Self-Diffusion Coefficient of fcc Mg: First-Principles Calculations and Semi-Empirical Predictions

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First-principles calculations and semi-empirical equations are employed to determine the self-diffusion mobility of fcc Mg. All factors entering the vacancy-mediated self-diffusion coefficient, which include the equilibrium lattice parameter, the enthalpy of vacancy formation and atom migration, and the vibrational entropy of vacancy formation as well as the effective frequency, are evaluated with the local density approximation (LDA) and generalized gradient approximation (GGA) in first-principles calculations. These computed quantities are then utilized to calculate the self-diffusion coefficient of fcc Mg. For comparison, four widely used semi-empirical equations are also used to estimate the self-diffusion coefficient of fcc Mg. The comparisons show that first-principles calculations and semi-empirical equations yield values close to the activation energy Q for self-diffusion of fcc Mg from the LDA calculation, but the diffusion prefactor D_0 predicted from the four semi-empirical equations are all about one order of magnitude larger than those from the first-principles calculations. Based on the comparison for the self-diffusion coefficients of fcc Al computed with the first-principles method and semi-empirical approaches, it is concluded that the self-diffusion coefficient of fcc Mg calculated with the LDA method is more accurate than the estimation from semi-empirical approaches.

Keywords fcc Mg, first-principles, self-diffusion, semi-empirical

1. Introduction

In recent years, much effort has been dedicated to investigating the diffusion coefficients utilizing fundamental electronic approach.^[1–11] These approaches are huge breakthroughs, transforming the kinetic problem into a thermodynamic one. Consequently, the diffusion coefficient can be directly calculated from first-principles calculations. These calculations are usually based on the vacancy-mediated scheme^[12] in either self-diffusion or impurity-diffusion. A short time ago, Sandberg et al.^[1] employed density functional theory (DFT) approach in conjunction with molecular dynamics (MD)¹¹ simulation to calculate the self-diffusion rates in Al. Jiang and Carter^[2] revised this approach and investigated the dissolution and diffusion of carbon in ferrite and austenite using DFT calculations. Afterwards, Mantina et al.^[5] improved this approach and developed an efficient parameter-free first-principles calculation scheme to compute the self-diffusion coefficients in face-centered cubic systems within the framework of TST (Transition State Theory).^[13] Recently, Mantina et al.^[8] extended this approach to predict the impurity diffusion coefficients in

Abbreviations

LDA	local density approximation
GGA	generalized gradient approximation
GGA-91	a method of calculation originally used by Perdew et al. ^[29]
GGA-PBE	a method of calculation originally used by Perdew et al. ^[30]
DFT	density functional theory
MD	molecular dynamics
TST	transition state theory
NEB	nudged elastic band
VASP	Vienna ab initio simulation package
ATAT	alloy theoretic automated toolkit
MEP	minimum energy path
DOS	density of states
NIST	National Institute of Standards and Technology

face-centered cubic systems based on the five jump frequency model proposed by LeClaire.^[14] Similarly, Huang et al.^[9] further extended this approach to the body-centered cubic systems using the nine jump frequency formalism of LeClaire^[15] and investigated the self- and impurity diffusivities in α -Fe. Furthermore, Simonovic and Sluiter^[6] carried out a systematic investigation of the impurity diffusion activation energy in Al across a wide range of elements. More recently, Ganeshan et al.^[11] extended this approach and investigated the self-diffusion in hcp Mg and Zn. The above work validates the high accuracy of this efficient approach.

In DICTRA (Diffusion Controlled Transformation)^[16,17] modeling, the self- and impurity diffusion mobilities for the fictitious configurations of certain elements are unknown.

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The majority of atomic mobility assessments employed semi-empirical equations to calculate the self- and impurity diffusion mobilities and adopted these quantities as the end-members for atomic mobility databases.^[18,19] However, the accuracy of semi-empirical equations is doubted. In the present work, we extend the efficient parameter-free first-principles calculation scheme to investigate the self-diffusion mobility of the fictitious face-centered cubic configuration of Mg. Still, four kinds of widely used semi-empirical equations are utilized to compute the self-diffusion mobility of fcc Mg for comparison with the result from first-principles calculations.

