Atomistic Modelling of Quantum Diffusion in Metals [and Discussion]

H. R. Schober, D. K. Ross and A. M. Stoneham

Phil. Trans. R. Soc. Lond. A 1995 **350**, 297-312
doi: 10.1098/rsta.1995.0016

Atomistic modelling of quantum diffusion in metals

By H. R. Schober
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, F.R.G.

Most theories of quantum diffusion start from model Hamiltonians. The diffusion rates are calculated in terms of parameters such as an effective tunnelling frequency. Often low temperature expansions are used. In this paper we present a calculation of diffusion rates from given interatomic interactions. The approximations leading to the model description are discussed and their breakdown with increasing temperature is shown. The experimental diffusion rates for H in Nb are reproduced by a parameter free calculation.

1. Introduction

Hydrogen diffusion is strongly influenced or even determined by quantum effects. This is evidenced particularly by the non-classical isotope effect and by the large diffusion rates at low temperatures which exceed those of other interstitial atoms by orders of magnitude. A study of these effects is facilitated by the large mass ratio of up to three between the isotopes hydrogen, deuterium and tritium or even thirty if one includes the muon μ^+ as an isotope.

In classical diffusion theory the activation energy is taken as the difference in potential energy between the equilibrium and saddle point configurations. Due to the small mass there is, in the case of interstitial hydrogen, also a considerable change in vibrational energy (zero point motion) between the two configurations. The activation energy is the sum of both changes and, therefore, is isotope dependent. The sign of this isotope effect will depend on the local structure and on the material. This effect might in some cases suffice to explain the observed non-classical behaviour.

In other materials, e.g. H in Nb, much more pronounced isotope effects are observed. Here diffusion is thought to be by tunnelling between sites and commonly the term quantum diffusion is used. Diffusion of μ^+ will be by tunnelling also in materials where the quantum effects for H are small.

This paper concerns itself with quantum diffusion in this narrower restricted sense. We restrict ourselves further to the low concentration limit where the hydrogen atoms occupy random interstitial sites. Diffusion is then by random hopping from one site to a neighbouring site and interaction with other hydrogen atoms is negligible.

The basic theories for quantum diffusion of light particles in metals were derived some 20 years ago. They start from the Børn–Oppenheimer approximation where it is assumed that the electrons adiabatically follow the nuclei. Having adiabatically eliminated the electronic degrees of freedom one is left with a tunnelling

Phil. Trans. R. Soc. Lond. A (1995) **350**, 297–312
Printed in Great Britain

particle coupled to the phonons of the host crystal. The defect-phonon problem is treated in the well-known papers on phonon assisted tunnelling by Flynn & Stoneham (1970), Kagan & Klinger (1974) and by Teichler & Seeger (1981). This work originates from the small polaron theory of Yamashita & Kurosawa (1958) and of Holstein (1959).

These earlier theories break down on both sides of a temperature scale. Conventionally, the dynamics of the system is decoupled into the fast dynamics of the hydrogen, determining the 'naked' tunnelling probability, and the slower dynamics of the host atoms, represented by a phonon heat bath which 'dresses' the tunnelling probability. The hydrogen is assumed to follow the host lattice adiabatically. As a second, more stringent approximation, the naked tunnelling probability is taken to be independent of the state of the phonons, i.e. the temperature (Condon approximation). Both these approximations hold as long as only long wavelength phonon states are populated. They break down at temperatures above *ca.* 50 K. At higher temperatures the strong coupling between hydrogen and host-lattice vibrations (Lottner *et al.* 1979) gains importance. The Condon approximation is the reason of the failure of the these theories to reproduce the experimentally observed kinks in the Arrhenius plots for the diffusion constants in Nb and Ta.

Standard small polaron theory is also unable to describe the low temperature limit correctly. In recent years, it has become clear that at low temperatures the tunnelling dynamics of light interstitials is strongly affected by a non-adiabatic interaction with the conduction electrons of the host metal. These non-adiabatic electron effects are ignored in the conventional Born–Oppenheimer approximation. Kondo (1984) introduced non-adiabatic electronic effects into the theory to explain the low temperature diffusion rate of muons in metals (Hartmann *et al.* 1980).

Besides these electronic terms there are also additional phononic terms which affect the low temperature rates. Small polaron theory considers only a bilinear coupling between the hydrogen coordinate and the host lattice (one phonon coupling). The next term in the hydrogen–lattice coupling, i.e. a two phonon coupling, has been considered in detail by Kagan & Prokof'ev (1989) who use the term fluctuational preparation of the barrier. The origin of this term is the change of host lattice phonon frequencies which is caused by the hydrogen interstitial and depends on the hydrogen position. The contribution of this term at low temperatures is formally similar to the electronic one but is also present in insulators.

Distortion fields, always found in real solids, will cause a bias ϵ between adjacent minima. For temperatures $kT \leqslant \epsilon$ this bias depresses the diffusion rate.

Calculations of diffusion rates can be done by either of two ways. In one approach the system is described by a model Hamiltonian which describes all or some of the above effects. One thus describes the physics by a number of parameters (effective tunnel frequency, one phonon coupling, two phonon coupling, electron coupling and bias) and additional parameters if excited states of the hydrogen vibration are to be included. In a Debye approximation the various couplings reduce to numbers and analytical results can be derived. For a detailed review see Kagan & Prokof'ev (1992). A problem with such an approach is that the parameters cannot be assigned uniquely and that they are effective quantities which can hide effects, e.g. of real spectra. Calculations using realistic spectra, but still based on small polaron theory, were reviewed by Vargas *et al.* (1991). The model parameters for different isotopes cannot be calculated from each other.

The other approach, which we follow in this article, is to calculate the rates from atomistic properties such as interatomic couplings and forces. Since to date no sufficiently accurate *ab initio* electronic simulations are available we describe the hydrogen–metal interaction by a pair potential fitted to the localized vibrations and the long range lattice displacement (dipole tensor). The host lattice is described by Born–von Karman parameters fitted to the phonon dispersion. The calculation of the phonon contribution to the diffusion rate is then parameter free.

To get an estimate of the various effects we first calculate the energies entering the problem. From this qualitative picture we proceed to derive the matrix elements needed to calculate the dynamics of the tunnelling process. From a general Hamiltonian we abstract through a number of approximations the Hamiltonian for the tunnelling system coupled to an electronic and phononic heat bath. We then extend the standard small polaron theory to higher temperatures by avoiding the low temperature approximations. This can be done conceptually fairly easily using Fermi's golden rule but involves numerical calculations (Schober & Stoneham 1988).

2. Statics and dynamics of hydrogen in metals

As a specific example we take hydrogen in Nb (Nb:H). To get numerical estimates we use the models of Klamt & Teichler (1986) and of Sugimoto & Fukai (1980). In figure 1 we give a schematic view of the energy landscape encountered. It should be kept in mind that in reality this landscape is multidimensional and cannot be mapped onto a single reaction coordinate.

