

Correlation functions for simple hopping among the octahedral and tetrahedral sites in a body-centered-cubic lattice

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The correlation functions for one and a pair of specific particles are calculated for an ensemble of particles making nearest-neighbor simple jumps among the tetrahedral and octahedral interstitial sites in a bcc lattice. These 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. Our results are compared to previous theories and to existing experimental results.

I. INTRODUCTION

In previous publications^{1,2} we have used our hopping formalism to obtain expressions for the correlation functions describing the motion of a single and a pair of specific (distinguishable) particles in an ensemble of particles making nearest-neighbor simple jumps in sc and fcc lattices. These expressions were then used to calculate NMR T_1 spin-relaxation times which were compared to experimental results on metal hydrides. In this paper we apply our formalism to perform similar calculations and comparisons for particles occupying the octahedral (O) and tetrahedral (T) interstitial sites in a bcc lattice. Thus the results apply directly to a number of transition-metal hydrides in the α or α' phases.

As in our previous work, the calculations described in this paper are based on the "simple hopping model" which is defined in Ref. 3. 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 the time nor on the occupancy of sites other than α and β . Obviously there is a question of whether this is a good model for any given substance. We note that the O sites and especially the T sites in bcc transition-metal hydrides are very close together and thus are prime candidates for looking for the effects of repulsive interactions. However, in order to make meaningful comparisons of theory and experiment, one needs accurate theoretical predictions. As discussed in detail in earlier work,^{1,2} there are a number of approximations used when working with the simple hopping model. These approximations include the single-relaxation-time (SRT) approximation, the random-walk (RW) approximation, the mean-field (MF) approximation, and the multiple-scattering (MS) approximation. The MF approximation is exact at low concentrations (c) of particles and high frequencies and the MS approximation is good to about 1% at all concentrations. On

the other hand, even at small concentrations of particles, the SRT and RW approximations introduce errors of 300% and 30%, respectively, in calculations of T_1 due to like-spin dipolar interactions for the lattices under consideration here. At higher concentrations these errors increase.

In the rest of this section we shall briefly discuss the relevant correlation functions and their relationship to T_1 dipolar relaxation. Section II contains a description of the calculation and may be omitted by readers not interested in the calculational details. Section III contains a discussion of the results and a comparison with existing experimental data.

The necessary correlation functions are discussed in detail in Refs. 1 and 2. The single specific particle correlation function is defined as

$$D(\vec{R}_\alpha, \vec{R}_\beta; t) = \langle \rho_{i\alpha}(t) \rho_{i\beta}(0) \rangle \Theta(t), \quad \rho_{i\alpha} = N^{1/2} p_{i\alpha}, \quad (1)$$

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

$$G(\vec{R}_\alpha, \vec{R}_{\bar{\alpha}}, \vec{R}_\beta, \vec{R}_{\bar{\beta}}) = \langle \rho_{i\alpha}(t) \rho_{j\bar{\alpha}}(t) \rho_{i\beta}(0) \rho_{j\bar{\beta}}(0) \rangle \Theta(t). \quad (2)$$

Since we only want the correlations between the particles, we shall ultimately use a form G which is averaged over all initial and final center-of-mass positions. In this paper we consider the spin-relaxation time T_1 of the hopping spins due to the motionally altered dipolar interaction. There are two contributions to this quantity and we write

$$(1/T_1) = [1/T_1(I-I)] + [1/T_1(I-S)]. \quad (3)$$

The quantity $T_1(I-I)$ is due to the dipolar interaction

among the I spins which are hopping and $T_1(I-S)$ is due to the dipolar interaction between the hopping (or I) spins and the stationary (or S) spins if any exist. $T_1(I-S)$ is not explicitly dependent on c , the concentration of hopping particles, but it does depend on c through the correlations described in D . The quantity $1/T_1(I-I)$ is explicitly proportional to c and has a further c dependence through the correlations described in G . We would expect $T_1(I-I)$ to be affected by interactions among the hopping particles and, even at small concentrations, would be drastically affected even if $T_1(I-S)$ was not. This point will be discussed further in Sec. III.

Finally, as a matter of notation, c is defined as the number of hopping particles divided by the number of available sites. On the other hand in formulas such as $M-H_x$, x denotes the number of hopping particles (hydrogen) divided by the number of host atoms (M). In the case of the O and T interstitial sites in a bcc lattice, $c = \frac{1}{3}x$ and $\frac{1}{6}x$, respectively, because a unit cell contains three octahedral sites or six tetrahedral sites.

