Diffusion of Hydrogen in Niobium

H. R. Schober
Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, West Germany

and

A. M. Stoneham
Theoretical Physics Division, Harwell Laboratory, Didcot, Oxfordshire OX11 0RA, England

(Received 19 January 1988)

The diffusion rate of H and D in Nb is calculated with avoidance of the usual adiabatic, linear-coupling, and Condon approximations. The method employed is a generalization of the standard small-polaron theory with explicit account taken of the coupled interstitial-host vibrations. It is applicable in the medium temperature regime, $50\ \mathrm{K} \leq T \leq 300\ \mathrm{K}$, and is not limited to light interstitials. Whereas a harmonic calculation exhibits the qualitative features, anharmonic terms have to be included to get quantitative results.

PACS numbers: 66.30.Jt, 61.70.Bv, 63.20.Mt

The diffusion of hydrogen in metals has been the subject of numerous investigations both theoretically and experimentally; see, e.g., Fukai and Sugimoto[1] for a review. Apart from the technological aspects one of the reasons for this interest is the small mass of the hydrogen which makes it ideally suited for studies of the transition from quantum-mechanical behavior (tunneling) to a more classical diffusion process. A particular advantage is the large mass ratio between its isotopes H, D, T, and the analogous case of μ^+. Most recent work in this field is limited to the low-temperature regime ($T < 50$ K). In this Letter we present a method suitable to intermediate temperatures ($50\ \mathrm{K} < T < 300$ K). As a test system we take H and Nb at low H concentrations.

Let us first summarize the experimental results relevant to this work, taken from the review[2] if not stated otherwise. Hydrogen occupies tetrahedral sites in the Nb lattice. The induced long-range displacement field is isotropic and the nearest neighbors are displaced by about 0.1 Å.[3] The vibrational spectrum of the H is dominated by two localized vibrations with frequencies of 27 and 43 THz, respectively. These localized vibrations account for nearly 99% of the spectral intensity. Additionally the H participates in the lattice vibrations (band modes) and its amplitudes are strongly enhanced for some of these vibrations (resonantlike behavior).[4] These latter vibrations determine, because of their lower frequencies, the temperature dependence of the Debye-Waller factor below 1000 K indicating their importance for mobility at not too high temperatures. Coherent (bandlike) tunneling of H cannot be observed in pure Nb but has been found for H trapped at O and N impurities; see, e.g., Wipf and Neumaier.[5] The diffusion rate in Nb has been measured by numerous groups for temperatures ranging from 110 to 500 K. It can be described by an Arrhenius law, $D = D_0 \exp(-E_a/kT)$, where for H the activation energy, E_a, changes at $T = 250$ K from 68 to 106 meV, whereas for D a constant value of 127 meV was found above $T = 150$ K.

In a theoretical treatment, one can distinguish various temperature regimes of the coupled H-host system. In the limit $T \rightarrow 0$, all phonon and electron degrees of freedom are frozen and the H can only move by coherent tunneling. In this process the H plus its surrounding displacement field and its electron cloud move from one site to an equivalent one without excitation of phonons or electron-hole pairs. With increasing temperature, tunneling will also occur between excited states, so that the coherent tunneling rate becomes temperature dependent. However, even at very low temperatures transitions between nonequivalent configurations, i.e., with excitations of phonons and electron-hole pairs, will dominate. With increasing temperature, first the electronic excitations and later the phononic ones dominate.[6] This changeover causes a minimum in the transition rate which has been seen for μ^+ in metals.[7] For H itself, evidence for electronic dressing effects is gained from the change of the tunnel splitting at the transition to superconductivity.[8] The first phonons to be excited are the long-wavelength ones. In this regime the incoherent transition rate can be calculated by path-integral techniques if we assume that Debye phonons are linearly coupled to the H position.[9,10] If we increase the temperature further, the detailed structure of the coupled H-Nb vibrational system becomes important until finally the localized H vibrations are excited. It is this temperature region which is the subject of this note. The transition rate will be dominated by the phononic degrees of freedom. Summing[10] over the electronic states, one gains an electronic shape function which accounts for the energy exchange with the electronic heat bath. This electronic shape function eliminates the divergence in the purely phononic problem caused by the coherent terms, i.e., those involving no phonon absorption or emission in the transition.[10] We will make use of this property in following the standard procedure of omitting these singular terms whose weight goes rapidly to zero with increasing temperature. Otherwise we will neglect the electronic shape function since it is much narrower than its phononic counterparts and since our results do not depend strongly on the width of the total shape function.

