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Correlation functions for simple hopping in a face-centered-cubic lattice

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The correlation functions for a single specific particle and for a pair of specific particles are calculated for an ensemble of particles making nearest-neighbor simple jumps in a fcc lattice. The correlation functions are used to obtain diffusion coefficients and NMR relaxation times due to $I-S$ (unlike spin) and $I-I$ (like spin) dipolar interactions for various concentrations of particles. Our results are compared to previous theories and to experimental results on PdH_x.

I. INTRODUCTION

Although the problem of atomic motion in a crystal lattice and the NMR relaxation times due to the motionally altered dipolar interaction between particles have been studied for years, many commonly used expressions in the field have only semiquantitative validity. However, we have developed a formalism[1] which in principle allows one to calculate all correlation functions and thus all relevant relaxation times for any simple hopping system. Recently this formalism has been used to obtain the correlation functions for an arbitrary concentration of particles hopping in a simple cubic lattice.[2] In this case we found, for example, that the commonly used random walk approximation could be in error by as much as 18% at low concentrations and by as much as 100% at high concentrations.

In this paper we derive expressions for the correlation functions for a single specific particle and for a pair of specific particles in an ensemble of particles hopping in a fcc lattice. These correlation functions are then used to calculate spin-lattice relaxation times T_1.

In the rest of this section we shall briefly discuss the relevant correlation functions and some of the commonly used approximations for these functions. In Sec. II, T_1 is given explicitly in terms of these functions. Further, expressions are derived for these correlation functions and compared to expressions derived using other models. In Sec. III numerical results for T_1 obtained from the various models are presented and compared to existing experimental data on hydrogen hopping in PdH_x.

When discussing problems involving atomic motion, there is a possibility of confusing various approximations to a model with the model itself. Throughout this paper the only model which we use is the "simple hopping model", which is defined in Refs. 1 and 2. In this model one assumes that the probability per unit time that a particle at the site α will hop to a nearby vacant site β is given by the hopping rate $\Gamma_{\alpha\beta}$ and that this rate depends neither on time nor on the occupancy of sites other than α or β. Obviously there is a question of whether this model is a good description of a given physical substance. In fact, this question is addressed in Sec. III.

However, given the simple hopping model, there is the question of what approximations are made in order to obtain the correlation functions for one or more specific particles. For example the single relaxation time approximation[3] and the random walk approximation[4] refer to approximations for the simple hopping model. The term "random walk" is particularly confusing. One reason for this is that for a lattice of equivalent sites, the occupancy of the sites by any particle can be correctly described as a random walk. However, the movement of one or more distinguishable particles cannot be described as a random walk! Unfortunately the random walk approximation[4,5] is sometimes presented as or thought to be the exact solution to the simple hopping problem. This definitely is not the case.

A particle hopping through a lattice feels an effective time-dependent dipolar field due to other hopping particles and possibly also due to stationary particles. T_1 is determined by the frequency spectrum of the correlation functions describing the relative coordinates between these interacting particles. The information on how a particle hops is thus given by the particle correlation functions. The first and simplest attempt at these functions is the Bloembergen, Purcell, and Pound[3] (BPP) or single relaxation time (SRT) approximation, where the time dependence is a single time decaying exponential. This actually describes a particle at a fixed position disappearing, not a hopping process at all. A much improved theory, which actually takes into account the hopping nature and the lattice structure, was presented by Torrey.[4] This approximation describes the particle motion as a random walk (RW) through the lattice. Later, Sholl[5] repeated Torrey's calculations improving on the numerical techniques.

However, neither SRT nor RW takes into account any correlation between hopping particles. These correlations give rise to diffusion constants which are lower than those in the RW approximation by as much as 25% for a high concentration of particles in a fcc lattice. Further, errors of nearly 200% and 50% in T_1 are found for the BPP and RW approximations respectively, when compared with the present correlated theory in certain limits. Recently Wolf[6] has developed the monovacancy model (MV) which treats correlations exactly in what is essentially a computer simulation. However, this model is only applicable when the concentration of vacancies approaches zero.

