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## On the theory of spin–lattice relaxation due to the hopping motion of light interstitials; the role of excited states

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**Abstract.** The dipolar contribution to the spin–lattice relaxation rate  $\Gamma_1$  of spin-carrying light interstitials is calculated assuming nearest-neighbour hopping among tetrahedral sites of a BCC lattice. As a new element, which was missing in previous treatments, we took into account explicitly the existence of localized excited states of the interstitials. The model considers two states per site, i.e., the ground state and one excited state, and takes into account transitions between the ground states, the excited states, and between an excited level and a ground state of two neighbouring interstitial sites as well as intrasite transitions between ground and excited states of the same site. If the intrasite transitions from the ground to the excited state are not fast compared with the tunnelling rate among the ground states of neighbouring tetrahedral sites, which is likely to be the case for hydrogen in BCC metals like Nb and Ta, the extended model predicts deviations from the results obtained for the usually considered model which describes the interstitial motion by a single effective hopping frequency among tetrahedral sites. The product  $\alpha = \Gamma_1 D$ , in which  $D$  is the diffusivity of the interstitial, may be considerably larger for the extended model than for the single-hopping-frequency model. Moreover the various hopping frequencies do not drop out from  $\alpha$  as does the effective hopping frequency in the latter case. This may lead to a strong increase of  $\alpha$  with temperature in contrast to the temperature independence of  $\alpha$  for the single-frequency model. The theoretical results are compared qualitatively with NMR experiments performed on the  $\alpha$ -phases of NbH<sub>x</sub> and TaH<sub>x</sub>.

### 1. Introduction

During the past few years considerable effort has been spent on the investigation of the diffusion of hydrogen and its isotopes in metals. Marked deviations from the predictions of the classical rate theory have been found which indicate that the diffusion of light particles is affected in an essential manner by quantum effects. In many cases this is true even at high temperatures.

A powerful technique for studying the diffusion of hydrogen (or its isotopes) is nuclear magnetic resonance (NMR) (see, e.g., Messer *et al* 1986 or Cotts 1978). The diffusion of positive muons ( $\mu^+$ , where  $\mu^+$  can actually be regarded as a light hydrogen isotope for our purposes) may be investigated by the related  $\mu^+$ SR (muon spin rotation, relaxation) method (see, e.g., Seeger 1984 or Schenk 1985). The hydrogen motion is detected via its effect on the proton (deuteron, triton) spin relaxation rates,

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which is due to the fact that diffusion of spin carriers (the hydrogen nuclei or the  $\mu^+$ ) leads to a random time-dependent modulation of the spin-dependent interaction. In order to interpret spin relaxation rates in terms of diffusion processes their relation to microscopic diffusion models has to be established.

For testing theories of quantum diffusion it is desirable to investigate samples containing hydrogen in very low concentrations ( $< 1\%$ ) in order to minimize the hydrogen-hydrogen interaction which otherwise would make it difficult to identify the elementary diffusion processes. It is the purpose of this paper to give expressions for the hydrogen spin relaxation rates in this concentration regime and for a certain microscopic diffusion model to be specified below. We restrict our treatment to situations where hydrogen is dissolved in para- or diamagnetic samples and where the spin-lattice relaxation rate,  $\Gamma_1$ , is determined by the interaction between the magnetic dipole moments of the hydrogen nuclei and the magnetic moments of the host nuclei. This dipolar contribution to  $\Gamma_1$  is directly related to the diffusion of hydrogen. We further confine ourselves to the regime where diffusion proceeds by small-polaron hopping and we thus exclude coherent propagation. For hydrogen, and even muons, the hopping regime extends down to the lowest temperatures investigated so far with the possible exception of local tunnelling centres (see, e.g., Wipf *et al* 1984, 1987).

To our knowledge all previous discussions relating nuclear spin relaxation rates with small-polaron hopping proceeded as for classical over barrier jumps, i.e., first one considered a number of sites corresponding to local minima of the quasiparticle energy as a function of its spatial coordinates and then one introduced transitions among them described by various hopping frequencies. A difference between quantum motion and classical hopping appears only in so far as the temperature and isotopic dependence of the hopping frequencies is given in the first case by the laws of quantum hopping (see, e.g., Flynn and Stoneham 1970, Teichler 1977, Emin *et al* 1979, Kondo 1984 and Grabert *et al* 1986) whereas in the second case they are given by the classical transition state theory<sup>†</sup>. The hydrogen diffusivity is dominated at low temperatures by tunnelling transitions between the particle ground states of neighbouring sites (Flynn and Stoneham 1970, Teichler 1977 and Grabert *et al* 1986). At higher temperatures, however, transitions between excited states, well separated in energy from the ground state, gain more and more importance (Emin *et al* 1979, Klamt and Teichler 1986). If we want to describe hopping among a particular pair of sites by just one hopping frequency we have to define an effective frequency which is an average over the various contributions weighted according to the thermal occupation of the initial states.

This average description is certainly sufficient as long as one considers diffusion over a macroscopic distance as measured, e.g., by the Gorski effect (Qi *et al* 1983) or by NMR using the pulsed field gradient method (Stejskal and Tanner 1965, Mauger *et al* 1981, Hampele *et al* 1989). Spin relaxation rates, however, are to a large extent determined by the time correlations between a few successive hops. In this case the rate of transitions among the various states which are localized within the 'same potential well' (at the same site)—they will be called intrasite transitions in the following—determines whether the average description is correct. If the intrasite transitions are not fast compared to transitions between different sites a description which regards the various states localized at a specific site as a single entity and which describes

<sup>†</sup> Note, sometimes the finite extension of the hydrogen wave function is taken into account (see Mc Mullen and Zaremba 1978).

hopping to a neighbouring site by an averaged frequency is in general inadequate. Since for hydrogen in metals the energy separation between the lowest excited state and the ground state is usually large compared to a typical phonon frequency of the host lattice many phonons are required to take up the energy imbalance associated with a transition between these levels. Phonon-induced transitions between these levels are therefore expected to be relatively slow. Additional coupling to electrons will speed up the intrasite transitions. However, for the systems considered below (NbH, TaH), there is experimental evidence (see section 2) that the deexcitation transitions, of whatever origin, are not faster, at least, than the tunnelling transitions between the excited states in neighbouring wells. We therefore believe that in many instances the more detailed treatment outlined below is required. This statement should hold similarly for quasielastic neutron scattering on metal hydrogen systems. Indeed one motive for doing the following investigations has been the quasielastic neutron scattering results on NbH and TaH obtained by Lottner *et al* (1979) and one of the interpretations given by these authors. We therefore investigate the consequences that the existence of discrete excited states and the concomitant occurrence of several hopping paths connecting a certain pair of sites may have for spin relaxation rates. Specifically we consider hopping among tetrahedral sites in BCC metals like Nb and Ta and we take into account only two states per site, i.e., the ground state and one further state which exists for several excited states. Our explicit calculations contain the simplifying assumptions that hydrogen is localized point-like at tetrahedral sites for both states, and furthermore we do not take into account lattice distortions in the vicinity of the hydrogen atom.

As is well known (see, e.g., Cotts 1978 or Fedders and Sankey 1978) a simultaneous discussion of the macroscopic diffusivity  $D$  and the spin-lattice relaxation rate  $\Gamma_1$  may give information on the diffusion mechanism. Under suitable experimental conditions (see section 3) the quantity  $\alpha$  which is proportional to the product  $\Gamma_1 D$  is independent of temperature for a simple diffusion mechanism such as in a hopping process between nearest-neighbour tetrahedral sites in the average frequency description. We discuss the conditions under which our model leads to deviations from the simple average frequency description, i.e., under what conditions  $\alpha$  becomes temperature dependent, and we show which kind of deviations may be expected. Through a careful analysis along this line one can hope that existing quantum diffusion theories can be critically tested and existing microscopic diffusion models further developed. Finally we will discuss NMR experiments performed on the  $\alpha$ -phases of Nb and Ta in view of our theoretical considerations.

## 2. The hopping model

The physical picture on which we base our microscopic diffusion model is related to Emin's semi-quantitative treatment of the diffusion of light interstitials (in BCC metals) (Emin *et al* 1979) which is a generalization of Holstein's occurrence probability *ansatz* (Holstein 1959). More quantitative calculations for hydrogen in niobium and tantalum along the same lines have been performed by Klamt and Teichler (1986).

The total transition rate between two sites  $i$  and  $j$  is expressed as

$$\nu_{ij} = \sum_{\nu\mu} \exp(-E_i^\nu/kT) \nu_{ij}^{\nu\mu} / \sum_{\nu} \exp(-E_i^\nu/kT) \quad (2.1)$$

where  $\nu$  and  $\mu$  denote the various particle states (including the corresponding distortion cloud) localized at sites  $i$  and  $j$ ,  $E_i^\nu$  are the corresponding (minimum) energies, and  $\nu_{ij}^{\nu\mu}$  are the transition rates between this special pair of states, calculated with the help of the occurrence probability *ansatz*. In the following we restrict our treatment to hopping between nearest-neighbour tetrahedral (T) sites and thus we will skip the indices  $i$  and  $j$  and write  $\nu$  for the hopping frequency among T sites. The diffusivity is given by

$$D = (a_0^2/12)\nu \quad (2.2)$$

where  $a_0$  is the lattice constant. As pointed out in the introduction this averaged description which uses just one hopping frequency  $\nu$  might be insufficient for the calculation of spin relaxation rates. Therefore  $\nu$  is split into partial contributions. In principle we should introduce all states still reasonably localized within one potential well and all transitions among all states located at nearest-neighbour sites. In the notation of Klamt and Teichler (1986) these would be the ground state (g) and the excited states  $1^y, 1^x, 1^z$  and  $2^y$ . To simplify our treatment without losing the essential physics, we consider only two states per site, i.e., the ground state denoted by T and one further state T' which stands for the assembly of all localized excited states. This subdivision is sensible because the hopping rates  $\nu_{ij}^{\mu\nu}$ , where both  $\mu$  and  $\nu$  are excited states, are usually comparable in magnitude whereas  $\nu_{ij}^{gg}$ , the hopping rate among ground states, may be orders of magnitude smaller. The possible transitions between the levels of two nearest-neighbour sites  $i$  and  $j$  are indicated by the arrows in figure 1. Besides ground state to ground state transitions we have transitions between excited states described by  $\nu_{T'T'}$ , transitions between a ground state and an excited state of neighbouring wells ( $\nu_{TT'}$  and  $\nu_{T'T}$ ), which all lead to a jump between two nearest-neighbour T sites, and intrasite transitions  $\nu_{T'T}^i, \nu_{T'T}^j$ , which do not lead to jumps to neighbouring sites. We may relate  $\nu_{T'T'}$  and  $\nu_{T'T}$  to the hopping frequencies between states introduced in equation (2.1) (we again omit the indices  $i$  and  $j$ ) by

