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Temperature-Dependent Diffusion Coefficients from *ab initio* Computations: Hydrogen in Nickel

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The temperature-dependent mass diffusion coefficient is computed using transition state theory. *Ab initio* supercell phonon calculations of the entire system provide the attempt frequency, the activation enthalpy, and the activation entropy as a function of temperature. Effects due to thermal lattice expansion are included and found to be significant. Numerical results for the case of hydrogen in nickel demonstrate a strong temperature dependence of the migration enthalpy and entropy. Trapping in local minima along the diffusion path has a pronounced effect especially at low temperatures. The computed diffusion coefficients with and without trapping bracket the available experimental values over the entire temperature range between 0 and 1400 K.

Diffusion in solids is of broad interest and fundamental importance for understanding the properties of materials including segregation, phase transformation, hydrogen embrittlement, and corrosion. Despite this importance, there is a serious lack of reliable experimental mass diffusion data. For example, experimental values for the diffusion coefficients of hydrogen in metals such as titanium [1] and aluminum [2] are scattered over many orders of magnitude and values for many important systems are not reported in the literature at all. Only in a few cases such as hydrogen in nickel, experimental data from different groups are reasonably consistent to serve as reliable benchmarks for computational approaches [3,4].

As a result of progress in *ab initio* computational methods, it is now possible to calculate an increasing number of materials properties at a level of accuracy close to and

sometimes better than available from experiment. The present work demonstrates that this can be achieved for hydrogen diffusion in nickel, provided that thermal effects are consistently taken into account. The approach is based on *ab initio* theory and it is applicable to a range of diffusion mechanisms including interstitial diffusion of impurities, self-diffusion, and vacancy-assisted diffusion of substitutional atoms. The computations provide novel insight into the thermodynamic aspects of the diffusion process including the change of the entropy of the entire system between the stable state and the transition state as a function of temperature.

Ab initio methods at various levels of approximation have been used in the study of solid-state diffusion [5-11]. However, no previously reported study has taken advantage of *ab initio* phonon calculations of the entire system to obtain attempt frequencies, enthalpies, and entropies as a function of temperature.

The present work is based on Eyring's concept of the activated complex [12] as applied by Wert and Zener [13] to impurity diffusion in solids. Density functional theory combined with the direct approach for phonon dispersions are employed in the *ab initio* computation of the energy hypersurface, vibrational frequencies, activation enthalpy, and the activation entropy. All vibrational degrees of freedom of the entire supercell are taken into account. In addition, effects due to thermal expansion are included in a self-consistent manner.

The interstitial diffusion of hydrogen atoms in solid nickel consists of jumps between octahedral sites involving a transition state and a metastable tetrahedral site (*cf.* Figs. 1 and 2). In their original work Wert and Zener [13] assumed the vibrational entropy of the transition state to be higher than that of the stable state due to the strain-induced reduction of the elastic moduli when the diffusing atom is at the transition state. The present calculations for H in Ni show that this is true only up to a temperature of 500 K. For higher temperatures, the situation is reversed. This *ab initio* result demonstrates the importance of the temperature-dependence of the vibrational entropy in diffusion processes.

In the case of H in Ni, the presence of a metastable tetrahedral site along the diffusion path causes an additional complication. To elucidate the role of this feature of the H-Ni system, the diffusion coefficient is computed with and without trapping in the intermediate tetrahedral site. The numerical results of the two extreme cases bracket the experimental diffusion data summarized by Völkl [3] over the entire temperature range, thus indicating a partial trapping of hydrogen atoms along the diffusion path.

Eyring's theory of the activated complex [12] assumes that the reaction proceeds over a transition state, which is in thermodynamic equilibrium with its surrounding. The reaction rate is given by (i) the ratio between the partition functions of the system in the transition state and the initial state including the Boltzmann factor $\exp[-\Delta E/(RT)]$, which involves the activation energy ΔE , and (ii) the mean velocity of the reactants crossing the transition state. In the present case, the first term is obtained from electronic structure total energy and phonon calculations. Following Eyring, the second term is taken from the temperature-dependent velocity distribution of classical particles at a temperature T .