When the hydrogen is introduced into the periodic lattice it will distort the lattice and thus lower its energy. In Nb:H the hydrogen occupies tetrahedral sites and the four nearest neighbour atoms are displaced by about 0.1 Å. This lattice distortion breaks the translational symmetry; neighbouring sites are no longer equivalent. The hydrogen wave function becomes localized in the minimum (*self-trapping*). From the model calculations one estimates the difference between the total energies of the undistorted and the relaxed lattices, respectively, to $E_{\mathrm{ST}} \approx 450\,\mathrm{meV}$. This so called self-trapping energy consist to about equal parts of gain in potential energy and of the reduction of the zero-point vibrational energy. For a μ^+ interstitial we get $E_{\mathrm{ST}} \approx 900\,\mathrm{meV}$ where only about 10% is potential energy. The potential energy gain for an infinitely heavy hydrogen isotope would be about 300 meV. Comparing these numbers we see that it is advantageous to sacrifice potential energy to reduce vibrational energy. This implies a strong coupling between the hydrogen vibrations and the lattice and an isotope dependence thereof.

One of the basic assumptions of standard quantum diffusion theory is that the hydrogen is, on a relevant timescale, localized at a site and that tunnelling is from one such site to the next. To check the validity of this assumption different possible sites have to be compared. One finds localization to the tetrahedral site for H and the heavier isotopes, whereas for the μ^+ no certain answer can be given due to the predominance of the vibrational energy and the uncertainties in the interaction models.

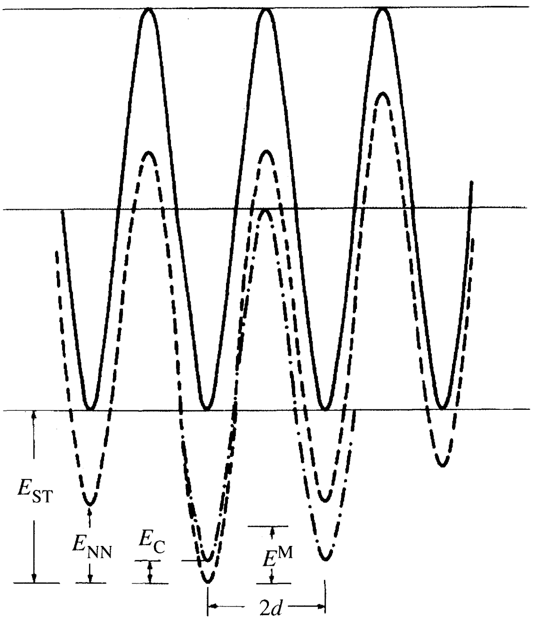

Figure 1. Schematic potential energy curves for a hydrogen interstitial ($2d$ is the distance between neighbouring interstitial sites). Solid line, metal host lattice unrelaxed; broken line, host lattice relaxed (self-trapped configuration); dot-dashed line, coincidence configuration; E_{ST} is the self-trapping energy; E_{NN} is the nearest neighbour site energy; E_c is the coincidence energy; E_M is the classical migration energy.

The dynamics of the hydrogen on its site is dominated by the localized vibration modes with frequencies of $\hbar\omega_0 = 100\,\mathrm{meV}$ and $170\,\mathrm{meV}$, respectively, where the latter mode is double degenerate. The frequencies of the localized vibrations are strongly affected by lattice distortions. In the unrelaxed lattice they would be 50–100% higher. The localized modes account for nearly 99% of the spectral intensity of the hydrogen. Additionally, the H participates in the host lattice vibrations (band modes). These modes are at much lower frequencies, the relevant energy scale is given by the Debye frequency of Nb, $\hbar\omega_D = 22\,\mathrm{meV}$. The amplitude of the H is strongly enhanced for some of these vibrations and shows a resonant like behaviour (Lottner *et al.* 1979). These latter vibrations determine, because of their lower frequencies, the temperature dependence of the thermal mean square displacements of the H below 1000 K which is a strong indication that they will also be important for the hydrogen mobility. The resonant like vibrations of the H result from the near neighbour geometry of the tetrahedral sites and consequently couple to short wavelength phonons. The coupling of the hydrogen to the long wavelength phonons is much weaker, the vibrational amplitude of the hydrogen about equals the one of the host atoms for these modes. It is important to distinguish between the three different groups of vibrations: The frequencies of the localized modes determine the order of magnitude of the tunnelling matrix element between sites (cf. (2.1)), the weakly coupled low frequency phonons give the temperature dependence in the standard small polaron theory and the excitation of resonant and localized vibrations causes the breakdown of this description towards higher energies as will be shown later.

In addition to these intrasite energies a number of intersite energies are relevant for diffusion. First, if the hydrogen is moved from its initial site i to a nearest neighbour site f without allowing the lattice to relax, the potential energy will be raised by $E_{\mathrm{NN}}^{\mathrm{elastic}} \approx 100$–$150\,\mathrm{meV}$. The change of the localized modes will add an additional contribution. These values are of the order of the localized mode energy. They prevent tunnelling in the vibrational ground state of the hydrogen but tunnelling in the excited state might be possible.

To enable tunnelling in the groundstate between sites i and f either the hydrogen has to tunnel together with its deformation field (dressed tunnelling, small polaron) or the lattice has to be deformed such that sites i and f become equivalent. There is of course an infinite number of such deformations. The minimal energy needed is called coincidence energy. It can be estimated by hypothetically putting half the hydrogen into each of the two sites. The models give values for the total coincidence energy E_{c} between 35 and 50 meV of which approximately 10 meV is the vibrational part. This coincidence energy is a measure for the strength of the phonon dressing effects.

Finally one can define a classical activation energy $E_{\mathrm{M}}^{\mathrm{cl}}$. This is the energy needed to move the hydrogen by an adiabatic deformation of the lattice from one site to the next. The saddle point configuration is then the lowest coincidence configuration for which the distance between the two sites vanishes. The model calculations give values between 70 and 130 meV as classical activation energy, of which again typically 10 meV is the vibrational part. Extrapolating from the measured vibrations of the Nb:H one obtains similar values for $E_{\mathrm{M}}^{\mathrm{cl}}$ (Lottner *et al.* 1979). This energy is of the same order or even smaller than the energies of the localized vibrations and the usual condition $E_{\mathrm{M}}^{\mathrm{cl}} \gg \hbar\omega_0$ holds only for the lattice vibrations but not for the localized ones. Hence, deviations from a classical hopping behaviour have to be expected in the Nb:H system even at high temperatures.

The similarity between classical activation energy and vibrational energy has an important consequence for the vibrational states of the hydrogen. If one takes a hydrogen in its relaxed position and excites one of the localized modes, energy can be gained by deforming the lattice towards that classical saddle-point configuration where that localized mode is unstable. The elastic energy needed is gained from the vibrational energy. In the model calculations of Sugimoto & Fukai (1980) and of Klamt & Teichler (1986) this results in delocalization of the excited states whereas experimentally even the higher excited states are observed (Hempelmann *et al.* 1981). However, an important consequence of this strong coupling between relaxations and localized modes for the diffusion of hydrogen will be the breakdown of the Condon approximation of the small polaron theory where just this dependence is neglected.