The remainder of the manuscript is organized as follows. In section 2, we will present the methodology of first-principles prediction of self-diffusion based on vacancy-mediated scheme. In section 3, the details of the computation and simulation are presented. In section 4, the calculated results associated with phonon stability, quantities entering the self-diffusion coefficient, and self-diffusion mobility of fcc Mg are discussed. This is followed by a summary in section 5.

2. Computational Approaches

2.1 First-Principles Calculations

The calculation of a self-diffusion coefficient is usually based on the vacancy-mediated mechanism. In the present work, the self-diffusion coefficient is investigated on the basis of the assumption that diffusion is governed by a single-vacancy mechanism mediated by nearest neighbor vacancy jumps. The equation that connects macroscopic phenomena of self-diffusion and microscopic transportation of atoms based on the single-vacancy formalism is as follows:

$$D^{\text{self}} = fa^2 C_v w \quad (\text{Eq 1})$$

where f is the correlation factor that takes a value of 0.7815 for a face-centered cubic configuration.^[20] a is the lattice constant. C_v is the equilibrium vacancy concentration and is described by an equation of the form^[21]:

$$C_v = \exp\left(\frac{\Delta S_f^{\text{vib}}}{k_B}\right) \exp\left(-\frac{\Delta H_f^{\text{vac}}}{k_B T}\right) \quad (\text{Eq 2})$$

where ΔH_f^{vac} and ΔS_f^{vib} are the enthalpy and vibrational entropy of vacancy formation, respectively. k_B is the Boltzmann's constant, and T is the absolute temperature. Considering only vibrational (phonon) contributions to the free energy, and employing the high-temperature limit of the harmonic approximation in the lattice dynamics,^[22] ΔH_f^{vac} and ΔS_f^{vib} can be treated as constants, which are independent of temperature. The enthalpy of monovacancy formation ΔH_f^{vac} in bulk fcc Mg can be evaluated with

$$\Delta H_f^{\text{vac}} = E(\text{Mg}_{n-1}\text{Va}) - \frac{n-1}{n}E(\text{Mg}_n) \quad (\text{Eq 3})$$

where $E(\text{Mg}_{n-1}\text{Va})$ denotes the energy of a supercell containing $n-1$ lattice sites with Mg atoms and one vacancy,

while $E(\text{Mg}_n)$ represents the energy for the same supercell containing n Mg atoms. The vibrational entropy of monovacancy formation ΔS_f^{vib} is evaluated in a similar manner:

$$\Delta S_f^{\text{vib}} = S^{\text{vib}}(\text{Mg}_{n-1}\text{Va}) - \frac{n-1}{n}S^{\text{vib}}(\text{Mg}_n) \quad (\text{Eq 4})$$

In Eq 4, the $S^{\text{vib}}(\text{Mg}_{n-1}\text{Va})$ and $S^{\text{vib}}(\text{Mg}_n)$ are the high-temperature values of the vibrational entropy for a single-vacancy-defected and non-defected supercell. They are computed within the methodology of harmonic approximation^[22]:

$$S^{\text{vib}} = k_B \int \left\{ \frac{\hbar v}{2k_B T} \coth\left(\frac{\hbar v}{2k_B T}\right) - \ln \left[2 \sinh\left(\frac{\hbar v}{2k_B T}\right) \right] \right\} g(v) dv \quad (\text{Eq 5})$$

According to the Eyring reaction rate theory,^[23] the jump frequency w is described and calculated with the following equation:

$$w = \nu^* \exp\left(-\frac{\Delta H_m^{\text{vac}}}{k_B T}\right) \quad (\text{Eq 6})$$

where ΔH_m^{vac} is the vacancy migration enthalpy, i.e., the energy barrier to be overcome for an atom to jump into the vacancy. This quantity is usually evaluated utilizing the Nudged Elastic Band method (NEB).^[24] ν^* is the effective frequency which is described by means of the Vineyard's TST (transition state theory)^[13]:

$$\nu^* = \frac{\prod_{i=1}^{3n-3} v_i}{\prod_{i=1}^{3n-4} v'_i} \quad (\text{Eq 7})$$

In Eq 7, v_i and v'_i are the phonon frequencies at the normal and saddle-point configurations, respectively. The product in the denominator specifically excludes the negative frequency corresponding to the unstable mode for the transition state.

