling of μ^+ diffusion and trapping. The general discussion and the conclusions are presented in Sec. VII.

II. H IN SOLID SOLUTION IN SCANDIUM AND YTTRIUM

It is well known that a number of hcp rare-earth metals (e.g., Sc, Lu, and Y) can retain substantial amounts of hydrogen at low temperatures without precipitation into ordered hydride phases.^{2,3} Neutron diffraction studies^{4,5} have shown that the dissolved hydrogen (deuterium) atoms reside in the tetrahedral (T) interstices of the metal (M) lattice, rather than in the octahedral (O) interstices. Diffuse elastic neutron-scattering studies^{6,7} have indicated that the hydrogen exhibits unusual short-range pairing ordering, which apparently stabilizes the solid-solution α phase to much higher concentration at low temperatures than in other metal-hydrogen systems. In this metastable phase, called α^* ,⁸ the basic H- M -H unit consists of a c -axis aligned pair of H atoms in second-nearest-neighbor T sites straddling a metal atom. These pairs are ordered in chains along the c direction

in a zigzag fashion, with each consecutive hydrogen pair undergoing a lateral displacement step—see Fig. 1 (from Refs. 9,10; for hcp Sc/ α -ScH_x the cell parameters are $a \approx 3.31$ Å and $c \approx 5.27$ Å). In addition, interchain correlations become significant with increasing H concentration and decreasing temperature. The electrical resistivity anomaly occurring between 150 and 170 K in these systems¹¹ is believed to coincide with the formation of these chains.¹² The details of the short-range hydrogen pairing (e.g., the fraction of paired hydrogen and the distribution of chain lengths) depend not only on H concentration and temperature, but also vary among the different rare-earth metals. With increasing atomic volume (Sc→Lu→Y) ordering takes place on fewer, but longer chains. This may be explained by a difference in elastic anisotropy as it is thought that elastic interactions play an important role in the ordering.

These differences have also been manifested by changes in the hydrogen vibrational dynamics characterized via incoherent-inelastic neutron-scattering studies.^{13–21} The T -site potential in the various rare-earth metals has been found to be anisotropic, with a markedly anharmonic vibration along the c direction being 25–30% lower in energy than the almost harmonic, doubly degenerate H vibrations in the basal plane. Moreover the c -axis vibration mode was found to be split by ~ 4 –5 meV due to the dynamic coupling of hydrogen-pair members.¹³

The mobility of H consists of long-range and local motions and has been observed on at least three different time scales:

(I) The relatively slow motion, which gives rise to long-range diffusion via T - O - T jumps, is characterized by an ac-

tivation energy of ~ 0.6 eV and has been observed in quasi-elastic neutron-scattering (QNS),^{22,6,7} NMR,^{23,24} and Gorsky effect²⁵ studies of YH_x , LuH_x , and ScH_x .

(II) Faster motion with rates of the order of 10^7 – 10^{10} s⁻¹ between 10 and 100 K associated with local tunneling between first-nearest-neighbor T sites (separation ≈ 1.0 – 1.2 Å) has been observed by NMR,^{26,27} acoustic spectroscopy—anelastic relaxation (AR),²⁸ and ultrasonic attenuation.^{29–31}

(III) The fastest motion with rates 10^{11} – 10^{12} s⁻¹ between 10 K and 200 K, also due to local hopping between neighboring T sites has been observed by QNS.^{22,6,7}

Analysis of the QNS data proves that the very fast local hopping is due to protons tunneling in an approximately symmetric T - T potential, protons that are, therefore, not involved in the pairing, which leads to short-range ordering at low temperature. Hence the population of these “free protons” decreases with decreasing temperature. Furthermore, the hopping rate measured by QNS goes through a minimum at ~ 100 K and then increases with further decrease in temperature following an approximate T^{-1} dependence. This behavior has been attributed to the nonadiabatic effects of weak coupling of the proton to the conduction electrons.²¹ The problem was originally studied from a theoretical point of view by Kondo,³² who later considered particularly the case of diffusing muons³³ after the first experimental results obtained for μ^+ , e.g., in Al (Ref. 34) and Cu.³⁵

Considering the lower H-hopping rate deduced from the NMR measurements in the α - M -H system, associated with a wide distribution of activation energies, it is likely that the corresponding relaxation is in fact due to slower moving protons involved in short-range order and hence experiencing a distribution of strongly asymmetric potentials.²⁷

More recently Cannelli and co-authors^{28,36} have presented evidence from acoustic measurements of H tunneling and trapping by oxygen atoms in α -phase YH_x at low H concentration. In the presence of O, three new anelastic-relaxation peaks are observed in addition to those observed in a pure sample. The peak at low temperature is attributed to tunneling of H, trapped by O, between adjacent- T sites with typical rates of 10^4 – 10^6 s⁻¹ between 10 and 60 K. The remaining peaks are postulated as being due to classical hopping of H in the distorted environment of the O atom. The main interaction of the trapped-tunneling system seems to be related to multiphonon processes and not to conduction electrons.

In summary, H tunneling between adjacent- T sites has been observed by QNS, NMR, and AR measurements, with decreasing rates due to the increasing asymmetry between the two-site energies, associated with (1) an isolated H atom (QNS), (2) the H pair along the c axis (NMR), and (3) a H atom (or pair) trapped by an O atom (AR).

Two recent reviews cover the details on tunnelling of H and D in metals and semiconductors,³⁷ and the theoretical and experimental aspects of quantum diffusion of muons and muonium atoms in solids.³⁸

III. BASIC FORMULAS FOR THE μ^+ -POLARIZATION DECAY

We recapitulate here the basic expressions that are to be used in evaluating the data. Unlike in usual treatments, the formulas below account for degenerate nuclear states explic-

itly. The approximate uniaxial Kubo-Toyabe formula (Sec. III B) is applied to μ SR measurements.

A. Relaxation rate for precession in transverse field

The muon is subjected, during a *residence time* τ_c separating eventual jumps between interstitial sites $\mathbf{R}_\mu$, $\mathbf{R}_{\mu'}$, to a magnetic field $\mathbf{B}_{loc} = \mathbf{B}_f + \mathbf{B}_{ext}$, where $\mathbf{B}_f$ is a random field, with $\bar{\mathbf{B}}_f = 0$, determined by the magnetism of electrons and atoms in the solid environment, and $\mathbf{B}_{ext}$ is the applied field. In the TF geometry, $\mathbf{B}_{ext}$ is (ideally) perpendicular to the initial μ^+ polarization $\mathbf{P}(0)$, while its orientation relative to the single-crystal sample is variable. In a “normal” TF experiment $B = |\mathbf{B}_{ext}|$ should not be too low: (i) $\mathbf{B}_{ext}$ should serve as an axis of quantization, $B \gg B_f = |\mathbf{B}_f|$, and also (ii) the nuclear precession frequencies have to be larger than the μ^+ -nucleus dipolar coupling. As a result of the ensemble average over B_f , the Larmor precession of the polarization $\mathbf{P}(t)$ is observed as a damped oscillation in the directions perpendicular to $\mathbf{B}_{ext}$,

$$P_x(t) = P(0) G_x(t) \cos(\gamma_\mu B t), \quad (1)$$

parallel to the initial polarization $\mathbf{P}(0)$. Here $\gamma_\mu = 2\pi \times 135.5388$ MHz/T is the gyromagnetic ratio for μ^+ . The transverse relaxation function $G_x(t)$ can often be approximated by the “Abragam” formula^{39,1}

$$G_x(t) = \exp[-M_2 \tau_c^2 (e^{-t/\tau_c} - 1 + t/\tau_c)], \quad (2)$$

where the “second moment” $M_2 = \sigma^2 = -(d^2 G_x / dt^2)_{t=0} = \gamma_\mu^2 \overline{B_{f,z}^2}$ is the mean square of the projection of $\mathbf{B}_f$ along $\mathbf{B}_{ext}$. For $t \ll \tau_c$ one has $G_x(t) \approx \exp\{-\frac{1}{2} \sigma^2 t^2\}$; therefore σ is called the *static (Gaussian) relaxation rate*.

In the absence of electron magnetism, $\mathbf{B}_f$ is the sum of *nuclear* dipole fields at the μ^+ , arising from the nuclear spins I_j . Except for temperatures well below 1 mK, the probabilities for a nucleus to be in any of the eigenstates of its spin Hamiltonian can be taken as equal. If these states are stationary during the stay of the muon at a given site (or during the time of observation $\tau_o \sim 10^{-5}$ s, if $\tau_o < \tau_c$), the calculation of M_2 amounts to summing up the quantum statistical averages $\overline{B_{fj\parallel}^2}$ for the dipolar field components along $\mathbf{B}_{ext}$, of each nuclei (j) about the muon.

