Self-learning kinetic Monte Carlo simulations of Al diffusion in Mg

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Abstract
Vacancy-mediated diffusion of an Al atom in the pure Mg matrix is studied using the atomistic, on-lattice self-learning kinetic Monte Carlo (SLKMC) method. Activation barriers for vacancy-Mg and vacancy-Al atom exchange processes are calculated on the fly using the climbing image nudged-elastic-band method and binary Mg–Al modified embedded-atom method interatomic potential. Diffusivities of an Al atom obtained from SLKMC simulations show the same behavior as observed in experimental and theoretical studies available in the literature; that is, an Al atom diffuses faster within the basal plane than along the c-axis. Although the effective activation barriers for an Al atom diffusion from SLKMC simulations are close to experimental and theoretical values, the effective prefactors are lower than those obtained from experiments. We present all the possible vacancy-Mg and vacancy-Al atom exchange processes and their activation barriers identified in SLKMC simulations. A simple mapping scheme to map an HCP lattice onto a simple cubic lattice is described, which enables simulation of the HCP lattice using the on-lattice framework. We also present the pattern recognition scheme which is used in SLKMC simulations to identify the local Al atom configuration around a vacancy.

Keywords: kinetic Monte Carlo, defect diffusion, point defects, vacancy diffusion

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(Some figures may appear in colour only in the online journal)
studied primarily with various broken bond models in fcc and bcc alloys using the KMC method [6–17]. To the best of our knowledge, no such simulations have been performed in HCP alloys. This paper focuses on the development and our implementation of the SLKMC method [18] and its application to the study of vacancy and Al atom diffusion in the Mg matrix.

This paper is organized as follows. In section 2, we describe very briefly the SLKMC method. In sections 3 and 4 we describe in detail the mapping scheme used to map the HCP lattice onto the simple cubic lattice and the pattern recognition scheme to identify the local Al atom neighborhood around a vacancy. In section 5, we present simulation results for a vacancy diffusion and an Al atom diffusion in pure single-crystal Mg. We then present a comparison of Al atom diffusivities obtained from SLKMC simulations with experimental and theoretical values available in the literature. In section 6, we discuss some of the vacancy-Mg and vacancy-Al atom exchange processes and their activation barriers. In addition, we present all vacancy-Mg and vacancy-Al atom exchange processes responsible for Al atom diffusion and their activation barriers identified in SLKMC simulations. Finally, in section 7, we summarize our results. Note that the details of the parameters of the MEAM interatomic potential are provided in the supplementary information.

2. Self-learning kinetic Monte Carlo method

The SLKMC method [18] is a variant of the on-the-fly KMC method [19], which identifies all the possible processes and calculates their activation energies based on the local atomic neighborhood on the fly. In addition, it uses a pattern-recognition scheme to store and retrieve these identified processes and their activation energies from a database to avoid redundant calculations. A pattern-recognition scheme [18, 20–23] is used to generate a unique tag or an identifier for a particular arrangement of neighboring atoms (for short, ‘configuration’) around an atom. All the identified diffusion processes the atom can perform along with their activation barriers are attached to the unique tag and are stored in a database. Note that the KMC algorithm we used is also based on the so-called ‘n-fold-way’ or Bortz–Kalos–Lebowitz (BKL) [24] or residence-time algorithm.

3. Mapping of HCP lattice onto a cubic lattice

To use an integer coordinate system in on-lattice KMC simulations, the crystal structure of a material should be mapped onto the simple cubic lattice. Since the HCP lattice is a non-Bravais lattice, it has to be first converted into a Bravais lattice before the mapping. Note that any non-Bravais lattice can be mapped onto a simple cubic lattice by transforming it into a Bravais lattice. An HCP lattice consists of two interpenetrating 2D hexagonal layers called A and B layers as shown in figure 1(a1). By combining A and B layers into a single layer, the HCP lattice is transformed into a stack of 2D hexagonal planes with each lattice point representing two atoms (one from the A layer and another from the B layer) or a basis of 2 as shown in figure 1(b2) and with an inter-layer spacing equal to \( c \) (=5.21 Å). A cubic lattice with a basis requires four integer coordinates, \( x, y, z \) and \( b \) (basis). For an HCP lattice, \( b = 0 \) or 1 indicates whether the atom is in the A or B layer, respectively. Figure 1(b) shows an illustration of the mapping of the integer coordinate system onto a hexagonal lattice. The coordinates of each atom in real space are obtained from the integer coordinates using the following expressions:

\[
\begin{align*}
\text{x}_{\text{real}} &= a_0 \left( \frac{x_{\text{int}} + y_{\text{int}}}{2} \right) \\
\text{y}_{\text{real}} &= \frac{a_0}{\sqrt{3}} \left( \frac{3}{2} y_{\text{int}} + b \right) \\
\text{z}_{\text{real}} &= c \left( z_{\text{int}} + \frac{b}{2} \right)
\end{align*}
\]

where \( x_{\text{int}}, y_{\text{int}}, z_{\text{int}}, b \) are integer coordinates in the cubic lattice and \( x_{\text{real}}, y_{\text{real}}, z_{\text{real}} \) are the coordinates in real space. \( a_0 \) and \( c \) are HCP lattice constants.