$$\nu_{T'T'} = \sum'_{\nu\mu} [p(\mu)/p_{T'}] \nu^{\mu\nu} \quad \nu_{T'T'} = \sum'_{\nu} \nu^{g\nu} \quad p_{T'} = \sum'_{\nu} p(\nu) \quad (2.3)$$

where  $p(\nu)$  is the probability that state  $\nu$  is occupied. The ground state is denoted by g and the primed summation sign indicates that the ground state is excluded from the sum. Detailed balancing gives us

$$\nu_{T'T} = [p_T/p_{T'}] \nu_{T'T'} \quad (2.4)$$

where

$$p_T = 1 - p_{T'}$$

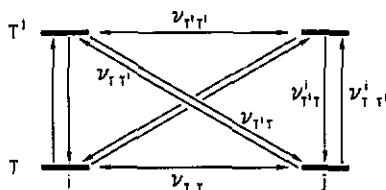


Figure 1. Transitions between the levels of two nearest-neighbour sites  $i$  and  $j$ .

The transitions  $\nu_{T'T}^i$  and  $\nu_{T'T}^i$  do not appear in (2.1) since they do not lead to diffusion.  $\nu_{TT}$  is simply given by  $\nu^{ss}$ . The diffusivity may now be written as

$$D = \frac{a_0^2}{12} [p_T (\nu_{TT} + \nu_{TT'}) + p_{T'} (\nu_{T'T'} + \nu_{T'T})] \quad (2.5)$$

which is equivalent to (2.2) with (2.1). In the following sections we shall assume that the jump distances for all hops, described by  $\nu_{TT}$ ,  $\nu_{T'T'}$ ,  $\nu_{TT'}$  and  $\nu_{T'T}$  are all equal and are given by the distances between nearest-neighbour T sites. Furthermore we assume that the transitions  $\nu_{T'T}^i$  and  $\nu_{T'T}^i$  do not lead to a displacement. Both assumptions are not exactly correct since for the excited states the center of gravity of the probability distribution for the hydrogen position might be slightly shifted from the ideal T position (Klamt and Teichler 1986). Nevertheless (2.5) is still correct since the various shifts average out in the calculation of  $D$ . The spin-lattice relaxation rate (see section 3), however, could be (slightly) affected by those shifts. We neglect this complication to keep our treatment as simple as possible and the number of parameters within reasonable bounds.

To obtain the temperature dependence of  $\Gamma_1$  we still need that of the hopping frequencies. In the temperature regime in which we are interested the Arrhenius law

$$\nu^{\mu\nu} = \nu_0^{\mu\nu} \exp(-E^{\mu\nu}/kT) \quad (2.6)$$

gives a good description for all transitions. A better choice for the ground state to ground state transition would be the multiphonon transition rate of Flynn and Stoneham (1970) or its modification given by Teichler (1977), but (2.6) is sufficient for our purposes even for ground state transitions. Therefore we have used

$$\nu_{TT} = \nu^{ss} = \nu_{TT}^0 \exp(-E^s/kT). \quad (2.7)$$

Instead of putting expressions (2.6) into (2.3) and (2.4) we choose

$$\nu_{T'T'} = \nu_{T'T'}^0 \exp(-E^e/kT) \quad (2.8)$$

$$\nu_{T'T} = \nu_{T'T}^0 \exp(-E^{es}/kT) \quad (2.9)$$

which does not introduce any qualitative modification in the behaviour of  $\Gamma_1$  compared to the procedure described above but reduces the number of parameters. The occupation probabilities  $p_T$  and  $p_{T'}$ , however, will still be calculated according to (2.3).

Whether the effects we are looking for do exist or not depends on the ratios between the intrasite and the intersite transition rates. That  $\nu_{T'T}^i$  in Nb and Ta can not be much larger than  $\nu_{T'T'}$ , follows from experiment (Richter and Shapiro 1980, Hempelmann *et al* 1981, Rush *et al* 1984, Magerl *et al* 1986) by attributing the linewidths of the inelastic neutron scattering spectra entirely to lifetime broadening due to  $\nu_{T'T}^i$  and by comparing the resulting  $\nu_{T'T}^i$  with the value of  $\nu_{T'T'}$  estimated from a fit of the diffusivity to equation (2.5) (if  $\nu_{T'T} = \nu_{TT'} \equiv 0$  is assumed). Since  $\nu_{T'T'}$  is typically almost as high as the Debye frequency, the condition that  $\nu_{T'T}^i$  should not be much larger than  $\nu_{T'T'}$ , in order that the effects to be discussed occur, does not constitute in our opinion a severe restriction from the viewpoint of theoretical expectations. For the phonon contribution to  $\nu_{T'T}^i$  this is obvious (see

below) but it seems to be reasonable for a possible contribution due to coupling to electrons, too. Furthermore, as will be discussed in section 4,  $\nu_{T'T}^i < \nu_{T'T'}$  is less important for the behaviour of  $\Gamma_1$  than the condition  $\nu_{T'T}^i < \nu_{TT}$ . The latter condition is frequently even less restrictive than the former due to the Boltzmann factor which relates  $\nu_{T'T'}$  to  $\nu_{T'T}^i$ . Thus taking into account the excited states explicitly may become relevant for the interpretation of  $\Gamma_1$ .

Little theoretical information is available as to the dependence of the intrasite transition rates on temperature. In the following we only consider contributions to  $\nu_{T'T}^i$  due to multiphonon transitions. If multiphonon transitions are dominant it is expected that  $\nu_{T'T}^i$  sharply rises at about the Debye temperature  $\theta_D$  as the temperature is increased. A possible additional contribution to  $\nu_{T'T}^i$  due to coupling to electrons is not expected to show this strong increase at  $\theta_D$  and might be taken therefore as temperature independent in a crude approximation. In the following discussion of the temperature dependence of  $\alpha$  such a temperature-independent contribution, however, is set equal to zero since the qualitative results can be reproduced without it. Even for multiphonon transitions we are not aware of any treatment of intrasite transitions for hydrogen in metals. Because of its simplicity we have chosen to describe the temperature dependence of the intrasite transitions by the expression

$$\nu_{T'T}^i = \nu_{T'T}^{i(0)} \frac{\exp(\Delta/kT) - 1}{[\exp(\hbar\langle\omega\rangle/kT) - 1]^p} \quad (2.10)$$

with

$$p = \Delta/\langle\omega\rangle$$

where  $\langle\omega\rangle$  is a characteristic phonon frequency of the host lattice (we set it equal to the Debye frequency  $\omega_D$ ) and  $\Delta$  is the energy of the excited state (the ground state energy is set equal to zero) or rather a suitable average over the various states contributing to the 'state'  $T'$ ;  $\nu_{T'T}^{i(0)}$  is the transition rate  $\nu_{T'T}^i$  as the temperature  $T$  approaches absolute zero. The reverse process  $\nu_{T'T'}$  is obtained from detailed balancing. An expression of that form results for multiphonon transitions between localized vibrational states with energy difference  $\Delta$  if the lattice phonons are treated in the Einstein approximation (see, e.g., Englman 1979).  $p$  gives the order of the process (number of phonons required to guarantee energy balance). The detailed form of (2.10) is of little importance for us. We believe, however, that (2.10) gives a qualitative description of intrasite transitions if they are dominated by particle phonon couplings, at least at temperatures not too far above  $\theta_D$ . In particular, (2.10) gives, as expected, a sharp rise of  $\nu_{T'T}^i$  at around the Debye temperature as the temperature is increased. A possible saturation of  $\nu_{T'T}^i$  at higher temperatures, however, is not described by (2.10). Since  $p$  typically has a value of 6-8 for localized H-vibrations in Nb and Ta the processes are of high order and are therefore expected to be comparably slow (i.e.,  $\nu_{T'T}^i < \nu_{T'T'}$  or at least not much larger).

### 3. Calculation of $\Gamma_1$

#### 3.1. Theory of relaxation by dipolar coupling

The isotopes  $p$  and  $t$  and the light 'isotope'  $\mu^+$  of element no 1 (hydrogen) all have

spin  $S = \frac{1}{2}$  and therefore no quadrupole moment. In para- or diamagnetic metals (Nb, Ta, V...)  $\Gamma_1$  of the nuclear spin of these hydrogen isotopes is determined by the electronic contribution (Korringa 1950) and the dipolar contribution which is affected by the hydrogen diffusion, and will therefore be of interest to us. For low hydrogen concentrations, and if there is no tendency for the formation of hydrogen clusters, the dipolar contribution to  $\Gamma_1$  is determined by the interaction between the magnetic moments of the hydrogen nuclei and those of the host nuclei whereas the interactions between the magnetic moments of the hydrogen nuclei may be neglected. Under these conditions and for a high applied static magnetic field  $B_0$  and if the spin system of the host nuclei remains in equilibrium (both conditions are fulfilled in the NMR experiments discussed in section 4), the relaxation of the spin polarization of the hydrogen nuclei is described by a single relaxation rate  $\Gamma_1$  given by (see Abragam 1962)

$$\Gamma_1 = g \left[ \frac{1}{12} J^{(0)}(\omega_S - \omega_I) + \frac{3}{2} J^{(1)}(\omega_S) + \frac{3}{4} J^{(2)}(\omega_S + \omega_I) \right] \quad (3.1)$$

where

$$g = \gamma_I^2 \gamma_S^2 \hbar^2 I(I+1)$$

and  $\omega_S = \gamma_S B_0$ ,  $\omega_I = \gamma_I B_0$  are the spin precession frequencies of the nuclear spins of hydrogen (gyromagnetic ratio  $\gamma_S$ ) or the host atoms (gyromagnetic ratio  $\gamma_I$ , spin quantum number  $I$ ) in the applied field  $B_0$ . The spectral densities  $J^{(\rho)}(\omega)$  are defined by