A basic quantity characterizing quantum effects is the tunnelling matrix element J in the coincidence configuration. Assuming a sine like potential between the two sites, the tunnelling matrix element can be evaluated using the eigenvalues of the Mathieu equation,

$$J = \hbar\Delta = \hbar\omega \frac{4}{\pi\sqrt{\pi}} \sqrt{\sigma} \exp{(8/\pi^2)\sigma}, \tag{2.1}$$

with

$$\sigma = 4m\omega d^2/\hbar, \tag{2.2}$$

where Δ is the tunnelling frequency, m is the mass of the tunnelling particle, ω the effective vibrational frequency and $2d$ is the distance between the two equilibrium sites. σ scales with $\sqrt{m}$ and due to the exponential dependence the tunnelling matrix element shows a very strong isotope effect. Kehr (1978) has evaluated (2.1) for Nb ($2d = 1.17$ Å) and gets the estimates $J_{\mathrm{H}} = 1.5$ meV, $J_{\mathrm{D}} = 0.14$ meV and $J_{\mu} = 85$ meV for hydrogen, deuterium and μ^+, respectively. These values are large enough to make tunnelling observable and for diffusion to be dominated by quantum effects at least at low temperatures. The observed tunnelling matrix element is of course reduced from this naked one by the effects of phonon and electron dressing which are the main subject of this paper.

3. Hamiltonian of the hydrogen–phonon system

As a first approximation the dynamics of interstitials in metals can be treated within the Born–Oppenheimer approximation which assumes that the electron distribution adjusts itself instantaneously to the ionic configuration, i.e. the electrons always occupy the momentary ground state and there is a smooth transition between these states. The only elementary excitations are then the phonons whose energies can be calculated well in this approximation. In a metal there are of course additionally electronic excitations with arbitrarily low energies and these will affect the dynamics at very low temperatures where the phonons are frozen out due to the ω^2-dependence of their spectrum. The low temperature formulae for the phononic contributions can easily by augmented by the electronic terms.

In the Born–Oppenheimer approximation the dynamics of the hydrogen metal system is determined by the kinetic energy and an effective interionic potential. The Hamiltonian can be written as

$$H = T_{\mathrm{H}} + T_{\mathrm{M}} + V_{\mathrm{M}} + V_{\mathrm{HM}}. \tag{3.1}$$

Here T_{H} and T_{M} are the kinetic energies of the hydrogen and the metal ions, respectively, V_{M} is the potential energy of the ideal metal host lattice and V_{HM} is the change due to the hydrogen. Since the displacements of the metal ions by the hydrogen are not too large, a reasonable, often used model for V_{M} is given by the harmonic approximation,

$$V_{\mathrm{M}} = \tfrac{1}{2} \sum_{\substack{m,n \\ \alpha,\beta}} s_{\alpha}^{m}\, \varPhi_{\alpha\beta}^{mn}\, s_{\beta}^{n}, \tag{3.2}$$

where $\boldsymbol{s}^m = \boldsymbol{R}^m - \boldsymbol{R}^{0m}$ is the displacement of the metal ion m from its ideal position $\boldsymbol{R}^{0m}$ and the coupling constants $\varPhi$ are taken from Born–von Karman fits to the phonon dispersion. In second quantization the displacements are expressed by phonon creation and annihilation operators $b_{q\lambda}^{+}$ and $b_{q\lambda}$:

$$\boldsymbol{s}^n = \left(\frac{\hbar}{2NM}\right)^{1/2} \sum_{q,\lambda} \frac{e(\boldsymbol{q},\lambda)}{\sqrt{\omega_{q\lambda}}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\boldsymbol{R}^n} (b_{q\lambda} + b_{-q\lambda}^{+}) \tag{3.3}$$

and

$$H_{\mathrm{ph}} = T_{\mathrm{M}} + V_{\mathrm{M}} = \sum_{q\lambda} \hbar\omega_{q\lambda}\, b_{q\lambda}^{+}\, b_{q\lambda}. \tag{3.4}$$

Here $\boldsymbol{q}$ is the wave vector, λ the polarization and $\omega_{q\lambda}$ the frequency of the phonon. The change in potential energy due to the hydrogen will, in general, be a many body potential depending on the hydrogen coordinate $\boldsymbol{R}^{\mathrm{H}}$ and on the lattice coordinates $\boldsymbol{R}^m$. The most simple approximation is to take pairwise potentials between the hydrogen and its near neighbours.

$$V_{\mathrm{HM}} = \sum_m V(|\boldsymbol{R}^{\mathrm{H}} - \boldsymbol{R}^m|). \tag{3.5}$$

The pair potential is then fitted to the experimental values of the lattice expansion and of the localized hydrogen vibrations. This Hamiltonian has the full translational symmetry of the lattice. Assuming self-trapping, i.e. that the hydrogen atom is localized at one site sufficiently long for the lattice to relax, the various energies given in the previous section can be calculated. For a truly quantum mechanical calculation this Hamiltonian is still too complex and one therefore resorts to an expansion in terms of displacements from a suitably chosen reference configuration.

Due to the exponential distance dependence of the tunnel splitting Δ (equation (2.1)), direct transitions to all but the nearest neighbour sites can be neglected. The tunnelling problem can be reduced to the tunnelling between two sites only. We introduce approximate total wave functions $\boldsymbol{\Psi}^{(\mathrm{i})}_{n_\mathrm{i}}(\boldsymbol{R}^{\mathrm{H}}, \boldsymbol{s})$ and $\boldsymbol{\Psi}^{(\mathrm{f})}_{n_\mathrm{f}}(\boldsymbol{R}^{\mathrm{H}}, \boldsymbol{s})$ for the hydrogen localized at its initial and final site, respectively. These wave functions are many body wave functions depending both on the hydrogen coordinate $\boldsymbol{R}^{\mathrm{H}}$ and on the lattice displacements $\boldsymbol{s}^n$. We enumerate the states of the system such that for $n_\mathrm{i} = n_\mathrm{f}$ the wave functions belong to equivalent states related to each other by the symmetry of the lattice of interstitial sites. The wave functions $\boldsymbol{\Psi}^{(\mathrm{i})}_{n_\mathrm{i}}$ and $\boldsymbol{\Psi}^{(\mathrm{f})}_{n_\mathrm{f}}$ are eigenfunctions of the Hamiltonians $H^{(\mathrm{i})}$ and $H^{(\mathrm{f})}$, respectively, where the potential energy in (3.1) was modified such as to produce stable potential energy wells for the hydrogen at sites (i) and (f), respectively.