II. CALCULATION

In this section we describe the calculations for the correlation functions and for the spin-lattice relaxation times. The two approximations that we use in this section, the MF and MS, have been extensively discussed in earlier publications.^{1,2} Thus, in this paper, we shall mainly focus on the computational complications that arise for non-Bravais lattices.

The O and T lattice sites can be described as a bcc lattice with a basis with three basis sites for the O case and six for the T case. In both cases the number of nearest neighbors is four. The location of these sites is shown in Fig. 1 which also shows our convention for numerically labeling these sites. Each site α is designated as

$$\alpha = (\bar{T}_\alpha, i_\alpha) \quad (4)$$

where \bar{T}_α is a lattice vector for the unit cell and i_α is the basis index. The four-nearest-neighbor sites to a given basis site in the cell at $\bar{T}=0$ are listed in Table I. From this table the hopping rates $\Gamma_{\alpha\beta} = \Gamma_{i_\alpha, i_\beta}(\bar{T}_\alpha, \bar{T}_\beta)$ can be constructed and Fourier transformed according to the usual prescription

$$A_{i_\alpha, i_\beta}(\bar{q}) = \sum_{\bar{T}_\alpha} A_{\alpha\beta} \exp[-i\bar{q} \cdot (\bar{T}_\alpha - \bar{T}_\beta)] \quad (5)$$

The results for the O sites are

$$\Gamma_{ii}(\bar{q}) = 0 \quad (6)$$

$$\Gamma_{ij}(\bar{q}) = \Gamma_{ji}^*(\bar{q}) = 2\Gamma_0 \cos Q_k \exp[i(Q_i - Q_j)] \quad (6)$$

$$\bar{Q} = \frac{1}{2} \bar{q} a_0 \quad (6)$$

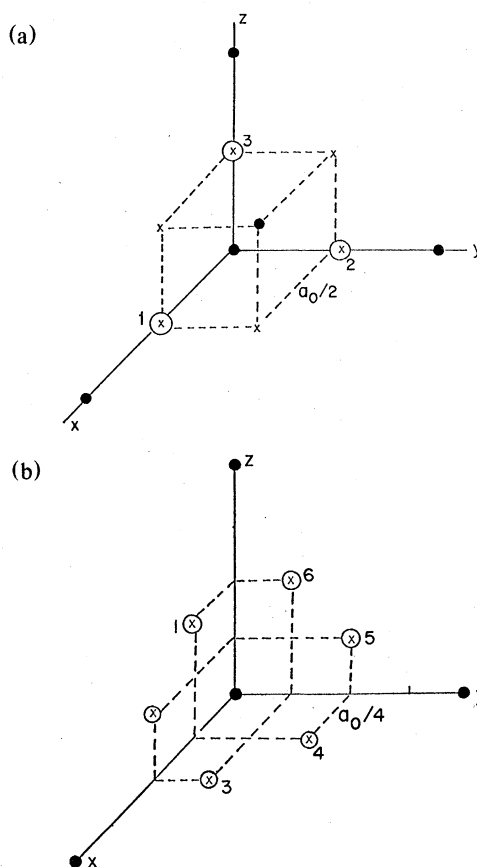


FIG. 1. (a) Position of the octahedral interstitial sites in a bcc lattice. The solid dots represent the host lattice and the interstitial sites are denoted by x . The three octahedral sites which belong to the unit cell at $\bar{T} = (0, 0, 0)$ are circled and labeled 1, 2, and 3. (b) Position of the tetrahedral interstitial sites in a bcc lattice. The solid dots represent the host lattice and the interstitial sites are denoted by x . The six tetrahedral sites which belong to the unit cell at $\bar{T} = (0, 0, 0)$ are circled and labeled 1-6.

where i, j , and k are cyclic variations of 1, 2, and 3, and Γ_0 is the rate for a particle at a given site to hop to an unoccupied nearest neighbor. For the T case, using the notation in Fig. 1 and Table I, we obtain

$$\Gamma_{ij}(\bar{q}) = \Gamma_0 \begin{pmatrix} 0 & 1 & e_z & 0 & e_y^* & 1 \\ 1 & 0 & 1 & e_y^* & 0 & e_x \\ e_z^* & 1 & 0 & 1 & e_x & 0 \\ 0 & e_y & 1 & 0 & 1 & e_z^* \\ e_y & 0 & e_x^* & 1 & 0 & 1 \\ 1 & e_x^* & 0 & e_z & 1 & 0 \end{pmatrix} \quad (7)$$

$$e_x = \exp[i(Q_x - Q_y - Q_z)] \quad (7)$$

with cyclic variations.