4. Pattern recognition scheme

To properly include their effect, Al atoms in the 56 neighborhood sites around a vacancy (greenish-yellow sphere at the center of the middle layer) as shown in figure 2 are included in the calculation of activation barriers for vacancy-Mg and vacancy-Al atom exchange processes. A unique binary bit pattern is generated for each local Al atom configuration (i.e. the arrangement of Al atoms around a vacancy) based on the occupancy of only Al atoms. That is, the presence of an Al atom at a site is taken as 1 and otherwise 0. For simplicity’s sake, 56 sites are grouped into eight rings as shown in figure 2. Accordingly, each configuration is given by a set of eight decimal numbers corresponding to the bit patterns of the eight rings, and from here on referred to as ring numbers. For each Al atom configuration, the set of ring numbers along with vacancy-Mg and vacancy-Al atom exchange processes and their activation barriers are stored in a database in the format shown in figure 3.

Note that, if the local neighborhood around an Mg atom is used instead, then each neighborhood lattice site has three states: 0, 1 and 2, representing a vacancy, an Mg atom and an Al atom, respectively. As shown in figure 4, one can either use a single decimal ring number for each ring corresponding to the ternary (radix-3 or base-3) number [25] generated based on Mg and Al atom occupancy, or two decimal numbers for each ring corresponding to the two binary bit patterns based on Al and Mg atom occupancy. To make the database concise we used the set of ring numbers which represent the local Al atom neighborhood around a vacancy (a non-real object) as described in the previous paragraph.

In present simulations a vacancy in the HCP lattice is only allowed to hop to 12 nearest neighbor (NN) sites; six NNs are within the basal plane and six NNs are in the adjacent basal planes (three each in the plane above and below). Local Al atom configuration dependent activation barriers for vacancy hop (jump) or vacancy-atom exchange processes are calculated using the climbing image nudge-elastic band (CI-NEB) method [26] as implemented in LAMMPS, an MD simulation package [27]. For the CI-NEB calculations, we used a periodic
orthorhombic simulation cell with 512 HCP lattice points and consists of 511 Mg and Al atoms, and one vacancy. Al atoms are placed at lattice sites around the vacancy according to the Al atom configuration not found in the database and the rest of the sites are occupied by Mg atoms. Note that the number of Mg and Al atoms varies based on the unknown Al configuration, but their sum is always equal to 511 atoms.

During the course of a simulation, if an Al atom configuration or its symmetric equivalent is not found in the database, then the CI-NEB module within LAMMPS is invoked. To reduce the number of CI-NEB calculations, we exploited the sixfold symmetry of the HCP lattice along the basal plane and mirror symmetry along the \( c \)-axis. The following eight unique symmetry operations were used to recognize equivalent configurations: (1) 120° (\( \theta_{120} \)) and (2) 240° (\( \theta_{240} \)) rotation around the \( c \)-axis, mirror reflection in (3) \( xy \)- (\( R_{xy} \)) and (4) \( yz \)- (\( R_{yz} \)) planes (figure 1(a)), (5) \( \theta'_{120} \) and \( R_{xy} \), (6) \( \theta'_{240} \) and \( R_{yz} \), (7) \( \theta_{240} \) and \( R_{xy} \), and (8) \( \theta_{240} \) and \( R_{yz} \). Note that the choice of using the Al atom environment around a vacancy also reduces the frequency of usage of symmetry operations during a simulation.

For the inter-atomic interactions, we used a second nearest neighbor (2NN) modified embedded-atom method (MEAM) potential as developed by Lee et al [28, 29]. The original MEAM potential parameters for Mg–Al systems were taken from [30] and were adjusted to obtain material parameters of pure Mg and Al, Al in Mg and Mg in Al, and Mg₁₇Al₁₂ close to first-principles and experimental values available in the literature. Modified MEAM parameters and comparison of material parameters with those obtained using density functional theory (DFT) calculations and from experiments are given in the supplementary information.