The solution of the tunnelling problem involves the calculation of the matrix element

$$\begin{aligned} M_{n_\mathrm{i}n_\mathrm{f}} &= \left\langle \boldsymbol{\Psi}^{(\mathrm{i})}_{n_\mathrm{i}}(\boldsymbol{R}^{\mathrm{H}}, \boldsymbol{s}) \left| H - \tfrac{1}{2}(H^{(\mathrm{i})} + H^{(\mathrm{f})}) \right| \boldsymbol{\Psi}^{(\mathrm{f})}_{n_\mathrm{f}}(\boldsymbol{R}^{\mathrm{H}}, \boldsymbol{s}) \right\rangle \\ &= \left\langle \boldsymbol{\Psi}^{(\mathrm{i})}_{n_\mathrm{i}}(\boldsymbol{R}^{\mathrm{H}}, \boldsymbol{s}) \left| V_\mathrm{T}(\boldsymbol{R}^{\mathrm{H}}, \boldsymbol{s}) \right| \boldsymbol{\Psi}^{(\mathrm{f})}_{n_\mathrm{f}}(\boldsymbol{R}^{\mathrm{H}}, \boldsymbol{s}) \right\rangle. \end{aligned} \tag{3.6}$$

The kinetic energy terms cancel in this expression and the transition operator V_T is the change in the potential energies only. The main contribution to the matrix element is from V_T at the region of maximal overlap between the two wave functions. To calculate the matrix elements one has to integrate the potential energy surface over all coordinates.

The standard solution in the framework of small polaron theory involves four additional approximations, all of them valid only at low temperatures. First the *adiabatic approximation* for the hydrogen motion: as in the Born–Oppenheimer approximation for the electrons it is assumed that the hydrogen wave function follows the metal ions instantaneously. At any given time the hydrogen tunnelling is determined by the frozen lattice configuration at that time. The total wave function is then approximated by

$$\boldsymbol{\Psi}^{(\mathrm{i})}_{n}(\boldsymbol{R}^{\mathrm{H}}, \boldsymbol{s}) = \Phi^{(\mathrm{i})}_{n}(\boldsymbol{R}^{\mathrm{H}}; \boldsymbol{s})\chi^{(\mathrm{i})}_{n}(\boldsymbol{s}), \tag{3.7}$$

where $\Phi^{(\mathrm{i})}_n$ represents the hydrogen wave function which depends parametrically on the lattice configuration. Second, since the adiabatic approximation is only valid at low temperatures, the hydrogen wave function is restricted to the ground state $\Phi^{(\mathrm{i})}$ (*truncation approximation*).

The wave function $\Phi^{(\mathrm{i})}$ satisfies

$$(T_{\mathrm{H}}+V_{\mathrm{HM}}^{(\mathrm{i})}(\boldsymbol{R}^{\mathrm{H}},\boldsymbol{s}))\Phi^{(\mathrm{i})}(\boldsymbol{R}^{H};\boldsymbol{s})=\epsilon^{(\mathrm{i})}(\boldsymbol{s})\Phi^{(\mathrm{i})}(\boldsymbol{R}^{H};\boldsymbol{s}) \tag{3.8}$$

and the lattice wave functions $\chi_n^{(\mathrm{i})}$ satisfy

$$(T_{\mathrm{M}}+V_{\mathrm{M}}+\epsilon^{(\mathrm{i})}(\boldsymbol{s}))\chi_n^{(\mathrm{i})}(\boldsymbol{s})=E_n\chi_n^{(\mathrm{i})}(\boldsymbol{s}). \tag{3.9}$$

Inserting these into (3.6) we can define a 'naked' tunnel splitting,

$$J(\boldsymbol{s})=2\left\langle\Phi^{(\mathrm{i})}(\boldsymbol{R}^{\mathrm{H}};\boldsymbol{s})\left|V_{\mathrm{T}}(\boldsymbol{R}^{\mathrm{H}},\boldsymbol{s})\right|\Phi^{(\mathrm{f})}(\boldsymbol{R}^{\mathrm{H}};\boldsymbol{s})\right\rangle, \tag{3.10}$$

where the integration is over the hydrogen coordinates only. This tunnel splitting depends still on the lattice configuration. At low temperatures when only long wavelength phonons are excited this dependence is weak and the tunnel splitting is taken as a constant (*Condon approximation*). Some theories have already discussed the configuration dependence of $J(\boldsymbol{s})$ formally in linear approximation in $\boldsymbol{s}$. This gives rise to the so called 'barrier fluctuation effect' (Kagan & Prokof'ev 1989).

The matrix element (3.6) is obtained by averaging $J(\boldsymbol{s})$ over the lattice wave functions $\chi_{n_{\mathrm{i}}}^{(\mathrm{i})}(\boldsymbol{s})$ and $\chi_{n_{\mathrm{f}}}^{(\mathrm{f})}(\boldsymbol{s})$,

$$M_{n_{\mathrm{i}}n_{\mathrm{f}}}=\tfrac{1}{2}\langle\chi_{n_{\mathrm{i}}}^{(\mathrm{i})}(\boldsymbol{s})\,|J(\boldsymbol{s})|\,\chi_{n_{\mathrm{f}}}^{(\mathrm{f})}(\boldsymbol{s})\rangle, \tag{3.11}$$

which simplifies in the Condon approximation to

$$M_{n_{\mathrm{i}}n_{\mathrm{f}}}=\tfrac{1}{2}J\langle\chi_{n_{\mathrm{i}}}^{(\mathrm{i})}(\boldsymbol{s})|\,\chi_{n_{\mathrm{f}}}^{(\mathrm{f})}(\boldsymbol{s})\rangle. \tag{3.12}$$

The naked tunnelling term is dressed by the overlap of the initial and final state lattice wave functions, the polaron term.

As a next step, in accordance with the harmonic Ansatz for the intermetallic coupling V^M, we expand in (3.9) the energy term $\epsilon^{(\mathrm{i})}(\boldsymbol{s})$ in powers of the displacements

$$\epsilon^{(\mathrm{i})}(\boldsymbol{s})=\epsilon^{(\mathrm{i})}-\sum_{m\alpha}F_{\alpha}^{(\mathrm{i})m}s_{\alpha}^{m}+\tfrac{1}{2}\sum_{\substack{mn\\ \alpha\beta}}s_{\alpha}^{m}\,V_{\alpha\beta}^{(\mathrm{i})mn}\,s_{\beta}^{n}+\dots \tag{3.13}$$

The first term is a constant 'chemical' binding energy of the hydrogen, the second is the relaxation energy in lowest order and the third term is a change of the vibrational coupling parameters to lowest order. Taking the displacements $\boldsymbol{s}^m$ from the coincidence configuration instead of the ideal lattice position, the expansion (3.13) converges much more rapidly. The force term is reduced to

$$\tilde{\boldsymbol{F}}^{(\mathrm{i})m}=\boldsymbol{F}^{(\mathrm{i})m}-\boldsymbol{F}^{(\mathrm{c})m}\approx\tfrac{1}{2}(\boldsymbol{F}^{(\mathrm{i})m}-\boldsymbol{F}^{(\mathrm{f})m}) \tag{3.14}$$

and similarly the force constant change

$$\tilde{\boldsymbol{V}}^{(\mathrm{i})mn}=\boldsymbol{V}^{(\mathrm{i})mn}-\boldsymbol{V}^{(\mathrm{c})mn}\approx\tfrac{1}{2}(\boldsymbol{V}^{(\mathrm{i})mn}-\boldsymbol{V}^{(\mathrm{f})mn}). \tag{3.15}$$

The bulk of the force constant change is now absorbed in $\boldsymbol{V}^{(\mathrm{c})mn}$ which is no longer translationally invariant. Expressing $\boldsymbol{s}^n$ by phonon creation and annihilation operators, one sees that (3.13) is an expansion in powers of phonon operators. Normally, only the first order term is taken (*linear coupling approximation*).