$$J^{(\rho)}(\omega) = \int_{-\infty}^{\infty} \exp(i\omega\tau) K^{(\rho)}(\tau) d\tau \quad (3.2)$$

where the  $K^{(\rho)}(\tau)$  are time correlation functions of certain contributions to the dipole-dipole coupling which show a random temporal modulation due to atomic hopping. They are given by

$$\begin{aligned} K^{(\rho)}(\tau) &= \sum_j \langle F_{\alpha_j}^{(\rho)*}(t+\tau) F_{\alpha_j}^{(\rho)}(t) \rangle \\ F_{\alpha_j}^{(0)} &= r_{\alpha_j}^{-3} (1 - \cos^2 \Theta_{\alpha_j}) \\ F_{\alpha_j}^{(1)} &= r_{\alpha_j}^{-3} \sin \Theta_{\alpha_j} \cos \Theta_{\alpha_j} \exp(i\varphi_{\alpha_j}) \\ F_{\alpha_j}^{(2)} &= r_{\alpha_j}^{-3} \sin^2 \Theta_{\alpha_j} \exp(i2\varphi_{\alpha_j}) \end{aligned} \quad (3.3)$$

where  $\langle \rangle$  denotes an ensemble average over the stochastic hydrogen motion. The summation in (3.3) is over all host nuclei.  $r_{\alpha_j}$  is the distance vector between the hydrogen and a host nucleus and is time dependent due to atomic motion.  $r_{\alpha_j}$ ,  $\Theta_{\alpha_j}$  and  $\varphi_{\alpha_j}$  are the polar coordinates of  $r_{\alpha_j}$ , the  $z$ -axis being parallel to the applied magnetic field. If the host nuclei are assumed to be immobile (this is a very good approximation since the mobility of hydrogen is very large compared to that of the heavy host nuclei) the time dependence of  $r_{\alpha_j}$  is completely determined by the hydrogen motion.



For cubic symmetry

$$J^{(\rho)}(\omega) = A^{(\rho)}(\omega) + B^{(\rho)}(\omega)f(\Theta, \varphi) \quad (3.4)$$

where

$$f(\Theta, \varphi) = \sin^2 2\Theta + \sin^4 \Theta \sin^2 2\varphi$$

depends on the orientation of the applied magnetic field relative to a cube axis and is given as a function of the polar angles  $\Theta$  and  $\varphi$  (see Wolf 1975 and Sholl 1986). The expressions for  $A^{(\rho)}$  and  $B^{(\rho)}$  may be found in the paper by Wolf (1975). In the following we are interested only in the extreme motional narrowing regime defined by  $\omega_I \tau_c \ll 1$  and  $\omega_S \tau_c \ll 1$ , where  $\tau_c$  is the correlation time characterizing the fluctuations of the dipolar interactions. In this case their limits as  $\omega$  tends towards zero may be taken for all spectral densities appearing in (3.1). Furthermore, because of the relation  $B^{(2)}(\omega) = -B^{(1)}(\omega) = \frac{1}{3}B^{(0)}(\omega)$  (see Wolf 1975),  $\Gamma_1$  is given by

$$\Gamma_1 = g\left[\frac{1}{12}A^{(0)}(0) + \frac{3}{2}A^{(1)}(0) + \frac{3}{4}A^{(2)}(0)\right] \quad (3.5)$$

and is therefore independent of the strength and orientation of the applied field. This holds for any diffusion process. In this regime and for simple diffusion mechanisms described by a single correlation time,  $\tau_c$ ,  $\Gamma_1$  is proportional to  $\tau_c$  whereas the diffusion coefficient  $D$  is proportional to  $\tau_c^{-1}$ . Therefore the product  $\Gamma_1 D$  is independent of  $\tau_c$ . To omit individual material parameters one defines

$$\alpha = \frac{a_0^4 \Gamma D}{g} \quad (3.6)$$

which is dependent on the lattice type and the diffusion mechanism but, as already stated, is independent of  $\tau_c$  for a simple diffusion mechanism (for nearest-neighbour hopping among T sites in a rigid BCC lattice one obtains  $\alpha = 14.8$ , see Sankey and Fedders 1980). Furthermore, since no other temperature-dependent parameter remains in (3.6) (only the temperature dependence of the lattice relaxation in the vicinity of hydrogen could introduce a further temperature dependence, which is expected, however, to be extremely small),  $\alpha$  is also temperature independent in this case. Hence, if it is possible to measure simultaneously  $\Gamma_1$  and  $D$ , and if the effects on both  $\Gamma_1$  or  $D$  due to the presence of lattice defects or composition variations with temperature in the  $\alpha$ -phase, etc, may be safely excluded, the temperature dependence of  $\alpha$  may be used to decide whether a simple diffusion mechanism may be ruled out or not. We would like to emphasize that the diffusion model introduced in section 2 is not simple in this sense. A calculation of  $\alpha$  for this model and a comparison with experimental results may thus provide additional insight to the mechanism of quantum diffusion.

### 3.2. Reciprocal space formalism

Having set the general framework we proceed with the calculation of  $K^{(\rho)}(t)$  and  $J^{(\rho)}(\omega = 0)$  which are required for the determination of  $\Gamma_1$  and  $\alpha$ . Since the time correlation functions are totally determined by the hydrogen motion they may be expressed by means of the conditional probabilities  $P(\mathbf{R}_\beta + \mathbf{r}_\beta - [\mathbf{R}_\alpha + \mathbf{r}_\alpha], t)$

to find a hydrogen atom which occupied a 'site'  $R_\beta + r_\beta$  at time  $t = 0$  but later occupied 'site'  $R_\alpha + r_\alpha$  at time  $t$ . Here  $R_\alpha$  are lattice vectors,  $r_\alpha$  characterize the various interstitial sites within one unit cell (T sites in our case) as well as the different states localized at a certain interstitial site. Thus  $r_\alpha$  contains not only the meaning of a spatial coordinate but the index  $\alpha$  also characterizes the state. Later we will restrict our treatment to the idealized situation where all states localized within one interstitial well are characterized by the same vector  $r_\alpha$  independent of the state index. In writing the conditional probability as a function of a time difference and a difference of spatial coordinates (and state variables) we assume stationarity (thermal equilibrium) and spatial homogeneity (we consider only crystalline materials). We obtain

$$K^{(\rho)}(t) = \sum_{R_j} \sum_{R_\beta + r_\beta} \sum_{R_\alpha + r_\alpha} N^{-1} p(r_\beta) P(R_\beta + r_\beta - [R_\alpha + r_\alpha], t) \times F^{(\rho)}(R_j - [R_\beta + r_\beta]) F^{(\rho)*}(R_j - [R_\alpha + r_\alpha]). \quad (3.7)$$

In (3.7)  $p(r_\beta)$  is the probability of finding a hydrogen atom at any site characterized by  $r_\beta$  and  $N$  is the number of unit cells. For very low concentrations of the spin-carrier the conditional probabilities in (3.7) are the solutions of a system of simple rate equations of dimension  $nN \times nN$  (where  $n$  is the number of different 'sites' in the unit cell) to the initial conditions  $P(R_\alpha + r_\alpha, t = 0) = \delta_{R_\alpha + r_\alpha, R_\beta + r_\beta}$ . Making use of the translational symmetry of the crystal one obtains after spatial and (one-sided) temporal Fourier transformation of these equations a system of  $n \times n$  algebraic equations (see, e.g., Fedders and Sankey 1977), namely

$$\sum_{\gamma} [(\tau_\alpha^{-1} - i\omega)\delta_{\alpha\gamma} - \nu_{\gamma\alpha}(q)] P(q, r_\gamma - r_\beta, \omega) = \delta_{\alpha\beta} \quad (3.8)$$

with

$$\nu_{\gamma\alpha}(q) = \sum_{R_\gamma} \nu(R_\gamma + r_\gamma, R_\alpha + r_\alpha) \exp[-iq(R_\gamma - R_\alpha)] \quad (3.9)$$

and

$$\tau_\alpha^{-1} = \sum_{R_\delta + r_\delta} \nu(R_\alpha + r_\alpha, R_\delta + r_\delta). \quad (3.10)$$

In (3.9) and (3.10)  $\nu(R_\gamma + r_\gamma, R_\alpha + r_\alpha)$  is the hopping frequency from 'site'  $R_\gamma + r_\gamma$  to  $R_\alpha + r_\alpha$ . It depends only on the difference  $R_\gamma - R_\alpha$ . The Fourier transforms  $P(q, r_\gamma - r_\beta, \omega)$  are defined analogously. Equation (3.8) may be rewritten as

$$[-i\omega \mathbf{1} + \mathbf{W}] P(q, \beta, \omega) = \mathbf{I}(\beta) \quad (3.11)$$

where  $\mathbf{1}$  is the  $n \times n$  unit matrix and the components of the  $n \times n$  matrix  $\mathbf{W}$  are given by

$$W_{\alpha\gamma} = \tau_\alpha^{-1} \delta_{\alpha\gamma} - \nu_{\gamma\alpha}(q). \quad (3.12)$$

The vector  $P(q, \beta, \omega)$  has elements  $P(q, r_\gamma - r_\beta, \omega)$ ;  $\gamma$  is the running index and  $\beta$  is fixed. The inhomogeneity is specified by the vector  $\mathbf{I}(\beta)$ . Its elements are  $\delta_{\alpha\beta}$

(running index  $\alpha$ ), which specify the initial condition that the hydrogen atom started at a 'site' characterized by  $r_\beta$ . The solution of equation (3.11) is

$$P(q, \beta, \omega) = [-i\omega \mathbf{1} + \mathbf{W}]^{-1} \mathbf{I}(\beta) \quad (3.13)$$

or for the components

$$P(q, r_\alpha - r_\beta, \omega) = \sum_\gamma [-i\omega \mathbf{1} + \mathbf{W}]_{\alpha\gamma}^{-1} \delta_{\alpha\gamma} = [-i\omega \mathbf{1} + \mathbf{W}]_{\alpha\beta}^{-1}. \quad (3.14)$$

We may now rewrite the spectral densities  $J^{(\rho)}(\omega)$  in terms of these quantities. We get

$$J^{(\rho)}(\omega) = N^{-1} \sum_{r_\beta} \sum_{r_\alpha} \int_{q \in BZ} p(r_\beta) 2\Re P(q, r_\beta - r_\alpha, \omega) \\ \times F^{(\rho)}(q, r_\beta) F^{(\rho)*}(q, r_\alpha) d^3q \quad (3.15)$$

where  $F^{(\rho)}(q, r_\beta)$  is the spatial Fourier transform of  $F^{(\rho)}(\mathbf{R}_j - [\mathbf{R}_\beta + r_\beta])$ .  $\Re$  in (3.15) denotes that the real part is to be taken. The integration is over the Brillouin zone. Equation (3.15) could be used to perform all calculations in reciprocal space. In some cases, however, a partial back transformation into real space turns out to be more convenient. This leads to

$$J^{(\rho)}(\omega) = N^{-1} \sum_{R_j} \sum_{R_\alpha} \sum_{r_\beta} \sum_{r_\alpha} \int_{q \in BZ} p(r_\beta) 2\Re P(q, r_\beta - r_\alpha, \omega) \\ \times \exp(-iq \cdot R_\alpha) F^{(\rho)}(\mathbf{R}_j - r_\beta) F^{(\rho)*}(\mathbf{R}_j - R_\alpha - r_\alpha) d^3q. \quad (3.16)$$

This formula will be used in the following.

