# Anomalous high-temperature hopping in metal hydrides

Peter M. Richards

*Sandia National Laboratories, Albuquerque, New Mexico 87185-5800*

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Recent NMR $T_1$ data on metal hydrides and earlier data on $PbF_2$ indicate the jump rate of hopping protons or fluorine ions decreases with increasing temperature at high temperature. This behavior is attributed to strong repulsions at the saddle point which increase with temperature as vibrational amplitudes increase. It consequently becomes harder to move through the saddle point at elevated temperature. Model potentials are used to obtain agreement with the data.

Recent NMR studies[1,2] of fcc metal dihydrides ($MH_{2-\epsilon}$ with $\epsilon \ll 1$) have shown that the relaxation time $T_1$ as a function of temperature goes through a maximum at $T_{max} \sim 800$ K, well above $T_{min} \sim 500$ K (these specific figures are for the $^{45}Sc$ resonance in $ScH_{1.83}$) where $T_1$ goes through its expected minimum for relaxation by diffusion.[3] Since theories of NMR relaxation by diffusion[3] all show $T_1 \propto v$ in the high-temperature region above $T_{min}$, the conclusion is that the proton jump rate $v$ *decreases* with increasing temperature above $T_{max}$. Another possibility, that there is a strongly temperature-dependent relaxation mechanism, seems unlikely in view of the fact that the anomaly is seen for both $^{45}Sc$ and $^1H$ NMR, which relax differently (electric-field-gradient fluctuations due to hydrogen hopping in the case of $^{45}Sc$ and fluctuating proton-proton dipole interactions in the case of $^1H$). The effect is seen in all the fcc dihydrides thus far investigated at high temperature,[1] which include $M =$ Sc, Y, La, Zr, Ti. It was also seen[4] several years ago in the NMR of superionic $PbF_2$, which has the same structure. There it was speculated that highly correlated motion and/or "melting" of the fluorine sublattice might be responsible. However, neutron scattering[5] and molecular-dynamics simulations[6] give no indication of such behavior.

Here I attribute the anomalous temperature dependence of $v$ to hydrogen-hydrogen repulsions at the saddle point which increase with temperature as the vibrational amplitudes increase. The same idea was used[7,8] to explain the equally anomalous octahedral- ($o$) site occupation in $YH_2$ and $LaH_2$. Instead of increasing with temperature, the $o$-site occupation shows a monotonic decrease as temperature is increased. As sketched in Fig. 1, modes which vibrate toward the $o$ site are strongly affected when a proton is at the $o$ site or an intermediate $s$ site. Occupation of these sites thus becomes less favorable at elevated temperature from energy and entropy considerations. If the vibrations occur, the $o$- and $s$-site energies are raised by the increased repulsion. If the vibrations are inhibited because the strong repulsion makes them unfavorable, the entropy is correspondingly decreased. Either case leads to a temperature-dependent increased free energy when the $s$ or $o$ site is occupied.

For equilibrium-site occupation as treated in Ref. 7, one calculates thermal equilibrium partition functions and compares their values with the site occupied and unoccupied. In this case the entropy effect dominates for large repulsion since the particles in the neighboring tetrahedral ($t$) sites must stay in their ground states if the $o$ site is occupied. The situation envisioned here for hopping *through* a site is somewhat different. I assume an adiabatic scenario whereby the time to pass over the saddle point is long compared with a vibrational period but short compared with the lifetime of the vibrational modes. Referring to Fig. 1, this means that the six other protons surrounding the $o$ site through which the labeled proton hops are treated as the "electrons" in a Born-Oppenheimer approximation. That is, as sketched in Fig. 2, when the hopping proton is at position $r$, any one of the other six follows the potential adiabatically and has a set of levels $E_n(r)$. If the lifetime of these levels is long, the quantum number $n$ will not change. Conse-
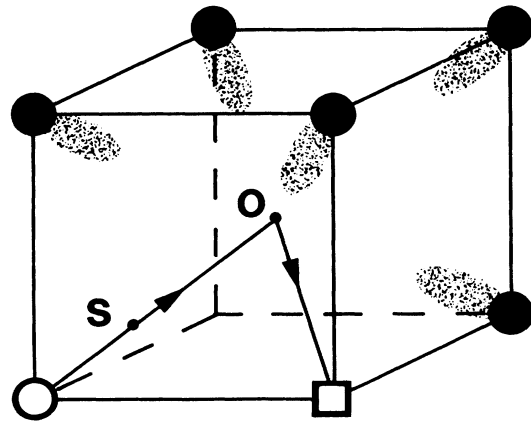


