

Tunneling and spin-lattice relaxation of hydrogen dissolved in scandium metal

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Some published NMR spin-lattice relaxation data for H in ScH_x metal solid solutions below 100 K [Lichty *et al.*, Phys. Rev. B **39**, 2012 (1989)] have been reinterpreted in terms of local tunneling motion in two-well potentials rather than classical over-the-barrier hopping. The asymmetry A between the wells strongly influences the electron- and phonon-induced tunneling transition rates and also the intensity of the relaxation in the two-level system. The fit to the data uses distributions of A that broaden with increasing concentrations of H. For the local motion of H in Sc, we find the barrier $V_0/k_B \approx 3200$ K, the ground-state tunnel splitting $\Delta E_{T0}/k_B \approx 0.37$ K, and coupling constants to electrons and phonons that have the same orders of magnitude as those for H in Nb.

I. INTRODUCTION

Barnes and co-workers^{1,2} have recently reported measurements of hydrogen spin-lattice relaxation times T_1 in very pure scandium-hydrogen solid solutions ScH_x with $x=0.57$, 0.11, and 0.27 at several NMR frequencies ω_0 and at temperatures T from 6 to 625 K. After the Korringa relaxation, $T_{1e}T=123$ s K, induced by the conduction electron spins has been subtracted, two relaxation rate maxima due to hydrogen motion stand out. (i) A large maximum centered near 520 K can be ascribed¹ to classical over-the-barrier hopping of H between well-separated interstitial sites in the hcp Sc lattice, whereby this motion gives the long-range diffusion. (ii) A second, much weaker maximum T_{1L}^{-1} near 60 K can be ascribed² to local H motion between two closely spaced sites that are arranged in pairs along the c axis.

The experimental data by Lichty *et al.*,² partly reproduced in Fig. 1, show that the relaxation maximum near 60 K displays a behavior as a function of ω_0 and T which cannot be fitted by a Bloembergen, Purcell, and Pound (BPP)-type formula² $T_{1L}^{-1} \propto \tau / (1 + \omega_0^2 \tau^2)$ with a single correlation time $\tau = \tau_0 \exp(E_a/k_B T)$ for classical hopping over a fixed barrier E_a . Furthermore, one has to account for the fact that the relaxation-rate maximum near 60 K is anomalously small.

Lichty *et al.* fitted the 60-K relaxation peak by assuming wide distributions of small activation energies E_a for the local motion, and with asymmetries A between the potential wells in a site pair that would lead to depopulation of the upper well. However, classical barriers with $E_a/k_B < 1000$ K are hard to reconcile with the greater H oscillation energy from recent inelastic-neutron-scattering experiments.³

In this paper we present an alternative interpretation of the NMR results based on a detailed model for the

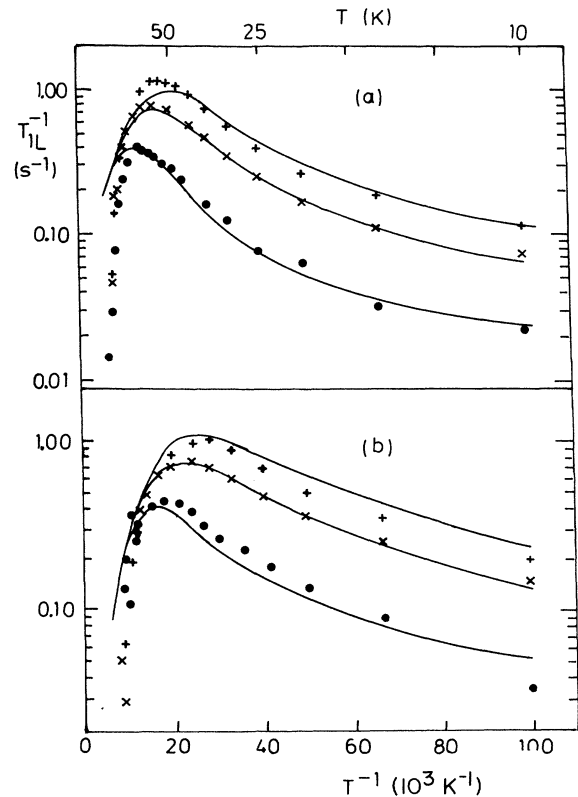


FIG. 1. Spin-lattice relaxation rates T_{1L}^{-1} of H in ScH_x where the Korringa contribution is subtracted. The symbols are T_{1L}^{-1} as measured by Lichty *et al.* (Ref. 2) at $\omega_H/2\pi=24$ MHz (+), 40 MHz (x), and 90 MHz (●) for the concentrations $x=0.27$ (a), and $x=0.11$ (b). The lines are the calculated fits from the parameters listed in Tables I and II, as described in the text.

hopping and tunneling motions of H in Sc where we show the observed relaxation rates can be explained quantitatively and consistently with a reasonable choice of parameters. The present reinterpretation of the data is justified by the similarity between the low-temperature motion of H in a two-well potential in Sc, and the tunneling of H in the two-well potential near oxygen or nitrogen impurities in niobium, a problem which has been investigated successfully by inelastic neutron scattering⁴⁻⁶ and other⁷⁻¹⁰ methods.

The local motion of H in ScH_x appears to be an excellent model system for testing the theories of hydrogen tunneling, for which several very different approaches have been proposed in the literature even for the simplest two-well system. Some theories of tunneling motion that have been applied to H in Nb focus on self-trapping^{11,12} or strong-coupling¹³ effects. However, the most successful approach^{6,10} to this system appears to be the direct interactions with electrons that have been used for two-level tunneling systems^{14,15} in disordered metallic glasses. For H in Sc we will use the two-level approach where the transitions are made possible by the tunneling overlap of the symmetrized wave functions and where the asymmetry A between the wells can be very important for the calculated rates. We will also include the related two-phonon transition rates, which seem to explain¹⁶ the ordinary diffusion of H in Nb, V, and Ta above 100 K.

II. STRUCTURE OF SCANDIUM WITH DISSOLVED HYDROGEN

Scandium has the hexagonal cell shown in Fig. 2(a) with dimensions $a = 3.31 \text{ \AA}$ and $c = 5.27 \text{ \AA}$. The dissolved hydrogen is believed to occupy tetrahedral (T) interstitial sites that are arranged in pairs along the c axes. Some pairs of T sites A - B , C - D , and E - F in the a - c crystal plane are shown in Fig. 2(b). The distance \overline{AB} between the sites in a pair is only about $c/4 = 1.32 \text{ \AA}$, and the short-range repulsion between the hydrogens therefore means that an A - B pair of sites is very unlikely to contain two H. One H in the A - B site pair is expected to hop or tunnel rapidly between the A and B positions in a localized motion.

