

A First-Principles Study of the Vacancy-Mediated Silver Impurity Diffusion in fcc Nickel

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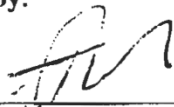


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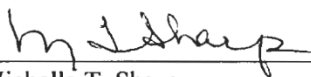
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ABSTRACT

In this report, *ab initio* techniques in Density Functional Theory, (DFT) are used to calculate the vacancy-mediated self-diffusion coefficient and impurity diffusion coefficient of silver (Ag) in pure fcc nickel (Ni). Prediction of diffusion coefficients is one of the most stringent tests of the ability of DFT calculations, because of the complex interplay of lattice constant, vacancy formation enthalpy, solute-vacancy binding enthalpy, and vibrational frequencies. The Ag diffusion and Ni self-diffusion coefficients calculated in the present work compare very favorably to previous experimental self-diffusion and Ag diffusion data. Extension of the methodology to nickel alloys is envisioned in future work.

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ACRONYMS & ABBREVIATIONS

DFT	Density Functional Theory
DFPT	Density Functional Perturbation Theory
fcc	face-centered cubic
GGA	Generalized Gradient Approximation
GW	One-body Green's function (G) and dynamically screened Coulomb interaction (W)
HTTR	High Temperature Test Reactor
LDA	Local Density Approximation
NEB	Nudged Elastic Band Method
PAW	Projector Augmented Wave
PBE	Perdew-Burke-Ernzerhof
TST	Transition State Theory
VASP	Vienna Ab initio Simulation Package

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1. INTRODUCTION

Silver possesses a peculiar ability to escape the silicon carbide layer of tristructural-isotropic (TRISO) fuel used in high-temperature gas reactors (HTGRs). While it is not thought to be a significant contributor to source terms, silver released in this manner may nevertheless be transported throughout the primary circuit. In an HTGR employing a direct Brayton cycle, ^{110m}Ag may deposit on turbine blades, and thus represents a potentially significant contributor to the dose received by personnel performing necessary maintenance on the turbine. If ^{110m}Ag deposited on the surface proceeds to diffuse into the bulk of the turbine blade material, it ceases to be removable contamination, exacerbating the problem. It is therefore of interest to understand the mechanisms of silver diffusion into candidate high-nickel superalloys, in order to inform alloy selection so as to mitigate this issue.

Diffusion is responsible for many different material properties and phenomena, such as diffusional phase transformations, high-temperature creep, and coarsening. One of the most common means of atomic diffusion in crystalline solids is via the vacancy mechanism [1], and vacancies are therefore of fundamental importance to the properties of metals and alloys.

Parameter-free first-principles approaches based on density functional theory (DFT) provide a powerful method for obtaining detailed point defect energetics. They are increasingly used to predict self- and impurity diffusion of elements in pure metals and multi-component alloys [1, 2-4]. In this report, we demonstrate the feasibility of combining a thermodynamics integration method with *ab initio* total energy calculations in order to evaluate thermodynamics properties, namely the impurity coefficient. We demonstrate the efficacy of the methodology by applying it to both self-diffusion in pure fcc nickel (Ni), and impurity diffusion of silver (Ag) in pure fcc Ni, and comparing with experimental data [5-7]. The ultimate objective is to apply similar methods as predictive models for Ag diffusion in high-nickel superalloys, and extension to these more complicated materials is discussed.

2. DIFFUSION THEORY AND EQUATIONS

The present work focuses on vacancy-mediated self-diffusion and Ag diffusion in the pure fcc Ni crystalline solid and calculates the lowest energy diffusion path of an atom between the initial and final states of an elementary atomic jump. Essentially, two processes are occurring. First, the defect, in this case a vacancy or Ag, is formed. Second, a thermally activated jump occurs, where the diffusing atom and the first nearest neighbor vacancy exchange lattice sites, known as vacancy-atom exchange. The macroscopic diffusion coefficient can then be written in terms of microscopic parameters; i.e., the atomic jump distance and jump frequency. In order to compare experimental data directly, one can represent the diffusion coefficient in Arrhenius form [8]:

$$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

in which D_0 is the prefactor (intercept), k_B is Boltzmann's constant and E_a is the activation energy for diffusion