By combining Eq 1-7, the self-diffusion coefficient would be described by the following equation:

$$D^{\text{self}} = fa^2 \frac{\prod_{i=1}^{3n-3} v_i}{\prod_{i=1}^{3n-4} v'_i} \exp\left(\frac{\Delta S_f^{\text{vib}}}{k_B}\right) \exp\left(-\frac{\Delta H_f^{\text{vac}} + \Delta H_m^{\text{vac}}}{k_B T}\right) \quad (\text{Eq 8})$$

The empirical equation for self-diffusion coefficient usually reads:

$$D^{\text{self}} = D_0 \exp\left(-\frac{Q}{k_B T}\right) \quad (\text{Eq 9})$$

where D_0 is the diffusion prefactor, and Q is the diffusion activation energy. By comparing Eq 8 with Eq 9, we have the expressions for D_0 and Q :

$$D_0 = fa^2 \frac{\prod_{i=1}^{3n-3} v_i}{\prod_{i=1}^{3n-4} v'_i} \exp\left(\frac{\Delta S_f^{\text{vib}}}{k_B}\right), \quad \text{and} \quad Q = \Delta H_f^{\text{vac}} + \Delta H_m^{\text{vac}} \quad (\text{Eq 10})$$

In order to investigate whether there exists a divacancy mechanism for self-diffusion in bulk fcc Mg, the binding energy for the divacancy is calculated according to the following expression^[25]:

$$\Delta H_{f,x}^{\text{vac}} = 2E(\text{Mg}_{n-1}\text{Va}) - E_x(\text{Mg}_{n-2}\text{Va}_2) \quad (\text{Eq 11})$$

where $E(\text{Mg}_{n-1}\text{Va})$ denotes the energy of a supercell containing $n-1$ lattice sites with Mg atoms and one vacancy, $E_x(\text{Mg}_{n-2}\text{Va}_2)$ represents the energy for a supercell containing $n-2$ lattice sites with Mg atoms and two vacancies. The subscript x indicates first nearest-neighbor (1nn) or second nearest-neighbor (2nn) divacancies.

2.2 Semi-Empirical Prediction

Many semi-empirical equations between the diffusion activation energy Q and prefactor D_0 and other physical properties of materials have been proposed.^[26] In the present work, four widely used equations are utilized to evaluate the self-diffusion activation energy of fcc Mg.

The first equation relating Q to physical properties is given as follows:

$$Q = AT_m \quad (\text{Eq 12})$$

Equation 12 is proposed by Askill,^[26] in which T_m is the melting temperature in Kelvin. A is a constant which is 38 for fcc structures and 32.5 for bcc structures.

A revised correlation between Q and T_m is described by the following equation:

$$Q = (K_0 + V)RT_m \quad (\text{Eq 13})$$

Equation 13 is proposed by Sherby and Simnad.^[27] V in Eq 13 is the valence. Values of V are 1.5 for group IVB (Ti, Zr, Hf), 3.0 for group VB (V, Nb, Ta), 2.8 for group VIB (Cr, Mo, W), 2.6 for group VIIB (Mn, Re), and 2.5 for other transition elements.

A similar equation, which is slightly better than Eq 13, is proposed by LeClaire^[15]:

$$Q = (K + 1.5V)RT_m \quad (\text{Eq 14})$$

where K is a constant, which equals 13 for bcc metals, 15.5 for fcc and hcp metals, and 20 for metals of the diamond structure.