The distance \overline{BE} to the nearest T site in another pair is 2.34 \AA . The hopping or tunneling between sites in different pairs is therefore expected to be hindered by a higher barrier than the motion within a pair. Hence such motion will be much slower than the local motion, but transitions to other pair sites are necessary for the long-range H diffusion. It has been suggested that the diffusion of H in the similar yttrium metal occurs by hops via metastable octahedral (O) sites that have small probability for being populated. The shortest distance between the T and O sites in Sc is 2.02 \AA , and the diffusion path T - O - T may be easier for H than the direct T - T transitions.

There are forces between the hydrogens from the electronic clouds, from the shielded Coulomb interactions and from the lattice deformations, that give asymmetries A in the potentials between otherwise equivalent T wells. The asymmetries influence the populations of the wells, and as we will see, also the tunneling rates between the

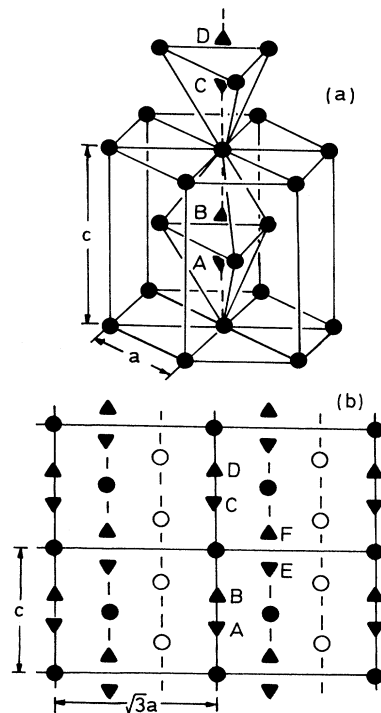


FIG. 2. (a) Hexagonal lattice of Sc (solid circles) showing the location of the tetrahedral interstitial sites for H (solid triangles). Sites A and B (and also C and D , etc.) form a closely spaced pair separated by about $0.25c$, but the ordering of H below 160 K is assumed to be on pairs of sites like B and C . (b) Cross section in the bc plane of the lattice showing both the stable tetrahedral (solid triangles) and the metastable octahedral (open circles) sites for H.

two wells in a close pair. Hence A is a very important parameter in our theory, and there will be a distribution $Z(A)$ of A values between the wells in a given sample.

Blaschko *et al.*¹⁷ have shown with neutron diffraction that the deuterons in ScD_x tend to order in pairs of type B - C in the c direction across the Sc atoms at T between 200 and 150 K. A similar ordering also occurs¹⁸⁻²¹ in the solutions LuD_x and YD_x . The ordering below 170 K of the hydrogens in ScH_x in pairs like B - C in Fig. 2(b) implies an asymmetry A_1/k_B of more than 200 K between the closely spaced sites A and B . This A_1 is large enough to depopulate site A and effectively stop the local hydrogen A - B motion below 100 K. However, the ordering of the H in pairs across the Sc is not complete and a small fraction of the H remains unpaired, as shown by the NMR relaxation at low temperatures.

Neutron diffraction indicates less order between hydrogens on neighboring c axes despite the shorter distance from the sites B to E than to C shown in Fig. 2(b), so the contribution A_2 to the asymmetry between A and B caused by a H sitting on E or equivalent sites, must be smaller than 150 K. The various interactions between all hydrogens contribute to the total asymmetry A in a pair of sites, and we will try to fit the NMR relaxation for H in Sc below $T = 160 \text{ K}$ with a T -independent multi-Gaussian distribution of A values around maxima at $\pm A_1$ and $\pm A_2$

$$Z(A) = (1/A_0)(2\pi)^{-1/2} \{ (1-P)\exp[-(A-A_2)^2/2A_0^2] + (1-P)\exp[-(A+A_2)^2/2A_0^2] \\ + P\exp[-(A-A_1)^2/2A_0^2] + P\exp[-(A+A_1)^2/2A_0^2] \}. \quad (1)$$

Here the majority fraction P of the hydrogens are ordered in pairs $B-C$ with average asymmetry A_1 , and the remaining unpaired fraction $(1-P)$ have values of A distributed around A_2 . We assume for simplicity that the distribution maxima for both the paired and the unpaired hydrogens have the same widths A_0 . This width is expected to increase with increasing H concentration. We have written the distribution with peaks at $\pm A_1$ and $\pm A_2$ so that it is reasonably shaped near $A=0$ and is normalized for positive values of A , $\int_0^\infty Z(A)dA=1$.

III. THEORY OF TUNNELING

We give here a simple but general model for the basic tunneling motions of hydrogen dissolved in metals, and we apply it to H in Sc. We use the same approach as has been used for two-level tunneling systems in disordered glassy structures, but we can be more specific and assume that the one-dimensional potentials between all well pairs have essentially the same sinusoidal shape and height V_0 . Since the distance d between the wells and the mass m of the tunneling particle are known, this model gives quantitative numerical results for the H oscillation frequencies and the tunnel splittings from only one adjustable parameter, V_0 . The numbers and the resulting effects can then be checked for consistency much better than in glasses where the microscopic nature of the two-level systems is poorly known. Other theories of tunneling will be considered only very briefly at the end of Sec. VI.

A. Tunneling eigenstates

We adapt¹⁶ the formulas obtained by Das²² for a tunneling particle in a sinusoidal periodic potential, to the double well shown in Fig. 3. The oscillation energies of the H in one of the wells are $E_n = a_n - a_0$ where

$$a_n \simeq (V_0/k^2) \{ (2n+1)k - [n^2 + (n+1)^2]/4 + \dots \}, \quad (2)$$

with $k = (d/\pi\hbar)(2mV_0)^{1/2}$. The tunnel splittings of the oscillation states are

$$\Delta E_{Tn} \simeq 8V_0 \frac{2^{3n} k^{(n-1/2)} e^{-2k}}{\pi^{1/2} n!} (1 + b_n/k + c_n/k^2). \quad (3)$$

If the energy E_1 of the first excited state is known from inelastic neutron scattering or otherwise, then V_0 is determined from (2), and ΔE_{Tn} can be calculated from (3). We use the bare mass m of the hydrogen isotopes in (2) and (3), which seems to give correct results¹⁶ for H, D, and T in Nb, Ta, and V. Thus, the effects of self-trapping and of the lattice polaron are included in the effective potential V_0 . The coefficients b_n and c_n in (3) are small²² for the lowest states. The approximation (3) breaks down for

the higher states near the top of the barrier. Furthermore, the assumption of a one-dimensional potential introduces uncertainties in the calculations of effects that involve the excited states.