FIG. 1. Schematic of hopping path and effect of vibrational amplitudes. Hydrogens are shown occupying tetrahedral ($t$) sites, one of which is vacant, in the fcc metal lattice. Particle represented by open circle jumps to vacant site represented by open square. It follows path indicated by arrows. $s$ is the center of a face of a tetrahedron formed by metal ions (not shown) and would be the likely saddle point in the absence of hydrogen-hydrogen interactions. $o$ is the octahedral site. Vibrational amplitudes of six "other" particles shown as solid circles at occupied $t$ sites are seen to raise repulsion along the path.
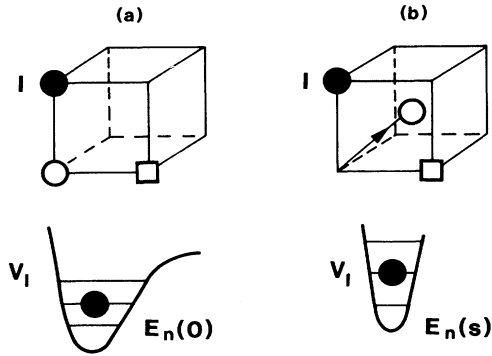
FIG. 2. Potential energy of one of the "other" particles in Fig. 1 when hopping particle is at (a) $t$ site and (b) saddle point (assumed to be at or near $o$ site at high temperature, as discussed in text. Adiabatic approximation described in text assumes particle maintains its quantum number as the hopper moves, as indicated by the level diagram.

quently the average potential-energy barrier the hopping particle must overcome is

$$U = z \sum_n \Delta_n \exp[-\beta E_n(0)] \bigg/ \sum_n \exp[-\beta E_n(0)] + U_A , \tag{1}$$

where $\Delta_n = E_n(s) - E_n(0)$ in which $s$ and $0$ (0 refers to the $t$ site) refer to the saddle point and equilibrium sites, respectively, $z$ is the number of hydrogen atoms assumed to interact equally with the hopping particle, $\beta = 1/k_B T$ with $T$ the absolute temperature; and $U_A$ is the barrier in the absence of hydrogen-hydrogen interactions. Use of $E_n(0)$ in the Boltzmann factors results from the long-lifetime assumption. Before the jump, the neighboring particle was in state $n$ of energy $E_n(0)$ with probability $\exp[-\beta E_n(0)]$. When the hopping particle reaches the saddle point, this neighbor particle has its energy changed to $E_n(s)$, but time has not been sufficient for it to reequilibrate by damping processes, so it retains the original quantum number $n$ and Boltzmann factor. That is, the process is adiabatic. The hopping rate $v$ is proportional to the probability of gaining enough energy to move from $0$ to $s$. It is convenient to express $v$ in a manner which explicitly shows the temperature dependence produced by the excited states, so it is written as

$$v = v_0 \exp(-\beta U_0)$$
$$\times \{\exp(-\beta U_T)[1 + Z_v(s)]/[1 + Z_v(0)]\} , \tag{2}$$

where $v_0$ is a prefactor which is of no concern here as long as it is temperature independent, and $U_0 = z\Delta_0 + U_A + E_q$ is the zero-temperature value of $U$ in Eq. (1) to which has been added a zero-point correction $E_q$, which has a negative contribution from the equilibrium site and a positive part from $s$. In general $E_q$ is temperature dependent, especially the part from the saddle point, since the repulsions raise the saddle-point vibrational frequencies. (Saddle-point frequencies refer to modes which vibrate in directions perpendicular