TABLE I. Tables show the four possible hops a particle at ($\vec{T}=0, i_0$) can make. (a) shows the possible hops between O sites and (b) shows the possible hops between T sites. The bcc lattice vectors $\vec{T}_x, \vec{T}_y,$ and \vec{T}_z define the unit cells at $\frac{1}{2}a_0(-1, 1, 1), \frac{1}{2}a_0(1, -1, 1),$ and $\frac{1}{2}a_0(1, 1, -1),$ respectively.

Position before hop i_0	\vec{T}_{1,i_1}	Position after hop \vec{T}_{2,i_2}	\vec{T}_{3,i_3}	\vec{T}_{4,i_4}
(a) O sites				
1	$\vec{T}_y, 2$	$\vec{T}_z, 3$	$-\vec{T}_x, 2$	$-\vec{T}_x, 3$
2	$\vec{T}_z, 3$	$\vec{T}_x, 1$	$-\vec{T}_y, 3$	$-\vec{T}_y, 1$
3	$\vec{T}_x, 1$	$\vec{T}_y, 2$	$-\vec{T}_z, 1$	$-\vec{T}_z, 2$
(b) T sites				
1	$\vec{o}, 2$	$\vec{o}, 6$	$-\vec{T}_z, 3$	$\vec{T}_y, 5$
2	$\vec{o}, 3$	$\vec{o}, 1$	$\vec{T}_y, 4$	$\vec{T}_x, 6$
3	$\vec{o}, 4$	$\vec{o}, 2$	$-\vec{T}_x, 5$	$\vec{T}_z, 1$
4	$\vec{o}, 5$	$\vec{o}, 3$	$\vec{T}_z, 6$	$-\vec{T}_y, 2$
5	$\vec{o}, 6$	$\vec{o}, 4$	$\vec{T}_y, 1$	$\vec{T}_x, 3$
6	$\vec{o}, 1$	$\vec{o}, 5$	$\vec{T}_x, 2$	$-\vec{T}_z, 4$

First we consider $D_{ij}(\vec{q}, \omega)$ the correlation function for a single specific particle. As in previous work, it is convenient to define this correlation function in terms of a self-energy or memory function $K_{ij}(\vec{q}, \omega)$ by the equation

$$\sum_k [\omega \delta_{ik} + iK_{ik}(\vec{q}, \omega)] D_{kj}(\vec{q}, \omega) = i \delta_{ij} \quad (8)$$

In the MF approximation the equation for K is particularly simple, taking the form

$$K_{ij}(\vec{q}, \omega) = \bar{c} \omega_{ij}(\vec{q}, \omega) \quad (9)$$

$$\omega_{ij}(\vec{q}, \omega) = 4\Gamma_0 \delta_{ij} - \Gamma_{ij}(\vec{q}) \quad ,$$

where $\bar{c} = 1 - c$ is the concentration of vacancies. In this approximation any site neighboring the site that the specific particle occupies is assigned a probability of c of being occupied. The inversion of Eq. (8) is straightforward but even in the MF approximation, somewhat messy. Readers interested in such algebraic details should consult Ref. 4.

As noted earlier, the mean-field approximation for D is exact in the limit as $c \rightarrow 0$. In the transition-

metal hydrides $M - H_x$, x is usually less than one in the α or α' phases. This means that $c < \frac{1}{3}$ if the O sites are occupied and $c < \frac{1}{6}$ if the T sites are occupied. For concentrations that are this small, we have found that rather simple corrections to Eq. (9) yield almost as good results as the much more complicated MS approximation. In fact, within the concentration limits stated above, the lowest-order Padé approximate yields results that are good to 1%. This approximation takes the form

$$K_{ij}(\vec{q}, \omega) = \bar{c} \omega_{ij}(\vec{q}) [1 - c \alpha_0 / (1 - 2i \alpha_0 \omega / \Gamma_0)] \quad (10)$$

