Acta Materialia 109 (2016) 128–141

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

A comprehensive first-principles study of pure elements: Vacancy formation and migration energies and self-diffusion coefficients

Shun-Li Shang*, Bi-Cheng Zhou, William Y. Wang, Austin J. Ross, Xuan L. Liu, Yong-Jie Hu, Hua-Zhi Fang, Yi Wang, Zi-Kui Liu

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

ARTICLE INFO

Article history:
Received 28 August 2015
Received in revised form
2 February 2016
Accepted 3 February 2016
Available online xxx

Keywords:
Pure elements
Vacancy formation energy
Vacancy activation energy
Self-diffusion coefficient
First-principles calculations

ABSTRACT

A vast number of materials properties and phenomena are regulated by diffusion. However, diffusion coefficients from experiments and calculations are far from complete. Here, we report a compilation of vacancy formation energies (H_{Va}^{F}), vacancy migration energies (H_{Va}^{M}), vacancy activation energies (H_{Va}^{Q}), vacancy concentrations (C_{Va}), and vacancy-mediated self-diffusion coefficients (D_{Va}) as a function of temperature for 82 pure elements in bcc, fcc, and hcp structures by means of a comprehensive first-principles study. We assess the accuracy of four exchange-correlation (X–C) functionals for first-principles calculations, including the local density approximation (LDA), two generalized gradient approximations (PW91 and PBE), and PBEsol – the focus of the present work. To gain temperature-dependent diffusion properties, transition state structure searches are performed by the climbing image nudged elastic band method; and the needed equilibrium properties of energy (E_0), volume (V_0), bulk modulus (B_0) and its pressure derivative (B') for each structure of each element are estimated via an energy versus volume equation of state. Examination of the predicted quantities and available experimental data indicates that (i) PBEsol is a better selection in terms of getting accurate equilibrium and diffusion properties; (ii) the facility of vacancy migration can be understood from the redistribution of differential charge density, and anomalous energy pathways for vacancy migration are found for hcp Ce, La, Pr, Ti, and Zr within the basal plane; (iii) H_{Va}^{Q} can be predicted well from the melting point of a pure element and in particular a new relationship ($H_{Va}^{Q} = B_0V_0/6$), suggesting diffusivity is governed by interatomic bonding strength; and (iv) the computed quantities such as C_{Va}, D_{Va}, H_{Va}^{F}, H_{Va}^{M}, and H_{Va}^{Q} are in favorable accord with available experiments for most elements, but fall short for entropy-related properties. The present study of pure elements provides not only diffusion-related properties and a new understanding of diffusivity, but also a benchmark of first-principles calculations and a foundational dataset for the *Materials Genome Initiative*.

1. Introduction

Diffusivity measures the intermingled motion of atoms or molecules due to thermal excitations [1]. As a consequence, diffusion regulates a vast number of materials properties and phenomena during materials synthesis and when a material is in-service, for example, mass transfer, materials ductility, composition segregation, phase transitions, oxidation, corrosion, creep, fatigue, and fracture. The thermally activated process of diffusion can be described by a migrating atom passing through an energy barrier from a local energy minimum site to an adjacent vacant site [2], with the decisive role being vacancy formation and migration energies/enthalpies (H_{Va}^{F} and H_{Va}^{M}, respectively) for substitutional solutions and the present focus of pure elements [1,3].

The temperature dependence of vacancy concentration (C_{Va}) or of the diffusion coefficient (D_{Va}) is frequently, but certainly not always [4], found to obey the Arrhenius equation [1,3,5,6],

$$C_{Va} = A_{Va}^{C} \exp\left(\frac{-H_{Va}^{F}}{k_B T}\right) \tag{1}$$

$$D_{Va} = A_{Va}^{D} \exp\left(\frac{-H_{Va}^{Q}}{k_B T}\right) \tag{2}$$

where A is a pre-exponential factor or the entropy (S) related

---

* Corresponding author.
E-mail address: sus26@psu.edu (S.-L. Shang).

http://dx.doi.org/10.1016/j.actamat.2016.02.031

parameter with $A = \exp(S/k_B)$, H the enthalpy (the symbol Q is also frequently used in the literature [3,5,6]), k_B the Boltzmann constant, and T the absolute temperature. Specifically, $A_{\mathrm{Va}}^{\mathrm{C}}$ represents the maximum vacancy concentration (when $T \to \infty$), and $A_{\mathrm{Va}}^{\mathrm{D}}$ represents the frequency factor of diffusion, i.e., the maximum diffusion coefficient. $H_{\mathrm{Va}}^{\mathrm{Q}}$ is the vacancy activation energy/enthalpy of diffusion. For the case of substitutional solutions and the present case of self-diffusion,

$$H_{\mathrm{Va}}^{\mathrm{Q}} = H_{\mathrm{Va}}^{\mathrm{F}} + H_{\mathrm{Va}}^{\mathrm{M}} \tag{3}$$