At low temperatures one is interested in the coupling to long wavelength phonons which can still be described by plane waves which are slightly shifted between the initial and final states. In terms of the force dipole tensors $\boldsymbol{P}^{(\mathrm{i})}$ and $\boldsymbol{P}^{(\mathrm{f})}$ of the initial and final state configurations, respectively, one has for the long wavelength limit

$$\sum_{n\alpha} \tilde{F}^{(\mathrm{i})n}_{\alpha}\, s^{n}_{\alpha} = \left(\frac{\hbar}{2NM}\right)^{1/2} \frac{1}{2} \sum_{\boldsymbol{q}\lambda} \left[i\left(P^{(\mathrm{i})}_{\alpha\beta} - P^{(\mathrm{f})}_{\alpha\beta}\right) \frac{e(\boldsymbol{q},\lambda)_{\alpha}}{\sqrt{\omega_{\boldsymbol{q}\lambda}}} q_{\beta} \cos(2\boldsymbol{qd}) \right] + \left[\left(P^{(\mathrm{i})}_{\alpha\beta} + P^{(\mathrm{f})}_{\alpha\beta}\right) \frac{e(\boldsymbol{q},\lambda)_{\alpha}}{\sqrt{\omega_{\boldsymbol{q}\lambda}}} q_{\beta} \sin(2\boldsymbol{qd}) \right] (b_{\boldsymbol{q}\lambda} + b^{+}_{-\boldsymbol{q}\lambda}). \quad (3.16)$$

To lowest order in $\boldsymbol{q}$ this gives in view of $\omega_{\boldsymbol{q}\lambda} \sim q$

$$\sum_{n,\alpha} \tilde{F}^{n}_{\alpha}\, s^{n}_{\alpha} = \sum_{\boldsymbol{q}\lambda} c_{\boldsymbol{q}\lambda} (b_{\boldsymbol{q}\lambda} + b^{+}_{-\boldsymbol{q}\lambda}), \quad (3.17)$$

where

$$c_{\boldsymbol{q}\lambda} = u_{\lambda} \omega^{s-1/2}_{\boldsymbol{q}\lambda}. \quad (3.18)$$

Here $s = 1$ applies for tunnelling between sites with different orientation and therefore changing the dipole tensor $\boldsymbol{P}$, e.g. tetrahedral sites in bcc lattices, and $s = 2$ applies if the site symmetry does not change, e.g. octahedral sites in fcc lattices. It should be noted, however, that in Nb and Ta an isotropic dipole tensor is found so that the $s = 2$ term dominates despite the site symmetry.

Under the above approximations, which are reasonable at low temperatures, the hydrogen metal system can be mapped onto the much simpler spin boson Hamiltonian (Grabert & Schober 1994).

4. Evaluation of diffusion rates

With increasing temperature the different approximations leading to the spin boson Hamiltonian break down. First corrections to the long wavelength limit will become noticeable. These can at first be incorporated by taking a more accurate expression for the linear coupling term (3.17). When short wavelength phonons become excited the local geometry will fluctuate strongly and the Condon approximation will break down. Eventually, the localized modes of the hydrogen are excited causing a failure of the truncation approximation. Furthermore, hydrogen has been found to vibrate not only with localized modes but also with quasi-resonant modes inside the band of lattice modes. Such vibrations are not properly accounted for by the adiabatic approximation. The aim of the theory of diffusion of hydrogen at higher temperatures is therefore to circumvent the approximations, most importantly the Condon approximation.

We retain the picture that the hydrogen is in well defined states in the initial and final interstitial sites, i.e. we assume that the hydrogen occupies each site sufficiently long for self-trapping to be effective. The transition probability can than be found by the use of the Fermi golden rule expression for quantal transition rates:

$$\Gamma = \langle\langle\, w^{\mathrm{if}}\, \rangle\rangle_{n_{\mathrm{i}}} \quad (4.1)$$

with the partial rates,

$$w^{\mathrm{if}} = \frac{2\pi}{\hbar} \left| \left\langle \boldsymbol{\Psi}^{(\mathrm{i})}_{n_\mathrm{i}}(\boldsymbol{R}^\mathrm{H}, \boldsymbol{s}) \left| V_\mathrm{T}(\boldsymbol{R}^\mathrm{H}, \boldsymbol{s}) \right| \boldsymbol{\Psi}^{(\mathrm{f})}_{n_\mathrm{f}}(\boldsymbol{R}^\mathrm{H}, \boldsymbol{s}) \right\rangle \right|^2 \delta(E^{(\mathrm{i})} - E^{(\mathrm{f})}), \qquad (4.2)$$

which follows directly from (3.6). Here $E^{(\mathrm{i})}$ and $E^{(\mathrm{f})}$ are the total energies of the initial and final states, respectively and $\langle\langle \quad \rangle\rangle_{n_\mathrm{i}}$ denotes thermal averaging over initial states n_i and summation over final states n_f.

The validity of this expression is restricted to the purely incoherent regime. To study the transition from coherent to incoherent tunnelling different methods have to be used (see Grabert & Schober 1994). Also correlations between single jumps which become important at high temperatures are not included.

Since in the region of incoherent tunnelling, the hopping rate Γ is the same whether the interstitial moves in a double well potential or in a periodic crystal potential, the rate (4.2) also determines the quantum diffusion coefficient D. For a crystal with cubic symmetry one has

$$D = \tfrac{1}{6} z (2d)^2 \Gamma, \qquad (4.3)$$

where z is the number of neighbouring interstitial sites and $2d$ the distance between two sites.