The mapping method described earlier is implemented in a general way such that different types of lattice structure can be mapped onto a simple cubic lattice, as part of a larger KMC simulation package, AKSOME (Atomistic Kinetic Simulations of Microstructural Evolution). All the required input, which includes locations of neighborhood sites in each ring relative to a vacancy location, symmetry operations and simulation parameters, is provided via input files. AKSOME is a flexible, on-lattice, self-learning kinetic Monte Carlo code.
and $z$ is the equilibrium. Substituting for $\Gamma_A$ and $\Gamma_B$ are partial correlation factors for in-plane diffusion ($2D$ diffusion in $xy$ plane). The $\langle x^2 \rangle$ is the mean square displacement and entropy of a vacancy, respectively. $\gamma_A$ and $\Delta S_A^V$ are the formation energy and entropy of a vacancy, respectively. $\gamma_A = 0.89 \text{ eV}$, which is calculated using the MEAM potential and $\Delta S_V = 1.49 k_B$, is taken from the DFT study by Ganeshan et al [31].

5.2. Single-vacancy diffusion in pure Mg

In its most general form, the diffusion coefficient of an atom along any arbitrary axis, $x$, is given by [32]

$$D_x = \frac{1}{2} \Gamma \langle x^2 \rangle$$

where $f$ and $\Gamma$ are the jump correlation factor and jump frequency, respectively. $\langle x^2 \rangle$ is the mean square displacement along the axis, averaged over a large number of jumps. In the HCP lattice, an atom has two independent jumps to nearest neighbor (NN) vacant sites: (a) between adjacent basal planes (out of plane) and (b) within a basal plane. A jump within a basal plane contributes to the diffusion only in the $xy$-plane, while the jump out of the plane contributes to diffusion in both the $xy$-plane and along the $z$-axis, as shown in figure 5. Diffusivities along the $c$-axis ($1D$ diffusion along $z$-axis, $D_c$) and in plane ($2D$ diffusion in $xy$-plane, $D_{\parallel}$) are given as [32–34]

$$D_{\parallel} = \frac{1}{4} \left( f_{a\alpha} \Gamma_A \frac{c^2}{4} \right)$$

$$D_c = \frac{1}{4} \left( f_{b\alpha} \Gamma_B a^2 + f_{a\alpha} \Gamma_A \frac{a^2}{3} \right)$$

where $\Gamma_A$ and $\Gamma_B$ are the total jump frequencies between adjacent basal planes and within a basal plane, respectively. $f_{a\alpha}$ and $f_{b\alpha}$ are partial correlation factors for in-plane diffusion due to out-of-plane and in-plane jumps, respectively, and $f_{a\alpha}$ is the partial correlation factor for the diffusion along the $c$-axis due to out-of-plane jumps.

For a vacancy, all the jump sequences are random, and hence all the correlation factors are equal to unity. Total jump frequency, $\Gamma = Zw$, where $Z$ is the number of NN sites into which a vacancy can jump to and $w$ is the frequency for individual jumps. Since an HCP lattice has six in-plane and six out-of-plane NN sites, $Z_A = Z_B = 6$. Substituting for $\Gamma$ in equations 3 and 4 gives

$$D_{\parallel} = \frac{3}{4} c^2 w_A$$

$$D_c = \frac{1}{2} a^2 (3w_B + w_A)$$

\[\text{Figure 2.} \] 56 neighborhood atoms around the central vacancy (greenish yellow sphere in the center of the middle layer). Atoms that belong to a ring are given the same color.

5. Results and discussion

We will first describe simulation details and then determine the diffusivity of a single vacancy in the pure Mg matrix, which is compared with the values calculated using analytical expressions. Finally we will determine the diffusivity of an Al atom in the pure Mg matrix.

5.1. Simulation details

We used a periodic simulation cell of $128 \times 128 \times 128$ lattice points, which corresponds to $410.88 \times 355.83 \times 664.80 \text{ Å}^3$ in real space. Note that, with a basis of 2 at each lattice point, the simulation cell consists of 222 atoms ($N_A$). The Mg lattice constants in our calculations are taken as $a = 3.21 \text{ Å}$ and $c/a = 1.623$. For this simulation cell size, the presence of one vacancy corresponds approximately to the equilibrium vacancy concentration at a temperature of 677.3 K (404 °C) in pure Mg, which is $1.03 \times 10^{22}$ vacancies m$^{-3}$. Therefore, the actual physical time ($t_{\text{real}}$) at other temperatures is obtained by rescaling the KMC simulation time ($t_{\text{kmc}}$) as [6, 7]