For $I > 1/2$ the nuclear spin eigenstates $|\nu\rangle$ are determined by the interplay of the magnetic dipole and electric quadrupole couplings. The Hamiltonian for the j -th nucleus, without the interaction with the muon, is

$$\hat{H}^{(j)} = -h \nu_Z \mathbf{b} \cdot \mathbf{I}_j + h \nu_Q^{(j)} [3I_{j,z}^2 - I(I+1) + \eta^{(j)}(I_{j,x}^2 - I_{j,y}^2)], \quad (3)$$

where $\nu_Z = (\gamma_I/2\pi)B$ and γ_I is the gyromagnetic ratio for the nuclei. The unit vector $\mathbf{b} = \mathbf{B}_{ext}/B$ has the components $(\sin \Theta \cos \Phi, \sin \Theta \sin \Phi, \cos \Theta)$ in the crystal frame, while (ξ, η, ζ) denote components along the principal axes of the electric-field gradient tensor $F_{ik}^{(j)} = \partial E_i(\mathbf{r}_{j\mu}) / \partial x_{jk}$ ($\mathbf{E}$ is the electric field and $\mathbf{r}_{j\mu} = \mathbf{r}_j - \mathbf{R}_\mu$ is the vector pointing from the muon to the j -th atom). The quadrupole frequency is $\nu_Q^{(j)} = eQF_3^{(j)} / [4I(2I-1)h]$, where Q is the nuclear quadrupole moment. The eigenstates of the j th nucleus depend on

(Θ, Φ) , on $|\mathbf{B}_{\text{ext}}|$ through the ratio $\nu_Z/\nu_Q^{(j)}$, on the *directions* of the principal axes of the EFG tensor, and on the “asymmetry parameter” $\eta^{(j)} = (F_1^{(j)} - F_2^{(j)})/F_3^{(j)}$, where $F_l^{(j)}$ are the eigenvalues of $F^{(j)}$ in the order $|F_3| \geq |F_2| \geq |F_1|$.

The static moment M_2 , a function of these 7 parameters per atom determining the eigenstates $|\nu\rangle$, is given by

$$M_2(\mathbf{B}_{\text{ext}}) = (\hbar \gamma_\mu \gamma_I)^2 \sum_j r_{j\mu}^{-6} (2I+1)^{-1} \times \sum_{\nu_j} \sum_{\nu'_j}^{|\epsilon_\nu - \epsilon_{\nu'}| < \Delta} |\langle \nu_j | (\mathbf{I}_j \mathbf{b}) - 3r_{j\mu}^{-2} (\mathbf{r}_{j\mu} \mathbf{b}) \times (\mathbf{r}_{j\mu} \mathbf{I}_j) | \nu'_j \rangle|^2. \quad (4)$$

This expression takes into account not only, as usual, the diagonal matrix elements of $\mathbf{I}_j$, but also the contribution from transitions between degenerate or “quasidegenerate” nuclear eigenstates $\nu(\mathbf{B})$, $\nu'(\mathbf{B})$, for which $|\epsilon_\nu - \epsilon_{\nu'}|$ is within the line width $\Delta \approx \hbar \gamma_\mu B_f$ of the μ^+ signal. Besides accidental degeneracies at isolated $\mathbf{B}_{\text{ext}}$ values, nearly degenerate states come *necessarily* into play for a half-integer nuclear spin $I > 1/2$ in the quadrupole-dominated, *weak-field* regime, where

$$M_2 \rightarrow M_{2Q}(\mathbf{b}) = \sum_{i,k=xyz} A_{ik} b_i b_k, \quad \nu_Z/\nu_Q^{(j)} \ll 1, \quad (5)$$

is a *second-order* polynomial in the components of $\mathbf{b}$. [To arrive at this result, the nondiagonal matrix elements in Eq. (4) are essential.] The coefficients A_{ik} depend on the site geometry *and* on the EFG tensors $F^{(j)}$.

The dependence of M_2 on $|\mathbf{B}_{\text{ext}}|$, implicit in the nuclear spin eigenstates $|\nu_j\rangle$ in the general expression Eq. (4), disappears also for sufficiently *large* fields, $\nu_Z/\nu_Q^{(j)} \gg 1$: in this “van Vleck limit” $\mathbf{I}_j \rightarrow \mathbf{b}(\mathbf{I}_j)$ gives

$$M_2 \rightarrow M_{2V}(\mathbf{b}) = \frac{4I(I+1)}{3} (\hbar \gamma_I \gamma_\mu)^2 \sum_j [P_2(\hat{\mathbf{r}}_{j\mu} \mathbf{b})]^2 / r_{j\mu}^6, \quad \nu_Z/\nu_Q^{(j)} \gg 1, \quad (6)$$

with $P_2(x) = \frac{1}{2} - \frac{3}{2}x^2$. Unlike for the weak-field limit, M_{2V} is a *fourth-order* even polynomial of b_i ,

$$M_{2V}(\mathbf{b}) = \sum_{iklm=xyz} C_{iklm}^{(4)} b_i b_k b_l b_m + C_{ik}^{(2)} b_i b_k + C_0, \quad \nu_Z/\nu_Q^{(j)} \gg 1, \quad (7)$$

with the coefficients C determined, like the A 's of Eq. (5), by the site geometry, but unlike those, the C 's do not depend on $F^{(j)}$. Thus, data obtained in a strong field ($\nu_Z/\nu_Q^{(j)} \gg 1$ for all j) can directly be used to determine the μ^+ position. (For any given site symmetry the polynomials M_{2Q} and M_{2V} reduce to the corresponding “symmetry harmonics.”⁴⁰)

A more general formulation is necessary when the μ^+ wave function is not localized at a single interstice but extends to a group G of neighboring sites. This is the case of “fast tunneling”: the frequency of μ^+ tunneling between the n_G sites of G is much larger than that of the nuclear preces-

sion. Then, for the perturbing effect of the muon at the nuclear sites, the μ^+ wave function can be taken as static, extended in a symmetrical way to the sites $\{\mathbf{R}_\mu, \mathbf{R}_{\mu'}, \dots\}$ of G . Assuming sharp (δ -like) localization about these positions, one obtains

$$M_2^{(G)}(\mathbf{B}_{\text{ext}}) = (\hbar \gamma_\mu \gamma_I)^2 \sum_j (2I+1)^{-1} \times \sum_{\nu_j} \sum_{\nu'_j}^{|\epsilon_\nu - \epsilon_{\nu'}| < \Delta} \left| n_G^{-1} \sum_{\mu \in G} \langle \nu_j | r_{j\mu}^{-3} \times \{(\mathbf{I}_j \mathbf{b}) - 3r_{j\mu}^{-2} (\mathbf{r}_{j\mu} \mathbf{b})(\mathbf{r}_{j\mu} \mathbf{I}_j)\} | \nu'_j \rangle \right|^2, \quad (8)$$

which, in the high-field van Vleck limit of negligible quadrupole coupling ($\nu_Z/\nu_Q^{(j)} \gg 1$), becomes^{41,42}

$$M_2^{(G)} \rightarrow M_{2V}^{(G)}(\mathbf{b}) = (\hbar \gamma_\mu \gamma_I)^2 \frac{4I(I+1)}{3} \sum_j \left| n_G^{-1} \sum_{\mu \in G} r_{j\mu}^{-3} P_2(\hat{\mathbf{r}}_{j\mu} \mathbf{b}) \right|^2. \quad (9)$$

Like M_{2V} above, $M_{2V}^{(G)}$ is an even polynomial of fourth order in the components of $\mathbf{b}$, but the fast tunneling leads to “interference” terms between the n_G muon sites. The weak-field limit $M_{2Q}^{(G)}$ is, like M_{2Q} , quadratic in b_i .

The possible μ^+ sites in hcp metals are tetrahedral (T) and octahedral (O) interstices. The T sites [see Fig. 1(a)] are grouped in adjacent pairs along the atomic chains in the c direction, the two sites T_1 , T_2 of a pair transforming into each other by mirror reflection through the separating $\mathbf{ab}$ atomic plane. For nonideal packing ratios $[(c/a)_{\text{Sc}} = 1.592]$ the distance z_0 of the T positions from the plane is not fixed by the site symmetry (C_{3v}). If the minima of the potential energy happen to be near the basal plane, tunneling of the μ^+ across the mirror plane becomes easy, and the muon state, extended over the pair of interstices, has the higher D_{3d} symmetry.

The O sites within a cage of six equidistant atoms at the corner of a nonregular octahedron have the symmetry D_{3d} , including also inversion: there is no free “position parameter” and the muon-atom distances are determined by the lattice parameters.