Using the adiabatic, Condon and linear coupling approximations of the previous section one gets the simple expression,

$$\Gamma = \frac{\pi}{2\hbar} J_0^2 \langle\langle |\, \langle \chi^{(\mathrm{i})}(\boldsymbol{s}) | \chi^{(\mathrm{f})}(\boldsymbol{s}) \rangle \,|^2 \, \delta(E^{(\mathrm{i})} - E^{(\mathrm{f})}) \rangle\rangle_{n_\mathrm{i}}, \qquad (4.4)$$

where J_0 is the tunnel splitting of the naked hydrogen in the fixed potential of the host ions and the temperature dependence is given by the averaged overlap of the total vibrational wave functions of the host ions with the hydrogen in its initial and final position, respectively. Even in this approximation the evaluation of the transition rate is non-trivial since any vibrational mode in the initial configuration will have a non vanishing overlap with many modes in the final configuration. Only in the long-wavelength limit will the modes be only weakly affected by the local defect geometry and it is reasonable to approximate them by identical normal modes with only the mean positions of the atoms changed. The total overlap integrals (3.12) factorize then into products of the single mode overlaps which can easily be calculated. The transition rate follows as (Flynn & Stoneham 1970)

$$\Gamma = \frac{J_0^2}{4\hbar^2} \int_{-\infty}^{+\infty} \mathrm{d}t \, \exp\left\{ -\sum_q S_q \left[\coth(\hbar\omega_q / 2k_\mathrm{B}T)[1 - \cos(\omega_q t)] + \mathrm{i} \sin(\omega_q t) \right] \right\}. \qquad (4.5)$$

Here we have used the index q to denote the phonon $\boldsymbol{q}$-vector as well as the polarization. Each mode contributes with a weight given by its Huang–Rhys factor which is given in terms of the difference of the mode displacements of the initial and final configurations,

$$S_q = \frac{1}{2} \frac{m\omega_q}{\hbar} \mid d_q^{(\mathrm{i})} - d_q^{(\mathrm{f})} \mid^2, \qquad (4.6)$$

with m the host atom mass. These Huang–Rhys factors can be evaluated from (3.16). For $q \rightarrow 0$ they are $\propto q$ in the isotropic case and $\propto q^{-1}$ in the anisotropic case. The above result for the transition probability contains a divergent part due to diagonal transitions, i.e. transitions without phonon excitation. These transitions are not dealt with properly in this model. In fact a main effect of the interaction with the conduction electrons is a suppression of the diagonal transitions. Since we are interested here in the high temperature regime we follow the standard procedure and eliminate them from (4.5) which then after some transformations takes the form (Holstein 1959)

$$\Gamma = \frac{J_0^2}{4\hbar^2}\mathrm{e}^{-S(T)}\int_{-\infty}^{\infty}\mathrm{d}t\left[\exp\left\{\sum_q S_q\frac{\cos(\omega_q t)}{\sinh(\hbar\omega_q/2k_\mathrm{B}T)}\right\}-1\right]. \tag{4.7}$$

The average Huang–Rhys factor $S(T)$ describes the average phonon dressing of the tunnelling matrix element

$$S(T)=\sum_q S_q\coth\left(\frac{\hbar\omega_q}{2k_\mathrm{B}T}\right). \tag{4.8}$$

For low temperatures $S(T)$ is of the form,

$$S(T)=S(0)+W(T), \tag{4.9}$$

where the temperature dependent part $W(T)$ is proportional to T^{2s}, with the exponent s introduced in (2.27). The zero temperature dressing factor may be absorbed into a renormalized tunnelling frequency

$$\Delta=(J_0/\hbar)\mathrm{e}^{-S(0)/2} \tag{4.10}$$

and the transition rate can be written as

$$\Gamma=\tfrac{1}{4}\Delta^2\mathrm{e}^{-W(T)}\int_{-\infty}^{+\infty}\mathrm{d}t\left[\mathrm{e}^{-\Xi(T,t)}-1\right], \tag{4.11}$$

where

$$\Xi(T,t)=-\sum_q S_q\frac{\cos(\omega_q t)}{\sinh(\hbar\omega_q/2k_\mathrm{B}T)}. \tag{4.12}$$

Going to the high temperature limit using the Debye approximation of the phonon spectrum Γ takes the simple form (Flynn & Stoneham 1970)

$$\Gamma=(\pi/16\hbar^2E_\mathrm{c}k_\mathrm{B}T)^{1/2}J^2\exp(-E_\mathrm{c}/k_\mathrm{B}T). \tag{4.13}$$

This describes a near Arrhenius behaviour with the coincidence energy E_c as activation energy. Even by fitting the values of J and E_c this result cannot reproduce the measured diffusion constants, in particular the observed change in slope of the measured diffusion constant in Nb and Ta. One remedy would be to introduce transitions between excited states or different sites with a second set of parameters J and E_c (Vargas *et al.* 1991).

A more satisfactory approach is to avoid the serious approximations made, in particular the Condon approximation. In the 'occurrence probability' method (Emin *et al.* 1979; Klamt & Teichler 1986) the adiabatic approximation is partially retained but one averages over possible coincidence configurations. Also transitions between differently excited localized H states are included. Since different coincidence configurations have different tunnelling probabilities for the 'naked' H an additional temperature dependence is found which can explain the change in slope of the Arrhenius-plot of diffusion of H in Nb. Gillan (1987) uses quantum molecular dynamics to identify the symmetric coincidence configurations. A direct calculation of the transition rate is not yet possible and the influence of asymmetric coincidence configurations is difficult to estimate. Both methods allow a comparison with classical diffusion.

We follow here another approach, the embedded cluster method (Schober & Stoneham 1982). There one makes use of the spatial localization of the resonant and localized modes. We do not separate the hydrogen and host degrees of freedom but treat a cluster of atoms (typically 6–21 atoms) explicitly and use the above approximations only for the embedding of the cluster into the rest of the host crystal. The limitations of this method are mainly due to computer capacity. The number of degrees of freedom one can treat explicitly is limited owing to the number of integrations involved in calculating a single transition element w^{if}. On the temperature side one is limited by the rapid increase in terms w^{if} contributing to the total transition rate Γ.

To see the temperature range where the polaron expression breaks down we calculate first an average coherent tunnelling rate, given by thermally averaging the diagonal elements ($n_{\mathrm{i}} = n_{\mathrm{f}}$) of (3.16)

$$\hbar\Delta(T) \approx 2\langle \boldsymbol{\Psi}^{(\mathrm{i})}_{n_{\mathrm{i}}} | V_{\mathrm{T}} | \boldsymbol{\Psi}^{(\mathrm{f})}_{n_{\mathrm{i}}} \rangle_{n_{\mathrm{i}}}. \tag{4.14}$$

Using the simplifications leading to (4.5) for the transition rate in the incoherent case, (4.14) simplifies to

$$\hbar\Delta(T) = J\mathrm{e}^{-S(T)/2}, \tag{4.15}$$

where $S(T)$ is again the average Huang–Rhys factor. The total dressing $\mathrm{e}^{[-S(T)/2]}$ of the tunnelling matrix element is of order 0.1 for Nb:H at low temperatures.