$$t_{\text{real}} = \frac{C_v^{\text{kmc}}}{C_v} t_{\text{kmc}}$$

where $C_v = \exp(\Delta S_V^V / k_B) \exp(-\gamma_A / k_B T)$ is the equilibrium vacancy concentration at temperature $T$ and $C_v^{\text{kmc}} = 1/N_A$ is the vacancy concentration in the simulation cell. $k_B$ is the Boltzmann constant; $\gamma_A^V$ and $\Delta S_A^V$ are the formation energy and entropy of a vacancy, respectively. $\gamma_A^V = 0.89 \text{ eV}$, which is calculated using the MEAM potential and $\Delta S_V = 1.49 k_B$, is taken from the DFT study by Ganeshan et al [31].

\[\text{AKSOME is still under development; therefore, some aspects (e.g. object type, number of rings being specified twice, ring ID) of the format of the database shown in figure 3 are redundant for the present simulations, but are needed for the additional functionality not described in the present article.}\]
where $w_{A,B} = D_0 \exp(-E_{A,B}/k_BT)$ are the frequencies for individual out-of-plane and in-plane jumps and $E_{A,B}$ are their activation barriers, $D_0$ is the pre-exponential factor and is taken as $2 \times 10^{13}$ s$^{-1}$ [35] and $T$ is the absolute temperature. In all our present simulations we assumed that the pre-exponential factors are independent of temperature, which varies only 1.67-fold from 300 K to 500 K ($D = D_0 \exp(S_m/k_BT)$, where $S_m$ is the entropy of migration). Activation barriers for the out-of-plane and in-plane jumps calculated using the MEAM potential are $E_A = 0.563$ eV and $E_B = 0.547$ eV, respectively. The total diffusivity ($D_{\text{total}}$) of a vacancy is given as

$$D_{\text{total}} = \frac{1}{3}(2D_A + D_B).$$  \hspace{1cm} (7)

The diffusion coefficient ($D$) of a randomly diffusing entity, which in our case is a vacancy, is obtained using the Einstein equation [36]:

$$D = \frac{1}{2d} \lim_{t \to \infty} \frac{\langle \Delta r(t)^2 \rangle}{t} = \frac{1}{2d} \langle \text{MSD} \rangle$$  \hspace{1cm} (8)

where $\Delta r(t)$ and $\langle \Delta r(t)^2 \rangle$ are the position and mean square displacement (MSD) at time $t$, respectively, and $d$ is the dimensionality of the diffusion. MSD/$t$ is obtained from the slope of the MSD versus time plot. Note that the dimensionality of vacancy diffusion within and perpendicular to the basal plane are 2 and 1, respectively. Table 1 shows a comparison of vacancy diffusivities in pure Mg obtained from KMC simulations and analytical equations (5)–(7) at temperatures of 300, 400 and 500 K. Good agreement between KMC simulation and analytical values shows that the KMC code is working correctly and the HCP lattice is mapped correctly onto the simple cubic lattice.

5.3. Al atom diffusion in Mg

Vacancy mediated solute diffusivity is given as

$$D_s = f_2^2 \Gamma_2 C_V(s) E_2$$  \hspace{1cm} (9)

where $f_2$ is the solute correlation factor, $\Gamma_2$ is the vacancy-solute exchange frequency, $C_V(s) = C_V^0 \exp(-E_b/v/k_BT)$ is the vacancy concentration near a solute atom and $E_{V-x}$ is the vacancy-solute binding energy. In the case of solute diffusion,
Table 1. Comparison of vacancy diffusivities within a basal plane and along the c-axis in pure Mg obtained from KMC simulations and those calculated using equations (5)–(7) at 300, 400 and 500 K.

| Temperature (K) | KMC | Equation (5) | KMC | Equation (6) | KMC | Equation (7) |
|-----------------|-----|--------------|-----|--------------|-----|--------------|
| 300             | 1.43 × 10^3 | 1.45 × 10^3 | 2.32 × 10^3 | 2.36 × 10^3 | 2.06 × 10^3 | 2.12 × 10^3 |
| 400             | 3.40 × 10^3 | 3.32 × 10^3 | 4.80 × 10^7 | 4.80 × 10^7 | 4.30 × 10^7 | 4.32 × 10^7 |
| 500             | 8.80 × 10^8 | 8.70 × 10^8 | 1.18 × 10^9 | 1.17 × 10^9 | 1.17 × 10^9 | 1.16 × 10^9 |

Table 2. Effective activation energies and diffusion prefactors for an Al atom diffusion in Mg matrix obtained from SLKMC simulations and a comparison with those obtained from an eight-frequency model and experiments.