Our formalism allows for the calculation of single particle and pair correlations at any concentration. The hopping rate does not depend on the particle's past history and, in the present case, is symmetric, in that the hopping rate from site 1 to 2 is equal to hopping rate from 2 to 1. Hopping to occupied sites is forbidden which blocks a particles path and increases the likelihood of a particle hopping back to it's previous site as the concentration increases. A more serious assumption is that hopping to a particular site is independent of occupancy of that site's neighboring environment. This means that the potential well of an unoccupied site does not depend on the occupancy of it's neighbors.

There are two distinct contributions to T_1 for the nuclei of the hopping particles. One contribution, denoted by $T_1(I-I)$, is from the motionally altered dipolar interaction between pairs of hopping particles. The correlation function for a pair of hopping particles is necessary for calculating this contribution. The other contribution to T_1, denoted by $T_1(I-S)$, is due to the motionally altered dipolar interaction between a hopping spin and other spins at fixed lattice positions. For this term the correlation function for a single particle with respect to the fixed lattice is required. In general, both mechanisms can be important. However, for the protons in PdH_x, the $I-I$ interactions dominate at all but the lowest concentrations of hydrogen.

The necessary correlation functions are discussed in detail in Ref. 2. The single specific particle correlation function is defined as

$$D_i(\vec{\mathrm{R}}_\alpha-\vec{\mathrm{R}}_\beta,t)=\langle\rho_{i\alpha}(t)\rho_{i\beta}(0)\rangle\theta(t)\ ,$$
$$\rho_{i\alpha}\equiv(N)^{1/2}P_{i\alpha}\ , \tag{1}$$

where α is a lattice site, N is the number of sites in the lattice, and $P_{i\alpha}$ is a stochastic variable whose value is one if the particle i is at site α and zero if not. θ is the step function, $\vec{\mathrm{R}}_\alpha$ the position of the site α, and $\langle\ \rangle$ denotes an ensemble average. The correlation function for a pair of specific particles is defined as

$$\begin{aligned}D_{ij}(\vec{\mathrm{R}}_\alpha,\vec{\mathrm{R}}_{\bar\alpha};\vec{\mathrm{R}}_\beta,\vec{\mathrm{R}}_{\bar\beta};t)=\langle&\rho_{i\alpha}(t)\rho_{j\bar\alpha}(t)\\&\times\rho_{i\beta}(0)\rho_{j\bar\beta}(0)\rangle\theta(t)\ ,\end{aligned} \tag{2}$$

where i and j refer to different specific particles. Since we only need the correlations between the particles i and j, we define

$$\begin{aligned}\tilde{D}_{ij}(\vec{\mathrm{R}}_\alpha,\vec{\mathrm{R}}_\beta,t)=\frac{1}{N^2}\sum_{\gamma\bar\gamma}D_{ij}(&\vec{\mathrm{R}}_\alpha+\vec{\mathrm{R}}_\gamma,\vec{\mathrm{R}}_\gamma\ ;\\&\vec{\mathrm{R}}_\gamma+\vec{\mathrm{R}}_{\bar\gamma},\vec{\mathrm{R}}_{\bar\gamma};t)\ ,\end{aligned} \tag{3}$$

which is the average of D_{ij} over all initial and final center of mass positions.

II. RESULTS

In this section we develop the expressions necessary to evaluate the two contributions to the spin-lattice relaxation time T_1 and compare our model to previously used models. The notation used is identical to or a slight generalization of the notation used in Ref. 2. In particular, quantities which depend on space and time are Fourier transformed as in Eq. (6)–(8) found in Ref. 2. In addition, the nuclei associated with the hopping particles will be referred to as I-spins while the host or stationary spins will be referred to as S-spins. We let c denote the concentration (the number of particles divided by the number of sites) of the I-spins.