(slope). The activation energy for diffusion, E_a , is

the summation of enthalpies of vacancy formation, H_v , and binding with impurity X, H_b , and impurity

migration:

$$D = D_0 \exp\left(-\frac{H_v + H_b + H_m}{RT}\right) \quad (2)$$

The prefactor, D_0 , includes the change in the entropy of the lattice vibrations that arises from the constriction of the diffusing atom when it is at the top of the barrier. It may be defined as

$$D_0 = \frac{1}{4} \nu \lambda^2 \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (3)$$

where f is the jump correlation factor, here equal to 0.7815 [9] for the fcc lattice, a is the lattice parameter,

and ΔS_v and ΔS_b are the changes in the vibrational entropies due to the introduction of one vacancy and the

vacancy binding with impurity X (here, Ag). They are related to changes in the vibrational frequencies of

atoms surrounding the vacancy or vacancy-impurity pair. The effective jump frequency is ν , which can be

determined according to the harmonic approximation within the transition state theory (TST) [10].

In particular, the effective jump frequency is expressed as the ratio of the product of normal vibration frequencies of the initial state of atomic migration to that of the non-imaginary normal frequencies of the transition state,

$$\nu = \frac{\prod \nu_i}{\prod \nu_i^\ddagger} \quad (4)$$

where ν_i and ν_i^\ddagger are the normal vibrational frequencies

in the initial well and in the activated transition state, respectively, for a system of N atoms. The vacancy

formation energy, E_f , can be obtained from

$$E_f = E_{vac} - E_{host} \quad (5)$$

where H is the total enthalpy of the corresponding system, and V_N indicates the vacancy in an N -site

supercell. The solute–vacancy binding energy, E_b , is defined as

$$E_b = E_{X-V} - E_X - E_V \quad (6)$$

where X indicates the substitutional element in an N -site supercell.

3. COMPUTATIONAL METHODOLOGY

Ab initio calculations are used in this work to determine lattice constants, defect formation enthalpies, migration barriers, binding enthalpies, and vibrational frequencies for the Ni self-diffusion and Ag impurity diffusion coefficients in a pure fcc Ni system. All calculations were performed using the projector augmented-wave (PAW) method [11] as implemented in the *Vienna ab initio simulation package* (VASP) [12-13] with the provided GW PAW potentials [14]. The potentials used treat all semi-core states as valence. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [15] parametrization was utilized for the exchange-correlation functional.

We employed supercells with 32 lattice sites (2x2x2 conventional fcc cells), replacing one host atom with Ag as the impurity atom, or removing one host atom to form a vacancy. The energy cutoff for the plane wave basis was 500 eV. The Brillouin zone was sampled with a Monkhorst–Pack k point mesh of $12 \times 12 \times 12$. All degrees of freedom of the crystal structures were allowed to relax, including cell shape, cell volume, and atomic positions using the conjugate gradient algorithm as implemented in the VASP code, until the forces on all unconstrained atoms were ≤ 0.01 eV/Å. The energy convergence in self-

consistent field calculations was chosen to be 10^{-5} eV. All calculations were spin polarized and allowed for magnetic ordering. Migration barriers were determined by the nudged elastic band method (NEB) [16]. Vibrational frequencies were determined via the calculation of the interatomic force constants, using density functional perturbation theory (DFPT) as implemented in VASP 5.4.

4. RESULTS AND DISCUSSION

The methods outlined in Section 2 have been used to calculate vacancy-mediated Ni-self and Ag diffusion coefficients in pure fcc Ni. The parameters needed for vacancy-mediated impurity diffusion are summarized in Table 1. All values are determined using *ab initio* methods, and all optimized structures are ferromagnetic.

Table 1. Calculated properties from current PBE calculations to, in comparison with, experimental data and other theoretical calculations.