### 3.3. Expansion in powers of the hopping frequencies

To evaluate equation (3.14) for the model introduced in section 2 we have to invert a  $12 \times 12$  matrix since we have 12 'sites' in the unit cell (6 T and 6 T' sites). In general it is not possible to disentangle the  $q$  dependence of the inverse matrix from the dependence on the hopping frequencies  $\nu_{TT}$ ,  $\nu_{T'T'}$ , etc, and on  $\omega$ . Hence, one has to perform the  $q$  integration for very many different combinations of hopping frequencies and for different frequencies  $\omega$  to calculate  $K^{(\rho)}(\omega)$  as a function of these parameters. Since we are interested only in the limit  $\omega \rightarrow 0$  the latter dependence is unimportant anyway and the matrix to be inverted is just  $\mathbf{W}$ . To avoid the countless number of  $q$  integrations still required to determine the dependence of  $\Gamma_1$  on the hopping frequencies we take refuge in a method discussed already in the appendix of a paper by Messer *et al* (1986). There  $\mathbf{W}^{-1}$  is expanded in powers of the matrix  $\nu(q)$  with matrix elements  $\nu_{\gamma\alpha}(q)$ . The  $q$  dependence of  $\nu_{\gamma\alpha}(q)$  is contained in geometric factors of the form  $\exp(iq \cdot r_i)$ , where  $r_i$  is a lattice vector which characterizes the unit cell reached in a certain hop (the cell from which the particle started is taken as the origin). A term  $(\nu)^s$  in the expansion thus is a sum of contributions containing factors of the form  $\exp(iq \sum_i r_i)$  where the sequence of the  $r_i$  in the sum characterizes a possible sequence of  $s$  jumps, hence,  $\sum_i r_i$  is a lattice vector of the cell (relative to the cell where the particle started) which is reached with this sequence of  $s$  hops.

The precise position within the start and final cells are given by the position in the  $n \times n$  matrix  $\nu^s$ . In calculating  $\nu^s$  we obtain the endvectors of all possible diffusion paths with exactly  $s$  hops of a particle starting at a site  $r_\beta$  corresponding to the row index of this matrix. The occurrence probabilities of the possible endvectors are given by the prefactors of the exponentials which depend on the hopping frequencies and the number of different diffusion paths leading to the same result. The  $q$  dependence in all terms is of the form  $\exp(iq \cdot R_\gamma)$ . Therefore the  $q$  space integration in (3.16) is trivial and is performed using

$$N^{-1} \sum_q \exp[iq \cdot (R_\gamma - R_\alpha)] = \delta_{R_\gamma, R_\alpha}. \quad (3.17)$$

The evaluation of (3.16) consequently is reduced to the calculation of lattice sums in real space. The selection of the lattice points  $R_\alpha$  to be summed over is provided by (3.17) and the weights are given by the prefactors of the exponentials. In the paper by Messer *et al* (1986) the expansion has been stopped at  $s = 6$ . Diffusion paths with more than 6 hops and those which lead outside of a diffusion sphere of radius  $\sqrt{3}a_0/2$  around the starting site  $r_\beta$  have been treated within the diffusion approximation. We follow the same procedure.

#### 3.4. Contribution of the first 6 hops

Instead of using the 12-component vector  $P(q, \beta, \omega)$ , where  $\beta$  characterizes one of the 12 different 'sites' in a unit cell, it turns out to be more convenient to use the 6-component vectors  $P_T(q, \beta, \omega)$  and  $P_{T'}(q, \beta, \omega)$ . The components of the first correspond to the 6 ground state levels of the 6 T sites within a unit cell whereas the latter comprise the excited levels of the 6 T sites. Furthermore, we distinguish two types of initial conditions. In the first case initially one of the ground states is occupied. This will be indicated by using an unprimed symbol to denote the initial condition, e.g.,  $\beta$  as above. If initially one of the excited states is occupied we will use a primed symbol instead, e.g.,  $P_T(q, \beta', \omega)$ . We will further use the convention that the contributions to  $\nu(q)$  of the different transitions shown in figure 1 have all, with the exception of the intrasite transitions  $\nu_{TT}^i$  and  $\nu_{T'T}^i$ , the same form. For instance, the  $6 \times 6$  block (the  $12 \times 12$  matrix  $\nu(q)$  may be decomposed into four  $6 \times 6$  blocks) corresponding to the T-T transitions may be written as

$$\nu^{TT} = \nu_{TT} \mathbf{A}(q) \quad (3.18)$$

with

$$\mathbf{A}(q) = \begin{pmatrix} 0 & e^{iq \cdot r_z} & 1 & 0 & 1 & e^{-iq \cdot r_y} \\ e^{-iq \cdot r_z} & 0 & 1 & 1 & 0 & e^{iq \cdot r_x} \\ 1 & 1 & 0 & e^{-iq \cdot r_y} & e^{iq \cdot r_x} & 0 \\ 0 & 1 & e^{iq \cdot r_y} & 0 & e^{-iq \cdot r_z} & 1 \\ 1 & 0 & e^{-iq \cdot r_x} & e^{iq \cdot r_z} & 0 & 1 \\ e^{iq \cdot r_y} & e^{-iq \cdot r_x} & 0 & 1 & 1 & 0 \end{pmatrix} \quad (3.19)$$

which is independent of the hopping frequencies and

$$r_x = (a_0/2)(1, -1, -1)$$

$$r_y = (a_0/2)(-1, 1, -1)$$

$$r_z = (a_0/2)(-1, -1, 1).$$

The other blocks of  $\nu(q)$  are obtained by replacing  $\nu_{TT}$  in (3.18) by the three further hopping frequencies. This is true even when a shift, relative to the ideal T sites, of the center of gravity of the particle probability distribution of the excited states is taken into account. This shift is absorbed in the basis vectors and comes into play only when doing the  $r_\alpha$  sum in (3.16). The quantities  $P_T(q, \beta, 0)$  and  $P_{T'}(q, \beta, 0)$  (we restrict our treatment to the limit  $\omega \rightarrow 0$ ) may be determined from two coupled systems of  $6 \times 6$  linear equations (we do not explicitly display the  $q$  dependence of  $A(q)$  in the following)

$$\begin{aligned} [\nu_c^g \mathbf{1} - \nu_{TT} \mathbf{A}] P_T(q, \beta, 0) - [\nu_{T'T}^i \mathbf{1} + \nu_{T'T} \mathbf{A}] P_{T'}(q, \beta, 0) &= I(\beta) \\ [\nu_c^a \mathbf{1} - \nu_{T'T'} \mathbf{A}] P_{T'}(q, \beta, 0) - [\nu_{T'T'}^i \mathbf{1} + \nu_{T'T'} \mathbf{A}] P_T(q, \beta, 0) &= \mathbf{0} \end{aligned} \quad (3.20)$$

with

$$\begin{aligned} \nu_c^g &= 4(\nu_{TT} + \nu_{T'T'}) + \nu_{T'T}^i \\ \nu_c^a &= 4(\nu_{T'T'} + \nu_{T'T}) + \nu_{T'T'}^i \end{aligned}$$

The component  $\alpha$  of the inhomogeneity  $I(\beta)$  is again given by  $\delta_{\alpha\beta}$ . Since we consider here the case where the particle is initially in a ground state the second equation is homogeneous. The intrasite hops  $\nu_{T'T}^i$  and  $\nu_{T'T'}^i$  do not shift the particle to another site and appear therefore only in connection with the unit matrix. The analogous quantities  $P_T(q, \beta', 0)$  and  $P_{T'}(q, \beta', 0)$  are obtained if the right-hand side of the first system of equations of (3.20) is set equal to  $\mathbf{0}$  and the inhomogeneity  $I(\beta')$  is introduced into the second system. The formal solutions of (3.20) are (the sequence of operations is unimportant here)

$$P_T(q, \beta, 0) = \frac{1}{g_1} \frac{\nu_{T'T'} \mathbf{1} + \nu_{T'T} f [4\mathbf{1} - \mathbf{A}]^{-1}}{1 - g_2 \mathbf{A}} I(\beta) \quad (3.21)$$

and

$$P_{T'}(q, \beta, 0) = \frac{[\nu_{T'T}^i \mathbf{1} + \nu_{T'T} \mathbf{A}] [\nu_{T'T'} \mathbf{1} + \nu_{T'T} f [4\mathbf{1} - \mathbf{A}]^{-1}]}{\nu_a g_1 [1 - g_3 \mathbf{A}] [1 - g_2 \mathbf{A}]} I(\beta)$$

with

$$\begin{aligned} f &= 4 + \nu_{T'T'}^i / \nu_{T'T'} = 4 + \nu_{T'T}^i / \nu_{T'T} \\ \nu_a &= 4\nu_{T'T'} + f\nu_{T'T} \\ g_1 &= 4k_1 + fk_2 \\ g_2 &= k_1 / g_1 \\ g_3 &= \nu_{T'T'} / \nu_a \\ k_1 &= \nu_{TT} \nu_{T'T'} - \nu_{T'T} \nu_{T'T'} \\ k_2 &= \nu_{TT} \nu_{T'T} + \nu_{T'T} \nu_{T'T'} + 2\nu_{T'T} \nu_{T'T'} \end{aligned}$$

Expression (3.21) is not defined in case all but the intrasite hopping frequencies are set equal to zero. In this case the calculation has to be done first with  $\omega \neq 0$ .