Despite numerous experimental methods developed, such as the well-established positron annihilation spectroscopy to determine C_{Va} [7] and the most reliable tracer sectioning techniques to determine D_{Va} [3], it is not trivial to measure diffusion-related properties at high temperatures. This is due to difficulties caused by corrosion, oxidation, and contamination of the specimen. As a result, measured data are scattered and very limited [3,5,6], see experimental data for pure elements listed in Supplemental Materials. For example, in bcc V measured values of $A_{\mathrm{Va}}^{\mathrm{D}}$ are scattered in the range of 0.1–214 cm^2 s^{-1} and $H_{\mathrm{Va}}^{\mathrm{Q}} = 2.82$–$4.24$ eV [6]. As another example, in hcp Ti [8] the measured values of $H_{\mathrm{Va}}^{\mathrm{Q}}$ ($\perp$ c-axis) are 3.14 eV and 2.0 eV for pure and less pure specimens, respectively. Correspondingly, the $A_{\mathrm{Va}}^{\mathrm{D}}$ values of hcp Ti are also scattered, i.e., 13.5 cm^2 s^{-1} and 1.7×10^{-4} cm^2 s^{-1} for pure and less pure specimens, respectively.

Compared with the experimental difficulty to determine diffusion properties, computational materials science, especially the one from first-principles calculations, offers powerful tools to provide fundamental understanding of materials behaviors and supports the design of materials that meet a wide range of application requirements [9,10]. Relevant to the present work, $H_{\mathrm{Va}}^{\mathrm{F}}$ has been widely studied from first-principles for pure elements. For example, Nazarov et al. [7] predicted the $H_{\mathrm{Va}}^{\mathrm{F}}$ values for 12 fcc metal elements in terms of four exchange-correction (X–C) functionals: the local density approximation (LDA) [11], the generalized gradient approximations (GGA) by Perdew-Wang (PW91) [12,13] and by Perdew-Burke-Ernzerhof (PBE) [14], and an improved GGA designed to describe point defects by Armiento-Mattsson (AM05) [15]. Nazarov et al. [7] concluded that (a) the predicted $H_{\mathrm{Va}}^{\mathrm{F}}$ values show a strong dependence on the selected X–C functional due to the different methods used to describe the internal surface created by vacancy; (b) $H_{\mathrm{Va}}^{\mathrm{F}}$ values from LDA and AM05 show similar results and are close to experiments; and (c) an accurate prediction of $H_{\mathrm{Va}}^{\mathrm{F}}$ needs an error correction. Medasani et al. [16] employed five X–C functionals: LDA, PBE, PW91, the revised PBE with a reduced gradient dependence for solids and surfaces (PBEsol) [17], and the meta-GGA of the revised-TPSS [18] to study $H_{\mathrm{Va}}^{\mathrm{F}}$ for 34 bcc, fcc, and hcp metal elements. Medasani et al. [16] drew similar conclusions to those from Nazarov et al. [7], pointing out the $H_{\mathrm{Va}}^{\mathrm{F}}$ values follow the trend of "revised-TPSS > PBEsol ~ LDA > PBE > PW91", and the results from the first three (revised-TPSS, PBEsol, and LDA) show a better agreement with experiments. A more complete $H_{\mathrm{Va}}^{\mathrm{F}}$ study of pure elements was performed by Angsten et al. [19] using PBE for 49 elements in the fcc structure and 44 in the hcp structure, indicating that the $H_{\mathrm{Va}}^{\mathrm{F}}$ values can be explained by properties related to the bonding strength such as the bulk modulus and the cohesive energy. It was also found that the $H_{\mathrm{Va}}^{\mathrm{F}}$ values for some fcc elements (e.g., Au, Rh, Pd, and Pt) show large discrepancies (>0.5 eV) between predictions and experiments [7,16]. An improved $H_{\mathrm{Va}}^{\mathrm{F}}$ prediction appeals to the more reliable X–C functionals [20]. For example, Xing et al. [20] indicated that a hybrid HSE functional predicts well the $H_{\mathrm{Va}}^{\mathrm{F}}$ values of Cu, Ag, and Au. It should be remarked that the ability of different X–C functionals to predict $H_{\mathrm{Va}}^{\mathrm{F}}$ stems from an internal free surface created by a vacancy, and $H_{\mathrm{Va}}^{\mathrm{F}}$ can be calculated satisfactorily using an X–C functional without a density gradient (such as LDA) or by using a correction to the density gradient (such as PBEsol and AM05) [7,16,21]. Note that the $H_{\mathrm{Va}}^{\mathrm{F}}$ values from AM05 and PBEsol are similar [7,16]. Note also that the reason LDA predicts a better $H_{\mathrm{Va}}^{\mathrm{F}}$ is due to a well-known cancellation effect [7]: LDA overestimates the exchange energy of a free metal surface but underestimates approximately the same magnitude of the correlation energy, resulting in a reasonable net total value of the surface energy. However, for a normal GGA, such as PBE, the exchange surface energy is underestimated but the correlation surface energy is only slightly overestimated, resulting in smaller vacancy formation energies [7]. Besides changing the X–C functional, another strategy to improve the $H_{\mathrm{Va}}^{\mathrm{F}}$ prediction is to use the temperature dependent (Gibbs) energy in terms of the quasiharmonic and/or the anharmonic approach [4,22,23].