The polynomial of fourth order in (b_x, b_y, b_z) [Eq. (7)], compatible with the above site symmetries, is for the O site

$$M_{2V}^O = a_{00} + a_{20} P_2(\cos \Theta) + a_{40} P_4(\cos \Theta), \quad (10)$$

and for the T site

$$M_{2V}^T = c_{00}(z_0) + c_{20}(z_0) P_2(\cos \Theta) + c_{40}(z_0) P_4(\cos \Theta) + c_{43}^{(i)}(z_0) P_4^3(\cos \Theta) \cos 3\Phi, \quad i=1,2 \quad (11)$$

(P_n are the Legendre polynomials, P_4^3 is the associated Legendre function), Φ is measured from a vertical mirror plane. (Note that $\cos 3\Phi \rightarrow -\sin 3\Phi'$ for the azimuthal angle $\Phi' = \Phi - 30^\circ$ measured from the a axis.) The coefficients a_{ik} and c_{ik} depend on the atomic positions around the μ^+ in the crystal frame: neglecting local atomic displacements, a_{ik} is

FIG. 2. TF relaxation rates $\sigma(\Theta)$ calculated in the van Vleck limit for the μ^+ at an O site (dash-dotted line), at the center of a T site (dashed line), at a shifted T site (long-dash-short-dash), and tunnelling between two adjacent- T sites (line dash-dot-dot-dot) in the undistorted Sc lattice. The measured low- T $\sigma(\Theta)$ relaxation rates for pure Sc at 503 mT are also shown.

determined by the lattice parameters, while c_{ik} depends also on the “height” z_0 of the T sites above and below the basal plane.

In Eq. (11) the index $i=1,2$ had to be introduced, since in the presence of $\mathbf{B}_{\text{ext}}$ the two T sites of a pair are no longer equivalent, as far as the average squared dipolar field M_2 is concerned. If Eq. (11) holds, with a set of c_{ik} , for the sites T_1 “above” the mirror plane, the same value of M_2 will be observed for the sites T_2 “below” the plane only if the field direction $\mathbf{b}$ is also reflected across the plane (see Fig. 1). This reflexion means $\cos \Theta \rightarrow -\cos \Theta$, showing that c_0, c_{20}, c_{40} are the same for T_1 and T_2 , but the invariance of M_{2V}^T implies $c_{43}^{(2)} = -c_{43}^{(1)}$. Since there is no reason to expect that the probabilities for the μ^+ to be stopped at T_1 or T_2 are different, the observable moment is $M_{2V}^T = \frac{1}{2}(M_{2V}^{T1} + M_{2V}^{T2}) = M_{2V}^T(\Phi = 30^\circ)$, i.e., independent of Φ (only in the van Vleck limit!). As a result, the c_{43} terms drop and the observable M_{2V}^T has the same algebraic form as M_{2V}^O . However, the coefficients a_{kl} and c_{kl} , and thereby the shapes of the $M_{2V}(\cos \Theta)$ functions, turn out to be markedly different for O and T sites (see Fig. 2).

For the tunneling- μ^+ state with mirror symmetry through the basal plane, the term c_{43} does not arise at all.

For the weak-field limit ($v_Z/v_Q^{(j)} \ll 1$) the quadratic Eq. (5) reduces for the present symmetries to

$$M_{2Q} = e_{00} + e_{20}P_2(\cos \Theta) \quad (12)$$

both for the T and O sites, but again with different coefficients e_{ik} .

B. Relaxation rate at zero applied field

For $\mathbf{B}_{\text{ext}}=0$ (i.e., $B \ll B_f$), the average polarization $\mathbf{P}(t)$ remains parallel to the unit vector $\mathbf{p} = \hat{\mathbf{P}}(0)$. For the second time derivative of G_x at $t=0$, M_2 , one has

$$M_2^{(\text{ZF})} = (\hbar \gamma_\mu \gamma_I)^2 \sum_j r_{j\mu}^{-6} (2I+1)^{-1} \times \sum_{v_j} \sum_{v'_j}^{|\epsilon_v - \epsilon_{v'}| < \Delta} |\langle v_j | \{ \mathcal{P}[\mathbf{I}_j - 3r_{j\mu}^{-2} \mathbf{r}_{j\mu}(\mathbf{r}_{j\mu} \mathbf{I}_j)] | v'_j \rangle|^2, \quad (13)$$

similarly to Eq. (4) but, instead of the components $(b\mathbf{I})$ along the field direction $\mathbf{b}$, this formula contains the projections $\mathcal{P}\mathbf{I} = \mathbf{I} - \mathbf{p}(\mathbf{p}\mathbf{I})$ of $\mathbf{I}$ (and of $\mathbf{r}_{j\mu}$) on the plane perpendicular to $\mathbf{p}$. For a tunneling state of the μ^+ one has, similarly,

$$M_2^{(\text{ZF},G)} = (\hbar \gamma_\mu \gamma_I)^2 \sum_j (2I+1)^{-1} \times \sum_{v_j} \sum_{v'_j}^{|\epsilon_v - \epsilon_{v'}| < \Delta} \left| n_G^{-1} \sum_{\mu \in G} \langle v_j | r_{j\mu}^{-3} \times \{ \mathcal{P}[\mathbf{I}_j - 3r_{j\mu}^{-2} \mathbf{r}_{j\mu}(\mathbf{r}_{j\mu} \mathbf{I}_j)] | v'_j \rangle \right|^2. \quad (14)$$

These formulas lead, both for localized or extended (tunneling) states of μ^+ , to

$$M_2^{(\text{ZF})} = D_0 + \mathbf{p} \cdot \mathbf{D} \cdot \mathbf{p}, \quad (15)$$

where the constant D_0 and the tensor $\mathbf{D}$ are determined by the μ^+ position ($\mathbf{r}_{j\mu}$) and the spin Hamiltonian of the nuclei, different for a localized or a tunneling state. The symmetry of $\mathbf{D}$ corresponds to that of the μ^+ site [Eq. (13)] or the tunneling center [Eq. (14)].

As to the evolution of $\mathbf{P}(t)$ for longer times, it can be calculated analytically only for some idealized cases of the classical distribution of B_f . With the assumption that this distribution is Gaussian and isotropic,⁴³ the result for $\mathbf{P}(t)$ is the familiar Kubo-Toyabe (KT) formula. However, the assumption of isotropy is certainly inadequate for noncubic site symmetry: it would predict $\mathbf{D}=0$, thus M_2 independent of $\mathbf{p}$, in striking contrast with the experiment. Fortunately, the generalization of the KT formula for a μ^+ site with uniaxial symmetry is still manageably simple.^{44,45} In this “uniaxial-Gaussian” approximation $M_2(\vartheta)$, as well as $P(t, \vartheta)$, vary with the polar angle ϑ of $\mathbf{p}$ relative to the crystal c axis, and contain as parameters $\Delta_1^2 = \overline{B_{f,x}^2}$ and $\epsilon = (\overline{B_{f,x}^2}/\overline{B_{f,z}^2}) - 1$ characterizing the magnitude and anisotropy of $B_{f,i}$. One has

$$M_2(\vartheta; \epsilon) = \Delta_1^2 \gamma_\mu^2 \left(\frac{\epsilon+2}{\epsilon+1} + \frac{\epsilon}{\epsilon+1} \cos^2 \vartheta \right), \quad (16)$$

and the function $P(t) = P^{(\text{ua})}(t)$ is well approximated by⁴⁴

$$P_{\text{KT}}^{(\text{ua})}(t, \vartheta) = P_a + (1 - a \gamma_\mu^2 \Delta_1^2 t^2) e^{-b \gamma_\mu^2 \Delta_1^2 t^2 \sin^2 \vartheta} + (1 - c_0 - c \gamma_\mu^2 \Delta_1^2 t^2) e^{-d \gamma_\mu^2 \Delta_1^2 t^2} \left(\frac{3}{2} \cos^2 \vartheta - \frac{1}{2} \right), \quad (17)$$

where the constants a, b, c, d depend only on ϵ ,

$$a = \frac{\sqrt{(\epsilon^2 + 4\epsilon + 3)}/3}{(\epsilon + 1)}, \quad b = \frac{2\epsilon + 3}{2(\epsilon + 1)} - a,$$

$$c = \sqrt{1 - (1 - c_0) \frac{4\epsilon + 5}{6(\epsilon + 1)}}, \quad \text{and} \quad d = (1 - c)/(1 - c_0),$$

$$\text{with } c_0(\epsilon) = 1 - \frac{\sqrt{1 + \epsilon}}{\epsilon} \left(\sqrt{1 + \epsilon} - \left\{ \frac{\sinh^{-1} \sqrt{\epsilon}}{\sqrt{\epsilon}} - \frac{\arcsin \sqrt{-\epsilon}}{\sqrt{-\epsilon}} \right\} \right),$$

for $\epsilon > 0$ or $\epsilon < 0$, and P_a , the large-time asymptotics of $P^{(\text{ua})}$, is $P_a = \frac{1}{2} \sin^2 \vartheta + (\frac{3}{2} \cos^2 \vartheta - \frac{1}{2}) c_0(\epsilon)$. For $\epsilon = 0$ the isotropic KT formula, with the unique parameter $\Delta_{\text{iso}} = \Delta_1$, is recovered:

$$P_{\text{KT}}(t) = \frac{1}{3} + \frac{2}{3} (1 - \gamma_\mu^2 \Delta_{\text{iso}}^2 t^2) e^{-(1/2) \gamma_\mu^2 \Delta_{\text{iso}}^2 t^2}. \quad (18)$$

C. On the electric-field gradient

The muon is a charged particle, the neighboring nuclei experience its spatially varying electric field. To deduce all the EFG parameters from the data, by application of the above formulas for weak or intermediate fields, is usually impossible: the number of the $F_{ik}^{(j)}$ components is normally too large (five quantities for each inequivalent atomic neighbor).