The above three equations (Eq 12-14) can be utilized to calculate the activation energy of self-diffusion. In order to compute the self-diffusion coefficient, the diffusion prefactor (D_0) has to be calculated. The widely used equation which can be employed to calculate the diffusion prefactor D_0 is the following^[26]:

$$D_0 = 1.04 \times 10^{-3} Qa^2 \quad (\text{Eq 15})$$

where Q is the diffusion activation energy, a is the lattice constant. Equation 15 is combined with Eq 12-14 to investigate the self-diffusion mobility of fcc Mg.

Apart from the above three semi-empirical equations, another widely used semi-empirical equation being able to predict the self-diffusion coefficient is as follows^[26]:

$$D = 3.4 \times 10^{-5} T_m \cdot a^2 \exp(-17.0T_m/T) \quad (\text{Eq 16})$$

In the present work, the above four semi-empirical equations are employed to investigate the self-diffusion coefficient of fcc Mg.

3. Computational Details

All calculations are performed using the local density approximation (LDA) of Ceperly and Alder^[28] as well as generalized gradient approximation (GGA) of Perdew-Wang^[29] and Perdew-Burke-Ernzerhof,^[30] as implemented in the efficient Vienna Ab initio Simulation Package (VASP) code.^[31,32]

For the calculation of equilibrium state of fcc Mg, a cutoff of 400 eV is used for the plane-wave expansion of the electronic wave functions. A Monkhorst-Pack scheme^[33] k -point sampling of $21 \times 21 \times 21$ is adopted to fully relax fcc Mg to get its equilibrium state. Convergence tests indicate that the plane-wave cutoff and k -point sampling are sufficient to limit the energy uncertainty to 1 meV/atom. The energy convergence criterion for electronic self-consistency is 10^{-6} eV/atom. The configurations are relaxed toward equilibrium until the Hellmann-Feynman force acting on each atom is less than 10^{-3} eV/Å.

In computing the phonon property of fcc Mg, the frozen-phonon approach as implemented in the ATAT (Alloy Theoretic Automated Toolkit) package^[34] is used. Three sizes of 8 atoms, 16 atoms and 32 atoms are used to calculate the phonon spectrum of fcc Mg in order to investigate the dependency of vibrational stability on the size of supercell. The displacement of 0.05 Å around the equilibrium positions of each atom in the supercell is applied and the calculated forces acting on each atom are then fitted to obtain the force constants. The vibrational frequencies are finally obtained with the Fourier transformation of the force constants. The fitting cutoff distance of 5 Å is adopted in the present work. The total number of k -points per reciprocal atom is at least 12000 for all the supercells.

With respect to the calculations of vacancy formation and migration enthalpies, periodic supercell containing 32 lattice sites ($2 \times 2 \times 2$ conventional fcc unit cells) is utilized. A plane wave cutoff of 300 and k -point sampling of $11 \times 11 \times 11$ are adopted to compute accurately the vacancy formation and migration energies. With VASP as the computational engine, the NEB method^[24] is used to obtain the minimum energy path (MEP) and migration barrier. In case there exists a local minimum along the diffusion path, three different sets of 1, 3, 5 images are adopted in the present work. The spring constant of $5.0 \text{ eV}/\text{\AA}^2$ is used for all the calculations. The total force convergence criteria for all the atoms of all images is set to 0.01 eV/Å.

As for the calculation of entropy of vacancy formation and effective frequency, supercells containing 32 lattice sites ($2 \times 2 \times 2$ conventional fcc unit cells) are utilized to compute the phonon density of state and Γ point vibrational

frequencies. It is worth noting that three configurations are employed in the present work: (I) perfect configuration—system with no vacancy; (II) initial configuration—system with a single vacancy, and all atoms and the vacancy of this configuration are at initial state; (III) saddle configuration—system with the diffusion atom at the saddle point. It should be noted that the saddle configuration is vibrationally unstable. The determination of the location of the saddle point for self-diffusion of fcc Mg is enforced utilizing the NEB method.^[24] The determination procedure is as follows: the diffusing atom is initially placed at the position halfway between the initial state and final state, and the structure of the supercell is subsequently relaxed using a quasi-Newton algorithm till the force convergence criteria. Again, the frozen-phonon approach is employed to calculate the phonon spectrum and related thermodynamic properties. Perturbation displacement of 0.05 Å is applied to evaluate the resulting force constants. Still, fitting cutoff distance of 5 Å is adopted to fit the force constants matrices within the harmonic approximation.