At the transition state, the particular degree of freedom corresponding to motion along the diffusion path is taken to be a free translation [12]. Thus, there is one more vibrational mode in the stable site than in the transition state. Furthermore, one particular vibrational mode leads the system from the initial geometry to the transition state. For the case considered here, the identification of this mode is readily obtained from an inspection of the phonon dispersions (*cf.* Fig. 3). It is a linear combination of the three degenerate vibrational modes of an H atom in an octahedral site with a frequency of 24.3 THz. One of these modes is separated, thus balancing the number of vibrational degrees of freedom in the transition state and in the ground state. When we apply these ideas [12] to the diffusion of an atom in a solid [13] we obtain the following expression for the diffusion coefficient, D ,

$$D = n\beta d^2 \nu^* e^{-\frac{\Delta G^*}{kT}} \quad (1)$$

where n is the number of nearest-neighbor stable sites, β is the probability that a jump to a nearest-neighbor site leads forward in the direction of diffusion, and d is the length of the jump projected onto the direction of diffusion. In the case of H in fcc Ni, we have $n=12$, $\beta = 1/3$ and $d=a/2$ with a being the lattice parameter of the conventional face-centered cubic unit cell of Ni.

The jump frequency ν^* is given by

$$\nu^* = \frac{kT}{h} \left(1 - e^{-\frac{h\nu}{kT}} \right) \quad (2)$$

where the frequency ν corresponds to the mode of the stable state leading to the transition state. Note that Wert and Zener [13] set $\nu^* = \nu$. This approximation is not justified for H in solids, where the frequencies are above 20 THz.

The effective free energy difference ΔG^* is given by

$$\Delta G^* = \Delta G + g_v \quad (3)$$

$$\Delta G = E_{el}^{TS} - E_{el}^0 + \tilde{E}_{TS}^{vib} - E_{vib}^0 - T(\tilde{S}_{vib}^{TS} - S_{vib}^0) \quad (4)$$

$$g_v = -dT \ln \left(1 - e^{-\frac{h\nu}{dT}} \right)^{-1} \quad (5)$$

The terms E_{el} are the electronic energies. $\tilde{E}_{vib}^{TS}$ and $\tilde{S}_{vib}^{TS}$ are the vibrational enthalpy and entropy of the transition state computed with one mode less than at the ground state. E_{vib}^0 and S_{vib}^0 are the corresponding terms of the stable state. The term g_v is the contribution to the free energy from the particular vibrational mode of the ground state, which leads to the transition state.

The electronic energies needed in eq. (4) are computed with density functional theory [14] in its spin-polarized form [15] with the generalized gradient approximation [16] and all-electron frozen-core projector-augmented-wave potentials [17] as implemented in the Vienna *ab initio* simulation package (VASP) [18]. Thermodynamic functions are obtained from phonon dispersions, which are computed by the direct method [19] with *ab initio* forces from VASP as integrated in the MedeA computational environment [20].

The system is described by a 2x2x2 Ni supercell containing 32 host atoms and one H impurity. In the geometry optimizations and the evaluation of the electronic energies, the one-particle wave functions are expanded in a plane wave basis with a cut-off energy of 337 eV. Integrations over the Brillouin zone are performed using a 5x5x5 Monkhorst-Pack k-mesh and a tetrahedron scheme with Blöchl corrections. In the phonon calculations, a non-spin-polarized Hamiltonian is used, the 5x5x5 k-mesh is maintained, and the plane wave cut-off is reduced to 270 eV.

The calculations give a lattice parameter for pure nickel of 3.5197 Å, which is 0.1 % larger than the experimental value (3.5238 Å) [21] when extrapolated to $T=0$ K (3.517 Å). The thermal expansion of the pure nickel lattice is computed from temperature-dependent free energies, as obtained from phonon calculations of five different lattice parameters. A fit leads to the form of $a(T) = 3.5197 + 3.12 \times 10^{-5} T$ with a in Å.