The asymmetry A between the potentials in the two wells will partly localize the H and its associated polaron to the left (L) or right (R) well in symmetrized ground eigenstates Ψ_{S0} and Ψ_{A0} that are split in energy by $\Delta E_0 = [\Delta E_{T0}^2 + A^2]^{1/2}$ with Ψ_{S0} lowest. We have

$$\Psi_{S0} = [(\Delta E_0 + A)/2\Delta E_0]^{1/2} \Psi_{R0} \\ + [(\Delta E_0 - A)/2\Delta E_0]^{1/2} \Psi_{L0} \quad (4a)$$

and

$$\Psi_{A0} = [(\Delta E_0 + A)/2\Delta E_0]^{1/2} \Psi_{L0} \\ - [(\Delta E_0 - A)/2\Delta E_0]^{1/2} \Psi_{R0}. \quad (4b)$$

These eigenstates are shown schematically in Fig. 3. The excited eigenstates Ψ_{Sn} and Ψ_{An} are similarly partly localized and split by $\Delta E_n = [\Delta E_{Tn}^2 + A^2]^{1/2}$, as long as the asymmetry is not so large that Ψ_{Sn} and $\Psi_{A(n-1)}$ perturb each other significantly.

The asymmetry A is caused by the interactions with neighboring hydrogens and perhaps with other impurities and defects. It is not caused by the hydrogen self-trapping, because this energy is the same whether the particle is in the left or the right well. We assume that some asymmetry up to A of order $V_0/10$ will not change

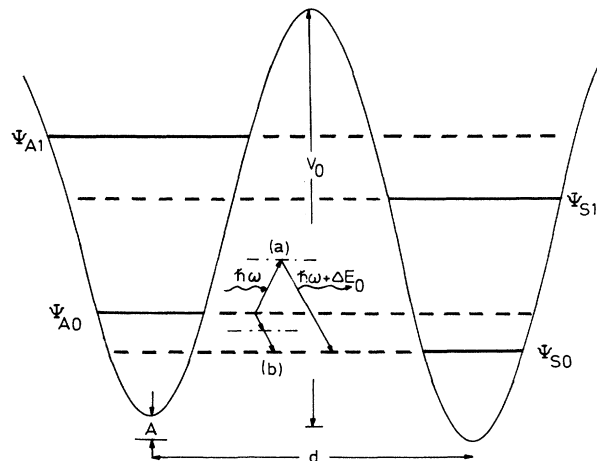


FIG. 3. Two-well potential with asymmetry A for H in Sc. The symmetrized eigenstates are shown with heavy lines where the H is likely to be in a state. Some two-phonon transitions via virtual states (dash-dot levels) are indicated for (a) one absorbed phonon with energy $\hbar\omega$, and one emitted phonon with $(\hbar\omega + \Delta E_0)$ and (b) two emitted phonons $\hbar\omega$ and $(\Delta E_0 - \hbar\omega)$.

significantly the well shape that gives E_n or the wave function overlaps that give ΔE_{Tn} . We also assume that the asymmetries over the well pairs will have the distribution form (1).

B. Direct tunneling transitions

Phonons and electrons will dynamically perturb the potential in Fig. 3, and thus induce transitions between Ψ_{S0} and Ψ_{A0} by taking up the energy difference ΔE_0 . The transitions shown schematically in Fig. 3 will clearly take the H from one well to the other when the wave functions are localized by $A > \Delta E_{T0}$. Motion between Ψ_{S0} and Ψ_{A0} is also possible via the excited states Ψ_{Sn} and Ψ_{An} . We will review the various transition processes that are made possible for H by the tunneling and that may contribute to the total transition rate between Ψ_{S0} and Ψ_{A0} , and how they are expected to vary with temperature T and asymmetry A .

The downward direct transition rate for a H in Ψ_{A0} going to Ψ_{S0} , caused by the free conduction electrons in a normal metal, is¹⁵

$$R_{e\downarrow} = \pi(K \Delta E_0 / \hbar) (\Delta E_{T0} / \Delta E_0)^2 / [1 - \exp(-\Delta E_0 / k_B T)], \quad (5)$$

where K is a dimensionless coupling factor that has to be fitted by experiments. The asymmetry reduces the overlap between Ψ_{S0} and Ψ_{A0} and is responsible for the reduction factor $(\Delta E_{T0} / \Delta E_0)^2$ in (5). The corresponding upward rate $R_{e\uparrow}$ for a H in Ψ_{S0} going to Ψ_{A0} is slower than $R_{e\downarrow}$ by the Boltzmann factor $\exp(-\Delta E_0 / k_B T)$. The rate (5) and its modification for superconducting metals have been used¹⁵ for two-level tunneling systems in metallic glasses, and for H in the two-well potential near O and N impurities in Nb where $K \approx 0.06$.^{6,10}

The downward rate for direct one-phonon transitions caused by a Debye spectrum of phonons has been used for two-level tunneling systems in insulating glasses¹⁵

$$R_{1p\downarrow} \approx F_{1p} \Delta E_{T0}^2 \Delta E_0 / [1 - \exp(-\Delta E_0 / k_B T)]. \quad (6)$$

The coefficient $F_{1p} = (H_{00R} - H_{00L})^2 (2v_t^{-5} + v_l^{-5}) / 8\pi\rho\hbar^4$ depends upon the coupling $(H_{00R} - H_{00L})^2$ to the phonons, the density ρ of the metal, and a proper average over the transverse and longitudinal velocities of sound v_t and v_l , but it is independent of T and A . The matrix elements of the phonon deformation potential of the ground states in the right or left well are formally

$$\begin{aligned} H_{00R,L} &= \langle \Psi_{0R,L} | \mathcal{H}_C | \Psi_{0R,L} \rangle \\ &= \int \Psi_{0R,L}^*(\mathbf{r}) \mathcal{H}_C(\mathbf{r}) \Psi_{0R,L}(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (7)$$

They are caused by the phonon modulations of the wells, while the modulation of the barrier and thus the tunnel splitting ΔE_{T0} , will have a smaller effect. Note that the

dynamic deformations of the potential by the phonons must be different in the two wells in order to give finite F_{1p} and R_{1p} , and a similar difference in perturbations is needed for a finite coupling K to the electrons in (5).