to the hopping path.) For simplicity, however, I neglect this dependence so that $U_0$ is constant and thus the coefficient of the term in curly brackets gives normal activated behavior. $U_T$ is the difference between $U$ and $U_0$ and hence given from Eq. (1) by

$$U_T = \left[ \left[ \sum_{n(>0)} \Delta_n \exp(-\beta \delta_n) \right] - \Delta_0 Z_v(0) \right] [1 + Z_v(0)]^{-1} , \tag{3}$$

where $\delta_n = E_n(0) - E_0(0)$ is the equilibrium-site energy relative to its ground-state value and $Z_v(0) = \sum_{n(>0)} \exp(-\beta \delta_n)$ is the contribution of excited states to the equilibrium-site partition function. A similar definition $Z_v(s) = \sum_{n(>0)} \exp\{-\beta[e_n(s) - e_0(s)]\}$ is used in Eq. (2) for the excited-state part of the partition function at the saddle point. The energy $e_n(s)$ differs from $E_n(s)$ in that the former is an energy level of a particle which is at the saddle point while the latter, used in Eq. (1), is an energy level of a particle at the equilibrium site when the neighboring saddle point is occupied. The adiabatic Eq. (2) differs from the isothermal equilibrium probability $P(s)$ of being at the saddle point which is given by

$$P(s) = \exp(-\beta U_0)\{[1 + Z_v'(s)]/[1 + Z_v(0)]\}^z$$
$$\times [1 + Z_v(s)]/[1 + Z_v(0)] , \tag{4}$$

where $Z_v'(s) = \sum_{n(>0)} \exp\{-\beta[E_n(s) - E_0(s)]\}$ differs from $Z_v(s)$ in that it refers to levels of the "other" particles in the neighborhood of the saddle point. Both Eqs. (2) and (4) assume that the probability of being at $s$ is small so that the total partition function which involves states both at $s$ and at $0$ may be approximated by one which involves $0$ only. The difference between Eqs. (2) and (4) is notable in an intermediate region of interest $\beta \Delta_n \ll 1$, $\beta[E_n(s) - E_0(s)] \gg 1$ for excited states $n > 0$. Equation (2) would then give a strongly temperature-dependent $U_T$ proportional to the strength of the repulsion. Equation (4) would give a greatly reduced partition function ratio approximately equal to $[1 + Z_v(0)]^{-z}$, whereby $P(s)$ is independent of the strength of the repulsion but decreased because the neighbor particles are forced into their ground states when the saddle point is occupied. As mentioned, Eq. (4) was used in Ref. 7 for $o$-site occupation; but the time scales make Eq. (2) seem more appropriate for the hopping problem. That is, the inelastic neutron scattering[8] generally shows well-defined peaks whose lifetime is greater than $10^{-13}$ s, compared with $v_0^{-1} \sim 10^{-14}$ s; so it is reasonable to assume there is not sufficient time for the levels to reestablish equilibrium populations during the jump. The assumption that the excited-state levels of the neighbors can be treated by a Born-Oppenheimer approximation is more tenuous, since their vibrational periods are of the same order as, though no longer than, $v_0^{-1}$. The breakdown of this approximation is not regarded as serious at least insofar as the qualitative effect is concerned.

In order for $v$ to decrease with increasing temperature above $T_{max}$ the term in curly brackets of Eq. (2) must not only decrease, it must decrease faster than

$\exp(-\beta U_0)$ increases. Since[1] $U_0$ is about 0.7 eV for ScH$_{1.83}$, this can be a demanding requirement. (The value of $U_0$ is inferred from the temperature dependence of $T_1$ below $T_{\min}$.) I now show that it can be satisfied and reasonable agreement obtained with a large, strongly distance-dependent repulsion. Quantitative comparison is made for ScH$_{2-\epsilon}$ only since the data there are particularly striking and it is perhaps the most difficult case because of the large $U_0$. (By comparison YH$_{2-\epsilon}$, the other system with extensive published results,[2] has $U_0 = 0.33$ eV. The theoretical temperature dependence is insensitive to $\epsilon$ as long as it is small so that the $t$ sites are nearly fully occupied.) The model potential is shown in Fig. 3. For a proton in the neighborhood of a vacancy there is a softening in the direction of the intermediate $o$ site, which is taken as the saddle point for ScH$_{2-\epsilon}$. It is not unreasonable to take the $o$ site as the saddle point in the Sc compound since there is no evidence of equilibrium $o$-site occupation[9] in ScH$_2$. It even may not be unreasonable in YH$_2$ and LaH$_2$ at high temperatures where the $o$ site is depopulated.[7,8] For analytic simplicity a one-dimensional piecewise quadratic potential