The two contributions to T_1 can be combined as

$$(1/T_1)=[1/T_1(I-I)]+[1/T_1(I-S)]\ . \tag{4}$$

As discussed in Ref. 2, the expressions for T_1 are relatively simple if a given I-spin site possesses cubic site symmetry with respect to both the other I-spin sites and the S-spin sites. In this case, one obtains[7]

$$\begin{aligned}\frac{1}{T_1}(I-I)=(\tfrac{1}{20}A)[\,&\tilde{D}_{00}'(\omega)(2-5h)+\tilde{D}_{00}'(2\omega)(8-20h)+\tilde{D}_{11}'(\omega)(24+90h)+\tilde{D}_{11}'(2\omega)(96-240h)\\&+\tilde{D}_{22}'(\omega)(6-15h)+\tilde{D}_{22}'(2\omega)(24+90h)]\ ,\end{aligned} \tag{5}$$

$$\frac{1}{T_1}(I-S) = (\tfrac{1}{20}B)\{(2-5h)[2D_{00}'(\omega_+) + D_{00}'(\omega) + 24D_{11}'(\omega_+) + 4D_{11}'(\omega_-) + 3D_{22}'(\omega) + 2D_{22}'(\omega_-)]$$
$$+ \tfrac{2}{3}D_{00}'(\omega_-)(1+10h) + 6D_{11}'(\omega)(4+15h) + 3D_{22}'(\omega_+)(4+15h)\} \ , \tag{6}$$

where

$$\begin{aligned} A &= I(I+1)\, \hbar^2\gamma_I^4 c/a_0^6 \ , \\ B &= S(S+1)\, \hbar^2\gamma_I^2\gamma_s^2 Q/a_0^6 \ , \\ h &= \sum l_i^4 - \tfrac{3}{5} \ . \end{aligned} \tag{7}$$

Here γ_I and γ_s are the gyromagnetic ratios of the I and S spins respectively, Q is the natural abundance factor for the S spins, l_1 are direction cosines of the external magnetic field with respect to the crystalline axes, ω is the resonant frequency of I-spins, $\omega_\pm = \omega \pm \omega_s$ where ω_s is the resonant frequency of S-spins and a_0 is the length of a cube edge. We have used

$$\begin{aligned} \tilde{D}_{\alpha\alpha}'(\omega) &= \frac{1}{N^2}\sum_{qq'} T_\alpha(\vec{q})\, \tilde{D}_{ij}'(\vec{q}, \vec{q}\,', \omega)\, T_\alpha^*(\vec{q}\,') \ , \\ D_{\alpha\alpha}'(\omega) &= \frac{1}{N}\sum_{q} T_\alpha(\vec{q}, \vec{r}_0) D_i'(\vec{q}, \omega)\, T_\alpha^*(\vec{q}, \vec{r}_0) \ , \end{aligned} \tag{8}$$

where $\tilde{D}'$, D' denote real parts of $\tilde{D}$, D and $T_\alpha(\vec{q})$, $T_\alpha(\vec{q}, \vec{r}_0)$ are given by

$$\begin{aligned} T_0 &= T_{xx} + T_{yy} - 2T_{zz} \ , \\ T_1 &= T_{xz} - iT_{yz} \ , \\ T_2 &= T_{xx} - T_{yy} - 2iT_{xy} \ , \end{aligned} \tag{9}$$

where $T_{ij}(\vec{q})$, $T_{ij}(\vec{q}, \vec{r}_0)$ are Fourier transforms of $T_{ij}(\vec{R})$, $T_{ij}(\vec{R}, \vec{r}_0)$ respectively where

$$\begin{aligned} T_{ij}(\vec{R}) &= a_0^3 R_i R_j/|R|^5, \quad \vec{R} \neq 0 \ , \\ T_{ij}(\vec{R}, \vec{r}_0) &= a_0^3(\vec{R}+\vec{r}_0)_i(\vec{R}+\vec{r}_0)_j/|R+r_0|^5 \ , \end{aligned} \tag{10}$$

where $\vec{R}$ is a lattice vector, $\vec{r}_0$ is the displacement of the I lattice from the S lattice, N is the number of lattice sites, and $\vec{q}$ is a wave vector in the first Brillouin zone.

The dipolar Fourier transforms can be evaluated numerically using Ewald's method[8] and the rates can be written conveniently as

$$\begin{aligned} \frac{1}{T_1}(I-I) &= \frac{A}{\omega}[g_0(\omega\tau_c) + hg_1(\omega\tau_c)] \ , \\ \frac{1}{T_1}(I-S) &= \frac{B}{\omega}[f_0(\omega\tau_c) + hf_1(\omega\tau_c)] \ , \end{aligned} \tag{11}$$

for a given ratio of ω_s/ω. In these equations we have defined a correlation time τ_c and a correlation rate Γ_c as

$$\begin{aligned} \Gamma_c &= (1/\tau_c) = z\,\bar{c}\,\Gamma_0 \ , \\ \bar{c} &= 1 - c \ , \end{aligned} \tag{12}$$

where z is the coordination number, $\bar{c}$ is the concentration of vacancies, and Γ_0 is the nearest neighbor hopping rate. For an fcc lattice, $z = 12$.