We propose a new method which allows us to take the actual structure of the vibrations into account and which overcomes some limitations of previous work. Our method is a generalization of the standard approach to absolute diffusion rates for light interstitials by Flynn and Stoneham[11] which involves several distinct ideas. The first is that sensibly localized states exist, between which transitions occur. The second, related, idea is that of self-trapping: The interstitial leads to a distortion of the host lattice which effectively immobilizes the interstitial. The transition probability can be found by use of the Fermi "golden rule" expression for quantal transition rates

$$W^{if} = \langle\langle w^{if} \rangle\rangle_m, \tag{1}$$

$$w^{if} = (2\pi/\hbar)\,|\langle \Psi_i(m)\,|\,H - E_{im}\,|\,\Psi_f(n)\rangle|^2\,\delta(E_{im} - E_{fn}), \tag{2}$$

where Ψ_i and Ψ_f are the initial- and final-state many-body wave functions, m and n denote the respective excitational states, $\langle\langle \cdots \rangle\rangle_m$ denotes thermal averaging over the initial states m and summation over the final states n, and finally $E_{im} = \langle \Psi_i(m)\,|\,H\,|\,\Psi_i(m)\rangle$. To evaluate this expression, additional approximations were introduced: (i) an adiabatic approximation to decouple the H and lattice degrees of freedom, (ii) the assumption of linear coupling between phonons and defect position, which means that the phonons are merely displaced in the transition but not altered, and (iii) the Condon approximation that the H tunneling element is independent of the phonon occupation. Under these approximations the Fermi "golden rule" expression becomes identical to the phonon part of the transition rate calculated by the path-integral method (both omitting the coherent terms).[10] One thus arrives at a simple expression

$$W^{if} = (2\pi/\hbar)\,|J|^2\,|\sigma^{if}|^2. \tag{3}$$

This equation can be evaluated approximately, and one finds in the high-temperature case

$$W^{if} = (\pi/4\hbar^2 E_c kT)^{1/2}\,|J|^2 \exp(-E_c/kT). \tag{4}$$

The activation energy, E_c, in (4) is the so-called coincidence energy, i.e., the minimal energy necessary to deform the lattice such that the initial and final configurations—of H plus lattice—are equivalent. The most successful extension of this simple model, still within the adiabatic approximation but improving on the Condon approximation, is the occurrence probability approach,[12,13] where one evaluates J for all coincidence configurations and averages with respect to lattice energy and excitation of the localized H vibrations. These approximations explain the observed H diffusion qualitatively at least.

Whereas the previous approximations relied on a linear (and, by implication, weak) hydrogen-phonon interaction, here we want to drop this restriction, which is inconsistent with the occurrence of resonant vibrations and with comparatively large self-trapping energies. We, therefore, do not treat separately the hydrogen and lattice degrees of freedom in (2) and thus we avoid the adiabatic, linear coupling, and Condon approximations of the earlier calculations. In a previous paper[14] we have shown how the rate can be evaluated by an "embedded cluster" method. The calculation can be broken down into the following stages: (i) choice of interaction model, (ii) calculation of structure, energies, and eigenmodes, (iii) evaluation of the tunnel splitting and of the transition probabilities w^{if} and the total rate W^{if}.