$$V_t(x) = \begin{cases} \infty, & |x| > x_0 \\ \frac{1}{2}kx^2, & -x_0 \leq x < x_1 \\ V_0 - b(x_0 - x)^2, & x_1 \leq x \leq x_0 \end{cases} \tag{5}$$

is used where $x = 0$ is the equilibrium $t$-site position, $x_0$ is the position of an $o$ site which neighbors the vacancy, and $-x_0$ is the position of an $o$ site in the opposite direction, away from the vacancy. Steep walls are assumed at $x = \pm x_0$ in order to keep a particle confined to the $t$ site for calculation of $t$-site properties. The force constant $k$ is chosen to give agreement with the observed[10] vibrational frequency $\hbar\omega = 129$ meV; for consistency $V_0 = U_0 - E_q$, since it should represent the same potential barrier to be surmounted at low temperature. I take $V_0 = 0.5$ as representative, which implies $E_q = 0.2$ eV. An $E_q > 0$ is reasonable since the saddle-point vibrational frequency is expected to be large because of the repulsion. A similar reduction $V_0 < U_0$ was also noted in previous work on the heat capacity[11] $C_p$ of ScD$_x$ to be necessary to fit the data for $x < 1.9$, but its possible origin in the zero-point energy of the saddle point was not recognized there. The parameters $b$ and $x_1$ are chosen to make $V_t(x)$ and $dV_t(x)/dx$ continuous at $x_1$. The potential $V_t(x)$ is for a particle at the $t$ site when neighboring $o$ sites are unoccupied, and is essentially of the same form used[11] in the $C_p$ work. When a neighbor $o$ site is occupied the potential is increased to

$$V_{t,o}(x) = V_t(x) + J(1 - x/x_o)^{-p} \tag{6}$$

for $x < x_o$, where $J$ is the strength of the repulsion when hydrogen atoms are separated by the $o$-$t$ distance $x_0 = 2.08$ Å for ScH$_2$ (i.e., when the particle in question is at $x = 0$ and the $o$ site is occupied by the hopping particle at $x = x_o$). The exponent $p$ is chosen as $p = 10$ for a typical strongly repulsive core. The levels of $V_t(x)$ are

the above $E_n(0)$ while those of $V_{t,o}$ are $E_n(s)$. As indicated in Fig. 3(b), the above $V_{t,o}(x)$ is approximated by