The limit  $\omega \rightarrow 0$  leads then to the well-defined expressions for the real part of  $P_T(q, \beta, 0)$  and so on. The conditional probabilities  $P_{T'}(q, \beta', 0)$  follow from (3.21) by the consistent interchange of T and T' in all expressions (thus, e.g., the expression for  $P_{T'}(q, \beta', 0)$  follows from that for  $P_T(q, \beta, 0)$ ) and the replacement of  $I(\beta')$  for  $I(\beta)$ . Expression (3.21) are now expanded in powers of  $\mathbf{A}$ . Again  $\mathbf{A}^s$  takes into account all possible paths with  $s$  diffusive hops. The non-diffusive intrasite hops  $\nu_{TT'}^i$ ,  $\nu_{T'T}^i$  are included up to arbitrary order. The result is expressed as

$$P_T(q, \beta, 0) = \sum_s f_T^{(s)}(\beta) (\mathbf{A}(q))^s I(\beta) \quad (3.22)$$

and an analogous expression for  $P_{T'}(q, \beta, 0)$  with  $f_T^{(s)}(\beta)$  replaced by  $f_{T'}^{(s)}(\beta)$ . The prefactors of  $(\mathbf{A})^s$  are given by

$$f_T^{(s)}(\beta) = \frac{1}{g_1} \left( \nu_{T'T'}(g_2)^s + \frac{1}{4} f \nu_{T'T} \sum_{l=0}^s \left(\frac{1}{4}\right)^{s-l} (g_2)^l \right) \quad (3.23)$$

and

$$f_{T'}^{(s)}(\beta) = \frac{1}{\nu_a} \left( \nu_{T'T'}^i \sum_{l=0}^s (g_3)^{s-l} f_T^{(l)}(\beta) + \nu_{T'T} \sum_{l=0}^s (g_3)^{s-l} f_T^{(l-1)}(\beta) \right) \quad (3.24)$$

where we define  $f_T^{(-1)} = 0$ . The two other conditional probabilities are obtained by the substitution described above and are also written in the form of (3.22) introducing corresponding prefactors  $f_T^{(s)}(\beta')$  and  $f_{T'}^{(s)}(\beta')$ . The advantage of using expansion (3.22) is that the time-consuming calculation of the lattice sums in (3.16) may be performed independently from  $f_T^{(s)}(\beta)$  and so on and therefore has to be carried out only once for all conceivable combinations of hopping frequencies. We assume further that hydrogen is localized point-like at the tetrahedral sites for ground as well as excited states. The lattice sums associated with  $(\mathbf{A}(q))^s$  are then those required to calculate  $\Gamma_1$  for the conventional model of hopping among T sites, which does not consider the excited states explicitly. Neglecting lattice distortions induced by hydrogen these have been calculated for  $s$  up to 6 (see Schmidt 1982). Putting these results into (3.16) and then into (3.5) or (3.1) one obtains

$$\frac{a_0^6 \Gamma_1}{g} = \sum_s \{ p(T) [f_T^{(s)}(\beta) + f_{T'}^{(s)}(\beta)] + p(T') [f_T^{(s)}(\beta') + f_{T'}^{(s)}(\beta')] \} G_s \quad (3.25)$$

with the occupation probabilities  $p(T)$ ,  $p(T')$  of the states T and T'. The lattice sums  $G_s$  are given in table 1. If hopping may be described by a single effective frequency the contribution of the first 6 hops to  $\alpha$  (see equation (3.6)) is

$$\alpha_{\leq 6} = 9.72. \quad (3.26)$$

Table 1. Lattice sums required to evaluate (3.25) (see Schmidt 1982).

$s$	0	1	2	3	4	5	6
$G_s$	195.3	380.6	969.9	2622.0	8220.0	22720.0	82730.0

### 3.5. Diffusion approximation

Outside a sphere of radius  $\sqrt{3}/2a_0$  surrounding the start site  $\beta$ ,  $P(\mathbf{R}_\alpha + \mathbf{r}_\alpha - \mathbf{R}_\beta - \mathbf{r}_\beta, \omega) \equiv P(\mathbf{r}, \omega)$  will be approximated by the solution of the diffusion equation for the appropriate initial condition, with  $D$  given by equation (2.5). Putting these expressions into the temporal Fourier transform of (3.7), restricting the sum over  $\mathbf{R}_\alpha$ ,  $\mathbf{r}_\alpha$  to sites outside the sphere and using (3.1) one obtains the contribution  $\alpha^{\text{out}}$  to  $\alpha$ . It depends only on the type of sites which are occupied but not on the diffusion mechanism. For tetrahedral sites one obtains

$$\alpha^{\text{out}} = 0.77. \quad (3.27)$$

The diffusion approximation is used again to take into account the contribution of diffusion paths with more than 6 diffusive hops which, however, end within the sphere. To avoid double counting, the time interval corresponding to the first  $s_0$  ( $s_0 = 6$  in our case) hops has to be excluded when calculating the Fourier transform. This interval is given by  $s_0\bar{\tau}$ , where  $\bar{\tau}$  is the mean time of stay at a site. We get

$$P(\mathbf{r}, \omega = 0) = 2 \int_{s_0\bar{\tau}}^{\infty} P(\mathbf{r}, t) dt = \frac{p(\mathbf{r}_\alpha)V_A}{4\pi D r} \operatorname{erf}[(r^2/4Ds_0\bar{\tau})^{1/2}] \quad (3.28)$$

with

$$\bar{\tau}^{-1} = 4p_T(\nu_{TT} + \nu_{T'T'}) + 4p_{T'}(\nu_{T'T} + \nu_{T'T'})..$$

The error function may be expanded for large  $s_0$  and small  $r$  which allows us to calculate the lattice sums for arbitrary values of  $s_0$ . The result is (see Schmidt 1982)

$$\alpha_{>6}^{\text{in}} = (D\bar{\tau}s_0)^{-1/2}1.581 - (D\bar{\tau}s_0)^{-3/2}0.0279 + (D\bar{\tau}s_0)^{-5/2}0.0022 \quad (3.29)$$

In equation (3.29)  $D$  is in units of  $a_0^2$ . For our model we obtain  $D\bar{\tau} = 1/48$  which with  $s_0 = 6$  leads to

$$\alpha_{>6}^{\text{in}} = 4.24. \quad (3.30)$$

Adding the three contributions we get

$$\alpha = \alpha_{\leq 6} + \alpha_{>6}^{\text{in}} + \alpha^{\text{out}}$$

which gives  $\alpha = 14.73$  if hopping is between tetrahedral sites and is describable by an effective frequency. This is in accordance with other treatments (Sankey and Fedders 1980). If the effective frequency description is inadequate,  $\alpha_{\leq 6}$  will depend on the ratios between the hopping frequencies and  $\alpha$  will become temperature dependent.

The diffusion approximation used to determine  $\alpha_{>6}^{\text{in}}$  and  $\alpha^{\text{out}}$  works well as long as  $\nu_{TT} \leq 6(\nu_{T'T'} + \frac{1}{4}\nu_{T'T}^i)$  and  $\nu_{T'T'} \leq 6(\nu_{T'T} + \frac{1}{4}\nu_{T'T'}^i)$ , where the second condition is less critical (see below). If on the contrary  $\nu_{TT} \gg 6(\nu_{T'T'} + \frac{1}{4}\nu_{T'T}^i)$  and  $\nu_{T'T'} \gg 6(\nu_{T'T} + \frac{1}{4}\nu_{T'T'}^i)$  one could split the system into two uncoupled subsystems T and T' described by two different diffusivities  $D_T$  and  $D_{T'}$  (see the appendix). To investigate how much our results are influenced by the diffusion approximation

introduced above we also studied a modified diffusion approximation. It is based on splitting  $P(r, t)$  (of section 3.4) into 4 contributions

$$P(r, t) = p_T((P_T(r, \beta, t) + P_{T'}(r, \beta, t)) + p_{T'}(P_T(r, \beta', t) + (P_{T'}(r, \beta', t))). \quad (3.31)$$

Let us consider  $P_T(r, \beta, t)$ , the probability of finding a hydrogen atom, which started at  $\beta$  (the ground state at a site  $r_\beta$ ) at a distance  $r = R_\alpha + r_\alpha - R_\beta - r_\beta$  at a later time  $t$ . Using the macroscopic diffusion coefficient  $D$  in a diffusion approximation for this probability is certainly not correct even for times larger than  $6\bar{\tau}$  if  $\nu_{TT} \geq 6(\nu_{TT'} + \nu_{TT'}^i)$  since a considerable fraction of the particles is still in a ground state after 6 hops. We describe the motion of particles which are still in a ground state at time  $t$  by the diffusivity

$$D_T = \frac{a_0^2}{12} \nu_{TT}. \quad (3.32)$$

The motion of particles that have changed into an excited state and back to the ground state at least once will be reasonably well described by the macroscopic  $D$ . Using these approximations we obtain

$$P_T(r, \beta, t) = \exp(-\bar{\nu}_{TT'} t) P(r, D_T, t) + p_{T'}(1 - \exp(-\bar{\nu}_{TT'} t)) P(r, D, t) \quad (3.33)$$

with

$$\bar{\nu}_{TT'} = 4\nu_{TT'} + \nu_{TT'}^i.$$

In (3.33)  $\exp(-\bar{\nu}_{TT'} t)$  gives the probability that until a time  $t$  no hop into an excited state occurred, and  $p_{T'}(1 - \exp(-\bar{\nu}_{TT'} t))$  is the probability that up until  $t$  at least one change into an excited state took place but that at  $t$  the ground state is occupied again.  $P(r, D_T, t)$  is the solution of the diffusion equation with diffusivity  $D_T$  for the initial condition  $\delta_{r,0}$ . Analogously we have

$$P_{T'}(r, \beta, t) = (1 - \exp(-\bar{\nu}_{TT'} t)) p_{T'} P(r, D, t) \quad (3.34)$$