For the interaction we used the model of Sugimoto and Fukai,[15] where the H-Nb interaction is via a double exponential potential smoothly cut off after the second neighbor and where the Nb-Nb interaction is described via Born–von Kármán parameters. The validity of this potential is certainly limited[4,16] but should be sufficient for our purpose since the nearest-neighbor displacement and the localized vibrations, which matter most, are correctly reproduced. In agreement with experiment, the stable configuration of the hydrogen interstitial is tetrahedral. We find for H a self-trapping energy of $E_{\mathrm{st}} = 470$ meV, where 300 meV is potential energy and the change of the zero-point vibrations contributes 170 meV. The minimal coincidence configuration energy is $E_c = 41$ meV (31 meV potential energy and 10 meV zero-point motion) and the classical saddle-point energy is $E_a = 61$ meV (potential energy only).

As a first approximation we take as eigenstates in the initial and final configurations the harmonic ones obtained by diagonalization of the dynamic matrix for clusters of 6 to 21 atoms. As in the full problem the eigenmodes are split into the three localized vibration modes and the rest in-band modes. Using these eigenmodes and a correction term for the rest of the lattice,[14] we find at $T = 0$ K a tunnel splitting of $\Delta E_T = 0.01$ meV, smaller than the value of 0.2 meV observed for H trapped in Nb-O. This underestimate is probably due to a slightly different geometry for Nb-O-H as compared with Nb-H. Our value will also be an underestimate because the overlap will be smaller for the harmonic wave functions than for the exact ones. Comparing our results with WKB results,[13] and assuming a sinusoidal potential shape, one gains a correction factor of approximately 1.3.

The total transition rate sums over all possible initial and final mode occupancies, with energy conservation as the only restriction. With increasing temperature, the number of terms diverges rapidly. In order to evaluate (2), therefore, we divide the modes into strongly and weakly coupled ones. The latter ones we treat by the usual small-polaron formalism, whereas we sum over the strongly coupled ones explicitly. Equation (2) is transformed into

$$w^{if}=2\pi/\hbar\,|\langle\Psi_i(m)\,|\,H-\tfrac{1}{2}(E_{im}+E_{fn})\,|\,\Psi_f(n)\rangle|^2 G(E_{im}-E_{fn}). \tag{5}$$

Here the δ function is replaced by a shape function which consists of two distinct factors. One comes from the line broadening, i.e., it accounts for the broadening of the sharp modes of the atomic cluster by the embedding lattice. We take a form

$$G_v(\omega)=(1/\sqrt{\pi})W_v\exp[-(\omega-\Omega)^2/W_v^2], \tag{6}$$

where $W_v=\sum_\sigma \omega^\sigma(m_\sigma+n_\sigma)$ is the total width and $\hbar\Omega=\sum_\sigma \hbar\omega^\sigma(m_\sigma-n_\sigma)$ is the difference in vibrational energy between the initial and final states. As widths w^σ of the individual modes σ, we took zero and 1.0 THz for the localized and band modes, respectively. The final result shifts only slightly when we change the width of the band modes from 0.5 to 2.0 THz. The second factor in the shape function stems from the change in mean displacement of the weakly coupled modes outside of the cluster as the hydrogen atom jumps. It corresponds to the dressing terms in (3). Its magnitude is, however, strongly reduced since we have included the bulk of the dressing explicitly in (5). It accounts mainly for the long-wavelength phonons. To simplify the evaluation we may take the high-temperature limit of this term,

$$G_R(\omega)=(16\pi E_R kT)^{-1/2}\exp[-(\hbar\omega+4E_R)^2/16E_R kT], \tag{7}$$

where we estimate from the overlap of $T=0$ K that $E_R=6$ meV. To evaluate (5) it was found sufficient to include excitation levels up to $n,m=4$ and transitions up to $n=m\pm2$. Figure 1 shows our results for the diffusion coefficients of H and D, together with the experimental values. From $T\simeq50$ K upwards, we find an Arrhenius behavior with a sudden change in activation energy at $T\simeq250$ 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) with an activation energy of ≈ 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, $m_{\text{loc}}=0\rightarrow n_{\text{loc}}=1$. These transitions with an excited localized state have much larger tunneling elements and hence become dominant. At still higher temperatures, transitions between excited H vibrations become dominant. This general behavior is in qualitative agreement with the results gained by the occurrence probability approach.[13]