In particular, we apply the above relations to the hydrogen palladium system. It is believed that hydrogen goes into the palladium lattice in the interstitial octahedral sites[9] to form its own fcc lattice displaced from the host palladium by $\frac{1}{2}a_0$ in the x direction. In various temperature-concentration regions the hydrogen behaves as a simple hopping system. For the fcc lattice, the hopping rate from site α to β is

$$\Gamma_{\alpha\beta} = \Gamma_0 f(\vec{R}_\alpha - \vec{R}_\beta) \ ,$$

where

$$f(\vec{q}) = 2\sum_{i \neq j} \cos Q_i \cos Q_j \ , \tag{13}$$

and i,j refer to x,y,z components and $Q_i = \frac{1}{2}q_i a_0$. Also, $\vec{r}_0$ in Eq. (10) is $(\frac{1}{2}a_0)$ (1,0,0).

The heart of the hopping problem is the calculation of $\tilde{D}_{ij}(\vec{q}, \vec{q}\,', \omega)$ and $D_i(\vec{q}, \omega)$. As in earlier work,[1,2] it is convenient both physically and computationally to express the correlation functions in terms of self-energies or memory functions $\tilde{K}$ and K. These quantities are defined by equations

$$\omega\,\tilde{D}_{ij}(\vec{q}, \vec{q}\,', \omega) + i\frac{1}{N}\sum_{q''}\tilde{K}_{ij}(\vec{q}, \vec{q}\,'', \omega)\,\tilde{D}_{ij}(\vec{q}\,'', \vec{q}\,', \omega) = i(N\delta_{\vec{q},\vec{q}\,'} - 1) \ , \tag{14}$$

$$\omega D_i(\vec{q}, \omega) + iK_i(q, \omega) D_i(q, \omega) = i \ .$$

A summary of the various models used to find $\tilde{K}$ and K are discussed in Ref. 2. Briefly, the SRT approximation assumes that $\tilde{K}$ and K are independent of $\vec{q}$ and ω and leads to

$$\begin{aligned} \tilde{D}_{ij}(\vec{q}, \vec{q}\,', \omega) &= iN\delta_{\vec{q},\vec{q}\,'}/(\omega + 2i\Gamma_c) \ , \\ D_i(\vec{q}, \omega) &= i/(\omega + i\Gamma_c) \ . \end{aligned} \tag{15}$$

The RW approximation yields

$$\begin{aligned} D_{ij}(\vec{q}, \vec{q}\,', \omega) &= iN\delta_{\vec{q},\vec{q}\,'}/[\omega + 2i\omega_c(q)] \ , \\ D_i(\vec{q}, \omega) &= i/[\omega + i\omega_c(\vec{q})] \ , \end{aligned} \tag{16}$$

where

$$\omega_c(\vec{q}) = \bar{c}\,[12\Gamma_0 - \Gamma(\vec{q})] \ . \tag{17}$$

Neither of these approximations tackles the problem of correlations between particles in any detail. The

SRT approximation has no correlations while the random walk includes only the reduced hopping rate $\bar{c}\,\Gamma_0$, due to the average occupation of neighboring sites. Wolf's MV model does include correlations by following a single vacancy about in the lattice but applies only as c approaches unity.