A hydrogen impurity is placed at the octahedral (O) and tetrahedral (T) interstitial sites, near the transition state (TS), and at the local maximum between two octahedral sites (M). All atomic positions are then relaxed until the largest force on any atom is below the convergence criterion of 0.01 eV/Å. The resulting energy hypersurface shows that the

lowest-energy path from one octahedral site to an adjacent site leads over a transition state, which is located between the tetrahedral and the octahedral sites as illustrated in Fig. 2. An important feature of the energy hypersurface of interstitial H in Ni is a pronounced local minimum at the tetrahedral site. The shortest path between two adjacent octahedral sites leads over the point M, where a diffusing atom would be exactly at the midpoint of a Ni-Ni bond. The electronic energy of this point is a maximum on the energy divide as shown in Fig. 2. The critical points on the energy hypersurface are thus those at the stable octahedral site, the transition state, and the metastable tetrahedral sites.

The phonon dispersions of 32-atom Ni supercells with a hydrogen atom at one of these three characteristic sites are shown in Fig. 3. When the octahedral site is occupied, there is one three-fold degenerate dispersionless phonon branch at 24.3 THz which corresponds to the vibration of the interstitial hydrogen atom. All phonon frequencies are positive indicating a true minimum on the energy hypersurface. When the transition state is occupied, the highest H-related frequency is shifted to 47.1 THz. This doubly degenerate mode corresponds to a vibration of the H atoms perpendicular to the diffusion path. By definition, a transition state is characterized by the occurrence of one negative eigenvalue in the dynamical matrix. This corresponds to a motion of the H atom along the diffusion path. This mode has an imaginary frequency, which is plotted as a “negative” frequency at -21.4 THz. The magnitude of the curvature of the energy hypersurface across the transition barrier is nearly the same as the curvature around the minimum at the octahedral site (compare 21.4 THz and 24.3 THz). Inspection of the hypersurface (Fig. 2) makes this plausible. The energy profile along the diffusion path from the stable site to the transition state is well described by a sinusoidal energy profile, as originally suggested by Wert and Zener [13]. When the tetrahedral site is occupied, all phonon branches are positive indicating a local minimum. Due to the confined interstitial space in a tetrahedral site, the corresponding vibrational mode of an H atom has a higher frequency, namely 38.7 THz, compared with 24.3 THz in an octahedral site. Integration of the phonon dispersion over the entire Brillouin zone leads to phonon densities of states, thus allowing the evaluation of the zero-point energy, the temperature-dependent enthalpy, entropy, and free energy.

The phonon calculations are repeated for a lattice expanded by 2.1%. The total energies and thermodynamic functions are then interpolated between the results from the two reference lattice parameters, thus taking into account thermal expansion. As expected, an expansion of the lattice leads to a softening of vibrational modes. In particular, the frequency of the H atom in the stable octahedral site is shifted from 24.3 THz to 22.7 THz at a temperature of 1000 K.

The dependence of the enthalpy and entropy on the temperature and the effect of lattice expansion are investigated next. To this end, we take differences between the thermodynamic functions at the transition state and the octahedral ground state. The results are shown in Fig. 4. The enthalpy difference increases slightly at low temperatures and then decreases steadily for temperatures above room temperature. The entropy difference shows a similar behavior. At low temperatures, the vibrational entropy is larger when the H impurity occupies the transition state compared with an occupancy of the octahedral site. At temperatures above 500 K, the reverse is the case as the entropy in the octahedral geometry increases faster than that of the transition state. In their original work, Wert and Zener [13] assumed the term ΔS to be positive, since an impurity at the transition state might lower the shear modulus of the host lattice, which would lead to an increase in the entropy. The present calculations show that the situation is more complicated due to the strong temperature dependence of the entropy. In the difference of the free energy, the decrease in ΔH is offset by the entropy term $-T\Delta S$, so that the free energy difference between the transition state and the stable state decreases at low temperatures, reaches a minimum around 650 K and then increases at higher temperatures. Fig. 4 also illustrates the fact that the zero-point energy of the system at the transition state is higher than at the stable octahedral site.

A thermal expansion of the lattice lowers the diffusion barrier and increases the entropy of the transition state as shown in Fig. 4. Technically, the differences shown in Fig. 4 are taken between two systems, where the reference state has one more vibrational degree of freedom than the transition state. As will be shown below, this effect is small and introduces a noticeable correction only at high temperatures.