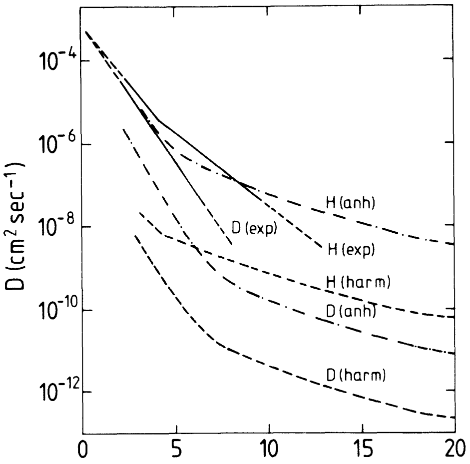

FIG. 1. Diffusion constants of H and D in Nb: solid line, experimental results (Ref. 2); dashed line, calculation with harmonic wave functions; dash-dotted line, calculation including anharmonic corrections.

The model so far is able to describe the general behavior. 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 we have included the actual potential shape only in the Hamiltonian in (2) but not in the wave functions. To get a better quantitative agreement we have to improve on the latter. For this we studied the anharmonic expansion parameters of the potential energy at the initial and final equilibrium sites. Three types of anharmonic terms were found to be important:

(i) Fourth- and higher-order terms in the localized H vibrations ($\phi^{(4)}u_{\text{loc}}^4$). Including these terms leads to an increased tunneling rate at $T=0$. This can be estimated from quasi one-dimensional models including only the localized modes.[14] We estimate that the "harmonic" tunneling frequency should be corrected by factors of 1.3 and 2.6 for H and D, respectively. These factors account basically for the difference in tunnel splitting in a sine-shaped potential with WKB-type expressions and an expression like (2) with harmonic wave functions.

(ii) Third-order couplings between localized and band modes ($\phi^{(3)}u_{\text{band}}u_{\text{loc}}^2$). These terms are important for the low-temperature behavior. They account for the reduction of the localized frequencies when the surrounding lattice is appropriately deformed.

(iii) A third-order coupling between two of the localized modes due to the extremum at the nearby octahedral interstitial site.

If we include the third-order anharmonicity by first-order perturbation theory for the wave functions, and take the correction factors of (i), the agreement with the experimental values is markedly improved without change in the general shape of the curves. The main remaining deficiency is the low-temperature activation energy which is too low. We think this is caused by deficiencies in the underlying model of the H-Nb interaction, which underestimates the effects of the H on the host lattice.[4]

As far as the method is concerned, we have demonstrated that a lattice-dynamical model of quantum diffusion is able to explain H diffusion. The advantage of such a model is the possibility of our studying the influence of the individual processes contributing to diffusion in detail. The applicability of such a model is not restricted to light interstitials.[14] The method is limited on the low-temperature side by the transition to coherent processes, and on the high-temperature side by the steep increase of the number of states which has to be included. However, this approach can bridge the gap between the low-temperature path-integral calculations[9,10] and the high-temperature calculations.[17] Moreover, the method avoids the restrictions of the adiabatic, linear-coupling, and Condon approximations, and can exploit any newer developments in interatomic potentials.

As regards the special case of H in Nb, our calculation shows that both the low- and high-temperature diffusion are quantum processes. This is evidenced by the isotope effect on the high-temperature activation energy which is much larger than the "classical activation energy" of the model.

Part of the work described in this report was undertaken as part of the Underlying Research Programme of the United Kingdom Atomic Energy Authority.

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