$$\widetilde{V}_{t,o}(x) = \begin{cases} \infty, & x < -x_0, \ x > x_2 \\ \frac{1}{2}k'(x - x_m)^2, & -x_0 \leq x \leq x_2 \end{cases} \tag{7}$$
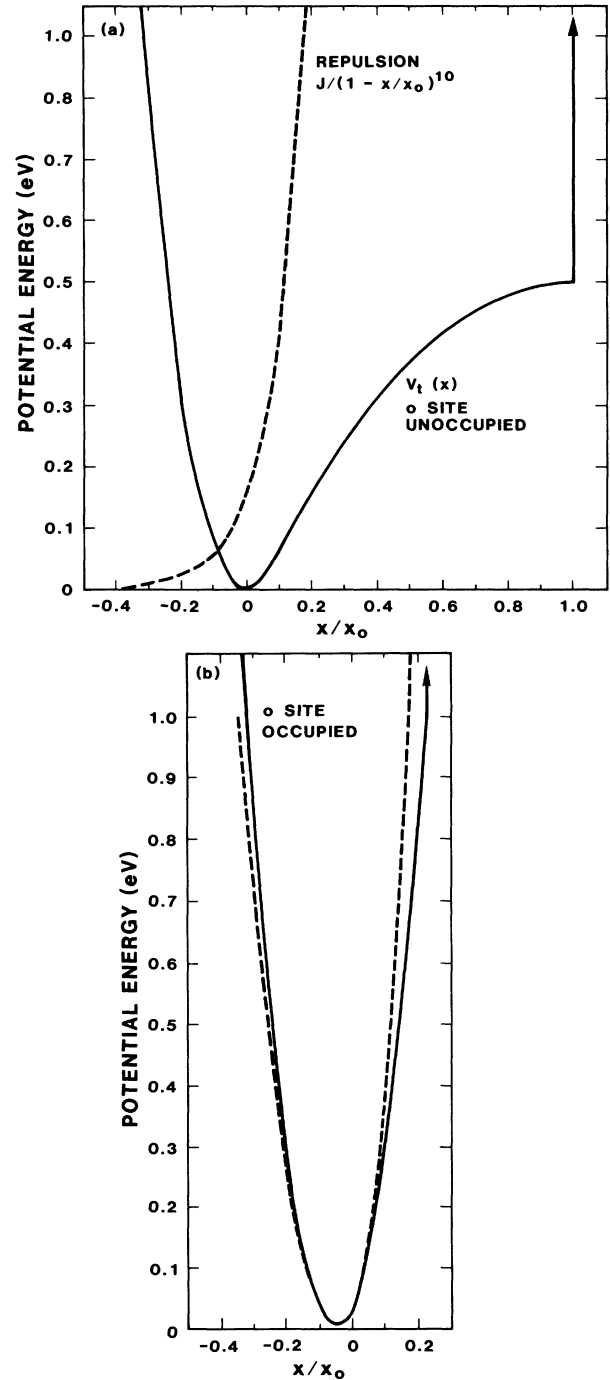


FIG. 3. Potential energy for "other" particle as actually used in fit to data. (a) $V_t(x)$ given by Eq. (5) and repulsive part with $J = 0.15$ eV. (b) Potential when $o$ site is occupied. Dashed curve is Eq. (6) which is the sum of the two curves in (a). Solid curve is the approximation Eq. (7) used in the calculation.

where $x_m$ $(x_m < 0)$ is the position at which the potential in Eq. (6) is a minimum and the new force constant is

$$k' = k + p(p+1)Jx_o^{-2}/(1 - x_m/x_o)^{p+2} .$$

The cutoff $x_2$ beyond which the repulsion acts like a hard core is chosen somewhat arbitrarily by $\frac{1}{2}k'(x_2 - x_m)^2 = 2V_0$, i.e., when the repulsion doubles the original saddle-point energy. A nonzero minimum value $\tilde{V}_{t,o}(x_m)$ can always be lumped into $U_0$ and thus is not shown in Eq. (7). Equations (6) and (7) are admittedly gross simplifications, but they have the advantage that the classical period when the particle has energy $E$, proportional to $\int_{x_a}^{x_b} dx [E - V(x)]^{-1/2}$ where $x_a, x_b$ are the classical turning points, may be determined analytically. Hence the energy levels are approximated by the correspondence principle $E_{n+1} - E_n = h/T_{cl}(n)$, where $T_{cl}(n)$ is the classical period for state $n$ and the ground state $E_0$ is that of an oscillator with force constant $k$ or $k'$ as the case may be. By this method, $E_n(0)$ and $E_n(s)$ are obtained from the potentials in Eqs. (5) and (7), respectively, and used in Eqs. (1)–(3) to get the temperature-dependent hopping rate. For a large $k'$ associated with strong repulsion, the vibrational levels for a particle at the saddle point, when it is surrounded by six other hydrogen atoms, are assumed to be sufficiently large that $Z_v(s) \ll 1$ is used in the formulas for the temperature range of interest.