The density of phonon modes in the Debye model is proportional to ω^2 up to the maximum frequency ω_D . This ω dependence counteracts the smaller overlap for larger values of A which implies larger transition energies, so the one-phonon rate (6) is nearly independent of A up to $k_B T$. The electron rate R_e may therefore dominate in the total rate at small values of A , while R_{1p} may be faster for large A . The Debye approximation in (6) is probably good for $\hbar\omega / k_B < 150$ K in Sc,²³ but it fails toward ω_D .

C. Two-phonon and multiphonon transitions

Above 20 K the two-phonon tunneling transitions will contribute to the total rate. Two-phonon mechanisms have been treated theoretically in electron²⁴ and nuclear²⁵ spin-lattice relaxation, but they have seldom²⁶ been discussed in the context of two-level tunneling systems, despite their importance there. Two-phonon processes will usually have a T^7 dependence for low temperatures, which decreases to a T^2 dependence for temperatures above θ_D . But transitions with a T^5 dependence are also possible²⁷ when there is a matrix element connecting Ψ_{S0} and Ψ_{A0} , and this is also the condition for the one-phonon processes.

The two-phonon transitions where one phonon i is absorbed and a phonon j of higher energy is emitted, is shown as the case (a) in Fig. 3, and this rate is

$$R_{2p(a)\downarrow} \approx [(2v_t^{-5} + v_l^{-5})^2 / 8\pi^3\rho^2] \int M_a^2 D_a d\omega. \quad (8)$$

Here the second-order matrix element connecting the states Ψ_{S0} and Ψ_{A0} is

$$\begin{aligned} M_a &= \frac{\langle \Psi_{S0} | \mathcal{H}_C^i | \Psi_{A0} \rangle \langle \Psi_{A0} | \mathcal{H}_C^i | \Psi_{S0} \rangle}{\hbar\omega} \\ &+ \frac{\langle \Psi_{S0} | \mathcal{H}_C^i | \Psi_{S0} \rangle \langle \Psi_{S0} | \mathcal{H}_C^i | \Psi_{A0} \rangle}{\hbar\omega + \Delta E_0} \\ &+ \frac{\langle \Psi_{S0} | \mathcal{H}_C^i | \Psi_{A1} \rangle \langle \Psi_{A1} | \mathcal{H}_C^i | \Psi_{A0} \rangle}{E_1 - \hbar\omega - \Delta E_0 / 2 + \Delta E_1 / 2} \\ &+ \frac{\langle \Psi_{S0} | \mathcal{H}_C^i | \Psi_{S1} \rangle \langle \Psi_{S1} | \mathcal{H}_C^i | \Psi_{A0} \rangle}{E_1 - \hbar\omega - \Delta E_0 / 2 - \Delta E_1 / 2}. \end{aligned} \quad (9)$$

It can be formally written out in terms of $H_{00R,L}$ from (7), or in terms of

$$\begin{aligned} H_{01R,L} &= \langle \Psi_{0R,L} | \mathcal{H}_C | \Psi_{1R,L} \rangle \\ &= \int \Psi_{0R,L}^*(\mathbf{r}) \mathcal{H}_C(\mathbf{r}) \Psi_{1R,L}(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (10)$$

for virtual excitations to E_1 . The Debye densities of phonon states, the deformations by the phonons and their thermal probabilities, are contained in the factor

$$D_a = \frac{(\omega + \Delta E_0 / \hbar)^3 \omega^3}{[1 - \exp\{-(\hbar\omega + \Delta E_0) / k_B T\}][\exp(\hbar\omega / k_B T) - 1]} \quad (11)$$

The T^7 two-phonon rate is the result when the terms with $E_1 \gg \hbar\omega$ as the intermediate states dominate in (9). This process have some terms¹⁶ proportional to $(\Delta E_{T_1} / \Delta E_1)^2$ that decrease with increasing A . But for larger values of A we find the rates

$$R_{2p(7a)\downarrow} \simeq F_{2p(7)} \Delta E_{T_1}^2 \int_0^{\omega_D - \Delta E_0 / \hbar} (E_1 - \Delta E_0 / 2 - \hbar\omega)^{-4} D_a d\omega \rightarrow \alpha T^7 \text{ for small } \Delta E_0 < k_B T \text{ and } T \rightarrow 0. \quad (12)$$

Here $F_{2p(7)} = H_{01L}^2 H_{01R}^2 (2v_t^{-5} + v_l^{-5})^2 / 32\pi^3 \rho^2$ is a proper average over all phonons, and $R_{2p(7a)\downarrow}$ vanishes for $\Delta E_0 > \hbar\omega_D$. The integral can be calculated numerically with $F_{2p(7)}$ as a coefficient to be determined by the fitting to experimental data. The variation of $R_{2p(7a)\downarrow}$ with A is small. The averaging involved in the integral makes the results rather insensitive to the details of the phonon spectrum, but the effect of the dispersion is uncertain.

Two phonons may be emitted as in the case (b) in Fig. 3. This requires the factor

$$D_b = \frac{(\Delta E_0 / \hbar - \omega)^3 \omega^3}{[1 - \exp\{-(\Delta E_0 - \hbar\omega) / k_B T\}][1 - \exp(-\hbar\omega / k_B T)]} \quad (13)$$

and a matrix element M_b where the signs of all $\hbar\omega$ in (9) have been changed. The resulting rates are

$$R_{2p(7b)\downarrow} \simeq F_{2p(7)} \Delta E_{T_1}^2 \int_0^{E_0 / \hbar} (E_1 - \Delta E_0 / 2 + \hbar\omega)^{-4} D_b d\omega \text{ for } \Delta E_0 < \hbar\omega_D \quad (14)$$

and

$$R_{2p(7c)\downarrow} \simeq F_{2p(7)} \Delta E_{T_1}^2 \int_{\Delta E_0 / \hbar - \omega}^{\omega_D} (E_1 - \Delta E_0 / 2 + \hbar\omega)^{-4} D_b d\omega \text{ for } \hbar\omega_D < \Delta E_0 < 2\hbar\omega_D. \quad (15)$$