|                  | Activation energy (eV) | Prefactor \((D_0)/10^{13} \text{Å}^2 \text{s}^{-1}\) |
|------------------|------------------------|--------------------------------|
|                  | SLKMC                  | Experimental                      |
|                  | Ganeshan Zhou Das Kammerer Brennan SLKMC Ganeshan Zhou Das Kammerer Brennan |
| Basal plane      | [37] [38] [39, 40] [41] | [37] [38] [42, 43] |
| c-axis           | 1.64 ± 0.04            | 1.12 ± 0.04                      |
| Total            | 1.48 ± 0.02            | 1.61 ± 0.02                      |
|                  | 1.65 ± 0.03            | 2.63 ± 0.03                      |
|                  | 1.44 ± 0.15            | 1.62 ± 0.15                      |
|                  | 1.53 ± 0.04            | 2.48 ± 0.04                      |

Figure 6. Arrhenius plot of vacancy diffusivities in Mg. Effective energy barrier and prefactors for a vacancy diffusion along ([||]) and perpendicular to (⊥) c-axis, and total diffusion.

concentration of Mg–Al solid solution using the Hall method [47]. Brennan et al [42] used depth profiling with secondary ion mass spectrometry (SIMS), and utilized the thin film method and the diffusion equation for the thin film solution to extract the Al atom diffusivities. Ganeshan et al [37] and Zhou et al [38] used an eight-frequency model [48] coupled with DFT-LDA and DFT-PBEsol calculated vacancy-atom (Mg and Al) exchange frequencies, respectively, to obtain Al atom diffusivities in single-crystal Mg. Note that the Al atom diffusivities obtained in the present simulations are also for a single crystal or a polycrystalline Mg with a very large grain size.
Al atom diffusivities obtained from SLKMC simulations using the MEAM potential are in qualitative agreement with the published experimental and eight-frequency model values. Our simulations also show that an Al atom diffuses faster within the basal plane than along the c-axis. The effective activation barriers obtained from SLKMC simulations are 0.1 eV higher when compared to the values obtained by Ganeshan et al [37] and Zhou et al [38]. While the effective prefactors have the same order of magnitude as those obtained by Zhou et al, the values obtained by Ganeshan et al are of order lower. Note that in a recent work Allnat et al [49] show that, to fully consider the anisotropy of an HCP lattice, 13 independent atom–vacancy exchange frequencies are needed in contrast to eight needed for the eight-frequency model. Also, no closed form expressions to calculate correlation factors exist for the 13-frequency model. In SLKMC simulation, the anisotropy of an HCP lattice is naturally included as well as all the possible vacancy-Mg and vacancy-Al exchange processes. In comparison to those obtained by Kammerer et al [41], the activation energy for the total diffusion is within the error bars and the effective prefactor has the same order of magnitude, but the effective prefactor has a very large error bar. On the other hand, prefactors obtained from diffusion couple experiments with single-crystal Mg by Das et al [39, 40] are two to three orders of magnitude higher than those obtained from the eight-frequency model and SLKMC simulations. Surprisingly, both activation energies and prefactors obtained by Das et al [39, 40] are in good agreement with those obtained by Brennan et al [42] using polycrystalline Mg with a grain size of 10 μm. In another study Brennan et al [43], using polycrystalline Mg with a grain size of 30 to 60 μm, obtained a prefactor which is four orders of magnitude lower than their previous value. Based on the available data, although the activation barriers differ only by a few tenths of an electronvolt, there seems to be a clear disagreement in the values of prefactors obtained using experiments and simulations.

6. Examples of vacancy hops in the presence of Al atoms

Here we show that the individual jump frequencies of a vacancy in an Mg matrix, within and out of a basal plane \(w_{Al,B}\) in various directions, are no longer equal to each other in the presence of an Al atom. Figure 7 shows examples for vacancy-Mg and vacancy-Al exchange processes, and the corresponding activation barriers are given in table 3. Figures 7(a)–(c) show vacancy jumps to NN sites within the basal plane and figure 7(d) shows vacancy jumps to the three NN sites in the adjacent plane above. Note that the directions shown in figure 7(d) are for a vacancy in an A layer, but the jump directions for a vacancy in a B layer are equivalent and can be obtained by rotating the directions shown in figure 7(d) by 120° either clockwise or anti-clockwise. Also, note that \(P_0\) to \(P_{11}\) in table 3 represent vacancy hops in directions 0 to 11 shown in figure 7.