Figure 4 shows the thus-calculated hopping rate $v$ versus temperature compared with the measured[1] $^{45}$Sc $T_1$ in $ScH_{1.83}$. Both the theory and data have been normalized to unity at their maximum values. In this temperature range $T$ is sufficiently greater than $T_{min}$ that $T_1$
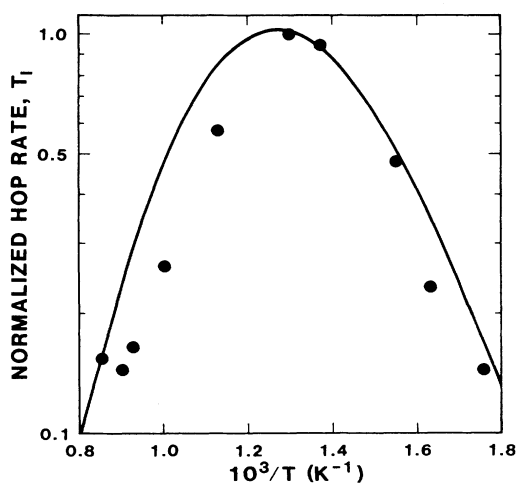


FIG. 4. NMR $T_1$ and theoretical hopping rate. Data points are from Ref. 1 for the $^{45}$Sc NMR in $ScH_{1.83}$. No distinction is made to frequency since, in the range shown, data are essentially the same where measurements were made at both 12 and 24 MHz. However, above 1000 K only 12-MHz data were presented in Ref. 1. Curve is Eq. (2) using the potentials of Eqs. (5) and (7) (Fig. 3) with parameter values as discussed in the text and seen in Fig. 3. Both data and theory are normalized to unity at their maximum values.

should be proportional to $v$, at least according to conventional theory.[3] The value of $J$ needed to obtain a reasonable fit is 0.15 eV. This may seem quite large, but may not be unreasonable in view of the small $o$-$t$ distance $x_o = 2.08$ Å. A generally accepted view[12] is that 2.1 Å is the closest two hydrogen atoms can get to each other in a hydride. Also, the value of $J$ used[13] to fit phase transition data in $PdH_x$ is 0.035 eV for hydrogen atoms 2.75 Å apart at neighbor $o$ sites. This scales to 0.56 eV for the $o$-$t$ separation in $ScH_2$, assuming an $r^{-10}$ dependence. $T_1$ appears to go through a second minimum above 1100 K or at least levels off. There are two possible explanations for this—apart from saying that $v$ has decreased so much that it is back to its value at $T_{min}$, in which case $T_1$ would again become frequency dependent. First, at very high temperatures the vibrational modes may have sufficiently short lifetimes that the adiabatic approximation breaks down and it would be more appropriate to use Eq. (4). The bracketed terms in this equation become temperature independent in the high-temperature limit so that $v$ would again show activation at $U_0$, but with a greatly reduced prefactor owing to the much softer potential associated with $Z_v(0)$ than with $Z_v'(s)$. Second, the present treatment has ignored the direct $t$-$t$ path, which is unfavorable at low temperature because of the close packing of the metal ions in the fcc structure. However, as the repulsion makes the $t$-$o$-$t$ path less favorable, the originally higher-activation-energy $t$-$t$ jump could have the greater $v$. Since the anharmonic vibrations are expected to be directly along the $t$-$o$ direction, they should have much less effect in limiting the jump rate in the $t$-$t$ direction.