The terms in (9) with Ψ_{S_0} and Ψ_{A_0} as the intermediate states may dominate for small A . We then find the rates²⁸

$$R_{2p(5a)\downarrow} \simeq F_{2p(5)} (\Delta E_{T_0} / \Delta E_0)^2 \int_0^{\omega_D - \Delta E_0 / \hbar} [1 / \omega + 1 / (\omega + \Delta E_0 / \hbar)]^2 D_a d\omega \rightarrow \alpha t^5 \text{ for small } \Delta E_0 < k_B T \text{ and as } T \rightarrow 0, \quad (16)$$

with

$$F_{2p(5)} \simeq (H_{00R} + H_{00L})^2 (H_{00L} - H_{00R})^2 \times (2v_t^{-5} + v_l^{-5})^2 / 128\pi^3 \rho^2 \hbar^2.$$

This rate decreases rapidly with A because of the overlap factor $(\Delta E_{T_0} / \Delta E_0)^2$. The analog rates $R_{2p(5b)\downarrow}$ and $R_{2p(5c)\downarrow}$ with two phonons emitted, appears to be unimportant for H in Sc compared to $R_{2p(7b)\downarrow}$ and $R_{2p(7c)\downarrow}$.

Above 150 K we also expect tunneling transitions via electron or multiphonon excitations to the states E_n . The simple formula²⁶

$$R_{E_n}^* \simeq (\Delta E_{T_n} / \hbar) \exp(-E_n / k_B T) \quad (17)$$

for tunneling interference in E_n seems¹⁶ to fit the experiments in many cases when $\Delta E_{T_n} \gtrsim A$ is fulfilled. Asymmetry will reduce the interference and we write

$$R_{E_n\downarrow} \simeq (\Delta E_n / \hbar) (\Delta E_{T_n} / \Delta E_n)^2 \exp(-E_n / k_B T). \quad (18)$$

At high T or for wide barriers with small ΔE_{T_n} in the lower n states, the dominant terms from (18) reduce to the formula for classical hopping over the top of a barrier $E_a \simeq V_0 - E_1 / 2$, and this rate is little affected by large A .

We have listed some of the various transition rates that are made possible by the tunneling in a two-well system, and the total rates are

$$R_{\downarrow} = R_{e\downarrow} + R_{1p\downarrow} + R_{2p(5a)\downarrow} + R_{2p(7a)\downarrow} + R_{2p(7b)\downarrow} + R_{2p(7c)\downarrow} + R_{E1\downarrow} = R_{\uparrow} \exp(\Delta E_0 / k_B T).$$

The various terms will be dominant in the total rate in different ranges of T and A , and not all of them will be important for the low-temperature relaxation of H in Sc. We have neglected many-electron transitions and possible interference terms between electrons and phonons, and the neglect of dispersion makes the phonon rates uncertain for large A and T . We also note that the expressions for R_e and $R_{2p(5a)\downarrow}$ that involve only the ground states may not be valid^{29,30} for small A and large T if it leads to $R_{\downarrow} > \Delta E_0 / \hbar$, but this case is not relevant for the nuclear relaxation of H in Sc.

IV. SPIN-LATTICE RELAXATION IN A TUNNELING SYSTEM

The hydrogen atoms make random tunneling transitions between the wells, and they thus experience a fluctuating local dipolar field that will cause nuclear spin-lattice relaxation. Note that most tunneling transitions conserve the nuclear spin state, but the spins will flip in a small fraction of the transitions determined by the mixing effect of the dipolar field.²⁸ The problem can therefore be

treated in the weak-collision approach where we assume a correlation function in terms of the total transition rates R_{\downarrow} and R_{\uparrow} calculated in the previous section. The correlation function for the hopping motion of a particle between two asymmetric wells has been derived by Look and Lowe³¹ in the context of hindered molecular rotations, and by Blinc³² for the hydrogen-bond systems. It was found to be exponential with a correlation time $\tau = 2/(R_{\downarrow} + R_{\uparrow})$ and with the intensity of the fluctuations proportional to $4a/(1+a)^2 = \cosh^{-2}(\Delta E_0/2k_B T)$ where $a = R_{\uparrow}/R_{\downarrow} = \exp(-\Delta E_0/k_B T)$.

For H in Sc, the dominant magnetic dipolar interaction for the relaxation is between H and Sc, while the H-H coupling is much smaller. This leads² to the spin-lattice relaxation rate for hydrogen making tunneling transitions between essentially localized states in a two-well potential with a particular asymmetry $A \gg \Delta E_{T0}$

$$T_1^{-1} \simeq \frac{C(i)/2}{\cosh^2(\Delta E_0/2k_B T)} \left[\frac{\tau}{1 + (\omega_H - \omega_{Sc})^2 \tau^2} + \frac{3\tau}{1 + \omega_H^2 \tau^2} + \frac{6\tau}{1 + (\omega_H + \omega_{Sc})^2 \tau^2} \right]. \quad (19)$$

The frequencies in (19) are $(\omega_H \pm \omega_{Sc}) = \omega_H(1.0 \pm 0.243)$ in terms of the measuring frequency ω_H . For smaller A and partly delocalized states we should probably reduce (19) by $(A/\Delta E_0)^2$, but this factor appears to be equal to 1 for almost all H in Sc. We also neglect the very small relaxation²⁸ $\propto (\Delta E_{T0}/\Delta E_0)^2$ caused by the coherent hydrogen tunneling oscillations with very high frequencies $\Delta E_0/\hbar \gg \omega_H$.

The coefficient $C(i)$ in (19) represents the mean-square fluctuating local field of the H-Sc dipolar interaction, and it can be written in terms of a contribution to the second moment of the resonance line. For an immobile H on a T site in Sc the total second moment has been calculated by Han *et al.*¹ to be $M_2(\text{rigid}) \simeq 12.2 \text{ Oe}^2$. Most of the $M_2(\text{rigid})$ is motionally averaged out only with the long-distance diffusion jumps that give the high-temperature relaxation. The fit to (19) of the relaxation maximum around 520 K required¹ a coefficient $C(\text{diff}) = \gamma_H^2 M_2(\text{diff})/2 \simeq 3.1 \times 10^9 \text{ s}^{-1}$ that corresponds to the component $M_2(\text{diff}) \simeq 8.8 \text{ Oe}^2$. Hence the dipolar field fluctuations from the local motion must correspond to the difference $M_2(\text{local}) \simeq 3.4 \text{ Oe}^2$ that give a coefficient $C(\text{local}) \simeq 1.2 \times 10^9 \text{ s}^{-1}$ in the expression (19) for the low-temperature relaxation T_{1L}^{-1} . Here $\gamma_H = 2.67 \times 10^4 \text{ s}^{-1}/\text{Oe}$ is the gyromagnetic ratio of protons.