4. Results and Discussion

4.1 Phonon Spectrum Calculations of fcc Mg

Table 1 shows the calculated and experimental lattice constants for bulk Mg including hcp and fcc structures. As can be seen that the GGA-PBE and GGA-91 calculated results show a better agreement with the experiment^[35] and previously calculated results by Wang et al.^[36] than LDA.

After the equilibrium structure of fcc Mg is acquired, the phonon dispersion relations are calculated employing the frozen-phonon approach. To verify the convergence of this approach, three different supercell sizes are used in the present work. The size of supercell is controlled in the *fitfc* module in ATAT^[34] by adjusting the range of desired interatomic forces. As mentioned above, this range is set to 8, 16 and 32 atoms supercells. In the present work, the phonon dispersion relations calculated with three different kinds of projector augmented wave pseudopotentials (LDA,

GGA-91, GGA-PBE) at the theoretical lattice parameter (see Table 1) are presented.

Figure 1(a) shows the LDA calculated phonon dispersion relations for fcc Mg. As can be seen that except for the deviation at the TA branches along the GX and GL directions, the dispersion curves for 8, 16 and 32 atoms agree with each other well. No imaginary frequencies in the phonon density of state (DOS) indicates the vibrational stability for the fcc configuration of Mg. Moreover, three supercells yielding similar phonon DOS of fcc Mg illustrate the convergence of the frozen-phonon approach. Figure 1(b) and (c) are the GGA-91 and GGA-PBE calculated phonon dispersion relations for fcc Mg which are analogous with the LDA result. Still, the phonon DOS with GGA-91 and GGA-PBE verifies the vibrational stability of fcc Mg. It should be noted that the TA branches along the GL directions of 16 atoms bear large deviations from that of 8 and 32 atoms for all the three pseudopotentials. Figure 2 gives comparison of the phonon dispersion relations calculated by 32 atoms supercell for fcc Mg among LDA, GGA-91 and GGA-PBE. As shown in Fig. 2, the predicted phonon dispersion relations by LDA are a little higher than GGA-91 and GGA-PBE, while the phonon dispersion by GGA-91 has a nice consistency with GGA-PBE. The vibrational stability of fcc Mg encourages the prediction of self-diffusion mobility of fcc Mg with first-principles calculations.

4.2 Self-Diffusion Coefficient of fcc Mg

Table 2 lists the calculated quantities concerned with monovacancy and divacancy formation for fcc Mg. As shown in Table 2, the enthalpy of vacancy formation ΔH_f^{vac} is evaluated using three different kinds of pseudopotentials. LDA gives the largest value. It should be noted that LDA has a better estimation of surface energy than GGA due to the cancellation of errors within the exchange and correlation functions of the total energy. That is why the presently calculated ΔH_f^{vac} yields a larger value with LDA than GGA-91 and GGA-PBE.

Figure 3(a)-(c) show the calculated phonon DOS of defect-free fcc Mg, fcc Mg with a single vacancy of the normal state, and fcc Mg with the diffusing atom at the saddle point. The phonon DOSs of the three configurations calculated using LDA, GGA-91 and GGA-PBE are analogous to each other. In the course of phonon DOS of initial configuration, a peak at lower frequencies appears. The explanation is that the partial vacancy-Mg bonds being softer than the Mg-Mg bonds leads to the lower vibrational frequencies for modes along the direction of vacancy. As shown in Fig. 3(a)-(c), the imaginary frequencies of phonon DOS indicate the instability of the saddle configuration. The nature of saddle configuration is verified by the fact that the vibrational spectra contained a single imaginary frequency with an associated eigenvector corresponding to a displacement of the diffusing atom along the transition path. The vibrational entropy of vacancy formation within the harmonic approximation is evaluated based on these phonon DOSs and plotted versus temperature in Fig. 4. The third column of Table 2 collects the evaluated entropy of vacancy formation using the three kinds of pseudopotentials. As