To simplify, one makes the physically plausible approximation that $F^{(j)}$ stems from an effective radial potential originating at the μ^+ , $F_{ik}^{(j)} \approx -(\partial^2 / \partial x_i \partial x_k) [\alpha^{(r)} f(r)]$, with a given normalized function f and a single “charge” parameter $\alpha^{(r)}$. (Due to the fast, $\sim r^{-6}$ decay of the muon-nucleus dipolar interaction, only nearest neighbors contribute to M_2 and the form of f is not crucial.) In addition, at the nuclear positions in a uniaxial lattice, the EFG is inherently nonzero, even without a perturbing μ^+ . It seems realistic to assume $F_{ik}^{(j)} = F_{ik}^{(j,\mu)} + F_{ik}^{(c)}$, where the radial term $F_{ik}^{(j,\mu)}$ is due to the μ^+ , while the “crystal” term $F_{ik}^{(c)}$ is oriented according to the site symmetry of the nuclei. Thus the quadrupolar term in the Hamiltonian Eq. (3) with $h\nu_Q^{(j)}$ is the sum of two interactions, both axially symmetric but along *two different axes* and with different frequencies $\nu_{Q,r}^{(j)}$ and $\nu_Q^{(c)}$, resulting in a nonzero asymmetry parameter $\eta^{(j)}$ in the frame where $F_{ik}^{(j)}$ is diagonal. For Sc a crystal component $\nu_Q^{(c)} = 24.0$ kHz has been measured by NMR (Ref. 46) in the pure crystal.

At fast tunneling, the “source” of $F^{(j,\mu)}$ is spatially extended. In this case, a reasonable approximation for F is to calculate the electrostatic perturbation at the nuclei as one due to a μ^+ located at the symmetry center $\mathbf{R}_G$ of the μ^+ -wave function.

IV. EXPERIMENT

The single-crystal samples of scandium were supplied by the Ames Laboratory Materials Preparation Center at Iowa State University, USA. Various samples were used: a block of approximately $28 \times 12 \times 10$ mm³ and three different

plates of ~ 3 mm thickness, later cut to form “blocks” of approximately $38 \times 9 \times 9$ mm³. The c axis was always oriented normal to the plate or the largest block faces. In the experiment the crystal orientation was changed by rotation around the long symmetry axis of the sample, i.e., an axis perpendicular to the crystal c axis.

One crystal was kept pure while the others were loaded at various stages during the experiments with hydrogen or deuterium to different compositions ScH_x, $x = 0.05, 0.10, 0.25$, and ScD_{0.10}. The hydrogen loading was accomplished by absorption from the gas phase using a calibrated volume to titrate the desired concentrations. After loading at 700 K the crystals were annealed for several hours at 800 K before cooling to room temperature.

The μ SR measurements were performed at the Ring Cyclotron of the Paul Scherrer Institute (PSI), Villigen, Switzerland. Several instruments were used on two muon-beam lines: “GPS” (line π M3, surface muons) and “GPD” (μ E1, decay muons) of the PSI- μ SR Facility, and our own modified “Strobo” set-up (μ E1, decay muons), operated in the classical time-differential mode. In the GPS we made use of the “veto-mode,” rejecting to a large extent the contributions from μ^+ not stopped in the Sc-samples, minimizing thereby the background signal from the sample environment. The samples were kept at the chosen temperature in He-flow cryostats or in closed-cycle He refrigerators, through exchange gas or contact with a cold finger, depending on the spectrometer used and the data-taking period. The T range extended from 300 K down to normally 10 K, a few times down to 2 K. In general the temperature was set and stabilized to better than 5% and ± 2 K.

The μ SR histograms accumulated in the different runs—with one to five positron telescopes in various positions, depending on the spectrometer and operation mode—were analyzed by using the formulas given in Sec. III.

V. μ^+ LOCALIZATION AT LOW TEMPERATURE

The transverse-field μ SR measurements show that, for all samples, the μ^+ probes a static environment below $T = 30$ K: the polarization decay in the observed time window is Gaussian [$P(t) \propto \exp(-\sigma^2 t^2/2)$], and the rate σ is anisotropic. The $\sigma(\Theta)$ patterns change their character as function of $|\mathbf{B}_{\text{ext}}|$, in accordance with Eqs. (10), (11), and (12): in high field σ varies approximately as $\cos(4\Theta)$, whereas in low field as $-\cos(2\Theta)$.⁴⁷ In Fig. 3 we show the low- T Gaussian relaxation rate measured as function of Θ in four samples in high and low field, respectively. For each sample $\sigma(\Theta)$ changes gradually when the TF is varied from the high to the low-field limit,^{48,49} limits that are found to correspond to ≈ 300 mT and ≈ 3 mT, respectively. The low-temperature patterns were followed down to 10 K for most samples and fields, in several cases even down to 2 K, but no significant changes with temperature were detected below 30 K.

The analysis of σ as function of $B = |\mathbf{B}_{\text{ext}}|$ for fixed Θ requires special care. For a given experimental set-up, the applied field, depending on its strength, may modify noticeably the time-independent background and the asymmetry of the μ SR signal, biasing to some extent the $\sigma(B)$ variation. To correct for such unwanted effects and to obtain the true $\sigma(B)$ behavior various consistency checks were made,

FIG. 3. Relaxation rate σ measured as function of the angle Θ between $\mathbf{B}_{\text{ext}}$ and the crystal c axis for high (a–d) and low (e–h) transverse field in Sc, α -ScH_{0.10}, α -ScH_{0.25}, and α -ScD_{0.10} at $T \leq 30$ K. The models (see text) give the two sets of three lines for high and low field, respectively.

mainly comparing results for different sample orientations; additional runs with calibration samples have also been used.

A. High TF measurements in pure Sc—the localized μ^+ T - T -tunneling state

The μ SR relaxation rates, measured by varying the applied field B , saturate for $B > 300$ mT. This indicates that M_2 , originating from the nuclear magnetic moments, has reached the van Vleck limit, independent of B .

Starting with an undistorted crystal lattice, the calculations of $\sigma(\Theta)$ by using Eq. (6), assuming various interstitial positions for the muon,⁴⁹ are summarized in Fig. 2. For the muon at an O site, the incompatibility with the data is obvious. The calculation for the ideal centered position in the T site ($z_0 \approx 0.12c$, z_0 defined as the distance along the c axis between the μ^+ and the “base” of the enclosing tetrahedron), labeled “ T -center,” approaches roughly the measured $\sigma(\Theta)$ pattern. An improvement is obtained with the μ^+ displaced towards the ab base of the occupied tetrahedron ($z_0 = 0.05c$, “ T -offset”). The data can be perfectly reproduced when fast tunnelling between the two adjacent- T sites⁷ is assumed: a calculation for the “ T - T -tunnelling” site with $z_0/c = \pm 0.09$ describes very well the measured $\sigma(\Theta)$ pattern. This state, represented in Fig. 1 by $T1$ – $T2$ is also required for a satisfactory description of the low-field results—see Sec. V C. The separation between the adjacent μ^+ tetrahedral sites determined for the *ensemble* of μ SR data, amounts to $2z_0 = 0.18c = 0.95 \text{ \AA}$,⁴⁹ which is remarkably near to the value $2z_0 = 0.194c$ found for the D position in α -ScD_{0.33} by neutron diffraction measurements.⁵

B. The trapped μ^+ -Sc-H state

Examining the high-field $\sigma(\Theta)$ -data for the α -phase samples [Fig. 3(b–d)], one notices a weak but increasing deviation from the T - T -tunneling model line (dash-dot-dot-dot) as the H or D content x increases. Assuming the muon enters into a pairing process with a H atom, similar to the H-H pairing of the α^* -phase, and finds itself in a μ^+ -Sc-H configuration along the c axis [represented by $T3$ – $T4$ in Fig. 1(a)], $\sigma(\Theta)$ is easy to calculate. The result differs very little from $\sigma(\Theta)$ for a static muon alone at a T site in a pure Sc-lattice, the effect of the paired H-atom being small.

Concentrating on the α -ScH_{0.25} sample [Fig. 3(c)], one sees that the data lay roughly between the calculations for the T - T tunneling and the static μ^+ at a centered T site (recall Fig. 2). A better bracketing of the data is realized if the centered static T site is replaced by a shifted T site with $z_0 = 0.09c$, a z_0 -value as for the T - T -tunneling state. Finally, one obtains a perfect fit with the simultaneous population of both the T - T tunneling state and the shifted T site with nearly equal weights ($w_{T-T \text{ tunnel}}/w_{\mu^+-\text{Sc-H}} = 1.0 \pm 0.1$ for $x = 0.25$), Fig. 3(c). [In Figs. 3(a) and 3(d) the three model calculations are displayed: line dash-dot-dot-dot for T - T tunneling in all graphs, dotted line for the shifted μ^+ -Sc-H state, in (c), and dashed line for the r.m.s. average of these two dependences, in (b)–(d).]