The temperature-dependent diffusion coefficients of H in Ni are evaluated for five different levels of theory of increasing complexity, thus providing detailed insight into the importance of each approximation. The first level neglects thermal expansion, it makes the approximation of $\nu^* = \nu$, and it ignores the fact that the number of vibrational degrees of freedom are different for the transition state and the ground state. Furthermore, the presence of metastable tetrahedral sites is ignored. This leads to the form

$$D_1 = a^2 \nu e^{-\frac{\Delta G}{kT}} \quad (6)$$

with ΔG being defined by eq. (4). The resulting diffusion coefficient is higher than the experimental values over the entire temperature range. The computed slope $d(\ln D)/d(1/T)$ decreases in magnitude for higher temperatures, but remains fairly similar to the experimental value (*cf.* Fig. 5). Inclusion of thermal expansion shifts the computed diffusion coefficients to higher values by a significant amount (see the red band between

curves D_1 and D_2 in Fig. 5). On the logarithmic scale of an Arrhenius plot, this effect is noticeable even at room temperature.

At the next level of theory, we maintain the inclusion of the thermal expansion and use ν^* as given by eq. (2). This has a substantial effect as can be seen from a comparison of D_2 and D_3 in Fig. 5. The computed diffusion coefficient is reduced and moves closer to the experimental data especially at low temperatures. The correction for the additional vibrational mode in the ground state has only a very small impact except at very high temperatures, where the present quasi-harmonic approach becomes less appropriate (compare D_3 and D_4 in Fig. 5).

The last step is the inclusion of trapping in the metastable tetrahedral site. Using the approach of McNabb and Foster [22], we introduce an effective diffusion coefficient

$$D_{eff} = \frac{D_{latt}}{1 + \frac{N_T}{N_L} e^{-\frac{E_b}{kT}}} \quad (7)$$

We take D_{latt} to be D_4 of the previous analysis. The ratio N_T/N_L represents the number of trapping sites per lattice site. In the case of an fcc lattice there are two tetrahedral sites per lattice sites, hence $N_T/N_L=2$. We identify ΔG_b with the difference in the free energy between the transition state and the metastable tetrahedral site. As in the case of the difference between the transition state and the stable octahedral ground state, we correct for the additional vibrational mode. In the present case, ΔG_b is of the order of -10 kJ/mol, which is approximately $\frac{1}{4}$ of the activation energy (*cf.* Fig. 4).

The inclusion of this term has a significant impact on the computed diffusion coefficient bringing the computed values well below the experimental results. (see D_5 in Fig. 5). Earlier it had been noted that the complete neglect of the tetrahedral sites gives a diffusion coefficient, which is too high. These results indicate that the diffusing hydrogen atoms are retarded by the metastable tetrahedral sites along the diffusion path, but not fully trapped as implied in eq. (7).

Given the overall agreement of the present *ab initio* calculations with the experimental data for this rather complex physical property, it is important to assess the uncertainties in the present computational approach.

- (1) Transition state theory assumes thermal equilibrium of the activated complex. Given the large difference in masses between hydrogen and nickel atoms, such equilibrium may not be achieved. On the other hand, the presence of a local minimum at the tetrahedral site may actually increase the residence time near the transition state. Therefore, the assumption of thermal equilibrium appears reasonable.
- (2) In his original paper Eyring [12] introduces a factor, c , which accounts for processes, when the activated complex crosses the transition barrier and then returns to the initial state. This factor reduces the diffusion rate. Wert and Zener [13] implicitly set $c=1$. It appears reasonable in the present case to retain this assumption.
- (3) A fundamental approximation in the present approach is the use of a quasi-classical description of the hydrogen atom rather than a quantum mechanical treatment of the proton describing lattice-assisted quantum tunneling in the framework of a Flynn-Stoneham model [23]. Recent work by Sundell and Wahnström [9] has demonstrated that H diffusion in transition metals such as Nb and Ta is best described in terms of an over-barrier motion for elevated temperatures. Given the relatively high barriers for H in Ni the present approach appears to be justified, especially at elevated temperatures. It should be stressed that the present calculations do include zero-point energies in the evaluation of the effective free energy of activation.
- (4) The dominant term in the diffusivity is the effective height of the diffusion barrier. There is some evidence and also accumulated lore to the effect that the DFT-GGA level of theory may underestimate barrier heights. To this end, we performed a sensitivity analysis by arbitrarily increasing the diffusion barrier by 20%. This lowers the diffusivity on average by an order of magnitude. “Good” agreement with experimental data would be obtained by ignoring trapping, by neglecting the lattice expansion, by using ν instead of ν^* and by scaling the barrier by 20%. However, in such an *ad-hoc* approach, the slope of $\log(D)$ vs $1/T$ would not agree well with experimental data [3,4]. While some shortcomings in the DFT-GGA approach cannot be ruled out, the present results indicate that the barrier height is probably correctly described and that all the other effects cannot be ignored, especially trapping in tetrahedral sites.
- (5) At higher temperatures, non-harmonic vibrational effects may start to play a role. A comparison of the present computed results with experimental data indicates that the actual diffusion coefficient at high temperatures is lower than that predicted with the quasi-harmonic approximation. However, recent studies of the temperature dependence of the thermodynamic functions of metal hydrides show [24] that the quasi-harmonic phonon approach is valid for a large range of temperatures even close to the melting point. Therefore, the present approach may be applicable up to fairly high temperatures.