Vacancy-Al atom exchanges always have the largest activation barriers when compared to vacancy-Mg atom exchange processes, irrespective of whether they are located at NN sites that are within the basal plane or in adjacent basal planes \(P_3\) in figures 7(a) and \(P_4\) in figure 7(d). The activation barrier when the vacancy and Al are at NN sites in adjacent planes is always the larger one. Accordingly, the exchange of a vacancy

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**Figure 7.** Al atom neighborhoods around a vacancy. White, purple and orange spheres represent Mg atoms, vacancies and Al atoms, respectively. (a) Vacancy and Al atom within the basal plane (A layer). (b) Al atoms at NN sites within the basal plane (B layer). (c) Al atom at diagonally opposite NN sites within the basal plane (A layer). (d) Vacancy and Al atom in adjacent planes (A layer).
and an Al atom occurs more often within the basal plane, and hence the Al atom diffuses faster perpendicular to the $c$-axis. The activation barrier for a vacancy and the Mg atom which is NN to both the vacancy and the Al atom has the lowest activation barrier ($P_0$ in figure 7(a)), while a similar exchange between adjacent planes has the second lowest activation barrier ($P_6$ and $P_9$ in figure 7(a)). Although the activation barriers are different, qualitatively similar behavior was observed even in DFT calculated activation barriers for the same processes [35]. From figures (b) and (c) and table 3 one can see that the activation barrier for the vacancy-Al atom exchange increases while that for the vacancy-Mg atom exchange decreases with increasing number of Al atoms. When the Al atoms are at NN sites on the same plane, the activation barrier for the exchange of a vacancy and an Mg atom located on adjacent planes, but NN to the Al atoms, is the lowest ($P_6$ and $P_9$ in figure 7(b)).

![Figure 8](image)

**Figure 8.** (a) Top view corresponding to figure 7(a). Blue and red arrows correspond to $P_0$ and $P_4$, respectively, while $S_1$ and $S_2$ represent their saddle points. (b) Top view corresponding to figure 7(b). $P_0$ & $P_4$ (red arrows) and $P_2$ & $P_5$ (blue arrows) are pairs of symmetric hops. (c) Top view corresponding to figure 7(c). $P_0$ & $P_5$ (blue arrows) and $P_2$ & $P_3$ (red arrows) are pairs of symmetric hops. Arrows show (approximately) the path of the Mg atom and the small circle in the middle represents the saddle point (for the sake of clarity, atoms on the top layer are shown as smaller circles).

### Table 3. Activation barriers for vacancy hops to 12 NN in the presence of an Al atom.

| Pattern      | Basis | $P_0$ | $P_1$ | $P_2$ | $P_3$ | $P_4$ | $P_5$ | $P_6$ | $P_7$ | $P_8$ | $P_9$ | $P_{10}$ | $P_{11}$ |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----------|----------|
| Figure 7(a)  | 0     | 0.283 | 0.538 | 0.533 | 0.533 | 0.543 | 0.574 | 0.398 | 0.643 | 0.554 | 0.398 | 0.643 | 0.554    |
| Figure 7(b)  | 1     | 0.313 | 0.646 | 0.646 | 0.313 | 0.464 | 0.464 | 0.154 | 0.644 | 0.644 | 0.154 | 0.644 | 0.644    |
| Figure 7(c)  | 0     | 0.520 | 0.601 | 0.275 | 0.275 | 0.601 | 0.520 | 0.391 | 0.392 | 0.729 | 0.392 | 0.391 | 0.729    |
| Figure 7(d)  | 0     | 0.424 | 0.424 | 0.627 | 0.546 | 0.546 | 0.627 | 0.414 | 0.637 | 0.414 | 0.550 | 0.588 | 0.549    |

**Note:** $P_0$ to $P_{11}$ represent vacancy hops in directions 0 to 11 as shown in figure 7. Bases of 0 and 1 represent whether the vacancy is in an A or B layer.