So far no lattice distortion around the μ^+ has been considered. We have found that the data cannot be explained by a mere expansion of the lattice. A lattice expansion of 1–2 % modifies, however, the calculated optimal value of z_0 by $\Delta z_0/z_0 \approx 5$ –10 %, while the overall good description of the

FIG. 4. Pure Sc at low temperature: field dependence of the measured TF $\sigma(\Theta=0^\circ)$ ($\times$), $\sigma(\Theta=45^\circ)$ ($\circ$), and $\sigma(\Theta=90^\circ)$ ($\triangle$). The lines represent a μ^+ -tunneling calculation with $z_0 = \pm 0.475$ Å, $\alpha^{(r)} = 2.4$, $\nu_Q^{(c)} = 9$ kHz; the splitting illustrates the effect of a distribution of the azimuthal orientation angle Φ (see text).

data is preserved. A complicating factor is that the lattice expansion around the muon is certainly anisotropic, with only uniaxial symmetry along the c axis. [Furthermore, the possibility that a small fraction of the muons paired with H undergoes T - T tunnelling, as postulated for H in α -YH_x (Refs. 28 and 36), cannot be totally ruled out.] However, the consistency of the analysis—see also the following sections—and the agreement found with the neutron data support the z_0 value determined by neglect of lattice distortion.

C. Low-TF measurements—electric-field gradients

When lowering, in the TF measurement, the field below the van Vleck limit, the electric quadrupolar coupling of the Sc nuclei becomes manifest [Eq. (4)]. Section III C describes the simplifications needed to calculate $\sigma(\Theta, B)$ —or $M_2(\Theta, B)$ —allowing comparison with the experiment, and the rationale behind it. The frequencies $\nu_{Q,r}^{(j)}$ and $\nu_Q^{(c)}$ are unknown parameters of the analysis. The various frequencies $\nu_{Q,r}^{(j)}$ depend on the “effective-charge” parameter $\alpha^{(r)}$ and the position vectors $\mathbf{r}_{j\mu}$, whereas the frequency $\nu_Q^{(c)}$ is independent of the muon position. For the given axial symmetry the *two* parameters $\alpha^{(r)}$ and $\nu_Q^{(c)}$ characterize the quadrupolar interaction. The value of $\alpha^{(r)}$ is difficult to estimate *a priori*, due to the antishielding via the electronic shell; the antishielding factor for Sc may be in the wide range of 10–50.³⁹

To interpret the data in pure Sc, Fig. 3(e), we assumed T - T tunneling with the μ^+ at $z_0 = \pm 0.09c = \pm 0.475$ Å and searched for the optimal combination of $\alpha^{(r)}$ and $\nu_Q^{(c)}$. A very good agreement was obtained with $\alpha^{(r)} = 2.4$, $\nu_Q^{(c)} = 9$ kHz (line dash-dot-dot-dot).

The low-field $\sigma(\Theta)$ data for the α -phase samples, Figs. 3(f)–3(h), show a flattening of the orientation dependence when x increases. Assuming, as for the high-field case, a growing fraction of the muons trapped in the μ^+ -Sc-H state, equal to the fraction of “free-tunneling” muons for α -ScH_{0.25} (i.e., the $\approx 1:1$ “mixed” state for $x = 0.25$), one can try to reproduce the data by varying the parameters $\alpha^{(r)}$ and $\nu_Q^{(c)}$ for the *trapped* state. Taking for $\alpha^{(r)}$ the same value as for the tunneling state, an excellent fit was obtained when $\nu_Q^{(c)}(\text{trap}) = 63$ kHz was chosen [dashed line in Fig. 3(g)]. Interestingly, the $\sigma(\Theta)$ dependence for the trapped state

FIG. 5. The coefficients $c_2(B)$ (circles) and $c_4(B)$ (triangles) of the $P_2(\cos \Theta)$ and $P_4(\cos \Theta)$ terms, respectively, in the development of $M_2(B, \Theta)$ obtained from TF data in Sc (a), α -ScH_{0.10} (b), and α -ScH_{0.25} (c) at low temperature. Model calculations are shown for T - T tunneling (line dash-dot-dot-dot), the “mixed” state (dashed line), and for the μ^+ -Sc-H trap (dotted line). The splitting illustrates the distribution of the Φ values (see text).

(dotted line) has the opposite asymmetry compared to the function calculated for the pure tunneling state (line dash-dot-dot-dot). As for the high-field dependences, the data of the intermediate H or D concentrations are bracketed by the calculations for the “mixed” state (dashed line) and the pure tunneling state, see Figs. 3(f) and 3(h).

Complementary information is obtained from the field dependence of σ , measured at different angles Θ . Figure 4 shows the raw $\sigma(B)$ data in pure Sc for $\Theta = 0^\circ$, 45° , and 90° , compared to the results of a μ^+ -tunneling calculation assuming the “standard” values $z_0 = \pm 0.475$ Å, $\alpha^{(r)} = 2.4$, $\nu_Q^{(c)} = 9$ kHz. This approach implies, however, additional complications. First, in intermediate fields the calculated $\sigma(B, \Theta)$ -values are also functions of the azimuthal orientation angle Φ of the crystal, with a periodicity of 60° (Φ was

FIG. 6. Pure Sc, ZF measurements at low T . The points show $\sqrt{M_2(\vartheta)}/2$ obtained from the measurements for each crystal orientation ϑ with respect to the μ^+ polarization. The solid line is the calculated $\sqrt{M_2(\vartheta; \Delta_1, \epsilon)}/2$ obtained by Eq. (16), with Δ_1 and ϵ determined from a global analysis with the uniaxial KT formula (all runs).

not specified in the experiment). This effect is illustrated by the splitting of the calculated lines assuming a variety of Φ values; it is particularly noticeable for $\Theta = 90^\circ$. Next, due to the difficulties mentioned at the beginning of Sec. V, $\sigma(B)$ is affected by several disturbing instrumental effects, which have to be corrected. We found that this could be largely simplified by developing the measured $\sigma^2(\Theta)$ functions in terms c_0 , c_2 , and c_4 of the Legendre polynomials P_0 , $P_2(\cos \Theta)$, and $P_4(\cos \Theta)$ [like the three first terms of Eq. (11)]: it appeared that mainly the c_0 term was affected by the experimental imperfections, and that it was adequate to use only the $c_2(B)$ and $c_4(B)$ coefficients to compare measurements and calculations.

Figure 5 shows the $c_2(B)$ and $c_4(B)$ data for Sc, α -ScH_{0.10}, and α -ScH_{0.25} compared to model results. The calculations are performed with $z_0 = 0.475$ Å, $\alpha^{(r)} = 2.4$, $\nu_Q^{(c)}(\text{tunnel}) = 9$ kHz, and $\nu_Q^{(c)}(\text{trap}) = 63$ kHz, as in Figs. 3 and 4, for T - T tunneling (line dash-dot-dot-dot), the 1:1 mixed state (dashed line), and for the μ^+ -Sc-H trap (dotted line). Because of the problems involved, the uncertainties in data and calculations are unavoidable and this comparison gives only a general indication. Nevertheless, the c_2 and c_4 data are close to the calculated tunneling state (line dash-dot-dot-dot) for pure Sc, and close to the calculated mixed state (dashed line) for α -ScH_{0.25}. The intermediate concentration data (α -ScH_{0.10}) are, as expected, bracketed by these two calculations. The fits are less satisfactory with other parameter values.

D. ZF measurements—“uniaxial” Kubo-Toyabe formula

At low temperature ZF measurements have been performed in pure Sc, α -ScH_{0.10}, α -ScH_{0.25}, and α -ScD_{0.10} as a function of ϑ . Special care was applied to obtain a precise knowledge of the *experimental* initial signal asymmetry A_0 , to determine its possible ϑ dependence (e.g., due to a small variable background contribution), and to estimate the effect of related imprecisions on the signal-fit results. This was achieved, among others, by extrapolating the orientation dependence of low-TF A_0 measurements to $B \rightarrow 0$.

First, the experimental value of $M_2(\vartheta)$ was determined by fitting $\Delta_{\text{iso}}(\vartheta) \gamma_\mu = \sqrt{M_2(\vartheta)}/2$ to the data for each orientation ϑ , using Eq. (18) (points in Fig. 6). For the analysis, however, we used the uniaxial-Gaussian approximation⁴⁴ summarized in Sec. III B. In this procedure the forward- and

backward-decay histograms of the ensemble of the runs obtained in one α -ScH(D) _{x} sample at different orientations ϑ are submitted to a combined fit with Eq. (17), using, as described above, the initial asymmetry values obtained by extrapolation. This yields the two *global* parameters, Δ_1 and ϵ , for each sample measured at low T . As an example, Fig. 7 shows the asymmetry signal in the pure Sc crystal (displayed is only the corrected forward-decay histogram for 8 orientations). The solid lines are results of the simultaneous fit of the whole Sc-data set. For the obtained parameters $\Delta_1 \gamma_\mu = 0.396(2) \mu\text{s}^{-1}$ and $\epsilon = 0.80(4)$, the measured orientation dependence of $\sqrt{M_2(\vartheta)}/2$ is shown as a solid line in Fig. 6.