In figure 2 we compare the temperature dependencies of $\Delta(T)$ in Nb:H for both the full expression evaluated in the embedded cluster approach and for the weak coupling formula (4.15). The calculations were done using the interaction potential of Sugimoto & Fukai (1980) with harmonic wave functions as basis. For low temperatures we find agreement between the two expressions but for $T > 40$ K the full expression predicts a strong isotope dependent structure absent in the simplified form. This indicates a breakdown of the adiabatic and Condon approximations at temperatures where the resonant-like (in-band) vibrations of the H are excited. The same effects are apparent in the variance of $\Delta(T)$ which increases rapidly with temperature. At $T \approx 50$ K it reaches 50%. In passing we want to note that an estimate of $S(T)$ from isotropic elasticity theory seriously underestimates $S(T)$ by about a factor 5 which again shows that the bulk of the dressing stems from short wavelength phonons.

For the same model we have evaluated the incoherent transition rate. In the embedded cluster approach the partial rates (4.2) take the form

$$w^{\mathrm{if}} = \frac{2\pi}{\hbar} |\langle \boldsymbol{\Psi}^{(\mathrm{i})}_{n_{\mathrm{i}}} | V_{\mathrm{T}} | \boldsymbol{\Psi}^{(\mathrm{f})}_{n_{\mathrm{f}}} \rangle|^2 G(E^{(\mathrm{i})} - E^{(\mathrm{f})}). \tag{4.16}$$

Here the wave functions $\boldsymbol{\Psi}$ are wave functions of the cluster only (or of selected important modes) and the δ function is replaced by a shape function which accounts for the broadening of the sharp modes of the atomic cluster by the embedding into the lattice and for the omitted long range displacements.

In doing the integrals in (4.16) V_{T} was expanded up to quadratic terms. We

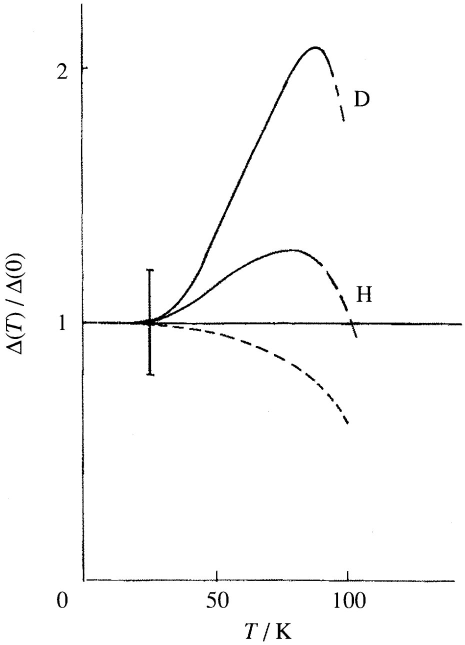

Figure 2. Temperature dependence of the average tunnelling rate for hydrogen and deuterium in Nb calculated from (4.14) (solid line) and in the weak coupling approximation (4.15) (dashed line), respectively. The error bar gives the variance (Schober & Stoneham 1991).

thus take both two phonon processes and barrier shaking into account. Excitation levels were included up to $n = 4$ for the single modes and transitions up to $n_{\mathrm{i}} = n_{\mathrm{f}} \pm 2$ for each mode were included. Figure 3 shows the results for the diffusion coefficients of H and D, together with the experimental values. From $T \simeq 50$ K upwards we find an Arrhenius behaviour with a sudden change in activation energy at $T \simeq 250$ K. This kink can be understood from the partial rates, w^{if}. At low temperatures transitions are only possible without exciting the localized vibrations of the H. The transition rate is therefore determined by the in-band excitations only and can be described by a formula as (4.13) with an activation energy of about 30 meV close to the coincidence energy of our model. At higher temperatures scattering from the band states into the localized vibrational states of the H becomes possible, $m_{\mathrm{loc}} = 0 \rightarrow n_{\mathrm{loc}} = 1$. These transitions with an excited localized state have much larger tunnelling matrix elements and hence gain importance. At still higher temperatures transitions between excited H-vibrations become dominant. This general behaviour is in qualitative agreement with the results of the occurrence probability approach (Klamt & Teichler 1986).

The model so far describes the general behaviour. It severely underestimates the diffusion constant, however. This has to be expected, since using harmonic wave functions, one underestimates the overlap between final and initial states. So far the actual potential shape was included in the Hamiltonian but not in the wave functions. To get a better quantitative agreement one has to improve on the latter. For this purpose the anharmonic expansion parameters of the potential energy at the initial and final equilibrium sites were studied. Three types of anharmonic terms were found to be important:

(i) Fourth and higher order terms in the localized H vibrations $(\phi^{(4)} s_{\mathrm{loc}}^{4})$ to

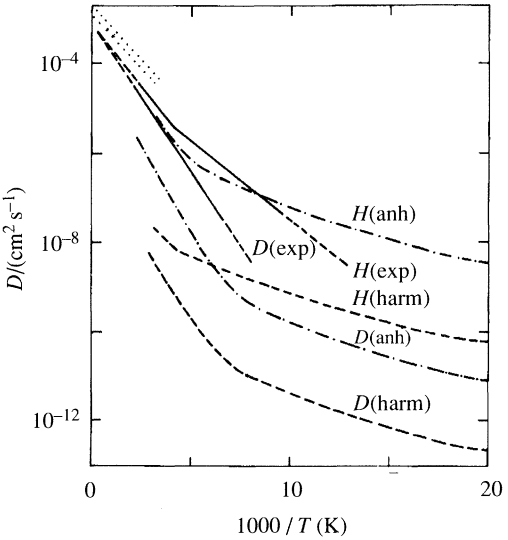

Figure 3. Diffusion constants of hydrogen and deuterium in Nb. Solid line, experimental results (Qi *et al.* 1983); broken line, calculation (Schober & Stoneham 1991) with harmonic wave-functions; dash-dotted line, calculation including anharmonic corrections; dotted line, Vineyard (1957) approximation for high temperatures.

bring the tunnelling frequency of the naked hydrogen up to the value of WKB type expressions.

(ii) Third order couplings between localized and band modes $(\phi^{(3)} s_{\text{band}} s^2_{\text{loc}})$. These terms account for a reduction of the localized mode frequency when the lattice is deformed.

(iii) Third order couplings between two of the localized modes due to the nearby extremum of energy at the octahedral site.

Taking anharmonicity into account by first order perturbation theory and taking appropriate correction factors to reproduce the WKB result for the naked hydrogen tunnelling, the agreement with the experimental results is markedly improved without changing the general shape of the curves. At low temperatures the activation energy is still much smaller than the experimental value. This might be due to the underlying interaction model. On the other hand in NMR experiments a value of 37 meV was found (Messer *et al.* 1984) in much better agreement to the calculated value of 30 meV.