In addition to $H_{\mathrm{Va}}^{\mathrm{F}}$, the vacancy migration energy $H_{\mathrm{Va}}^{\mathrm{M}}$ is another parameter used to determine the diffusion coefficient, but it is relatively less explored. A large study was performed by Angsten et al. [19] to predict $H_{\mathrm{Va}}^{\mathrm{M}}$ for pure elements (49 in the fcc structure and 44 in the hcp structure) by means of PBE and the climbing image nudged elastic band (CINEB) method [24]. Most first-principles calculations of $H_{\mathrm{Va}}^{\mathrm{F}}$ and $H_{\mathrm{Va}}^{\mathrm{M}}$, including the aforementioned ones [7,16,19,20], have been performed at 0 K. Only a few first-principles efforts were carried out to investigate the entropy-related parameter A and the enthalpy H at finite temperatures, see Eqs. (1) and (2). For example, the vacancy formation Gibbs energies of Al and Cu as a function of temperature, $G_{\mathrm{Va}}^{\mathrm{F}}$ $(= H_{\mathrm{Va}}^{\mathrm{F}} - TS_{\mathrm{Va}}^{\mathrm{F}})$, were studied in Neugebauer's group [4,23]. We developed approaches for predicting the self and impurity diffusion coefficients in Al, Cu, Fe, Mg, Ni, and Ti alloys with bcc, fcc, or hcp structure based on the vacancy-mediated diffusion mechanism [2,8,25–34], where the required vibrational properties were predicted from phonon calculations and/or the Debye model [35].

Attention should be paid to the fact that the vacancy formation energy $H_{\mathrm{Va}}^{\mathrm{F}}$ can be described well by the X–C functionals without a density gradient (i.e. LDA). On the other hand, GGA is the best X–C functional to use when obtaining the equilibrium and vibrational properties for metallic systems [36]. This makes the X–C functional PBEsol, a revised GGA with a reduced gradient dependence for solids and surfaces [17], one of the best choices when predicting temperature-dependent diffusion properties.

Despite efforts from first-principles calculations (see above), a systematic study of pure elements concerning the temperature-dependent diffusivity is still far from complete, motivating the present first-principles study for 82 pure elements in the commonly observed bcc, fcc, and hcp structures. Besides knowledge of diffusion properties, the present work is also a benchmark to examine the capability of first-principles calculations in predicting diffusion-related properties. In addition, the obtained properties of pure elements can serve as a starting point to model diffusion properties for multi-component systems using the general CALPHAD modeling approach [36–39], since in CALPHAD modeling the energetics of phases need to be defined using lattice stabilities, which include both stable and unstable structures of elements.

To achieve the aforementioned goals, vacancy-mediated self-diffusion coefficients as a function of temperature will be predicted for 82 pure elements in terms of the transition state theory (Eyring's reaction rate theory [40] used herein), the CINEB method [24] (to determine the transition state), and the quasiharmonic Debye model [35] (for vibrational thermodynamics at finite temperatures), see details in Section 2. In Section 3, we present the equilibrium properties of volume and bulk modulus from four X–C functionals of LDA, PW91, PBE, and PBEsol. Following this, the vacancy formation energy, vacancy migration energy, vacancy