Similar relations may be used for the other conditional probabilities. Their contribution to  $\alpha_{>6}$ , however, is small because  $p_{T'}$  is considerably smaller than  $p_T$  and in particular since  $D_{T'}$  ( $D_{T'} = (a_0^2/12)\nu_{T'T'}$ ) is much larger than  $D_T$ . The temporal Fourier transforms of (3.33) and (3.34) have to be calculated as in (3.28), however, the lower integration limit should be taken as  $6\tau_{TT}$  ( $\tau_{TT} = \frac{1}{4}\nu_{TT}$  is the average time between hops if transitions to excited states are excluded) in transforming the first term of (3.33), or  $6\bar{\tau}$  for the second term. If one wants to use the same lattice sums as calculated already to arrive at (3.29) a similar expansion has to be made which again converges reasonably well for large  $s_0$ , small  $r$ , and if in addition

$$\bar{\nu}_{TT'} 6\tau \leq 1 \quad (3.35)$$

with  $\tau = \bar{\tau}$  or  $\tau_{TT}$  depending on whether the lower integration limit is  $6\bar{\tau}$  or  $6\tau_{TT}$  and with

$$\bar{\nu}_{TT'} = 4\nu_{TT'} + \nu_{TT'}^i.$$

The result which should replace (3.29) is somewhat lengthy and will not be given here. Within the parameter regime investigated the numerical results obtained from both treatments are not too different anyway. In the case where inequality (3.35) is violated, (3.29) should be a good approximation.  $\alpha^{\text{out}}$  should be treated similarly. Since its contribution to  $\alpha$ , however, is very small and because the numerical modifications to be expected are even smaller than for  $\alpha_{>6}^{\text{in}}$  we continue to use (3.27).



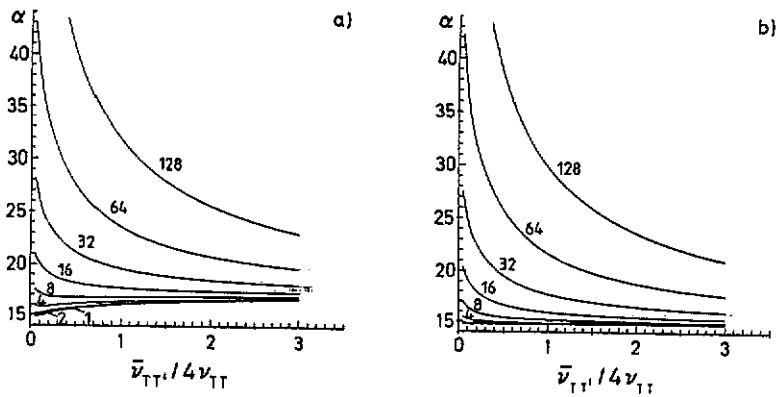


Figure 2.  $\alpha$  as a function of  $\bar{\nu}_{TT'}/4\nu_{TT}$  for different values of  $\nu_{TT'}/\nu_{TT}$  given by the numbers at the various curves and for (a)  $\nu_{TT'}/\nu_{TT} = 0.001$ , and (b)  $\nu_{TT'}/\nu_{TT} = 32$ . In both cases  $p_T = 0.95$ .

#### 4. Results and discussion

Since the various hopping frequencies do not drop out from  $\alpha$  for the extended hopping model,  $\alpha$  will depend on them. This dependence is shown in figures 2 and 3 for 5% and 0.5% occupation of the excited states. Because tunnelling among excited states can be expected to be faster than among ground states we have only investigated the regime  $\nu_{TT'}/\nu_{TT} \geq 1$ . In this regime  $\alpha$  is generally larger than 14.8 the value obtained for a simple diffusion process described by one hopping frequency  $\nu_{TT}$ .

Before discussing the dependence of  $\alpha$  on the various model parameters in detail we want to make some general remarks on the temperature dependence of  $\alpha$  that follow from its dependence on the hopping frequencies. A main prediction of our model is an increase in  $\alpha$  if the temperature is raised above a certain value given by the excitation energy of the state  $T'$ . The qualitative, but not quantitative, behaviour is insensitive to the precise form of the temperature laws of the hopping frequencies. A quantitative discussion will be given later in connection with figures 4-7 which show  $\alpha$  as a function of temperature if the temperature laws (2.7) to (2.10) are used for the hopping frequencies.

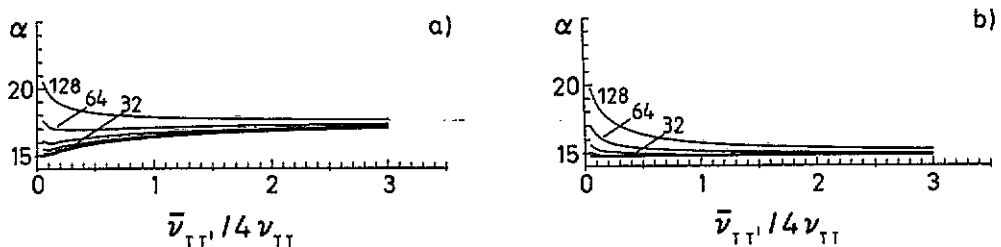


Figure 3.  $\alpha$  as a function of  $\bar{\nu}_{TT'}/4\nu_{TT}$  with the same values for  $\nu_{TT'}/\nu_{TT}$ ,  $\nu_{TT'}/\nu_{TT}$  as in figure 1 but with  $p_T = 0.995$ .

The behaviour of  $\alpha$  as a function of  $\bar{\nu}_{TT'}/4\nu_{TT}$  ( $\bar{\nu}_{TT'} = 4\nu_{TT} + \nu_{TT'}^2$ , as in equation (3.33)) for ratios  $\nu_{TT'}/\nu_{TT}$  ranging from 1 to 128 and two values of  $\nu_{TT'}/\nu_{TT}$  is

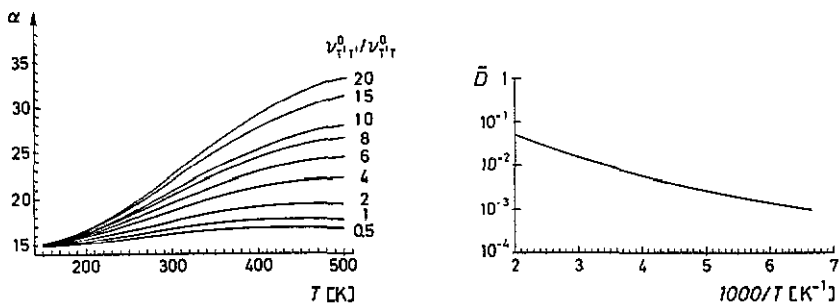


Figure 4. Left:  $\alpha$  as a function of temperature for  $\nu_{TT}^0 = 3.6 \times 10^{11} \text{ s}^{-1}$ ,  $E^s = 46 \text{ meV}$ ,  $E^e = 6.5 \text{ meV}$ ,  $E^{es} = 10 \text{ meV}$ ,  $1.0 \times 10^{12} \text{ s}^{-1} \leq \nu_{TT}^i/\nu_{TT}^0 \leq 4.6 \times 10^{12} \text{ s}^{-1}$ ,  $\nu_{TT}^{i(0)} \equiv 0$  and different ratios  $\nu_{TT}^i/\nu_{TT}^0$ . The excitation energies for the states  $1^y$ ,  $1^z(1^z)$  and  $2^y$  are 117 meV, 165 meV and 227 meV. Right:  $\bar{D} = D \times 10^{-12} \text{ [s]}/a_0^2$  as a function of  $1000/T$  calculated for the various parameter sets given above. The same  $D$  is obtained for all the  $\alpha$ -curves in the left-hand side of the figure.

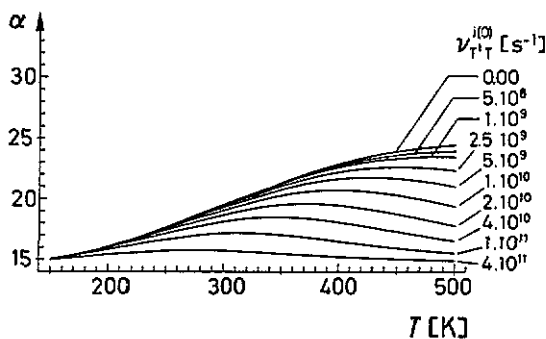


Figure 5.  $\alpha$  as a function of temperature for  $\nu_{TT}^0 = 3.6 \times 10^{11} \text{ s}^{-1}$ ,  $\nu_{TT}^i = 3.6 \times 10^{12} \text{ s}^{-1}$ ,  $\nu_{TT}^i/\nu_{TT}^0 = 6.0 \times 10^{11} \text{ s}^{-1}$  ( $\nu_{TT}^i/\nu_{TT}^0 = 6$ ),  $E^s = 46 \text{ meV}$ ,  $E^e = 6.5 \text{ meV}$ ,  $E^{es} = 10 \text{ meV}$ , the same excitation energies as in figure 4 are used for various values of  $\nu_{TT}^{i(0)}$ . The same diffusivity as in figure 4 is obtained for all the  $\alpha$ -curves.

shown in figure 2 for 5% occupation of the excited states. For large ratios  $\nu_{TT}^i/\nu_{TT}^0$ ,  $\alpha$  is, in the parameter range of figure 2, considerably larger than 14.8 and it decreases with increasing  $\bar{\nu}_{TT}^i/4\nu_{TT}^0$ . The reason for the high values of  $\alpha$  is that  $\Gamma_1$  does not decrease in the same proportion as the diffusivity  $D$  increases due to the occupation of the highly mobile excited states (see the discussion of (3.6)). This is because the first hops of a hydrogen atom starting from a ground state are to a large extent determined by  $\nu_{TT}^0$ , the hopping frequency between ground states. This leads to a contribution to  $\Gamma_1$  which is larger than that calculated with an effective hopping frequency because it corresponds to a smaller diffusivity  $D_{TT}^0$ . Analogously the contribution due to those particles starting at an excited state is reduced because  $\nu_{TT}^i$  is larger than the effective hopping frequency. Since, however,  $p_{T^i}$  is very small the main contribution to  $\Gamma_1$  comes from particles starting at a ground state (for this reason  $\bar{\nu}_{TT}^i/4\nu_{TT}^0$  is the relevant parameter and not  $\bar{\nu}_{TT}^i/4\nu_{TT}^i$ , where  $\bar{\nu}_{TT}^i = 4\nu_{TT}^i + \nu_{TT}^0$ ) and the net effect is an increase of  $\Gamma_1$  over the value expected from  $D$ . The contribution of  $\nu_{TT}^i$  to long range diffusion is nevertheless considerable for large  $\nu_{TT}^i/\nu_{TT}^0$ .