This is the first data analysis with the generalized “approximate” uniaxial Kubo-Toyabe formula.⁴⁴ Figure 7 shows how the “dip” of the KT curve varies and even crosses the zero line, and how the level corresponding to the “1/3-repolarization” tail of the isotropic formula is modulated as a function of the orientation ϑ in a crystal with uniaxial symmetry.

The parameters Δ_1 and ϵ obtained in Sc, α -ScH_{0.10}, α -ScH_{0.25}, and α -ScD_{0.10} at low T are presented in Fig. 8 as a function of the H(D)-content x . Δ_1 decreases approximately linearly, by 8% for x varying from 0 to 0.25. This is more than expected from the average lattice expansion due to a random-H distribution in the crystal, which amounts to $\Delta c/c < \Delta a/a \leq 0.7\%$ for the present concentration variation.² The decrease of ϵ is very pronounced—the calculation shows that such a decrease can be caused by an increase of the “crystal term” relative to the “radial term” in the EFG tensor (Sec. III C). This variation of the EFG tensors at the nuclear sites is consistent with the μ^+ -Sc-H bonds aligned along the c axis, thus increasing the maximal EFG at the Sc atoms. The strong decrease of the ZF second-moment anisotropy with increasing x is quite similar to the variation of the low-field M_2 anisotropy [Figs. 3(e–g)]. This is not surprising since in both cases the EFG plays the major role. In contrast, the concentration dependence of the M_2 anisotropy measured at high field [Figs. 3(a–c)] is weak: in the van Vleck limit the EFG interaction is negligible.

Equation (14) allows the exact calculation of $M_2 = M_2(\vartheta; z_0)$ and, by comparison to Eq. (16), it provides the parameters Δ_1 and ϵ as functions of the μ^+ position for the approximate uniaxial Kubo-Toyabe formula Eq. (17). This has been done for the case of pure Sc for the T - T -tunnelling muon with z_0 as free parameter, assuming the “standard” EFG parameters from the TF fits. One calculates $0.41 \mu\text{s}^{-1}$ for $\Delta_1 \gamma_\mu$, practically independent of z_0 , a value close to $0.397(2) \mu\text{s}^{-1}$ obtained from the ZF data. The ϵ parameter shows a strong variation with z_0 , see Fig. 9; comparing the calculated function with the measured value, one infers almost the same z_0 position as $z_0 = 0.09c = 0.475$ Å obtained from the TF data. This is a strong evidence for the consistency of the analysis for high-, low-, and zero-field data, and shows also that the values for the EFG parameters in the presence of the muon are realistic.

VI. μ^+ DIFFUSION AND TRAPPING

The temperature dependence of the muon depolarization was measured in pure Sc, in α -ScH _{x} for $x = 0.05, 0.10$, and 0.25 , as well as in α -ScD_{0.10}. For these scans various TF

FIG. 7. ZF μ^+ spin relaxation signals from low- T measurements in pure Sc (only forward-decay spectrum and 8 crystal orientations ϑ displayed). A simultaneous fit of all the data (both spectra and 11 orientations) with the uniaxial Kubo-Toyabe formula gives the solid lines. The dotted lines indicate $1/3$ of the initial signal asymmetry.

FIG. 8. Relaxation $\Delta_1\gamma_\mu$ and asymmetry ϵ of the ZF uniaxial Kubo-Toyabe formula determined in Sc and α -ScH(D)_x at low temperature, displayed as functions of x . The symbols ($\triangle$ for $\Delta_1\gamma_\mu$ and $\circ$ for ϵ) are filled for the deuterated sample.

FIG. 9. Parameter ϵ for the uniaxial Kubo-Toyabe approximation, as a function of z_0 , calculated by Eqs. (14) and (16) for pure Sc (solid line). The measured ϵ value (ZF data) and z_0 deduced from TF data are also indicated.

FIG. 10. Measured polarization-decay rates $\Lambda(T)$ for Sc (a), α -ScH_{0.05} (b), α -ScH_{0.10} (c), α -ScH_{0.25} (d), and for α -ScD_{0.10} (f), high-TF data. Solid lines from fits of the two-state model to the data (see Table I). Graph (e) shows the nonexponentiality index $\beta(T)$ for α -ScH_{0.05} obtained from a stretched exponential fit to the μ SR spectra, associated to $\Lambda(T)$ of graph (b).

and ZF conditions combined with different orientations of the single crystals in the external field or with respect to the initial muon polarization direction were chosen. Part of the measurements were repeated using different experimental set-ups both to achieve optimal conditions for the specific requirements and to perform consistency checks or determine corrections where needed. A few T -scan data were previously published,⁵⁰ but their interpretation, in terms of the Abragam-formula (see Eq. 2), was preliminary. ZF measurements were also performed as a function of T , however not as many as TF measurements. Compared to the latter, ZF measurements necessitated longer runs and additional tests to yield unbiased results (see explanation beginning of Sec. V D). Since the preliminary analysis of the ZF data shows a similar behavior for the parameters of the dynamics as the TF results, only the analysis of the TF data will be presented here.

A. The damping data $\Lambda(T)$

All μ SR T -scans show the same basic features, even if varying significantly with the H(D)-concentration in the samples. A representative set of depolarization data for Sc, three α -ScH _{x} samples, and α -ScD_{0.10} is displayed in Fig. 10; the selection corresponds to TF measurements with $\Theta=0^\circ$ in high field. Without making any assumption on its temperature dependence, the muon depolarization can be represented by the damping parameter Λ , obtained from the experimental spectra and defined as the inverse time for decay of the polarization $P_x(t)$ to 1/e of its initial value:

$$P_x(t=\Lambda^{-1})/P_x(t=0)=e^{-1}. \quad (19)$$

The exact form of the depolarization function is unknown, but a phenomenological description of the data is possible by a stretched exponential function:

$$P_x(t)=P_x(t=0)\exp[-(\Delta t)^\beta]. \quad (20)$$

For this functional form, Δ is precisely the above defined damping parameter Λ .

As an example, Fig. 10(e) shows the temperature dependence of β obtained in α -ScH_{0.05}. For all samples, at low temperature, say for $T<30$ K, the parameter β stays at the maximum value of 2.0: the damping is Gaussian, indicating the absence of long-range motion of the μ^+ . On the ‘‘high’’-temperature side of the studied range, when $\Delta<0.04\ \mu\text{s}^{-1}$, the relaxation is exponential and β levels at 1.0.

For α -ScH _{x} in the temperature range studied, i.e., below ~ 300 K, the dynamics of the proton diffusion is too slow to be noticed during τ_μ .² Therefore, features reflecting dynamics in the data must relate to that of the μ^+ . For the intermediate H-concentrations ($x=0.05$ and 0.10) $\Lambda(T)$ shows a characteristic shoulder between 75 and 110 K. [In this same T -domain the β -parameter of the stretched exponential fit deviates from its basically decreasing trend as the temperature increases and indicates an enhanced static character around 100 K—see Fig. 10(e).] These μ^+ polarization damping curves $\Lambda(T)$ resemble the ones observed for muon diffusion in niobium in the presence of traps, studied by Borghini and co-authors.⁵¹ We propose below a ‘‘two-state model,’’ analogous to the one used to interpret the Nb data and discussed by Kehr, Honig, and Richter,⁵² well suited to the μ^+ in α -ScH _{x} .

B. The two-state model

In the case of diffusion in a homogeneous crystal (pure Sc), the average muon polarization in TF geometry, $G_x(t)$, has the particular form of Eq. (2).³⁹ The function $G_x(t)$ is Gaussian for $t\ll\tau_c$, with $M_2=\sigma_F^2$, the second moment of

TABLE I. Fields and fit parameters characterizing the temperature dependence of the μ SR depolarization $\Lambda(T)$ in 5 samples (high transverse-field measurements with $\Theta=0^\circ$). A two-state model is used to describe the data—see text.

Sample	Field (mT)	$G_1(0)$	$\sigma_f/\sqrt{2}$ (μs^{-1})	Γ_c (μs^{-1})	$E_c=E_1$ (meV)	Γ_1 (μs^{-1})	$\sigma_t/\sqrt{2}$ (μs^{-1})	Γ_0 (μs^{-1})	E_0 (meV)	τ_c/τ_1
Sc ^a	503	1.0	0.252	200	33.2	0				0.0
α -ScH _{0.05}	600	0.975	0.252	190	32.7	14	0.262	220	62.9	0.07
α -ScH _{0.10}	510	0.915	0.268	170	32.3	19	0.279	170	59.5	0.11
α -ScH _{0.25}	503	0.5	0.255	80	31.0	18	0.265	33	49.1	0.22
α -ScD _{0.10}	520	0.915	0.258	140	32.3	19	0.268	120	57.7	0.14

^aFor the pure crystal $\Gamma_1=0$, and the trapped-state parameters σ_t , Γ_0 , and E_0 are absent.

the Gaussian frequency distribution, characterizing the randomness of the static internal fields to which the muon (now in a localized T - T -tunneling state) is exposed. τ_c is the average time during which correlation between the “observed” frequencies exists: τ_c is approximately the mean residence time τ of the muon at different interstitial (tunneling) sites.