Property	System	Present work	Experimental data	Other computations
a (Å)	fcc Ni	3.50	3.5238 [17] 3.5157 [18]	3.5239 [19]
ΔH_f (eV)	vacancy	1.48	1.4 [5] 1.73 [6] 1.56 [7]	1.40-1.45 [3] 1.63-1.81 [4]
ΔH_m (eV)	vacancy	1.19	1.5 [5] 1.04 [6]	
Q (eV) ($\Delta H_f + \Delta H_m$)	vacancy	2.67	2.90 [5] 2.81 [20] 2.77 [6]	2.62-3.03 [4]
$-\Delta H_b^{Ag-V}$ (eV)	Ag-V	-0.283		
$\Delta H_f^V - \Delta H_b^{Ag-V}$ (eV)	Ag-V	1.197		
$\Delta H_m^{Ag/Ni}$ (eV)	Ag-V	0.732		
$Q^{Ag/Ni}$ (eV) ($\Delta H_f - \Delta H_b + \Delta H_m$)	Ag-V	1.929	2.047 [5]	
	vacancy	11.272		
(THz)				
	Ag-V	1.053		
(THz)				
	vacancy	N/A	3.3 [7]	1.82 [19]
(K _B)				

(κ_B)	Ag-V	N/A		
D_0 (cm ² /sec)	vacancy	0.0666	1.9 [5] 0.534 [20]	0.0444-0.0745 [4]
D_0 (cm ² /sec)	Ag-V	0.0062	0.025 [5]	

4.1 Lattice Parameter

Table 1 lists the lattice parameter, a . The lattice parameter for pure Ni has been experimentally measured at room temperature to be 0.35238 nm [17] and 0.35157 nm at 50 K [18]. The *ab initio* calculated value used in this work is 0.35 nm (0.35239 nm [19]), which is considered to be at 0 K. Since the models are appropriate when there is only a dilute amount of solute present (~1% or less), the pure Ni lattice constant is used for all tracer diffusion calculations. The *ab initio* calculated lattice parameter value will be used in order to be consistent with the other *ab initio* determined values.

4.2 Thermodynamic Properties

In order to calculate the concentration of thermally created vacancy defects, the enthalpy of formation must be determined. The calculations of enthalpy of formation and the solute–vacancy binding energy are more or less routine nowadays; however, the evaluation of the vibrational entropy changes S_f and S_b is non-trivial due to problems obtaining converged values, which seems to require a very large effort to adjust DFT parameters. In this report, we have assumed values of $1.82 k_B$ [19] and $0.0 k_B$ for S_f and S_b , respectively. We are currently still performing actual calculations of these due to vibrational contributions.

The thermodynamic properties of the initial and transition states of a jump need to be determined to calculate its effective jump frequency, ν , using Equation (4). Each initial state is completely relaxed

with respect to internal coordinates, the volume, and shape. We quantitatively determine the transition state with the saddle point along the minimum energy diffusion path by NEB [16] calculations. Conducting NEB calculations is specifically important for the case of jumps with asymmetry between the initial and final states.

Table 1 illustrates our calculated enthalpy of vacancy formation *and migration barrier* in pure fcc

Ni, as well as the enthalpy of solute–vacancy binding (Δ) *and migration barrier* Q of Ag in Ni. Where

available, these quantities are compared with experimental measurements. We find a good

agreement between our first-principles-calculated energetics and experimentally measured quantities.

The corresponding Arrhenius parameters are presented in Table 1, along with the results from a previous DFT study [4], the Zhang mobility assessment [20] and selected single-crystal experimental data [5-6]. Table 1 shows that in the present work, the activation energies for self-diffusion and vacancy-

mediated Ag diffusion, , are within 10% (< 6% for Ag-Ni) of the single-crystal experimental data. In

general, the data appears lower than the prediction for finite temperature calculations. Similar trends are

observed for the diffusion prefactor, .

Note that our DFT calculations were performed at 0 K. There is clearly a discrepancy between the high-temperature (closer to the melting temperature) estimates from experiments and low-temperature approximations from DFT. We suspect that this discrepancy with experimental data may be due to the use of non-equilibrium quenching methods to obtain the experimental values [4], a large scatter in the data at lower temperatures, and a strong non-Arrhenius behavior in measurements close to the melting temperature [3], in contrast with the $T = 0$ K *ab initio* calculations.