The distribution of asymmetries (1) results in a distribution in the correlation times τ for the different protons and in a distribution in the intensity in the spectral density of fluctuations that each of them experience. These effects could result in a distribution of spin-lattice relaxation rates. However, the nuclear magnetization recovery was found² to be exponential at all temperatures and this

indicates that all protons are in dipolar contact and relax with a common spin temperature, as we expect from the relatively large H concentrations. Thus the measured spin-lattice relaxation rate is given by the average of (19) over positive values of A with the distribution $Z(A)$ from (1) where the contributions from the paired hydrogens automatically vanish at low temperatures because of the depopulation factor $\cosh^{-2}(\Delta E_0/2k_B T)$.

V. FIT OF THE RELAXATION DATA

We will first use the oscillation energies of H in Sc to estimate the barriers against the H motion. From inelastic scattering on ScH_x , Udovic *et al.*³ found $E_{1\parallel} = 101 \text{ meV}$ for oscillations parallel to the c axis and $E_{1\perp} = 148 \text{ meV}$ for motion perpendicular to the c axis. In the nearly perpendicular direction to the nearest O site or a T site in another pair of sites the oscillation frequency should therefore be of order $E_1/k_B \simeq 1500 \text{ K}$. From the relation (2) we then calculate the potential $V_0/k_B \simeq 14000 \text{ K}$ for $d = 2.34 \text{ \AA}$, corresponding to an activation temperature $E_a/k_B \simeq (V_0 - E_1/2)/k_B \simeq 13000 \text{ K}$ for classical hopping over the barrier to another T site, and a somewhat smaller $V_0/k_B \simeq 11000 \text{ K}$ for $D = 2.02 \text{ \AA}$, corresponding to $E_a/k_B \simeq 10000 \text{ K}$ for hopping over the barrier to an O site. Both of these calculated barriers are much higher than the activation temperature $E_a/k_B = 6300 \text{ K}$ measured by Han *et al.*¹ from the proton NMR relaxation maximum around 520 K in ScH_x . This means that the potential barriers against long-range diffusion must have narrower wells and flatter tops than a sine function. We note that (3) gives very small tunnel splittings of H in the lowest oscillation states through barriers of this magnitude, and transitions via the states near the top of the classical barrier is the only way for the H diffusion.

The barrier against the motion along the c axis to the other site in the pair $A-B$ is much thinner and lower, and the tunneling through it will be significant. With $d = 1.32 \text{ \AA}$ and $E_{1\parallel}/k_B = 1170 \text{ K}$ in (2) and (3) we calculate for the localized motion $V_0/k_B \simeq 3200 \text{ K}$, $E_2/k_B \simeq 2150 \text{ K}$, $\Delta E_{T0}/k_B \simeq 0.37 \text{ K}$, $\Delta E_{T1}/k_B \simeq 10 \text{ K}$, and $\Delta E_{T2}/k_B \simeq 90 \text{ K}$. These quantities have about the same magnitudes as have been found¹⁶ for tunneling H in Ta, and the tunnel splittings ΔE_{Tn} are slightly smaller than for H in Nb and V. The calculated second excited state for H in Sc is reasonably close to the measured³ $E_{2\parallel}/k_B \simeq 2090 \text{ K}$ and we conclude that the anharmonicity of the real potential is slightly greater than for the sine function. We also calculate from (2) that the energy at the top of the local barrier is $E_a/k_B \simeq 2560 \text{ K}$, but this number has little significance for the local motion if the H in ScH_x can tunnel faster through the barrier than by classical hopping over it.

We use the calculated tunnel splittings to evaluate the transition rates (5)–(18) for the local motion of H in Sc. The A and T dependencies of the rates are given, while the couplings to the electrons and the phonons and the distribution of asymmetries $Z(A)$ are unknown parameters that must be fitted with the relaxation data. The parameters obtained from T_{1L}^{-1} in Fig. 1 by using (19) and

TABLE I. Fitted parameters for the tunneling two-level system H in Sc. The oscillation energy is $E_1/k_B = 1170$ K and the tunnel splittings are $\Delta E_{T0}/k_B \approx 0.37$ K and $\Delta E_{T1}/k_B \approx 10$ K. The coupling K is to the electrons from (5), F_{1p} is the one-phonon coupling from (6), $F_{2p(5)}$ and $F_{2p(7)}$ are the two-phonon couplings from (16) and (12), and the deformation potentials are $H_{1p} = (H_{00R} - H_{00L})$, $H_{2p(5)} = (H_{00R} + H_{00L})(H_{00R} - H_{00L})$, and $H_{2p(7)} = H_{01R}H_{01L}$.

K	F_{1p} ($1/sJ^3$)	$F_{2p(5)}$ (s^4)	$F_{2p(7)}$ (s^6J^2)	H_{1p}/k_B (K)	$H_{2p(5)}/k_B$ (K)	$H_{2p(7)}/k_B$ (K)
0.06	3.8×10^{75}	5.0×10^{-54}	1.7×10^{-120}	3700	4100	6800

averaging over the distribution of asymmetries $Z(A)$ from (1), are given in Tables I and II. The fitted downward tunneling transition rates are shown in Fig. 4. In the integrals for the two-phonon rates we have used the Debye temperature $\theta_D = 280$ K, which is somewhat lower than the value 320 K obtained²³ from specific heat. The lower Debye temperature approximates better the slow transverse phonons with average $v_t \approx 2700$ m/s which dominate in the two-phonon rates.