There are some caveats which must be mentioned. Although the theory has the hydrogen atoms localized at $t$ sites as opposed to becoming liquidlike, it does assume a fair amount of anharmonicity in the vibrations. This might be expected to show up in neutron diffraction, but recent data[14] on $ScD_{1.8}$ show a linear temperature dependence of the deuteron mean-square displacement $\langle \delta r^2 \rangle$, with $\langle \delta r^2 \rangle \approx 0.4$ Å$^2$ at 1300 K, about what one would expect for a harmonic oscillator with $\hbar\omega = 91$ meV (reduced from the $ScH_2$ value by the $\sqrt{2}$ isotope factor). This is quite different from $PbF_2$, where the fluorine density is considerably spread out at high temperature although still centered at $t$ sites.[5,6] One possible explanation is that the present model requires anharmonicity only for those modes which vibrate toward an $o$ site which is a nearest neighbor of a vacant $t$ site, i.e., modes which influence a hopping particle (see Fig. 1). For $ScH_{1.8}$ where the vacancy concentration is 10% and assuming that only one of three modes is involved for each of those "other" hydrogen atoms in Fig. 1, I thus estimate that only about $\frac{1}{4}$ of the total number of optic modes need by softened. This may be a sufficient reduction to make $\langle \delta r^2 \rangle$ insensitive to the anharmonicity, especially in view of the fairly large experimental error[15] in the data of Ref. 14. However, as mentioned above, anharmonicity was also invoked[11] to explain the large high-temperature deuteron contribution to the heat capacity $C_p$ of $ScD_x$ near $x = 2$, and it is not so clear whether this interpretation of $C_p$ is compatible with the

diffraction data.

A second point is that the decrease of $v$ at high temperature is an inference from NMR $T_1$ data rather than a direct measurement, as might be accomplished by diffusion studies. In this light the older $PbF_2$ data[4] deserve some comment. There (see Fig. 2 of Ref. 4) $v$ was inferred to decrease in a region where the ionic conductivity $\sigma$ was still increasing with temperature, although at a greatly reduced rate. Thus there might appear to be evidence against the $F^-$ hop rate decreasing. However, the relation $\sigma \propto N_v v$ where $N_v$ is the number of $F^-$ vacancies shows than an increasing $\sigma$ and decreasing $v$ are not incompatible if the vacancy concentration is strongly increasing. Stoichiometric $PbF_2$ is considerably different from $ScH_{1.8}$ in that the former has an activated vacancy concentration whereas the latter has a constant 10% vacancy concentration up to very high temperatures. Indeed a possible explanation for the slow increase of $\sigma$ above 500 °C in $PbF_2$ is that $N_v$ continues to increase at a rapid rate but $v$ decreases.

The present theory should be equally applicable to $PbF_2$, and possibly even more palpable there where there is clear evidence of anharmonicity. So the $T_1$ data of Ref. 4 are nicely explained. But the model here does not explain the factor of 60 difference between $T_1$ and $T_{1\rho}$ found at high temperature in Ref. 4. $T_{1\rho}$ is essentially $T_1$ measured at a Larmor frequency corresponding to the rf magnetic field rather than the dc field, so the effective measurement frequency for $T_{1\rho}$ is orders of magnitude smaller than for $T_1$. Although $T_1$ was independent of frequency in the MHz range, as theory[3] says it should be above $T_{\min}$ where $T_1 \propto v$, the much smaller $T_{1\rho}$ was interpreted[4] as due to a much slower

cooperative motion. Since this work concerns only local hopping, it offers no insight into possible cooperative motions. Measurements of diffusion and $T_{1\rho}$ in the hydrides are clearly desirable.

An obvious test of the model is that, since it is based on hydrogen-hydrogen interactions, there should be no anomalous temperature dependence for low hydrogen concentration. Measurements[16] on $\alpha$-phase $ScH_{0.27}$ are in support of this. However, a similar anomaly has been reported[17] in $V_x Nb_{1-x} H_{0.2}$. The present theory, based on the structure of fcc dihydrides, has no explanation for this behavior in a bcc alloy.

In conclusion, the anomalous temperature dependence of proton hopping in fcc dihydrides can be explained by hydrogen-hydrogen repulsion which increases rapidly with temperature because of vibrational effects. This makes the saddle-point energy an increasing function of temperature and leads to the decrease in hopping rate at high temperature, which is inferred from NMR $T_1$ measurements. Open questions remain as to whether the proposed anharmonicity can be fully consistent with neutron diffraction and whether the decreased hopping rate can be verified in a direct diffusion experiment. The latter could settle whether the temperature dependence of $T_1$ might be caused by something other than an anomalous jump rate. Also, other mechanisms might be operable so that the present explanation is not unique.

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