Our mean-field approximation (MF) takes into account, in an average way, correlations of the particles. For D_i, this mean field is the same as the random walk approximation as long as the factor $(1-c)$ is included, which corrects for the average vacancy of neighbor sites. The mean field for $\tilde{D}_{ij}$ is made up of each particle i and j in the mean field of the rest of the hopping particles plus the restriction that the two particles can rigorously never occupy the same site. By methods similar to those in Ref. 2, the fcc generalization of Eqs. (22), (23) in Ref. 2 for the mean-field approximation becomes

$$\tilde{D}_{ij}(\vec{q},\vec{q}\,',\omega)=N\delta_{\vec{q},\vec{q}\,'}d_0(\vec{q},\omega)+8\,\bar{c}\,\Gamma_0 d_0(\vec{q},\omega)d_0(\vec{q}\,',\omega)\left\{\frac{1}{2}\sum_{i\neq j}\frac{\cos Q_i\cos Q_j\cos Q_i'\cos Q_j'}{1-8\,\bar{c}\,\Gamma_0 F(c_x^2c_y(c_y-c_z),\omega)}+\frac{1}{2}\sum_{i\neq j}\frac{\sin Q_i\sin Q_j\sin Q_i'\sin Q_j'}{1-8\,\bar{c}\,\Gamma_0 F(s_x^2s_y^2,\omega)}\right\}. \tag{18}$$

Here

$$d_0(\vec{q},\omega)=1/[\omega+2i\omega_c(\vec{q})]\ ,$$

$$F(t,\omega)=\frac{1}{N}\sum_q t(\vec{q})\,d_0(\vec{q},\omega)\ , \tag{19}$$

and c_x, s_x, etc., stand for cos Q_x and sin Q_x.

In Ref. 2 we developed an approximation scheme for computing D_i and $\tilde{D}_{ij}$ which we called the multiple scattering (MS) approximation. Since the scheme can be generalized to the fcc lattice in a perfectly straightforward (but tedious) manner, we shall not present any details of these calculations. In order to reduce the results for $D_i(\vec{q},\omega)$ to a managable form, we have fit the self-energy $K_i(\vec{q},\omega)$ numerically to

$$K_i(\vec{q},\omega)=\omega_c(\vec{q})\left[\frac{1-ca(\vec{q},c)}{1-i\omega a(\vec{q},c)/2\Gamma_0}\right], \tag{20}$$

where

$$a(\vec{q},c)=\alpha(c)+\beta(c)\omega(\vec{q})/12\Gamma_0\ ,$$

$$\omega(\vec{q})=\omega_c(\vec{q})/\bar{c}\ , \tag{21}$$

and α and β depend only on c and not on $\vec{q}$ or ω. The value of α is given by

$$\alpha=0.139(1+0.301c)/(1-0.173c)\ . \tag{22}$$

The value of β as a function of c is given in Fig. 1. As can be seen, β is or order 10^{-2} for $c<0.8$ but increases very rapidly for larger values of c. It turns out that β is a reasonably good measure of how good the numerical fit is. For values of $c<0.9$ Eqs. (20) and (21) yield a value of $D_i(\vec{q},\omega)$ that is correct to within about 1%. As c increases above 0.9, these equations give values of $D_i(\vec{q},\omega)$ that are rapidly becoming more unreliable. The tracer correlation factor f_t is defined by the equation

$$D=\tfrac{1}{12}f_t\Gamma_c a_0^2\ , \tag{23}$$

where D is the diffusion constant. From Eqs. (14) and (20) and the definition of $\omega_c(q)$, we obtain

$$f_t=1-c\alpha(c)\ . \tag{24}$$

This gives the correct published value of 0.781 when c approaches unity.[10]

As in Ref. 2, the MS approximation for the pair-correlation function $\tilde{D}_{ij}(\vec{q},\vec{q}\,',\omega)$ is obtained by using Eq. (18) with $d_0(\vec{q},\omega)$ replaced by $d_1(\vec{q},\omega)$, where

$$d_1(\vec{q},\omega)=\int\frac{d\omega'}{2\pi}D_i(\vec{q},\omega')D_i(\vec{q},\omega-\omega')\ . \tag{25}$$