However, for the diffusion of μ^+ in a crystal with distributed traps (H atoms in the α -phase of scandium, where the muon may be trapped in the μ^+ -Sc-H configuration discussed in Sec. V B), a model describing repeated capture and release is needed. The muon diffusing in the undisturbed lattice is captured by a trap, on the average after a time τ_1 , and a muon in a trap escapes after an average time τ_0 . The muons in a state of free diffusion or in a trap have different polarization decays. Following a reasoning similar to the one in Ref. 51, one assumes the depolarization in the free state, $G_1(t)$, to obey a generalized law [such that at the limit $\tau_1 \rightarrow \infty$ one has again Eq. (2)]. The polarization decay of the trapped state is governed by a similar expression, $G_0(t)$, where σ_f^2 is replaced by σ_t^2 , corresponding to the field distribution over the traps, and τ_c is replaced by τ_t , the correlation time for the muon in a trap. Thus, the time variation of the two polarizations is governed, in a good approximation, by the coupled equations^{51,52}

$$\begin{aligned} \frac{dG_1(t)}{dt} &= \sigma_f^2 \tau_c [e^{-t/\tau_c} - 1] G_1(t) - \frac{1}{\tau_1} G_1(t) + \frac{1}{\tau_0} G_0(t), \\ \frac{dG_0(t)}{dt} &= \sigma_t^2 \tau_t [e^{-t/\tau_t} - 1] G_0(t) - \frac{1}{\tau_0} G_0(t) + \frac{1}{\tau_1} G_1(t), \end{aligned} \quad (21)$$

and the observed polarization is

$$G_\Sigma(t) = G_1(t) + G_0(t). \quad (22)$$

For the correlation time in a trap, τ_t , one has $\tau_t \leq \tau_0$, where τ_0 is the lifetime of the trapping state. Neglecting dynamics for the traps, we make the simplest assumption $\tau_t = \tau_0$.

Various situations can be considered for the initial conditions $G_1(t=0)$ and $G_0(t=0)$, keeping in mind that the sum corresponds, of course, to the full initial polarization: $G_\Sigma(0) = G_1(0) + G_0(0) = 1$. In case of a pure (trap free) crystal and for low trap concentration the assumption $G_1(0) = 1$, as in Ref. 51, is justified. For higher trap concentration, $G_1(0)$ can be *estimated* in the following way. In α -ScH_{0.25} a fraction of 0.25/2 of the interstitial T sites is occupied by a H atom (there are two interstitial T sites per atom in the hcp lattice). Thus, assuming random distribution

of the hydrogen and a random thermalization location for the implanted muon, $\sim 0.25/1.75$ of the muons appear in the μ^+ -Sc-H-trap state at $t=0$. In *reality* this fraction may be either smaller, if e.g., an appreciable fraction of the hydrogen is itself locked in the H-Sc-H state (which is known to happen), or larger, if the last thermalization steps of the muon are directed preferentially towards a trap.

Equations (21) were solved using a Runge-Kutta procedure, with different initial conditions $G_1(0)$. From the resulting polarization $G_\Sigma(t)$ the damping parameter Λ was calculated for comparison with the experiment.

In applying Eqs. (21)–(22) to the experimental data, Arrhenius relations

$$\tau_i^{-1} = \Gamma_i \exp[-E_i/(k_B T)] \quad (23)$$

have been assumed for the times τ_c , τ_1 , and τ_0 . E_1 is taken equal to E_c since the trapping process is supposed to be diffusion controlled.

For the different samples and high-field measurements with $\Theta=0^\circ$, the $G_1(t=0)$ parameter and the values obtained for σ_f , Γ_c , E_c , Γ_1 , σ_t , Γ_0 , and E_0 are presented in Table I. The best fit functions $\Lambda(T)$ are shown as solid lines in Fig. 10. To arrive at this result, the following procedure was used:

(i) The “free-state” σ_f of the model is given by Eqs. (20) and (2) [$\sigma_f/\sqrt{2} \approx \Lambda$ at the low- T plateau of $\Lambda(T)$]. The difference between *experimental* “trapped-state” σ_t and σ_f is taken as the difference of the two *theoretical* dependences $\sigma_t(\Theta)$ and $\sigma_f(\Theta)$, as discussed in Sec. V B (the difference is small, which means that its calculation with limited relative precision is sufficient). Basically, σ_f , the two activation energies, and the three pre-exponential factors are determined by adjustment of the calculated $\Lambda(T)$ -function to the data. The seven “free” parameters $G_1(0)$, σ_f , Γ_c , E_c , Γ_1 , Γ_0 , and E_0 are, of course, too numerous to fit the T -dependence of Λ for just one sample without additional constraints — different parameter combinations lead to equally good fits.

(ii) *Considering all four α -ScH_x samples* (with $x=0$, 0.05, 0.10, and 0.25), we searched for further information yielding a consistent overall picture. The results of a large number of “quasifree” fits, covering more or less evenly a wide portion of the parameter space, indicate at first the necessity of an initial free-state population $G_1(t=0, x)$ decreasing more than linearly with increasing x , starting evidently at 1.0 for $x=0$. Assuming⁵¹ that x had no effect on the μ^+ behavior in *intrinsic* “free” and trapped states, i.e., that the

FIG. 11. $H(D)$ -concentration dependence for the parameters of the two-state model describing the $\Lambda(T)$ data. Solid lines: best relations for $G_1(t=0)$, (a), and for $E_c=E_1$ and E_0 , (b). Best fit results for Γ_1 , (c), and for Γ_c and Γ_0 , (d). Filled symbols for the deuterated sample.

parameter sets (Γ_c, E_c) , and (Γ_0, E_0) , representing local properties of the muon jump process, are independent of x , and that *only* Γ_1 can be a function of the H-content, no good overall fit could be achieved. We allowed instead a smooth variations for $E_c(x)$ and $E_0(x)$, without further constraints or limiting relations for the remaining parameters.

(iii) The fit results of a thorough parameter-space scan showed, as best solution, the three x -dependences represented by the solid lines in Figs. 11(a) and 11(b). One sees, (1) an approximately constant $E_c(x)=E_1(x)$, (2) a moderately varying $E_0(x)$, and (3) a decreasing $G_1(t=0, x)$ implying enhanced population of the trap site at $t=0$, with $G_1(t=0, x=0.25)=0.5 \pm 0.1$. The related results for the other parameters are displayed in Figs. 11(c) and 11(d), and for each sample the resulting $\Lambda(T)$ function is shown by a solid line in Fig. 10. For α -ScD_{0.10} a best fit is obtained with parameters close to the ones for α -ScH_{0.10}, see also Table I.

C. Discussion of the μ^+ -diffusion results

From inspection of the results of the two-state model one sees the following:

(a) The parameter $G_1(t=0)$, which is temperature independent in the model, follows a H-concentration dependence of the form $1 - Ax^2$ implying, as briefly discussed, enhanced thermalization of the μ^+ into the μ^+ -Sc-H configuration. The value of A is such as to give a 1:1 initial populations of free and trapped states in α -ScH_{0.25}, as deduced from the low-temperature $\sigma(\Theta)$ measurements.

(b) Although the values for σ_f (and consequently σ_t) slightly scatter (reflecting the varying experimental conditions), they are fully consistent with the $\sigma(\Theta)$ dependences determined at low temperature—see Sec. V.

(c) The factors Γ_c and Γ_0 decrease with increasing x , indicating the development of a “blocking effect” at higher H concentrations. From a simple consideration of the correlation between the attempt jump frequency to an adjacent site, $\Gamma_i \propto \tau_i^{-1}$, and the probability bx that such a site is occupied, one expects $\Gamma_i \propto (1 - bx)$; variations proportional to $-x$ are indeed observed. The apparently stronger decrease of Γ_0 (escape from the trap) compared to Γ_c (escape from the free-tunneling state) may be a consequence of the increased H ordering in the α^* phase.

(d) The factor Γ_1 grows from 0 to $19 \mu s^{-1}$ for x increasing from 0.0 to 0.10, but, at higher H concentrations, the sole data point (at $x=0.25$) indicates a leveling of Γ_1 . Thus, the probability of μ^+ capture by a trap rises with the trap concentration only for $x \leq 0.10$.

(e) The ratio $\Gamma_1/\Gamma_c = \tau_c/\tau_1$, also shown in Table I, can be simply interpreted. After each diffusion jump (occurring in negligibly short time $\tau \ll \tau_c$), a μ^+ ends either in a free-tunneling state or in a trap (where it resides for average times τ_c or τ_0 , respectively, before its next long-range step). Assuming the μ^+ makes “Markovian” jumps (with no memory of its state before the jump), the ratio of the muon probability to end in a trap to the probability to arrive at a free state is just τ_c/τ_1 . The inverse of this ratio, τ_1/τ_c , is the average number of free diffusion steps before trapping.