$$\alpha_0 = 2 / (6 - c) \quad .$$

Next we consider the correlation function for a pair of specific particles. $G(\alpha, \beta; \vec{\alpha}, \vec{\beta}; \omega)$ is Fourier transformed in space as

$$\begin{aligned} \bar{G}_{ij\bar{j}}(q, q'; \omega) = N^{-2} \sum G(\alpha, \beta; \vec{\alpha}, \vec{\beta}) \\ \times \exp[-i\vec{q} \cdot (\vec{T}_\alpha - \vec{T}_\beta) \\ - i\vec{q}' \cdot (\vec{T}_{\bar{\alpha}} - \vec{T}_{\bar{\beta}})] \quad , \quad (11) \end{aligned}$$

where

$$\alpha = (\bar{I}_\alpha, i), \quad \beta = (\bar{I}_\beta, j), \quad \bar{\alpha} = (\bar{I}_{\bar{\alpha}}, \bar{i}), \quad \bar{\beta} = (\bar{I}_{\bar{\beta}}, \bar{j}),$$

and the summation is over all four \bar{I} 's. Thus the initial and final center-of-mass unit-cell positions are averaged over but not the basis indices. We have found it convenient to express \bar{G} as

$$\bar{G}_{ij\bar{j}}(\bar{q}, \bar{q}'; \omega) = N \delta_{\bar{q}, \bar{q}'} \bar{G}_{ij\bar{j}}^{(0)}(\bar{q}, \omega) + \Delta G_{ij\bar{j}}(\bar{q}, \bar{q}'; \omega), \quad (12)$$

$$\bar{G}_{ij\bar{j}}^{(0)}(\bar{q}, \bar{\omega}) = \int \frac{d\bar{\omega}}{2\pi} D_{i\bar{i}}(\bar{q}, \bar{\omega}) D_{j\bar{j}}(-\bar{q}, \omega - \bar{\omega}), \quad (13)$$

where D is the correlation function for a single specific particle. The first term in Eq. (12) describes a situation where each of the specific particles propagates independent of the other and $\Delta \bar{G}$ contains the corrections to this picture. In the limit as $c \rightarrow 0$, the MF approximation for D is exact and is equivalent to the RW approximation. The RW approximation for \bar{G} consists of the first term in Eq. (12). However, this approximation is in error even as $c \rightarrow 0$. In earlier work we have found that ΔG introduces corrections of order $1/z$ where z is the number of nearest neighbors to a given site. This rule is also true in the present case.

Our approximation for $\Delta \bar{G}$ is the same as that used in earlier publications with appropriate modifications for the present lattices. It can be written

$$\begin{aligned} \Delta G_{ij\bar{j}}(\bar{q}, \bar{q}'; \omega) = & 2\bar{c} \sum_{kl, \bar{k}\bar{l}} G_{ijkl}^{(0)}(\bar{q}, \omega) \\ & \times [\Gamma_{kl}(\bar{q}) \Delta_{kl\bar{k}\bar{l}}(\omega) \Gamma_{\bar{k}\bar{l}}(\bar{q}')] \\ & \times G_{kl\bar{j}}^{(0)}(\bar{q}', \omega), \end{aligned} \quad (14)$$

where

$$\begin{aligned} \Delta_{ij\bar{j}}(\omega) = & \left(\delta_{i\bar{i}} \delta_{j\bar{j}} - \frac{2\bar{c}}{\Gamma_0} \frac{1}{N} \sum_q [\Gamma_{ji}(\bar{q}) \bar{G}_{ij\bar{j}}^{(0)}(\bar{q}, \omega) \right. \\ & \left. \times \Gamma_{j\bar{j}}(\bar{q}) \right]_{ij\bar{j}}^{-1}. \end{aligned} \quad (15)$$

Equations (14) and (15) give a complete, albeit complex, description of our approximation. Some additional comments on making the matrix inversion more manageable can be found in Ref. 4.

Finally, after obtaining D and \bar{G} , they can be inserted into standard expressions for $T_1(I-S)$ and $T_1(I-I)$, respectively. This is straightforward but tedious manipulations are again described in Ref. 4. We shall present the results of the numerical evaluations in Sec. III.

III. RESULTS

In this section we present the results of the calculations described in Sec. II, discuss these results, and

make comparisons with existing experimental data. These results are good to about 1%.