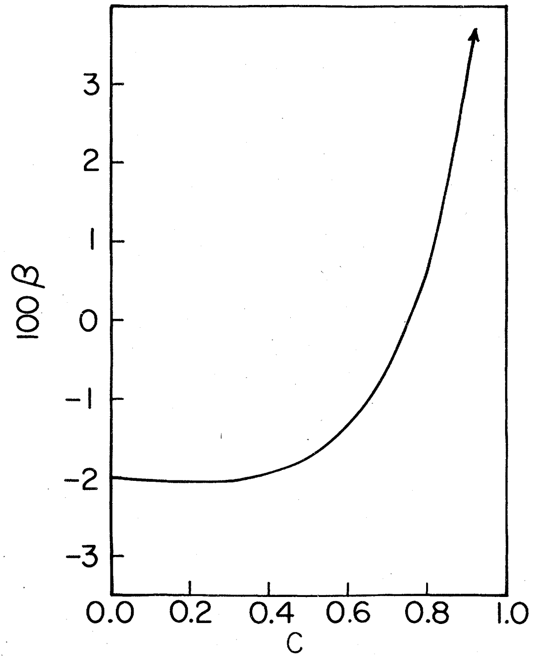

FIG. 1. Concentration dependence of β, defined by Eq. (21).

TABLE I. The dimensionless constants $b_\alpha(0)$, $b_\alpha(\infty)$, $a_\alpha(0)$, and $a_\alpha(\infty)$ defined by Eqs. (26) and (27). The quantities $a_1(0)$ and $b_1(0)$ are zero.

Theory		*I-I*			*I-S*	
	$b_0(0)$	$b_0(\infty)$	$b_1(\infty)$	$a_0(0)$	$a_0(\infty)$	$a_1(\infty)$
BPP (any c)	115.6	185.0	29.4	562.7	459.0	1.99
RW (any c)	215.1	156.5	24.5	651.8	634.9	2.17
MF (any c)	226.7	143.7	21.5	651.8	634.9	2.17
MS ($c \rightarrow 0$)	226.7	143.7	21.5	651.8	634.9	2.17
MS ($c=0.1$)	229.2	143.7	21.5	660.3	634.9	2.17
MS ($c=9.2$)	232.0	143.7	21.5	669.8	634.9	2.17
MS ($c=0.3$)	235.4	143.7	21.5	680.8	634.9	2.17
MS ($c=0.4$)	239.4	143.7	21.5	693.5	634.9	2.17
MS ($c=0.5$)	244.2	143.7	21.5	708.5	634.9	2.17
MS ($c=0.6$)	250.2	143.7	21.5	726.7	634.9	2.17
MS ($c=0.7$)	257.9	143.7	21.5	749.7	634.9	2.17
MS ($c=0.8$)	268.5	143.7	21.5	780.9	634.9	2.17
MS ($c=0.9$)	285.0	143.7	21.5	829.7	634.9	2.17

The first term in the ensuing equation describes each particle i and j hopping in the lattice without regard to each other. The second term is the lowest-order correction to the restriction that both particles cannot be at the same site simultaneously. This second term is roughly a 7% correction for the fcc lattice. The corresponding correction for the sc lattice (with half the number of nearest neighbors) was about twice as much.

III. COMPARISON WITH EXPERIMENT

In this section we summarize the results of our calculations and compare them to existing experimental data. The computations for $T_1(I-I)$ and $T_1(I-S)$ for any specified concentration and frequency are easily performed using the prescription described in Sec. II. The results of our computations in the asymptotic regions of $\omega\tau_c \gg 1$ and $\omega\tau_c \ll 1$ are given in Table I for a wide variety of concentrations. The results are displayed in terms of the dimensionless constants $b_m(0)$, $b_m(\infty)$, $a_m(0)$, $a_m(\infty)$ defined by the equations

$$g_m(x) \rightarrow b_m(\infty)/x\ , \qquad f_m(x) \rightarrow a_m(\infty)/x\ , \tag{26}$$

for $x \gg 1$ and

$$g_m(x) \rightarrow b_m(0)x\ , \qquad f_m(x) \rightarrow a_m(0)x\ , \tag{27}$$

for $x \ll 1$. The results for the b's are independent of the gyromagnetic ratio of the host nuclei but the values of the a's depend on Δ where

$$\omega_{\pm} = (1 \pm \Delta)\omega\ . \tag{28}$$

Table I has been constructed for $\Delta = -0.041$ which is appropriate for hydrogen in Pd. In general, for small values of Δ, corrections to the a's are of order Δ compared to one. The corresponding values for the a's and b's for other theories are also included in Table I.