From the above considerations the decrease of  $\alpha$  with increasing  $\bar{\nu}_{TT}^i/4\nu_{TT}^0$  and for large  $\nu_{TT}^i/\nu_{TT}^0$  is also evident, since fast hopping between ground and excited

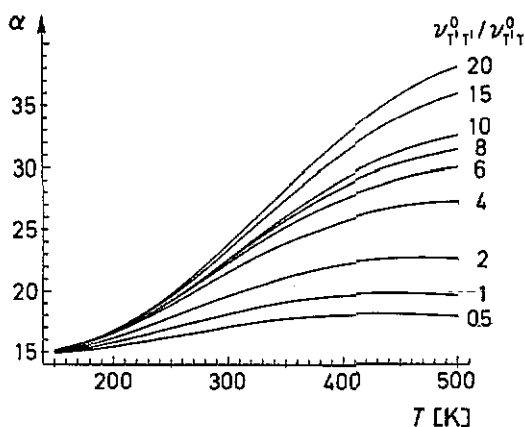


Figure 6.  $\alpha$  as a function of temperature for  $\nu_{T'T}^0 = 3.6 \times 10^{11} \text{ s}^{-1}$ ,  $E^{\text{e}} = 46 \text{ meV}$ ,  $E^{\text{eg}} = 6.5 \text{ meV}$ ,  $E^{\text{eg}} = 40 \text{ meV}$ ,  $2.0 \times 10^{12} \text{ s}^{-1} \leq \nu_{T'T}^0 \leq 4.6 \times 10^{12} \text{ s}^{-1}$ ,  $\nu_{T'T}^{i(0)} \equiv 0$  and different ratios  $\nu_{T'T'}^0 / \nu_{T'T}^0$ . Excitation energies are the same as in figure 3. Again the same diffusivity results for all the  $\alpha$ -curves are obtained as in figure 4.

states leads to an enhancement of the initial mobility of particles starting from a ground state.

For smaller ratios  $\nu_{T'T'}/\nu_{T'T}$ , we have to distinguish the cases of small and large values of  $\nu_{T'T'}/\nu_{T'T}$ .

(i) If the intrasite hopping frequency  $\nu_{T'T'}$  between states T and T' is much smaller than  $\nu_{T'T}$ , associated with a transfer to a nearest-neighbour site,  $\alpha$  increases with increasing  $\nu_{T'T'}/\nu_{T'T}$  and eventually reaches a plateau where  $\alpha$  is larger than 14.8. This plateau corresponds to a diffusion process dominated by successive T-T', T'-T hops and is described by two hopping frequencies  $\nu_{T'T'}$  and  $\nu_{T'T}$ .

(ii) If  $\nu_{T'T'}/\nu_{T'T}$  is large,  $\alpha$  attains, for not too small  $\nu_{T'T'}/\nu_{T'T}$ , the numerical value 14.8 characteristic for T-T hopping described by a single frequency. This means that the intrasite hops are fast enough to guarantee that the internal level structure associated with a site may be disregarded.

(iii) If  $p_T'$  is smaller, (see figure 3), we get (compared to figure 2) an overall reduction of  $\alpha$  for large  $\nu_{T'T'}/\nu_{T'T}$ . For small  $\nu_{T'T'}/\nu_{T'T}$  and large  $\nu_{T'T'}/\nu_{T'T}$ , however, the plateau reached by  $\alpha$  may be even slightly higher than for larger  $p_T'$ .

For a comparison with experiment we need  $\alpha$  as a function of temperature. In order to get this dependence we use the temperature laws (2.7) to (2.10) for the hopping frequencies. To calculate  $p_T$  and  $p_{T'}$  (see (2.3)) we fix the excitation energies at 117 meV for state  $1^y$ , 165 meV for  $1^x$  and  $1^z$ , and 227 meV for state  $2^y$ . These energies have been chosen to be almost identical to those obtained for the local excitation energies of hydrogen in Nb and Ta by inelastic neutron scattering (see Richter and Shapiro 1980, Hempelmann *et al* 1981) or the model calculations of Klamt and Teichler (1986). The results for various parameter sets are shown in figures 4–7. Besides the excitation energies we have fixed  $\nu_{T'T}^0$  and  $E^{\text{e}}$  in all the figures. Figures 4 and 5 show the temperature variation of  $\alpha$  when  $E^{\text{e}}$  and  $E^{\text{eg}}$  have very similar values.

In figure 4 all the curves are calculated with  $\nu_{T'T}^{i(0)} \equiv 0$ . The ratio  $\nu_{T'T'}^0 / \nu_{T'T}^0$  has been varied between 20 and 0.5. The absolute value has been chosen such that the

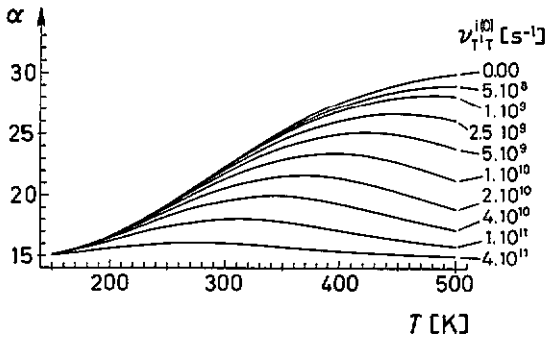


Figure 7.  $\alpha$  as a function of temperature for  $\nu_{T,T}^0 = 3.6 \times 10^{11} \text{ s}^{-1}$ ,  $\nu_{T,T'}^0 = 4.5 \times 10^{12} \text{ s}^{-1}$ ,  $\nu_{T',T}^0 = 7.5 \times 10^{11} \text{ s}^{-1}$  ( $\nu_{T',T}^0/\nu_{T,T}^0 = 6$ ),  $E^s = 46 \text{ meV}$ ,  $E^e = 6.5 \text{ meV}$ ,  $E^{es} = 40 \text{ meV}$ , and various values of  $\nu_{T,T}^{i(0)}$ . The excitation energies and diffusivity are the same as in figure 4.

diffusivity is the same within the line thickness for all  $\alpha$ -curves. The temperature dependence of  $D$  shown in the lower part of figure 4 exhibits a change of slope and has been chosen to be very close to that obtained for H in Nb by Gorski effect measurements (see Vökl and Alefeld 1978, Qi *et al* 1983).

In figure 5 we set  $\nu_{T',T}^0/\nu_{T,T}^0 = 6$  (see also one of the curves in figure 4) and we have varied  $\nu_{T,T}^{i(0)}$ . To evaluate  $\nu_{T,T}^{i(0)}$  from (2.10) we use 240 K as the Debye temperature and  $\Delta = 125 \text{ meV}$  as an 'average' excitation energy of T'. The temperature dependence (2.10) is such that  $\nu_{T,T}^{i(0)}$  approaches  $\nu_{T,T}^{i(0)}$  for  $T = 0 \text{ K}$  but increases drastically with increasing temperature and is a factor of 100 to 400 higher between 400 K and 500 K. For high values of  $\nu_{T,T}^{i(0)}$  the absence of a saturation effect in  $\nu_{T,T}^{i(0)}$  leads to a maximum of  $\alpha$  which would disappear if the temperature law (2.10) becomes invalid at higher temperatures and has to be replaced by a law showing saturation at about these temperatures. We want to emphasize that for  $\nu_{T,T}^{i(0)} = 10^{10} \text{ s}^{-1}$  the intrasite transition frequency  $\nu_{T,T}^{i(0)}$  is, over the whole temperature range of our figure, of the same order of magnitude as the hopping frequency  $\nu_{T,T'}$  between excited states. Because many phonons are required to take up the energy imbalance associated with an intrasite transition the ratio  $\nu_{T,T}^{i(0)}/\nu_{T,T'}$  is expected to be smaller than unity but even for this or somewhat larger values a measurable temperature dependence of  $\alpha$  persists. This is because actually  $\nu_{T,T}^{i(0)}/\nu_{T,T} < 1$  (where  $\bar{\nu}_{T,T'}/4\nu_{T,T}$  is the relevant parameter, see above) is the condition for the observation of deviations from the single-frequency hopping model and this latter condition is in some cases less restrictive than the former. The behaviour if  $E^{es}$  is considerably larger than  $E^e$  (figures 6 and 7) is quite similar to that just described. Again a marked temperature dependence of  $\alpha$  is observed for parameters which seem to be reasonable for hydrogen in metals like Nb or Ta.

Since the same correlation functions needed to calculate  $\Gamma_1$  are also important in quasielastic neutron scattering we expect that the 'complexity' of our model also shows up in these experiments. This is in agreement with the finding that it is impossible to explain the experimental results on NbH and TaH (see Lottner *et al* 1979) within a 'simple' diffusion model. A model, however, which can be regarded as a special case of ours ( $\nu_{T,T} = \nu_{T,T'} = \nu_{T,T} = 0$ ) can indeed be fitted to the data. However, a temperature-independent value  $p_{T'}$  results from the fit which excludes an interpretation in terms of excited states. This led the authors to the interpretation

that  $T'$  must be some unspecified mobile state. The temperature independence of  $p_{T'}$ , however, is likely to be an artefact due to setting  $\nu_{TT} = 0$ . A detailed discussion of neutron scattering in terms of our model should be carried out in the future.