4.3 Diffusion Coefficients

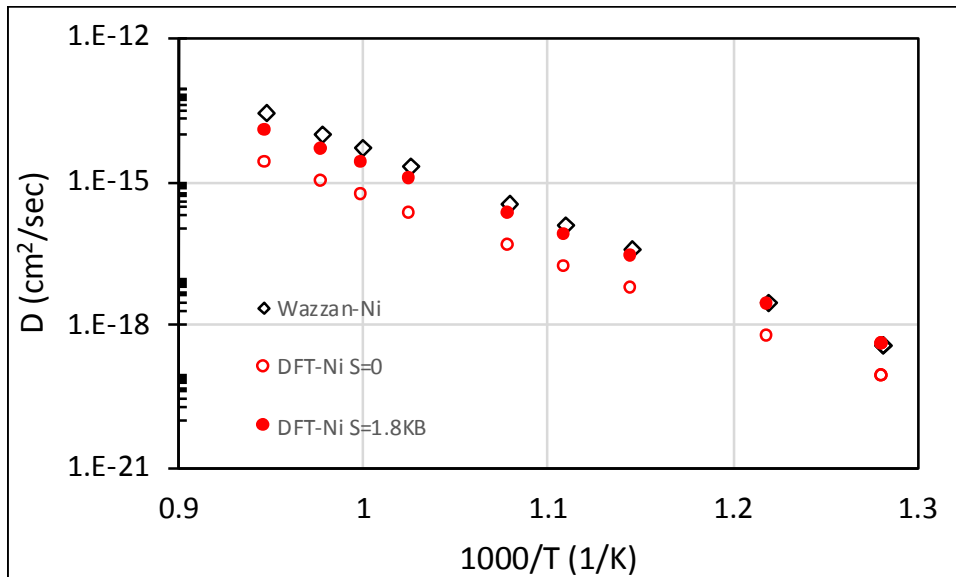
After Arrhenius diffusion data were determined within the GGA and DFPT, the diffusion coefficients were calculated according to Equation (1). Figure 1 shows our prediction results for self-diffusion and vacancy-mediated Ag diffusion in pure fcc Ni for two vacancy-formation vibrational entropies of $1.8 k_B$ and $0 k_B$, respectively, alongside experimental data. Prediction of diffusion coefficients is one of the most

stringent tests of the ability for DFT calculations, because of the complex interplay of lattice constant, vacancy formation enthalpy, solute-vacancy binding enthalpy, and vibrational frequencies in these supercell calculations including defects. As shown in the Arrhenius plot of D versus $1000/T$ in Figure 1, the accuracy in general is quite impressive, given the expected accuracy of current DFPT calculations, especially with the value of $1.82 k_B$ for the vacancy formation vibrational entropy adopted from previous DFT calculations [19]. In fact, the discrepancy is only significant in the case where the vacancy formation vibrational entropy is not taken into account, in which case the prediction is about half an order of magnitude lower than the experimental data at low temperatures, and about an order of magnitude lower at high temperatures.

With , *the most significant discrepancies* with the experimental data are underestimation by about

0.05 orders of magnitude at low temperatures for Ni self-diffusion, as well as overestimation by about 0.06 orders of magnitude at high temperatures for Ag diffusion. Even there, the discrepancy might be attributed to the fact that experimental data only exists in the higher-temperature paramagnetic regime above the Curie temperature of Ni around 625 K, and our DFPT calculations are at 0 K with spin-polarized and magnetic ordering leading to a ferromagnetic phase. In fact, nickel is ferromagnetic up below its Curie temperature, at which point it transforms to paramagnetic phase. This makes direct, quantitative comparison with experimental data very difficult. In addition, the discrepancy may also result from the small vacancy-formation entropy change due to vibrational frequencies at different temperature.

Previous first-principles studies of diffusion coefficients in the literature have used either the Debye model or the phonon supercell approach [4] for calculating finite temperature thermodynamic properties. Particularly at lower temperatures, the results on the Arrhenius plots in general underestimate the experimental diffusion data in all cases, and the most significant underestimation was about an order of magnitude. At high temperature, the underestimation is about half an order of magnitude. Consistent with other observations in the literature, the use of the phonon supercell approach (i.e., Debye model or quasiharmonic approximation) for the calculation of finite temperature thermodynamic properties within the local density approximation (LDA) and lower energy cutoff results in an underestimation of the diffusion coefficient with respect to experimental data. Apparently, present work using GGA-derived exchange and correlation functionals with the DFPT approach yields much better results [3].