It is interesting to see in Fig. 4 how the calculated rates from the various tunneling processes vary with A and T for the fitted parameters. Below $T = 20$ K the two-phonon contributions to the rates are negligible, and this makes the fitting of the direct processes easier. The electron-induced rates R_e are larger than the one-phonon rates R_{1p} for asymmetries up to $A/k_B \approx 50$ K. Above $T \approx 40$ K the two-phonon rates begin to dominate at medium asymmetries $50 < A/k_B < 150$ K, but the one-phonon rate is important up to $T = 150$ K for hydrogens with A close to the Debye energy, because the density of phonon states is very high there. The rate $R_{2p(5a)}$ is the largest of the two-phonon processes for $A/k_B < 30$ K, while $R_{2p(7a)}$ dominates for greater values of A/k_B up to 220 K where $R_{2p(7b)}$ and eventually $R_{2p(7c)}$ takes over. The contribution R_{E1} to the total rate from tunneling in E_1 is negligible below 160 K, tunneling in E_2 is negligible below 250 K, and the over-the-barrier hopping R_{Class} is negligible below 300 K.

The contributions to the spin-lattice relaxation from the H transitions depend upon how different the rate $\tau^{-1}(A)$ is from the measuring frequency ω_H , and upon the intensity factor $[\cosh^2(\Delta E_0/2k_B T)]^{-1}$ in (19). The ω_H is shown in Fig. 4 in order to indicate the efficiency of the total motion for the relaxation. The transition rates in Fig. 4 will give reasonable fits to the measured relaxation shown in Fig. 1. The frequency dependence of T_{1L}^{-1} below the maximum is less than ω_H^{-2} since the protons

that are moving rapidly because of small A , contribute less to the spin-lattice relaxation at increasing T . Most of the hydrogens must be locked in pairs with large A_1/k_B of order 800 K or more, because a tail below 500 K in the A/k_B distributions would contribute significantly to the NMR relaxation below $T = 160$ K. The fitted Gaussian distribution which refer to the unpaired hydrogen fraction $(1-P)$ is shown in Fig. 5. The shape of the high- A part of $Z(A)$ around A_1 referring to the majority fraction P of paired hydrogens is largely a guess since it cannot be determined from the low- T relaxation.

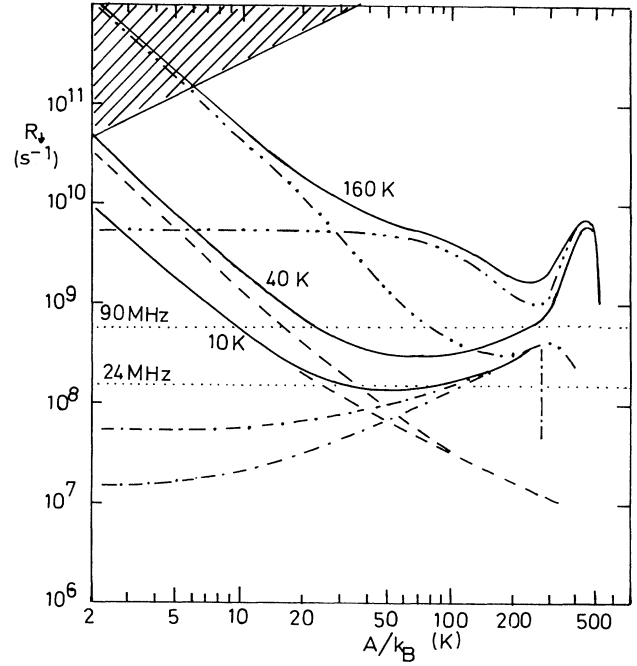


FIG. 4. Local tunneling transition rates of H in Sc calculated as function of asymmetry A as described in the text, using the tunnel splitting $\Delta E_{T0}/k_B = 0.37$ K and the coupling constants given in Table I. The solid lines are the total downward rates R_{\downarrow} at $T = 10, 40,$ and 160 K. The dashed lines are the electron contributions $R_{e\downarrow}$ and the dash-dotted lines are the one-phonon contributions $R_{1p\downarrow}$ at 10 and 40 K. The dash-dot-dot line is the two-phonon rate $R_{2p(5a)\downarrow} + R_{2p(5b)\downarrow} + R_{2p(5c)\downarrow}$ and the dash-dot-dot-dot line is the two-phonon rate $R_{2p(7a)\downarrow} + R_{2p(7b)\downarrow} + R_{2p(7c)\downarrow}$ at 160 K. The dotted lines show the rates corresponding to the range of measuring frequencies from 24 to 90 MHz. The hatched region for small A shows where the calculated rate may break down for $R_{\downarrow} > \Delta E_0/\hbar$.

TABLE II. Parameters for the fitted Gaussian distributions (1) of asymmetries A in the two samples of ScH_x . The paired fraction P of H has maximum for $A = A_1$, the unpaired fractions $(1-P)$ has maximum for $A = A_2$, and both maxima have widths A_0 .

x	$1-P$	A_1/k_B (K)	A_2/k_B (K)	A_0/k_B (K)
0.11	0.06	> 700	45	25
0.27	0.07	> 700	90	50

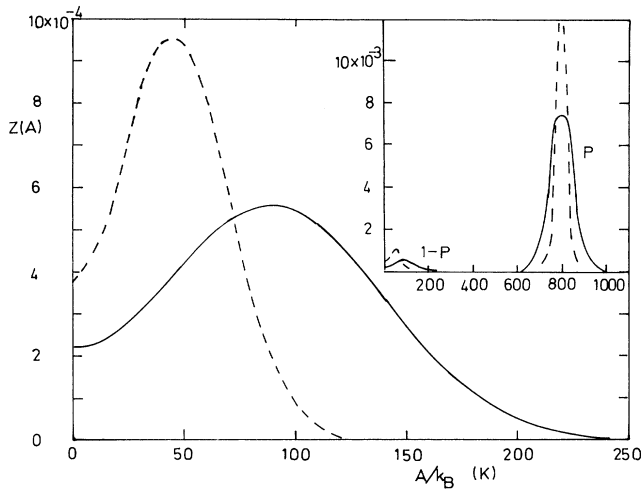


FIG. 5. Gaussian distributions of asymmetries $Z(A)$ from (1) fitted to the spin-lattice relaxation T_{1L}^{-1} of H in ScH_x . Solid line: fit to sample with $x=0.27$ using $A_2/k_B=90$ K, $A_0/k_B=50$ K, and $(1-P)=0.07$. Dashed line: fit to sample with $x=0.11$ using $A_2/k_B=45$ K, $A_0/k_B=25$ K, and $(1-P)=0.06$. The insert on the smaller scale shows the large fractions P of paired H with uncertain $A/k_B > 600$ K, where the H do not contribute to the relaxation below $T=160$ K.