(f) The activation energies $E_c=E_1 \approx 32$ meV and $E_0 \approx 49$ –63 meV are much smaller than the 500–600 meV observed for the long-range H (or D) diffusion in α -ScH(D) _{x} —Sec. II. The energy E_0 (escape from the H trap) has values close to the pair-binding energies E_b , obtained, e.g., from resistivity measurements (50 meV for α -ScH _{x} and 57 meV for α -ScD _{x} , Ref. 53) from neutron scattering (20 and 82 meV for ScH_{0.16},²¹) as well as to the

FIG. 12. Temperature dependence of various hopping or correlation rates for H, D, and μ^+ in α -ScH(D)_x (Arrhenius plot). The H/D motions are ranked in three mechanism, (I) long-range diffusion jumps, (II) tunneling in *asymmetric* T - T potential, (III) tunneling in *symmetric* T - T potential. For each domain the most usual experimental techniques and the isotopes involved are indicated. The observed μ^+ diffusion is described by the inverse of the three correlation times τ_c , τ_1 , and τ_0 of a two-state model. (For details and references see text.)

energy of fast localized motion observed below room temperature with NMR (broad binding energy distribution around 50 meV, Ref. 26—however, this interpretation of the data is questioned, Ref. 27). The difference between E_c and E_0 decreases with increasing x values. This could follow from a weakening of the trap-state potential well with increasing H concentration, due to average lattice expansion.

D. Comparison of H, D, and μ^+ dynamics

To illustrate the various channels of H, D, and μ^+ dynamics in α -ScH(D)_x systems, the behavior of H or D observed by different techniques is compared in the Arrhenius plot, Fig. 12, to the μ^+ -diffusion rates τ_c^{-1} , τ_1^{-1} , and τ_0^{-1} , deduced from μ SR measurements via the two-state model. (For better legibility only a fraction of the data is reported, the results for other H/D concentrations are hardly distinguishable from the presented selection.)

For H and D one encounters the three basic channels mentioned in Sec. II:

(I). Long-range diffusion jumps—the relatively slow motion for which in the figure practically all the data merge into a single Arrhenius line [e.g., the NMR measurements⁵⁴ (a) in α -ScH_{0.06} and (b) in α -ScH_{0.27}, the internal friction measurements⁵⁵ (c) in α -ScH_{0.1} and (d) α -ScD_{0.2}]. Interestingly, these values coincide also with a perfect Arrhenius line, (e), extending over 10 orders of magnitude, compilation of results from various techniques⁵⁶ for the α -YH(D)_x system.

(II). Tunneling in *asymmetric* T - T potential—the relatively fast rate, here represented by the relaxation “bands” calculated with a two-level-tunneling system model according to Leisure and co-authors³⁰ for their ultrasonic spectroscopy

(US) measurements in α -ScH_{0.25} and α -ScD_{0.18}. One sees a striking isotope effect for $T > 20$ K. An essentially identical motion is also observed by NMR, as discussed by Svare, Torgeson, and Borsa.²⁷

(III). Tunneling in *symmetric* T - T potential—the very fast motion, only observed by QNS, for which the measurements in ScH_{0.16}, Ref. 7, are displayed.

The low rate channel associated with O-impurity traps is not represented here.

From μ SR the μ^+ rates are (A) for τ_c^{-1} in Sc, (B) in α -ScH_{0.25}, (C) in α -ScD_{0.10}; (E) for τ_1^{-1} in α -ScH_{0.25}, (D) in α -ScD_{0.10}; (F) for τ_0^{-1} in α -ScH_{0.25}, (G) in α -ScD_{0.10}.

The observed μ^+ motion is long-range diffusion, to be compared with mechanism (I) of H or D. In the temperature range of the muon study ($T < 300$ K), the μ^+ -jump rates are, however, far higher than the H/D T -O- T -jump rates, whereas the μ^+ activation energies are about 10 times smaller than the practically identical H and D activation energies. Clearly, two different mechanism are involved. On one hand, the long-range H/D diffusion in hcp metals, due to the relatively high temperature at which the measurements are feasible, is not expected to show marked quantum effects, and the behavior is nearly classical.³⁷ On the other hand, for μ^+ in the α -ScH(D)_x systems, one has rather to follow theories like those of Flynn and Stoneham,⁵⁷ and Kagan and Klinger,⁵⁸ which take into account self-trapping or polaron effects due to relaxation of the lattice around the diffusing particle. Arrhenius-like T dependences are predicted, but the activation energies have different meaning in comparison to the classical rate theories. It would be interesting to follow the muon diffusion in pure Sc to higher temperature, where the extrapolated μ^+ -Arrhenius line crosses the H/D line (at about 400 K). There one would expect the muons to show steeper mobility increase to obey the H/D-diffusion mechanism. Unfortunately, such high μ^+ -jump rates are off-range for conventional μ SR measurements.

Likewise the “fast-tunneling” rate of the μ^+ in the free T - T state cannot be determined in our study. It is expected to be at least as high as the H-rate of mechanism (II), possibly as high as the rate observed for mechanism (III).

VII. CONCLUSIONS

(1) *Free μ^+ state—tunneling.* We have found that in pure scandium the free μ^+ occupies a localized fast-tunneling state extending over two adjacent interstitial- T sites. The average muon position is obtained consistently from high-, low-, and zero-field μ SR measurements. The tunneling rate is higher than the μ SR-window limit ($> 10^8$ s⁻¹), but no precise experimental value is available.

(2) *μ^+ states in the α -ScH(D)_x phase.* We have established the coexistence of the free- μ^+ -tunneling state and a static-trapped state associated with H, most likely the μ^+ -Sc-H state similar to the H-H pairing of the α^* -phase. The population of the trapped state increases approximately with the square of the hydrogen concentration in α -ScH_x.

(3) *Intrinsic and muon-induced EFG.* The electric-field gradients, of muonic as well as intrinsic-crystalline origin, acting on the μ^+ neighboring nuclei, influence the μ SR re-

laxation at low and zero magnetic fields. A consistent interpretation of the pure-Sc and the α -ScH_x data with only three EFG parameters, introduced in Sec. III C, can be achieved, assuming the values $\alpha^{(r)}=2.4$, $\nu_Q^{(c)}(\text{tunnel})=9$ kHz, and $\nu_Q^{(c)}(\text{trap})=63$ kHz.

(4) *Trapping of μ^+ . Enhanced trapping* of the μ^+ by hydrogen at thermalization is strongly indicated at low temperature (below 30 K) by the variation of the high-TF $\sigma(\Theta)$ -data as the H-content increases (Sec. V B). It is also indicated by the low-TF measurements (Sec. V C), and, for the entire temperature range up to 300 K, by the data very well explained by the two-state model for muon diffusion. At all temperatures a tendency for *enhanced trapping* of the muon during diffusion is also observed.

(5) *μ^+ diffusion.* A two-state model is used to describe the diffusion data, consisting of free muon jumps and repeated μ^+ -capture and release processes, with three characteristic correlation times, which follow Arrhenius laws. The difference in the long-range diffusion mechanisms of μ^+ compared to H or D is evident; for the muon the polaron effects are dominant.

(6) *μ^+ in α -ScH_x vs μ^+ in α -ScD_x.* Comparison of the μ SR data obtained in ScH_x and ScD_x hosts, i.e., for the

α -ScH_{0.10} and α -ScD_{0.10} samples, show practically no differences. This is the case for $\sigma(\Theta)$ measured in high and low fields (Fig. 3) and for the ZF relaxation data at low temperature (Fig. 8). A small difference appears in the polarization-decay rate $\Lambda(T)$, reflecting small variations of the Γ_c and Γ_0 parameters of the two-state model [Fig. 11(d)]. In the context of the present α -ScH(D)_x study the muon is not sensitive to H-isotope effects.

(7) *α^* -ordering temperatures.* The temperatures at which the H-H or D-D pairs condense into zigzagging chains in the α^* phases, 152.5(5) K for ScH_x and 160.5(5) K for ScD_x, were determined from subtle changes in resistivity measurements⁵³ and called “anomaly temperatures” in that context. No evident discontinuities are apparent around these temperatures in the present μ SR measurements.

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¹For a comprehensive treatment of the method, see, e.g., A. Schenck, *Muon Spin Rotation Spectroscopy* (Hilger, Bristol, 1985).

²For a general review, see, e.g., P. Vajda, *Hydrogen in Rare-Earth Metals, Including RH_{2+x}*, Handbook on the Physics and Chemistry of Rare Earths Vol. 20, edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier, New York, 1995), p. 207.

³See also L. Schlappbach, I. S. Anderson, and J. P. Burger, *Materials Science & Technology*, edited by K. H. J. Buschow (VCH, Weinheim, 1994), Vol. 3B, Chap. 12, pp. 271–331, and references therein.

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