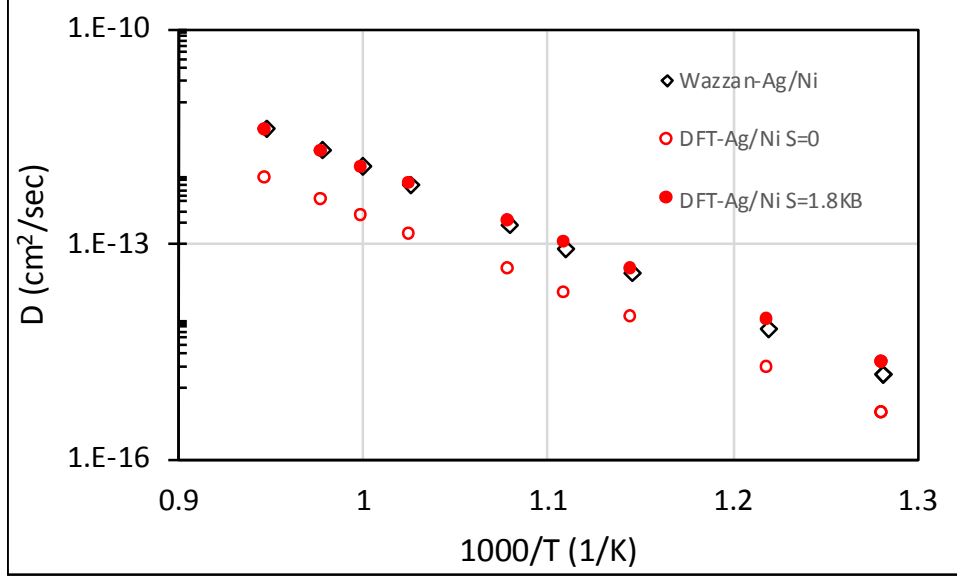


Figure 1. Coefficients of self-diffusion (top) and vacancy-mediated Ag diffusion (bottom) in pure fcc Ni for two vacancy formation vibrational entropies of $1.8 k_B$ and $0 k_B$, respectively, compared with experimental data.

5. RESULTS AND DISCUSSION

We have illustrated how impurity diffusion coefficients can be predicted directly from first principles without any empirical or fitting parameters. Specifically, we have used DFT static (energy) and DFPT (vibrational) calculations to obtain lattice constants, defect formation enthalpies, migration barriers, vacancy–solute binding enthalpies, vibrational frequencies, and the impurity-jump frequency within the framework of transition state theory. Prediction of diffusion coefficients is one of the most stringent tests of the ability of DFT calculations, because of the complex interplay of lattice constant, vacancy formation enthalpy, solute-vacancy binding enthalpy, and vibrational frequencies.

Using the DFPT approach, we were able to obtain the values of the individual diffusion parameters

along with the diffusion pre-factor *and activation energy* for Ni self-diffusion and Ag diffusion in

pure fcc Ni. The results match well with the experimental data. Both the diffusion prefactor and the

activation energy are key to a quantitative description of vacancy-mediated self-diffusion or solute diffusivities. It is also found that even the qualitative trends of diffusivity in fcc Ni may not always be inferred from activation energies or migration barriers alone. Especially given some limitations of the proposed methods (i.e., that all of the experimental data that exists is in the paramagnetic regime, while the calculations were performed in the ferromagnetic regime), the calculations provide very impressive agreement with experimentally measured diffusion coefficients for Ag in fcc nickel.

The present work shows that the DFPT approach may be a viable means to determine Ag diffusion coefficients accurately in Ni alloys. We are currently still performing actual calculations of entropies due to vibrational contributions, since the evaluation of

the vibrational entropy changes S_f and S_b is non-trivial. Future plans to utilize this DFPT approach would

extend initially to Ag diffusion in binary nickel alloys such as NiMo, NiCr and NiFe and ternary Ni alloys such as NiCrFe and NiCrMo. The ultimate goal is a predictive tool for determination of Ag diffusion coefficients in Ni super-alloys such as Inconel 713C, and Hastelloy X, or other prospective turbine blade materials.

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