Since we are dealing with a lattice with cubic symmetry the results can be conveniently expressed as^{3,4}

$$1/T_1(I-I) = (A/\omega) [g_0(\omega\tau_c) + hg_1(\omega\tau_c)], \quad (16)$$

$$1/T_1(I-S) = (B/\omega) [f_0(\omega\tau_c) + hf_1(\omega\tau_c)],$$

where

$$\begin{aligned} A &= I(I+1)\hbar^2\gamma_I^4c/a_0^6, \\ B &= S(S+1)\hbar^2\gamma_I^2\gamma_S^2Q/a_0^6, \end{aligned} \quad (17)$$

$$h = \sum_i \gamma_i^4 - \frac{3}{5}.$$

In these equations the mobile atoms have a spin I and gyromagnetic ratio γ_I while S and γ_S are the corresponding quantities for the host spins. The quantity a_0 is the length of a cube edge, c is the concentration of mobile atoms, and Q is the concentration or natural abundance of host spin S . The γ_i are the direction cosines of the static magnetic field with respect to the cubic axes and the angular average of h is zero. Finally, ω is the frequency of experiment and the correlation time τ_c is defined in terms of the basic hopping rate Γ_0 by

$$1/\tau_c = 4\bar{c}\Gamma_0. \quad (18)$$

The functions g_0 and g_1 depend only on the dimensionless variable $\omega\tau_c$ but the functions f_0 and f_1 also depend on the ratio of the gyromagnetic ratios Δ , where

$$\Delta = \gamma_S/\gamma_I. \quad (19)$$

For example, $\Delta = 0.244$ for NbH_x .

In many cases only the asymptotic forms of the f 's and g 's for large and small $\omega\tau_c$ are of interest.⁵ In these limiting cases it is convenient to express the results as

$$\left. \begin{aligned} g_m(x) &\rightarrow b_m(\infty)/x \\ f_m(x) &\rightarrow a_m(\infty)/x \end{aligned} \right\}, \quad x \gg 1 \quad (20)$$

and

$$\left. \begin{aligned} g_m(x) &\rightarrow b_m(0)x \\ f_m(x) &\rightarrow a_m(0)x \end{aligned} \right\}, \quad x \ll 1, \quad (21)$$

where $m = 0$ or 1 . The quantities $b_1(0)$ and $a_1(0)$ are zero and $a_0(0)$ is independent of Δ while $a_m(\infty)$ are proportional to $k_m(\Delta)$ where

$$\begin{aligned} k_0(\Delta) &= 0.6(1+\Delta)^{-2} + 0.3 + 0.1(1-\Delta)^{-2}, \\ k_1(\Delta) &= (1+\Delta)^{-2} - 2 + (1-\Delta)^{-2}. \end{aligned} \quad (22)$$

The nonzero a_m and b_m are compiled in Table II. For purposes of comparison we have included the values

TABLE II. The dimensionless constants $b_\alpha(0)$, $b_\alpha(\infty)$, $a_\alpha(0)$, and $a_\alpha(\infty)$ defined by Eqs. (20) and (21) for various theories of hopping. The a 's and b 's are listed for both the octahedral (O) and tetrahedral (T) models of site occupancy. The abbreviations SRT, RW, MF, and MS are used, respectively, for the single-relaxation-time approximation, the random-walk approximation, the mean-field approximation, and the multiple-scattering approximation. Only the MS approximation depends explicitly on the atomic fraction x . The quantities $a_1(0)$ and $b_1(0)$ are zero for all theories and $k_m(\Delta)$ is given by Eq. (22).

Theory	$b_0(0)$	$b_0(\infty)$	$b_1(\infty)$	$a_0(0)$	$a_0(\infty)/k_0(\Delta)$	$a_1(\infty)/k_1(\Delta)$
<i>T</i> sites						
SRT	2485	3976		195.2	195.1	
RW (any x)	5178	3117	660	712.0	100.0	3.36
MF (any x)	6478	2298	468	712.0	100.0	3.36
MS ($x=0$)	6478	2298	468	712.0	100.0	3.36
MS ($x=0.3$)	6589	2298	468	724.2	100.0	3.36
MS ($x=0.6$)	6705	2298	468	737.0	100.0	3.36
MS ($x=0.9$)	6829	2298	468	750.5	100.0	3.36
<i>O</i> sites						
SRT	376.7	588.3	-483.3	226.1	226.1	
RW (any x)	852.0	449.9	-310.9	460.0	178.1	49.3
MF (any x)	1029.0	347.5	-214.9	460.0	178.1	49.3
MS ($x=0$)	1029.0	347.5	-214.9	460.0	178.1	49.3
MS ($x=0.3$)	1065.0	347.5	-214.9	476.1	178.1	49.3
MS ($x=0.6$)	1107.0	347.5	-214.9	494.1	178.1	49.3
MS ($x=0.9$)	1156.0	347.5	-214.9	514.1	178.1	49.3