### Table 4. Activation barriers for vacancy hops to 12 NN for Al atom neighborhoods shown in figure 9.

| Pattern  | Basis | $P_0$ | $P_1$ | $P_2$ | $P_3$ | $P_4$ | $P_5$ | $P_6$ | $P_7$ | $P_8$ | $P_9$ | $P_{10}$ | $P_{11}$ |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----------|----------|
| Fig. 1   | 1     | 0.554 | 0.547 | 0.550 | 0.566 | 0.552 | 0.550 | 0.555 | 0.564 | 0.578 | 0.574 | 0.547 | 0.560    |
| Fig. 2   | 0     | 0.535 | 0.551 | 0.552 | 0.556 | 0.550 | 0.547 | 0.574 | 0.560 | 0.547 | 0.555 | 0.578 | 0.564    |
| Fig. 3   | 1     | 0.627 | 0.423 | 0.423 | 0.627 | 0.545 | 0.545 | 0.588 | 0.550 | 0.550 | 0.640 | 0.413 | 0.413    |
| Fig. 4   | 0     | 0.423 | 0.424 | 0.627 | 0.546 | 0.544 | 0.627 | 0.414 | 0.637 | 0.414 | 0.550 | 0.588 | 0.549    |
| Fig. 5   | 0     | 0.283 | 0.538 | 0.533 | 0.543 | 0.543 | 0.573 | 0.398 | 0.645 | 0.556 | 0.397 | 0.644 | 0.552    |
| Fig. 6   | 1     | 0.573 | 0.283 | 0.539 | 0.533 | 0.534 | 0.543 | 0.644 | 0.556 | 0.397 | 0.564 | 0.556 | 0.397    |
| Fig. 7   | 0     | 0.554 | 0.553 | 0.545 | 0.552 | 0.552 | 0.544 | 0.562 | 0.564 | 0.541 | 0.562 | 0.564 | 0.561    |
| Fig. 8   | 1     | 0.552 | 0.552 | 0.554 | 0.553 | 0.553 | 0.545 | 0.562 | 0.564 | 0.561 | 0.562 | 0.564 | 0.561    |
| Fig. 9   | 0     | 0.560 | 0.533 | 0.611 | 0.611 | 0.553 | 0.556 | 0.554 | 0.553 | 0.562 | 0.562 | 0.644 | 0.552    |
| Fig. 10  | 0     | 0.611 | 0.533 | 0.556 | 0.557 | 0.533 | 0.611 | 0.554 | 0.553 | 0.562 | 0.562 | 0.644 | 0.552    |
| Fig. 11  | 1     | 0.542 | 0.545 | 0.549 | 0.523 | 0.548 | 0.565 | 0.565 | 0.579 | 0.544 | 0.565 | 0.579 | 0.544    |
| Fig. 12  | 0     | 0.550 | 0.523 | 0.548 | 0.542 | 0.545 | 0.549 | 0.565 | 0.579 | 0.544 | 0.565 | 0.579 | 0.544    |
| Fig. 13  | 1     | 0.560 | 0.528 | 0.553 | 0.554 | 0.528 | 0.560 | 0.579 | 0.578 | 0.572 | 0.579 | 0.578 | 0.572    |
| Fig. 14  | 0     | 0.554 | 0.528 | 0.559 | 0.560 | 0.528 | 0.553 | 0.578 | 0.572 | 0.579 | 0.578 | 0.572 | 0.579    |
| Fig. 15  | 0     | 0.550 | 0.561 | 0.537 | 0.548 | 0.558 | 0.552 | 0.564 | 0.563 | 0.579 | 0.564 | 0.552 | 0.552    |
| Fig. 16  | 1     | 0.559 | 0.547 | 0.536 | 0.549 | 0.549 | 0.552 | 0.570 | 0.563 | 0.563 | 0.549 | 0.552 | 0.567    |
| Fig. 17  | 0     | 0.548 | 0.548 | 0.548 | 0.548 | 0.548 | 0.548 | 0.588 | 0.587 | 0.587 | 0.573 | 0.572 | 0.572    |
| Fig. 18  | 1     | 0.548 | 0.548 | 0.548 | 0.548 | 0.548 | 0.548 | 0.588 | 0.587 | 0.587 | 0.573 | 0.572 | 0.572    |

**Note:** Basis of 0 and 1 represent whether the vacancy is in the A or B layer.
on adjacent planes (not shown). This suggests that a single vacancy will diffuse faster with increasing Al concentration, but the Al atom diffusivity will decrease due an increase in the activation barrier for vacancy-Al atom exchange.