The given fit is not unique, and several slightly different sets of coupling constants may give equally good fits to the relaxation data. We have used the same electron coupling coefficient $K=0.06$ or H in Sc as has been derived^{6,10} for H in Nb. The two-phonon transitions $R_{2p(7)}$ are necessary for the fit, while it would have been almost as good without the contributions R_{1p} and $R_{2p(5)}$. The numerical values of the derived deformation potentials of the phonons depend strongly upon the average over the velocities of sound in ScH_x . When we use $\rho=2990$ kg/m³ and $v_t \approx 2700$ m/s $\ll v_l$, we calculate the deformation potentials listed in Table I. The fit requires that the fraction P of paired hydrogens is about the same for the two samples, while the width A_0 of the distributions increases with increasing concentration of H, as expected.

The only part of the data in Fig. 1 that cannot be well fitted in this way is for $T > 120$ K where the calculated two-phonon processes without dispersion do not increase rapidly enough with T . However, we note that for this temperature range the data represent the vanishing difference between the measured relaxation and the assumed Korringa electron-induced relaxation, and the error bars on the experimental points are large here. A slightly smaller Korringa rate might have changed the experimental data to agree with our calculated rate also above 120 K.

VI. DISCUSSION AND CONCLUSIONS

We have reinterpreted the observed² proton spin-lattice relaxation rate below 120 K in the metallic solid solution ScH_x as caused by the local tunneling of the un-

paired hydrogen between the closely spaced sites. The fit of the data leads to a determination of tunneling parameters which appears quite reasonable, and it supports the two-level approach to describe tunneling of H in metals.

A sinusoidal barrier $V_0/k_B \approx 3200$ K between the wells was chosen for the fit, consistent with the measured first excited oscillation state E_1 of H in the single well. The estimated tunnel splitting $\Delta E_{T0}/k_B \approx 0.37$ K is slightly smaller than for H in TaH_x , and it could possibly be directly measured by specific heat or by inelastic neutron scattering.

One-phonon, two-phonon, and electron-induced processes are found to be important in determining the tunneling transition rates in the two-level system. Some of these processes are very sensitive to the asymmetry A between the wells, but this has not always been recognized. The width A_0 of the distributions of asymmetries was found to broaden with increasing concentration of H in Sc, indicating that the interactions with other hydrogens are more important for A than the interaction with impurities and defects. The broadening is similar to, but weaker than the concentration effect found⁸ for H bound to 0 impurities in Nb.

The electron coupling coefficient $K \approx 0.06$ chosen to fit the data in Sc is the same value as measured^{6,10} for H bound to O or N impurities in Nb. This is consistent with the fact that the Korringa relaxation product³³ for H in Nb ($T_{1e}T=110$ sK) is close to the one² for H in Sc ($T_{1e}T=123$ sK). The deformation potentials that we derive for the H interacting with the phonons in Sc, are comparable to the potential barrier, and $(H_{01L}H_{01R})^{1/2}$ from $F_{2p(7)}$ have about the same magnitude as have been derived¹⁶ for H in Nb, although there only phonons with polarization along [111] were considered.

Two-phonon transition rates with T^5 dependence seems to be necessary to explain the spin-lattice relaxation of H in Sc. Such rates have been found³⁴ before in proton relaxation from rotational tunneling of NH_4^+ ions in ammonium salts. In comparisons of the two-phonon rates we note that H_{01R} connects states of opposite parity in one well, so we may expect it to be smaller than H_{00R} . However, $F_{2p(7)}$ does not require different deformations by the phonons in the two wells like $F_{2p(5)}$ and F_{1p} do.

The distributions of asymmetries $Z(A)$ shown in Fig. 5 and used in fitting the data, are temperature independent with a fraction of unpaired hydrogens $(1-P)$ of about 6%. This percentage may reflect the thermal equilibrium concentration of unpaired H at around 170 K where the long-range diffusion freezes. It is conceivable that the distributions of A should depend upon T , since the averaging effect of the increased motion of a given H with increasing T , should decrease its contribution to A for the neighboring H. The inverse of this effect may lead to a cooperative freezing of the unpaired hydrogens which is similar to, but distinct from the order-disorder pairing transition of the majority of the hydrogens observed¹⁷ around 170 K. A reduction in the width of $Z(A)$ with increasing T would cause a faster increase of the NMR relaxation up to the maximum near 60 K, and a faster decrease above, than we calculate from a constant $Z(A)$. The apparent increase in the Korringa relaxation term at

170 K ascribed² to a change in electronic structure with H pairing, may be due instead to the high- T tail of the relaxation from the local motion of the unpaired hydrogens.

The derived tunneling transition rates for H in Sc could possibly be checked with internal friction, ultrasonic attenuation, or quasielastic neutron scattering measurements. The heavier isotope D in ScD_x should have local tunneling rates that are smaller than for H by a factor 100 or more.

The model is probably valid also for the local tunneling motion of hydrogen in the similar hcp metals yttrium, lutetium, etc., that have been studied with NMR,³⁵⁻³⁷ neutron scattering,¹⁸⁻²¹ and other³⁸ methods. Theoretical calculations³⁹ on Y metal have recently confirmed the existence of a double-well potential for H along the c axis, although the calculated barrier $V_0/k_B \simeq 1800$ K appears too low when compared in Eq. (2) with the measured²¹ oscillation energy $E_1 \simeq 1100$ K. Furthermore, the calculated pairing energy for H in Y leads to predictions about the fraction of H involved in pairs that are in qualitative agreement with our findings for H in Sc.

Regarding other theories of hydrogen tunneling we note that the small-polaron theories^{11,12} use the coincidence configuration where the self-trapping energy is

overcome by the phonon deformations, as the intermediate state, and they do not consider the important effects of asymmetry. The theory predicting¹³ that the tunneling transition rate of H in Nb should decrease with T as $\propto T^{2K-1} \simeq T^{-0.9}$ is not experimentally proved,^{29,30} and it certainly does not fit the data for H in Sc. A T^{2K-1} behavior can perhaps not be excluded in the case where the calculated electronic transition rate is greater than $\Delta E_0/\hbar$. However, we see from Fig. 4 that this occurs only for $A/k_B < 5$ for T below 100 K, and we have found that only a negligible fraction of the H in Sc are tunneling between wells with such small asymmetry. Finally, it is gratifying that the electron rate (5) can be derived also as the low-temperature limit of the path-integral theory of tunneling by Weiss and Wollensak.⁴⁰

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