for the SRT and RW theories as well as our results. Since the concentration of hopping particles is rather small in all the cases considered, the dependence of x or c is not very great. Further, the tracer correlation factor in this regime is given by the formula

$$f_t = (6 - 3c)/(6 - c) \quad (23)$$

As mentioned in Sec. II, the random-walk model does not adequately describe the hopping of a pair of specific particles even when the concentration approaches zero. The effect of these correlations on $T_1(I-I)$ can be studied by examining the behavior of g_0 in Eq. (16). In Fig. 2 this function g_0 is plotted using a random-walk model for hopping and our mean-field theory which is exact as $c \rightarrow 0$. The mean-field correction to the random walk, Δg_0 , is defined by

$$g_0(\text{MF}) = g_0(\text{RW}) + \Delta g_0 \quad (24)$$

The first point to note about Fig. 2 is that the maximum value of g_0 [minimum value of $T_1(I-I)$] is

approximately the same in both models. This fact that T_1 at the T_1 minimum is nearly the same for any hopping model (even the SRT approximation) has appeared in every system we have studied. The second point to note about Fig. 2 is that the MF curve appears shifted from the RW result by nearly a

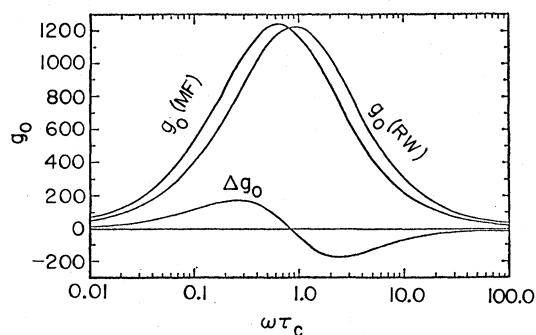


FIG. 2. A plot of $g_0(\omega\tau_c)$ in the mean-field (MF) and random-walk (RW) approximations assuming tetrahedral occupation in a bcc lattice. The difference between them, Δg_0 , is defined by Eq. (24).

constant amount. This can be physically interpreted as a shift in the hopping rate due to the correlations between the two particles. If the two hopping spins are nearest neighbors, the effective hopping rate for one of them out of its present site is reduced from $4\Gamma_0$ to $3\Gamma_0$. This obtains because hops to neighboring occupied sites are not allowed. These short-range correlations are extremely important since $1/T_1$ depends on d^{-6} , where d is the distance between the two hopping spins. Keeping the above two points in mind, it is clear that $T_1(I-I)$ in the asymptotic region is strongly dependent on correlations in the motion but that $T_1(I-I)$ at the minimum is not.

The discussion to this point ignores the possibility of interactions between the hopping particles except for the exclusion of double occupancy. Since the interstitial sites in a bcc lattice are quite close together, one might easily expect interactions, especially nearest-neighbor repulsion, to be important. However, at low concentrations, we would expect relatively minor effects on D , which describes the motion of a single specific particle. Thus we would expect only small changes in $T_1(I-S)$. On the other hand, we would expect strong interactions to have a dramatic affect on G and thus on $T_1(I-I)$. This should be obtained even at small concentrations because the largest part of the $T_1(I-I)$ relaxation occurs when pairs of particles are nearest neighbors.

Usually measurements of the dipolar part of T_1 for a metal hydride in the α or α' phases cannot be carried out over a wide temperature range. This occurs because at high temperatures the conduction electrons will dominate the spin relaxation and at low temperatures the α or α' phases cease to exist. Further, a serious comparison of theory and experiment would involve an independent measurement of τ_c . For these reasons, the ratio D/T_1 is especially important since it is independent of τ_c if $\omega\tau_c \ll 1$. For the two lattices considered this ratio is

$$D/T_1 = \alpha a_0^2 f_1 [Ba_0(0) + Ab_0(0)] \quad (25)$$

where $\alpha = \frac{1}{48}$ for the T sites and $\frac{1}{12}$ for the O sites.