Table 1 Calculated structure information of hcp Mg and fcc Mg

Space group:	hcp Mg			fcc Mg		
	<i>P6₃/mmc</i>			<i>Fm-3m</i>		
	Lattice constants, Å			Lattice constants, Å		
Method	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
LDA(a)	3.148	...	5.034	4.431	...	...
GGA-PBE(a)	3.211	...	5.127	4.516	...	...
GGA-91(a)	3.215	...	5.129	4.519	...	...
Exp.(b)	3.21	...	5.21	...	...	...
Calc.(c)	3.189	...	5.169	4.516	...	...

(a) Present calculation. (b) Reference 35. (c) Reference 36

Fig. 1 Calculated phonon dispersions for fcc Mg (a, LDA; b, GGA-91; c, GGA-PBE). The solid line corresponds to the phonon dispersions evaluated using supercells of 8 atoms. The dashed line corresponds to the phonon dispersions evaluated using supercells of 16 atoms. The dot dashed line corresponds to the phonon dispersions evaluated using supercells of 32 atoms

Fig. 2 Comparison of phonon dispersions for fcc Mg calculated with supercell size of 32 atoms between three pseudopotentials (LDA, GGA-91, GGA-PBE)

Table 2 Calculated enthalpy ΔH_f^{vac} (eV), vibrational entropy ΔS_f^{vib} (k_B) of monovacancy formation, formation volume ΔV_f^{vac} (V_0 is the volume for an atom in bulk fcc Mg) of monovacancy, and binding energy for the divacancy $\Delta H_{f,2nn}^{\text{vac}}$ (eV) of fcc Mg

Method	ΔH_f^{vac} , eV	ΔS_f^{vib} (k_B)	ΔV_f^{vac} (V_0)	$\Delta H_{f,1nn}^{\text{vac}}$, eV	$\Delta H_{f,2nn}^{\text{vac}}$, eV
LDA	0.887	0.947	0.664	-0.116	-0.017
GGA-PBE	0.844	0.641	0.640	-0.107	-0.015
GGA-91	0.794	0.839	0.683	-0.096	-0.012

Subscript 1 ($\Delta H_{f,1nn}^{\text{vac}}$) and 2 ($\Delta H_{f,2nn}^{\text{vac}}$) indicates first nearest-neighbor (1nn) or second nearest-neighbor (2nn) divacancies

shown in Table 2 and Fig. 4, LDA yields the largest value for entropy of vacancy formation, while GGA-91 produces a smaller value. This tendency is similar to the case in predicting the self-diffusion coefficient of fcc Al.^[5] GGA-PBE gives the smallest one, which is less by 32% than the value by LDA.

The fourth column of Table 2 illustrates the formation volume of a vacancy which is calculated with the formula:

$$\Delta V_f^{\text{vac}} = V(\text{Mg}_{n-1}\text{Va}) - \frac{n-1}{n}V(\text{Mg}_n) \quad (\text{Eq 17})$$

where $V(\text{Mg}_{n-1}\text{Va})$ denotes the volume of a supercell containing $n-1$ lattice sites with Mg atoms and one vacancy, while $V(\text{Mg}_n)$ represents the energy for the same supercell containing n Mg atoms. The evaluated data for formation volume of single-vacancy reveals that the introduction of vacancy leads to the reduction of volume of the system. The calculated values using three kinds of pseudopotentials yield nearly the same value. The rest of Table 2 gives the evaluated binding energy for the divacancy. As shown in Table 2, the first nearest-neighbor and second nearest-neighbor divacancy are unstable since $\Delta H_{f,1nn}^{\text{vac}} < 0$ and $\Delta H_{f,2nn}^{\text{vac}} < 0$ for all the three pseudopotentials. That means the energy cost to remove the second atom to form a divacancy is higher than the cost to create an additional monovacancy. Thus it can be concluded that the divacancy mechanism does not exist in the self-diffusion in bulk fcc Mg. This conclusion supports the assumption that the self-diffusion in bulk fcc Mg is governed by a single-vacancy mechanism.