According to this model the diffusion of H at room temperature is still influenced strongly by quantum mechanics. The calculation is not sufficiently accurate to see whether and how the classical limit is reached at higher temperatures. For comparison figure 3 shows also the results of a calculation of the Vineyard (1957) approximation for classical diffusion. The shift in the prefactor between H and D is about what one would expect from the mass difference. The activation energy is 97 meV and 96 meV for H and D, respectively. Here 90 meV is the potential energy part. The discrepancy between our quantum results and these classical ones is not sufficient to draw any definite conclusion. Gillan (1987) puts the classical to quantum transition already at the kink. Since there will be a smooth transition and due to differences in the model this need not be in contradiction to our results.

For the low temperature regime of diffusion (4.5) is a good starting point. One best transforms the sum over q-values to one over frequencies. The non-adiabatic electron coupling adds then an additional term to the Huang–Rhys factors. Due to its different ω dependence this additional term lifts the divergence due to diagonal transitions and causes the observed increase of the diffusion rates at low temperatures. A bias between the sites and two phonon terms lead to additional terms in the exponent (Kagan & Prokof'ev 1992; Grabert & Schober 1994).

5. Conclusions

Model descriptions of quantum diffusion suffer by the large number of parameters one has to introduce in order to take all possible mechanisms into account. To get simple results a number of approximations are usually introduced. The strong interaction between the hydrogen and the host lattice is not fully taken into account. Already at fairly low temperatures the approximations start to break down. In the embedded cluster method, using the interatomic interactions as only input, it is possible to calculate the diffusion rates of hydrogen in Nb. To get a fully quantitative description the knowledge of the hydrogen lattice interaction should be improved. Any such calculations have to take the hydrogen zero point motion into account.

References

Emin, D., Baskes, M. J. & Wilson, W. D. 1979 The diffusion of hydrogen and its isotopes in BCC metals. *Phys. Rev. Lett.* **42**, 791–794.

Flynn, C. P. & Stoneham, A. M. 1970 Quantum theory of diffusion with application to light interstitials in metals. *Phys. Rev.* B **1**, 3966–3978.

Gillan, M. J. 1987 Quantum simulation of hydrogen in metals. *Phys. Rev. Lett.* **58**, 563–566.

Grabert, H. & Schober, H. R. 1994 Theory of tunneling and diffusion of light interstitials in metals. In *Hydrogen in metals III* (ed. H. Wipf). Berlin: Springer Verlag.

Hartmann, O., Karlsson, E., Norlin, L. O., Niinikoski, T. O., Kehr, K. W., Richter, D., Welter, J. M., Yaouanc, A. & Hericy, J. L. 1980 Muon diffusion and trapping in aluminium. *Phys. Rev. Lett.* **44**, 337–340.

Hempelmann, R., Richter, D. & Kollmar, A. 1981 Localized vibrations of H and D in Ta and their relation to the H(D) potential. *Z. Phys.* B **44**, 159–165.

Holstein, T 1959 Studies of polaron motion. *Ann. Phys. (NY)* **8**, 325–389.

Kagan, Yu. & Klinger, M. I. 1974 Theory of quantum diffusion of atoms in crystals. *J. Phys.* C **7**, 2791–2807.

Kagan, Yu. & Prokof'ev, N. V. 1989 Special role of the two-phonon interaction in the problem of quantum tunneling with dissipation in a crystal. *Sov. Phys. JETP* **69**, 1250–1260.

Kagan, Yu. & Prokof'ev, N. V. 1992 Quantum tunneling diffusion in solids. In *Quantum tunneling in condensed media* (ed. Yu. Kagan & A. J. Legget), pp. 37–144. Amsterdam: North Holland.

Kehr, K. 1978 Theory of the diffusion of hydrogen in metals. In *Hydrogen in metals. I. Topics in applied physics*, vol. 28 (ed. G. Alefeld & J. Völkl), pp. 197–225. Berlin: Springer Verlag.

Klamt, A. & Teichler, H. 1986 Quantum-mechanical calculations for hydrogen in niobium and tantalum. *Phys. Status Solidi* (b) **134**, 103–114; 533–544.

Kondo, J. 1984 Diffusion of light interstitials in metals. *Physica* B **125**, 279–285.

Lottner, V., Schober, H. R. & Fitzgerald, W. J. 1979 Band modes of hydrogen in the BCC metals Nb, V, Ta. *Phys. Rev. Lett.* **42**, 1162–1165.

Messer, R., Blessing, A., Dais, S., Höpfel, D., Majer, G., Schmidt, C., Seeger, A., Zag, W. & Lässer, R. 1984 Nuclear magnetic resonance studies of hydrogen diffusion, trapping and site occupation in metals. *Z. Phys. Chem. (NF) Suppl.* H **2**, 62–119.

Qi, Z., Völkl, J., Lässer, R. & Wenzl, H. 1983 Tritium diffusion in V, Nb and Ta. *J. Phys.* F **13**, 2053–2062.

Schober, H. R. & Stoneham, A. M. 1982 Motion of interstitials in metals: quantum tunneling at low temperatures. *Phys. Rev.* B **26**, 1819–1828.

Schober, H. R. & Stoneham, A. M. 1988 Diffusion of hydrogen in niobium. *Phys. Rev. Lett.* **60**, 2307–2310.

Schober, H. R. & Stoneham, A. M. 1991 Diffusion of hydrogen in transition metals. *J. Less. Comm. Met.* **172–174**, 538–547.

Sugimoto, H. & Fukai, Y. 1980 Theory of light interstitials in BCC metals. *Phys. Rev.* B **22**, 670–680.

Teichler, H. & Seeger, A. 1981 One-phonon processes in phonon-assisted tunneling jumps at low temperatures. *Phys. Lett.* A **82**, 91–94.

Vargas, P., Miranda, L., Rodriguez, L., Lagos, M. & Rogan, J. 1991 Quantum diffusion in transition metals. *J. Less-Common Met.* **172–174**, 557–571.

Vineyard, G. H. 1957 Frequency factors and isotope effects in solid state rate processes. *J. Phys. Chem. Solids* **3**, 121–127.

Yamashita, J. & Kurosawa, T. 1958 Small polarons in metals. *J. Phys. Chem. Sol.* **5**, 34–45.

Discussion

D. K. Ross (*Salford University, U.K.*). Has the possibility of quantum tunnelling to next-nearest sites been included?

H. R. Schober. The tunnelling element for direct tunnelling to next nearest neightbours is much smaller than that for nearest neighbour tunnelling. Direct tunnelling to next nearest neighbours, therefore, should not contribute significantly to hydrogen diffusion. There is of course, just as in classical diffusion, correlation between subsequent tunnelling events. A calculation of this effect is difficult and I have not included it in my calculations.

A. M. Stoneham (*Harwell Laboratory, Oxfordshire, U.K.*). In principle Dr Schober's results include both the polaron and barrier lowering terms (following Dr Prokof'ev's choice of names). How do these compare?

H. R. Schober. My results incude both the polaron and the barrier fluctuation effect. I have not made a systematic separation of the two effects. To do this the adiabatic approximation for the hydrogen would have to be introduced. The data do, however, show that in the temperature region studied the quadratic effects (barrier fluctuation) are much smaller than the polaron ones.