Although it is generally agreed^{6,7} that hydrogen in the α and α' phases of Nb and V occupy the T sites, we shall include the possibility of O site occupation in our comparison with existing experimental results. For example, Table II can be used to reinterpret the work of Zogel and Cotts on NbH_{0.6} at high temperatures.⁸ Table III contains various theoretical and experimental values of D/T_1 at 103°C. The Torrey⁹ theory is a random-walk theory with a number of additional mathematical approximations.

The first point to note about Table III is that except for the SRT approximation, D/T_1 is nearly the same for either model of site occupancy. This occurs because both T_1 and D for the T sites is about one-half the value of the corresponding quantity for the O

TABLE III. A comparison between theory and experiment of D/T_1 in the high-temperature limit for NbH_{0.6}. Experimental values of T_1 have been corrected by subtracting off the electron contribution.

Lattice	SRT	D/T_1 (10^{-5} cm ² /sec ²)	
		Approximation Torrey	MS
O sites	0.67	1.27	1.44
T sites	0.41	1.14	1.33
Experiment	1.5 ± 0.2		

sites. This coincidence occurs largely because of the difference in the $I-I$ interaction. Unfortunately both models of site occupancy give values in the MS approximation which are within the experimental error. Although from these data alone it is difficult to determine the site location of the hydrogen, it does show that any possible repulsion between hydrogen must be smaller than expected by using the Torrey theory. Zogel and Cotts describe a modified Torrey model in which the probability of two-nearest-neighbor sites to be simultaneously occupied is zero. This modification appears to be necessary to bring the Torrey results in agreement with experiment. However this modification is unnecessary to bring the MS results within experimental error. The $T_1(I-I)$ contribution to D/T_1 assuming T site occupation is about $\frac{1}{3}$ of the total.

The high-temperature asymptote may also be applied to T_1 measurements¹⁰ of Lütgemeier, Arons, and Bohn in NbH_{0.03} in the temperature range 200–475 K at 44.4 MHz. The hopping rate for this system is so great that no minimum of T_1 appears. The analysis of their data is further complicated by the fact that the electron contribution dominates over much of the temperature range. Also, measurements of the diffusion constant by Schauman, Völkl, and Alefeld¹¹ indicate that the diffusion constant has a change in activation energy which occurs at around 300 K. Although there is considerable scatter in the T_1 data making a precise evaluation of the electron contribution difficult, the experimental ratio of D to T_1 is $D/T_1 = 1.9 \pm 0.2 \times 10^{-5}$ cm²/sec². This ratio was taken in the temperature range of 200–300 K where T_1 is dominated by dipolar interactions. The MS approximation gives $D/T_1 = 1.38 \times 10^{-5}$ cm²/sec² for the O sites and 1.08×10^{-5} cm²/sec² for the T sites.

This large discrepancy between theory and experiment is very difficult to understand. Since the concentration is small, the interaction is almost entirely $I-S$ and the hopping may be described as a random

walk. The disagreement is not altered substantially if the hydrogen occupation is not totally random due to a slight attraction or repulsion. The electron contribution appears to have been taken into account properly since the experimental D/T_1 is constant to within 5% in the region 250–200 K.

To agree with experiment, the theory needs to increase the diffusion constant or increase the relaxation rate. The diffusion constant may be increased if longer jumps occur such as jumps to next-nearest neighbors. An increase in the relaxation rate is obtained if other relaxation mechanisms are important such as paramagnetic impurities. A relaxation mechanism unique to interstitial sites is that caused by different static magnetic environments at interstitial sites of the unit cell. An effect similar to this has been discussed in connection with quadrupolar relaxation caused by changes in the electric field gradients.

Since the interstitial sites are not sites of cubic symmetry, the static magnetic field due to polarization of nuclear or electron spins does not vanish at these sites nor is each site equivalent. Thus a particle hopping within the unit cell sees fluctuations in the magnetic field allowing it to relax. It is difficult to estimate the size of this effect, however, it must be proportional to $(\chi H_0)^2$ where χ is the static susceptibility and H_0 the static field. Unlike the high-temperature limit of the I - S dipolar coupling which we considered, this mechanism depends on the magnetic field or ω .

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