We have compared our theory to the T_1 experiments of Cornell and Seymour[11] on PdH$_x$ powders with $x=c=0.7$. In Table II we have listed the results for T_{1m}(T_1 at the T_1 minimum) with $a_0=4.04$ Å and have also listed the value of $\omega_c\tau$ at which the T_1 minimum occurs. As can be seen, $T_1(I-S)$ contributes only about 3% of the total T_1. Further, all theories give virtually identical results for T_{1m} although the values of $\omega\tau_c$ at which this minimum occurs differ significantly.

All of the theoretically derived values of T_{1m} are about 10% smaller than the experimentally observed T_{1m}'s. This is a rather large discrepancy since we believe that our calculations are good to about 1%. The discrepancy could be resolved by a 2% increase in a_0 or a 10% decrease in c. However, these changes seem too large to be viable alternatives. Of course, as suggested by others, the discrepancy could also be due to a repulsion between nearest neighbors. This repulsion would lengthen T_1 because particles would

TABLE II. Values of T_1 at the T_1 minimum in msec for $PdH_{0.7}$. Experimental values have conduction electron relaxation subtracted off.

Theory	$\omega\tau_c$	T_1 (7 MHz)	T_1 (11 MHz)	T_1 (47 MHx)
Experiment		11.9 ± 0.4	19.4 ± 0.8	77 ± 6
SRT (*I-I* only)	1.23	9.71	15.25	65.17
RW (*I-I* only)	1.03	10.57	16.62	71.00
MF (*I-I* only)	0.95	10.52	16.54	70.65
MS (*I-I* only)	0.83	10.92	17.16	73.34
MS (*I-I* + *I-S*)	0.85	10.64	16.71	71.91

tend, on the average, to stay further apart. With a small concentration of vacancies this effect would be nonexistent because essentially all protons would have to have nearest neighbors. Thus we would expect this effect to be of order $\bar{c}^2$ which, for the present case, would be a 10% effect.

Another meaningful comparison with experiment can be made at high temperatures ($\omega\tau_c\to0$), where both diffusion and T_1 measurements have been made. In this limit the ratio of diffusion constant to T_1 is independent of Γ_c and, is given by the equation

$$\frac{D}{T_1}=\frac{Af_t(c)a_0^2}{Z}\left\{b_0(0)+\frac{B}{A}a_0(0)\right\}, \qquad (29)$$

where $f_t(c)$ is the tracer correlation factor of Eq. (24). The MS theory for $PdH_{0.7}$ with $a_0=4.04$ Å gives

$$\frac{D}{T_1}=21.25\times10^{-7}(\text{cm/sec})^2 .$$

In Table III, the experimental and theoretical values are listed using $D=9.0\times10^{-4}e^{-0.228}\,\text{ev}/k_BT\,\text{cm}^2/\text{sec}$ as given by Seymour, Cotts, and Williams.[12] However, as discussed in Ref. 2, the asymptotic values on the low-frequency (high-temperature) side of the T_1 minimum are not reached very quickly. Thus we have had to correct the value of D/T_1 by a factor δ to take this into account.

In this case the agreement between our MS theory and the experimental results is quite good although there is a 20% scatter in the experimental values of D/T_1. However, at frequencies of 11 and 7 MHz, the agreement is to within 2%. On the other hand, the three other theories give values of D/T_1 that are consistently significantly less than the measured values. The agreement with the T_1 data in Ref. 13 is roughly similar.

It is somewhat difficult to reconcile this good agreement with the discrepancies in T_{1m}. If, for example, the theoretical values of T_1 were raised by

TABLE III. Comparison of the experimental values of D/T_1 in the high-temperature regime with the theoretical values of various hopping models. The quantity δ is a model dependent quantity which is used to adjust the theoretical asymptotic values to small but finite values of $\omega\tau_c$.