Figure 5 shows the calculated vacancy migration enthalpy in bulk fcc Mg. As can be seen that the barrier by LDA is little higher than that of GGA-91 and GGA-PBE. The computed migration enthalpy using different images gives exactly the same value for the same pseudopotential (see detailed data in Table 3). It can be concluded that there is no local minimum state along the diffusion path in bulk fcc Mg.

After all factors entering the vacancy-mediated self-diffusion coefficient including the equilibrium lattice

Fig. 3 First-principles (a, LDA; b, GGA-91; c, GGA-PBE) calculated phonon DOS of defect-free fcc Mg, fcc Mg with a single vacancy of the normal state, and fcc Mg with the diffusing atom at the saddle point. The negative frequencies in phonon DOS of TS correspond to the unstable mode

Fig. 4 Comparison of calculated vibrational entropy of vacancy formation vs. temperature of fcc Mg for the three pseudopotentials (LDA, GGA-91, GGA-PBE)

Fig. 5 The minimum energy paths (MEP) for vacancy migration in fcc Mg calculated using NEB method

Table 3 Calculated migration energies (eV) of vacancy with different images in bulk fcc Mg

Method	1 image	3 images	5 images
LDA	0.324	0.323	0.323
GGA-PBE	0.314	0.314	0.314
GGA-91	0.305	0.305	0.304

parameter, the enthalpy of vacancy formation and atom migration, and the vibrational entropy of vacancy formation as well as the effective frequency are evaluated, the self-diffusion coefficient of fcc Mg is calculated using Eq 8.

Table 4 Calculated effective frequency ν^* , diffusion prefactor D_0 and activation energy Q of bulk fcc Mg

Method	ν^* , THz	D_0 , m ² /s	Q , eV	Q , kJ/mol
LDA	9.33	3.84×10^{-6}	1.211	116.82
GGA-PBE	14.03	4.25×10^{-6}	1.159	111.79
GGA-91	11.66	4.31×10^{-6}	1.100	106.14
Semi-empirical(a)	...	5.69×10^{-5}	1.162	112.16
Semi-empirical(b)	...	5.73×10^{-5}	1.169	112.83
Semi-empirical(c)	...	5.80×10^{-5}	1.185	114.29
Semi-empirical(d)	...	4.90×10^{-5}	1.033	99.64
Calc(e)	...	5.7×10^{-5}	1.166	112.50

(a) Present work, evaluated with semi-empirical Eq 12 combined with Eq 15. (b) Present work, evaluated with semi-empirical Eq 13 combined with Eq 15. (c) Present work, evaluated with semi-empirical Eq 14 combined with Eq 15. (d) Present work, evaluated with semi-empirical Eq 16. (e) Reference 38

Fig. 6 Self-diffusion coefficients predicted by first-principles calculations and semi-empirical equations in the present work. Subscript (a-c) indicates the self-diffusion coefficients of fcc Mg are evaluated from first-principles calculations using LDA, GGA-91, and GGA-PBE, respectively. Subscript (d-g) represents the self-diffusion coefficients of fcc Mg are predicted from the four kinds of semi-empirical equations in the present work. Subscript (f) indicates the self-diffusion mobility of fcc Mg is taken from Yao's result^[38]

In the course of semi-empirical prediction, with the melting temperature $T_m = 704.97$ K for fcc Mg being derived from the thermodynamic database^[37] and the lattice parameter $a = 4.516$ being taken from the present first-principles calculations, the self-diffusion coefficient of fcc Mg is evaluated based on the semi-empirical Eq 12-16. The obtained self-diffusion coefficients of fcc Mg are all collected in Table 4. The temperature dependency of the obtained self-diffusion coefficients are presented in Fig. 6. It can be seen in Fig. 6 that the first three kinds of semi-empirical equations (Eq 12-15) yield practically the same self-diffusion mobility of fcc Mg. The self-diffusion mobility predicted by Eq 16 bears large deviation from the other three kinds of semi-empirical equations especially at lower temperatures. Yao et al.^[38] has evaluated the self-diffusion