In summary, transition state theory has been applied to the diffusion of interstitial hydrogen in nickel. The key features of this approach are (i) all thermodynamic functions are computed with an *ab initio* phonon approach taking into account all vibrational degrees of freedom of the system, (ii) a metastable intermediate state at the tetrahedral sites of H in Ni is treated in the form of trapping, and (iii) effects due to the thermal expansion of the host lattice are included.

The key conclusion are (i) the temperature dependence of the thermodynamic functions is important; in particular, the entropy of the system at the transition state is larger than at the stable state only for temperatures below 500 K; above this temperature the reverse is true, (ii) the computed results of the diffusion coefficient with and without trapping in the metastable tetrahedral site bracket the experimental data indicating that the diffusing hydrogen is only partially trapped in the tetrahedral site, (iii) thermal expansion of the lattice has a significant effect on the computed diffusion coefficient. Thus, transition state theory combined with *ab initio* phonon calculations provides detailed insight into the thermodynamic and kinetic aspects of impurity diffusion in solids. The accuracy of the approach opens exciting perspectives for the *ab initio* calculation of diffusion coefficients for other systems, where experimental data are missing or difficult to obtain.

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FIG. 1 Conventional fcc unit cell with an interstitial impurity atom diffusing from an octahedral site O a distance d in the z -direction to a nearest-neighbor octahedral site O' . M denotes the midpoint between O and O' ; T denotes a tetrahedral interstitial site. The equivalent transition states are labeled TS and TS' .

FIG. 2. Energy hypersurface (electronic energy) of H diffusing in nickel between octahedral interstitial sites. Note the pronounced local minimum at the tetrahedral site (T) and two transition states (TS and TS') along the path from O to O'. The blue dashed-dotted line is the energy divide.

FIG. 3. Computed phonon dispersions of a 32-atom Ni supercell with an H atom in the stable octahedral site (oct), the transition state (TS), and the metastable tetrahedral site (tet). The computations were performed for a lattice constant of $a=3.5197$ Å. The isolated, dispersionless phonon branches are related to vibrations of the H atom. The mode with an imaginary frequency at the transition state (plotted as negative frequency) corresponds to the motion of the H atom across the barrier. The symmetry of the supercell describing the TS state is different from that of the octahedral and tetrahedral sites, which is reflected in the labeling of the special points in the Brillouin zone.

FIG. 4. Differences of the free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) between the transition state and the stable octahedral site as a function of temperature and lattice parameter. The changes in the electronic energy (ΔE_{el}) and the zero-point energy (ΔE_{zp}) are shown in connection with the enthalpy in the upper left of the graph. Values corresponding to a lattice parameter of $a=3.5197 \text{ \AA}$ and $3.5936 \text{ \AA}$ are shown in long and short-dashed lines, respectively. The thermodynamic functions corresponding to a temperature-dependent lattice parameter are drawn as solid lines. The free energy of trapping (ΔG_{trap}) is the difference between the free energy of the transition state and the tetrahedral site taking into account the expansion of the lattice.

FIG. 5. Computed and experimental diffusion coefficient of H in Ni. The narrower shaded band illustrates the increase of the diffusion coefficient due to the thermal expansion of the lattice. The broader shaded region is limited by a diffusion coefficient computed without trapping (D_4) and with full trapping (D_5). The experimental values fall between D_4 and D_5 .