Experiment			Theoretical asymptotic ($\omega\tau_c\to0$) $(D/T_1)_{asy}$				Nonasymptotic adjustment factor δ				Theory $\delta(D/T_1)_{asy}$			
ν (MHz)	T (°K)	D/T_1	SRT	RW	MF	MS ($c=0.7$)	SRT	RW	MF	MS ($c=0.7$)	SRT	RW	MF	MS ($c=0.7$)
47	329	15.1	9.64	17.7	18.7	21.3	0.969	0.748	0.795	0.760	9.34	13.3	14.8	16.2
47	318	15.9	9.64	17.7	18.7	21.3	0.938	0.680	0.701	0.678	9.04	12.8	13.1	14.4
47	311	13.8	9.64	17.7	18.7	21.3	0.932	0.661	0.684	0.665	8.98	11.7	12.8	14.2
11	321	18.7	9.64	17.7	18.7	21.3	0.996	0.865	0.879	0.866	9.60	15.3	16.4	18.4
11	308	17.7	9.64	17.7	18.7	21.3	0.993	0.843	0.855	0.846	9.57	14.9	16.0	18.0
7	324	19.3	9.64	17.7	18.7	21.3	0.995	0.909	0.918	0.919	9.59	16.1	17.1	19.6

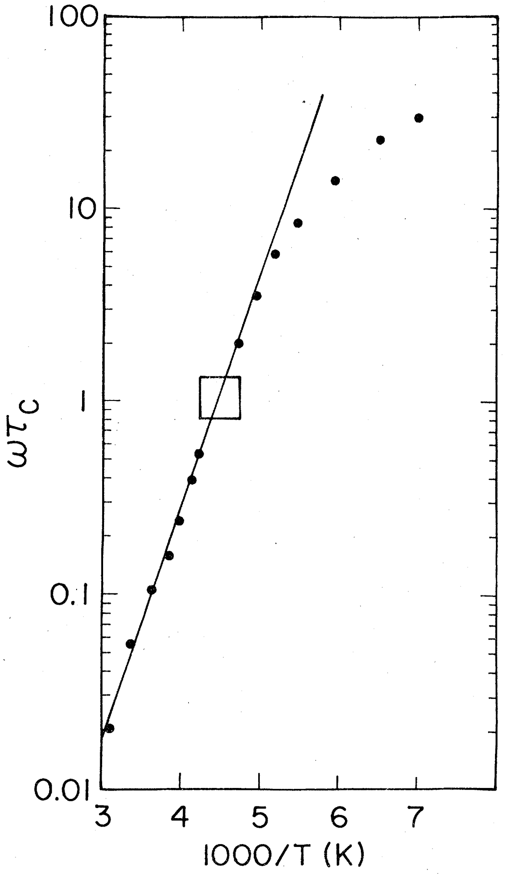

FIG. 2. Log $\omega\tau_c$ vs $1/T(K)$ for $PdH_{0.7}$.

about 10% for all values of $\omega\tau_c$ the experimental and theoretical values of T_{1m} would agree. However, the theoretical values of D/T_1 for the MS theory would be too small and the values of D/T_1 for the other theories would be even worse. It is also hard to believe that any effects due to repulsion could change D and $1/T_1$ by the same factor. At present, we have no solution to this dilemma.

The temperature dependence of Γ_0 can also be found using the experimental values of T_1 and temperature and comparing with the MS values of T_1 and $\omega\tau_c$. Our MS results were multiplied by an overall constant factor to give the exact T_1 minimum as reported by Cornell and Seymour at 7 MHz. In Fig. 2, log $\omega\tau_c$ is plotted versus $1/T$. The straight line segment at high temperaures gives an activation energy of 0.25 eV if an Arrhenius relation is assumed. Note that the Arrhenius behavior is obtained on both sides of the T_1 minimum but cease at about 200 °K. Points very near the T_1 minimum are not included because T_1 vs $\omega\tau_c$ is very flat near the minimum. Any differences then, between theory and experiment, could lead to large variations in the "derived" $\omega\tau_c$. Results similar to these were obtained by Torrey[14] using a random walk approximation at $c = 0.64$. Torrey finds the knee at 220 °K.

These comparisons between theory and experiment give credibility to the simple hopping model in PdH_x. For instance, as mentioned in Sec. I, the simple hopping model ignores any possibility that there may be a repulsion or nearest neighbors to be simultaneously occupied. This repulsion should lengthen the time T_1 considerably, because particles would tend to be, on the average, further apart making their dipolar interaction weaker. Our values at the T_1 minimum, possibly allow for this to be taking place, but it must be a very weak effect because of the short ranged $1/r^6$ dependence.

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