coefficient of fcc Mg using the semi-empirical equation (the third semi-empirical equation in the present work). In Fig. 6, we present the temperature dependency of self-diffusion coefficients of fcc Mg from first-principles calculations, semi-empirical calculations from the present work and Yao's prediction.^[38] As can be seen that the self-diffusion mobility of fcc Mg evaluated with semi-empirical equations (except for the fourth semi-empirical equation) in the present work agrees well with Yao's result. The first-principles evaluated self-diffusion mobility of fcc Mg using three pseudopotentials shows discrepancies from the semi-empirical equations. GGA-91 gives the largest self-diffusion mobility of fcc Mg among the three pseudopotentials. It should be noted that self-diffusion mobility of fcc Mg predicted by GGA-91 shares consistency with the mobility from semi-empirical equations at lower temperatures. As shown in the detailed data in Table 4, the calculated prefactors from first-principles calculations are about one order of magnitude smaller than those from semi-empirical equations. The evaluated activation energies of self-diffusion of fcc Mg with first-principles calculations are very close to those predicted with semi-empirical equations except for GGA-91 due to its underestimation of the surface energy.

In order to illustrate the high accuracy of first-principles calculations in calculating the diffusion coefficients, the self-diffusion mobility of fcc Al from first-principles calculations^[5] and the four semi-empirical equations in the present work are plotted versus temperature in Fig. 7. The predicted value through these two means of methods are compared with the NIST data from Zhang et al.^[39] As shown in Fig. 7, the predicted self-diffusion mobility of fcc Al with LDA pseudopotential shows an excellent agreement with the mobility by Zhang et al.^[39] It should be noted that LDA pseudopotential has a better estimation of self-diffusion mobility of fcc Al than GGA without correction (correction for surface energy^[25]). However, the self-diffusion mobilities evaluated with the first three kinds of semi-empirical equations bear large discrepancy from the NIST data. In addition, it has been verified that the LDA predicted self-diffusion mobility has a good agreement with the experimental data for Cu, Ni and Ag without correction.^[40]

Fig. 7 Self-diffusion coefficients of fcc Al predicted by first-principles calculations and semi-empirical equations in the present work. Subscript (a) represents the self-diffusion coefficients of fcc Al is from the NIST data.^[39] Subscript (b, c) indicates the self-diffusion coefficients of fcc Al are evaluated from first-principles calculations using LDA and GGA, respectively. Subscript (d-g) represents the self-diffusion coefficients of fcc Al are predicted from the four kinds of semi-empirical equations in the present work

These first-principles calculations on the self-diffusion coefficients for Al, Cu, Ni, and Ag validate the high accuracy of LDA pseudopotential in predicting the diffusion coefficients. Since there are no experimental data on the self-diffusion coefficient of fcc Mg, the self-diffusion coefficient of fcc Mg computed with LDA pseudopotential is judged to be the most accurate one in comparison with the other calculations, and such a self-diffusion coefficient is recommended as the standards for the establishment of atomic mobility data by means of DICTRA.

5. Summary

The self-diffusion mobility of fcc Mg has been investigated via first-principles calculations and semi-empirical predictions. With VASP as the computational engine, the phonon spectrum of fcc Mg has been calculated and its vibrational stability has been verified utilizing frozen-phonon approach.

The first-principles predicted self-diffusion coefficient of fcc Mg has been compared with those evaluated from semi-empirical equations. The comparison shows that the activation energy Q of self-diffusion of fcc Mg agrees well with each other, but the diffusion prefactor D_0 predicted from the four kinds of semi-empirical equations are all about one order of magnitude larger than those from first-principles calculations. The self-diffusion mobility of fcc Al from first-principles calculations and semi-empirical predictions have been compared with each other to validate the high-accuracy of LDA pseudopotential in predicting the diffusion

coefficients. Finally, The LDA generated self-diffusion coefficient of fcc Mg is believed to yield the most accurate self-diffusion mobility of fcc Mg when compared with others.

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