A further prediction of our model is a marked isotopic effect in  $\alpha$ . For deuterium and tritium the level distances are smaller than for hydrogen and therefore the excited states become important at lower temperatures. A temperature dependence of  $\alpha$ , corresponding to that described previously, should therefore begin at lower temperatures. However, for smaller level distances the ratio  $\nu_{T'T'}/\nu_{TT}$  should be considerably larger. This would lead to a strong reduction of the amplitude of the temperature variation of  $\alpha$ . On the other hand a very large increase of the ratio  $\nu_{T'T'}/\nu_{TT}$  could enhance this amplitude. If we compare H and D,  $\nu_{T'T'}/\nu_{TT}$  will increase since for H, and probably even for D, tunnelling between excited states is nearly adiabatic and therefore  $\nu_{T'T'}$  will not change very much in going from H to D whereas  $\nu_{TT}$  drops enormously due to its quadratic dependence on the tunnel integral. For tritium, however, tunnelling between low lying excited states becomes non-adiabatic. Therefore  $\nu_{T'T'}/\nu_{TT}$  should not be much larger for tritium than it is for hydrogen. Since the level spacing for tritium is much smaller than for hydrogen, and therefore the tunnel integrals for T-T and T'-T' transitions in the case of tritium are substantially less different, it is even conceivable that this ratio becomes smaller for tritium. These considerations show that a definite conclusion concerning the amplitude of the variation of  $\alpha$  can not be drawn for deuterium. In the case of tritium, however, a reduction of the effect is very likely. Unfortunately deuterium cannot be used for these investigations because it has a quadrupole moment and the quadrupolar contribution to  $\Gamma_1$  would obscure the effect. However, one *could* carry out experiments on tritium.

Quasielastic neutron scattering should show an analogous isotopic effect concerning the onset and 'strength' of deviations from a diffusion process describable by a single hopping frequency. The onset of the deviation, which shows the most transparent isotopic effect, unfortunately is too low in temperature to be detected by quasielastic neutron scattering, but a quantitative comparison of experiments performed on deuterated Nb and Ta with the model would give a dependence of the model parameters on the isotopic mass which could, together with corresponding measurements of the diffusivity, be used to check the consistency of the model.

Despite the immense amount of work done to investigate both the macroscopic diffusivity  $D$  (Völkl and Alefeld 1978, Qi *et al* 1983, Mauger *et al* 1981 and Hampele *et al* 1989) as well as that done to measure  $\Gamma_1$  (Messer *et al* 1986, Majer *et al* 1989) in the  $\alpha$ -phases of NbH<sub>x</sub> and TaH<sub>x</sub> the experimental situation concerning the quantity  $\alpha$  is still not completely clear. One reason is that both  $D$  and  $\Gamma_1$ , even for low hydrogen content, depend on the hydrogen concentration (Hampele 1989). This dependence may be due to some kind of blocking effect which leads to an influence on the motion of one hydrogen atom due to other hydrogens located nearby, or, in the case of  $\Gamma_1$ , by an additional relaxation contribution due to the magnetic dipole-dipole interaction between the moments of neighbouring hydrogen nuclei. This latter effect turns out to be small for the concentrations investigated, smaller than expected without the blocking of nearest-neighbour sites (Hampele 1989). These concentration dependencies show that many of the measurements are still not fully in the low concentration regime treated in this paper. Therefore a strict comparison of the experimental results with our calculations is only possible if the concentration dependence of the hydrogen mobility can be totally absorbed into concentration-

dependent effective hopping frequencies (i.e. if the mean field approximation is valid). A further probably more serious problem constitutes the influence of lattice defects (precipitates, dislocations, etc) on  $\Gamma_1$  and  $D$ . It has been found (Hampele 1989) that  $\Gamma_1$  in  $TaH_x$  depends on the strength of the applied magnetic field in a temperature range where, according to the observed diffusivity, we should still be on the high temperature side ( $\omega\tau_c \ll 1$ ) of the relaxation maximum. This was attributed to the influence of lattice defects on  $\Gamma_1$ . After subtracting the defect contribution from  $\Gamma_1$  (no correction of  $D$  has been considered) the temperature dependence of  $\alpha$  shown in figure 8 was obtained. The two curves correspond to two extreme frequency dependencies and thus two different corrections for defects compatible with the data. The full curve in figure 8 could be explained within our model if we assume that  $\alpha$  for the 'simple' diffusion model is reduced from 14.8 to about 10 due to lattice distortions around H and because of the extension of the hydrogen wavefunction. A temperature variation below 150 K as indicated by the broken curve, however, cannot be explained within our model. For  $NbH_x$  no dependence of  $\Gamma_1$  on the strength of the applied field has yet been observed. The resulting  $\alpha$  is shown in figure 9 (Hampele 1989).  $D$  for a hydrogen content of  $c_H = 0.05$ , which is close to the concentration  $c_H = 0.04$  of the  $\Gamma_1$  measurements, has been used to obtain this figure. It differs therefore quantitatively, not qualitatively, from that given in the paper of Majer *et al* (1989) who used  $D$  for  $c_H \rightarrow 0$  instead. Again the smooth increase above around 170 K could be explained by our model but the very fast drop to extremely low  $\alpha$ -values below that temperature must have another origin. One should keep in mind, however, that even above 170 K a comparison with our calculations still contains some uncertainties due to the dependence of  $\Gamma_1$  and  $D$  on the hydrogen concentration.

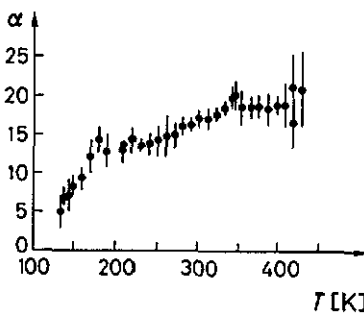


Figure 8. Temperature variation of  $\alpha$  obtained from measurements on  $TaH_x$  after correction of  $\Gamma_1$  for a defect contribution for two extreme cases compatible with the experimentally observed  $\Gamma_1$ . The curves are interpolations calculated from the data (see Hampele 1989).

## 5. Conclusions

We investigated the temperature range where hydrogen diffuses both via non-adiabatic transitions between the ground states of two nearest-neighbour interstitial wells as well as via (possibly adiabatic) transitions between excited levels or between ground states and excited levels. This is, e.g., the case for H-diffusion in Nb and Ta at

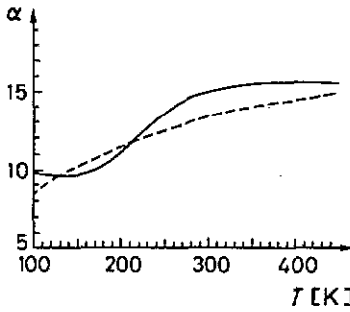


Figure 9. Experimentally determined temperature variation of  $\alpha$  for NbH<sub>x</sub> (see Hampele 1989).

elevated temperatures. We found that for a range of the model parameters, which are quite possibly relevant for hydrogen diffusion, the existence of these various diffusion paths has to be taken into account explicitly if one wants to establish the relation between hopping frequencies and quantities reflecting diffusion on a microscale, like the hydrogen spin-lattice relaxation rate  $\Gamma_1$  or quasielastic neutron scattering. It is important to realize this as a possibility of interpretation if measurements of  $\Gamma_1$  or quasielastic neutron scattering give indications of a non-simple diffusion mechanism.

The experimentally observed temperature variation of  $\alpha \sim \Gamma_1 D$  (see Messer *et al* 1986, Hampele *et al* 1989) indeed indicates the existence of an  $\alpha$  temperature dependence as predicted by a model which takes excited states into account explicitly. Our interpretation of the observed temperature variation of  $\alpha$  is completely in terms of this model which was successfully used to describe the change of slope in  $D$  versus temperature (see Emin *et al* 1979, Klamt and Teichler 1986). We neither have to introduce an unspecified mobile phase as has been done by Lottner *et al* (1979) for the interpretation of their quasielastic neutron scattering data, nor is it necessary to assume occupation of metastable octahedral sites at elevated temperatures as was done by Messer *et al* (1986) to account for the observed  $\alpha$ .

A quantitative comparison of the model with the data could provide information about the temperature variation and the absolute values of  $\nu_{TT}$  and  $\nu_{TT}^i$ , which are not accessible by an analysis of  $D$  alone and further improves on the precision of the determination of the other parameters. This quantitative comparison has not been carried out yet, since there are additional effects and still open questions concerning the dependence of  $\Gamma_1$  on the hydrogen concentration or the influence of defects on  $\Gamma_1$  and  $D$ . These questions have to be settled first by further experimental and theoretical investigations before the quantity  $\alpha$  may be used to gain a more detailed insight into the microscopic diffusion mechanism.

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## Appendix

If we neglect any hops between ground and excited states we have two entirely separated subsystems T and T'. Hopping among the different sites within one of these systems is described by just one hopping frequency and thus in the extreme motional narrowing limit the relation between  $\Gamma_1$  and  $D$  is given by (3.6) for each subsystem, i.e.,

$$\Gamma_1^T = \alpha_T g D_T^{-1} \quad \text{and} \quad \Gamma_1^{T'} = \alpha_{T'} g D_{T'}^{-1}$$

where  $D_T$  is given by (3.32) and  $D_{T'}$  by an analogous relation. If no energy exchange between the two spin systems corresponding to the systems T and T' occurs, the two spin systems would relax independently with relaxation rates  $\Gamma_1^T$  and  $\Gamma_1^{T'}$ . In reality, however, there is always sufficient energy exchange between the two spin systems on the time scales given by  $(\Gamma_1^T)^{-1}$  and  $(\Gamma_1^{T'})^{-1}$  to guarantee a common relaxation. This energy exchange could be provided, e.g., by some residual hopping between T and T' states. If this process is very slow compared to  $\nu_{TT}$  and  $\nu_{T'T'}$ , so that it may be neglected in the calculation of  $\Gamma_1$  (since it does not influence the mean time of stay at a lattice site) but is still sufficiently fast to guarantee a common relaxation, then the relaxation rate is given by

$$\Gamma_1 = p_T \Gamma_1^T + p_{T'} \Gamma_1^{T'}$$

For simplicity we put  $\alpha_T = \alpha_{T'}$  in the following. This is not very restrictive for the case which we are interested in, where  $\nu_{T'T'} \gg \nu_{TT}$  and therefore  $\Gamma_1^{T'} \ll \Gamma_1^T$ , and hence assumptions on  $\alpha_{T'}$  have very little influence on the resulting  $\Gamma_1$ . We obtain then

$$\alpha = \frac{D\Gamma_1}{g} = \left( p_T^2 + p_{T'}^2 + p_T p_{T'} \frac{D_T^2 + D_{T'}^2}{D_T D_{T'}} \right) \alpha_T$$

If the parameters of figures 4 or 6 are used to evaluate this expression we get a sharp increase of  $\alpha$  above 250 K but no leveling off (or even a reduction) at higher temperatures as in figures 4–6 where hopping between T and T' is included.

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