An interesting observation from figures 7(a)–(c) and table 3 is that the activation barriers for the in-plane exchange of vacancy and Mg atoms which are adjacent to the Al atom ($P_0$ and $P_4$ in figure 7(a)) are not equal to each other.
In figure 7(a), the exchange of Mg$_2$ and V and of Mg$_1$ and V represent $P_0$ $(0.283 \text{ eV})$ and $P_0$ $(0.543 \text{ eV})$ in figure 7(a), respectively. Similarly, in figure 7(c) activation barriers for seemingly symmetric vacancy hops $P_0$, $P_2$, $P_3$ and $P_5$ are not equal to each other. However, in figure 7(b) the activation barrier $P_0$ is equal to $P_3$, and $P_5$ is equal to $P_6$ due to symmetry. Seemingly symmetric vacancy hops in figures 7(a) and (c) are in fact not symmetric due to the unequal distance between the saddle points, $S_1$ and $S_2$, of Mg$_1$ and Mg$_2$, and the Al atom(s). As noted earlier, within each ring, a pair of two decimal ring numbers based on Al and Mg atom occupancy can represent the atomic neighborhood around Mg atoms. Accordingly, in figure 8(a) the neighborhoods of Mg$_1$ and Mg$_2$ in the first ring are given as $(1, 60)$ and $(16, 39)$, respectively. By performing symmetry operations, one can see that the atomic neighborhoods in the initial location around Mg$_1$ and Mg$_2$ are not symmetric to each other. In figure 8(a) one can see that the saddle point $S_2$ for Mg$_2$ is closer to the Al atom than saddle point $S_1$ for Mg$_1$. Therefore, the activation barrier $P_0$ is strongly influenced by the presence of the Al atom, whereas the activation barrier $P_1$ is very close to the activation barrier for the vacancy-Mg atom exchange in pure Mg. Also, note that the Al atom is smaller than the Mg atom. For Mg$_1$ and Mg$_2$, atomic neighborhoods in the initial state and at the saddle point are different. Similar reasoning also applies for the asymmetry in the activation barriers for the vacancy hops, $P_0$, $P_2$, $P_3$ and $P_5$ shown in figure 7(c).

A single Al atom and a vacancy will produce a limited number of configurations. A complete list of these Al atom configurations around a vacancy identified in SLKMC simulations of Al atom diffusion in Mg matrix is shown in figure 9, while corresponding vacancy-Mg and vacancy-Al exchange processes are given in table 4. Note that for convenience figure 9 and table 4 show patterns and the activation barriers for vacancy-exchange processes, respectively, for both A and B layers. One can also see the asymmetry mentioned in the previous paragraph in the activation barriers for vacancy hops within the basal plane as described in the previous paragraph.

7. Conclusions

On-lattice, self-learning KMC (SLKMC) simulations of Al atom diffusion in the HCP Mg matrix are presented. SLKMC simulations automatically take into account both the effect of asymmetry of the HCP lattice, and the effect of asymmetry in the local atomic environment due to the presence of Al atoms, on the activation barriers for vacancy-Mg and vacancy-Al atom exchange processes. We presented a simple mapping method to map an HCP lattice onto a simple cubic lattice, which enables the study of non-cubic systems using an on-lattice framework. A comparison of vacancy diffusivities in pure Mg matrix obtained from KMC simulations with those obtained from analytical expressions shows that the mapping accurately represents the HCP lattice.

In agreement with the behavior that was observed in both theoretical and experimental studies, we also find that an Al atom in an Mg matrix diffuses faster in the basal plane than along the $c$-axis. The effective energy barriers differ from experimental and theoretical values by a few tenths of an electronvolt, but there seems to be a clear disagreement in the literature for the values of effective prefactors. Note that SLKMC simulations can identify new processes and calculate their activation barriers on the fly, but not their pre-exponential factors, which are therefore provided as an input. As pre-exponential factors do not vary significantly between different vacancy-atom exchange processes, in our simulations they were assumed to be the same for all processes. Considering the fact that the MEAM potential shows good correlation with DFT and experimental values of material parameters, Al atom diffusivities obtained from SLKMC simulations are reasonable values. Importantly, more accurate effective activation energies and prefactors for Al atom diffusion can be obtained by performing KMC simulations using DFT calculated activation energies and pre-exponentials for vacancy-Mg and vacancy-Al exchange processes identified in present SLKMC simulations.

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References

[1] Mordike B and Ebert T 2001 Mater. Sci. Eng. A 302 37
[2] Luo A A 2002 JOM 54 42
[3] Kulecki M 2008 Int. J. Adv. Manuf. Technol. 39(9) 851
[4] Fichthorn K A and Weinberg W H 1991 J. Chem. Phys. 95 1090
[5] Amar J G 2006 Comput. Sci. Eng. 8 9
[6] Clouet E and Soisson F 2010 C. R. Phys. 11 226
[7] Soisson F, Barbu A and Martin G 1996 Acta. Mater. 44 3789
[8] Bouar Y L and Soisson F 2002 Phys. Rev. B 65 094103
[9] Molnar D, Niedermeier C, Mora A, Binkele P and Schmauder S 2012 Contin. Mech. Thermodyn. 24 607
[10] Schmauder S and Binkele P 2002 Comput. Mater. Sci. 24 42
[11] Soisson F, Becquart C S, Castin N, Domain C, Malerba L and Vincent E 2010 J. Nucl. Mater. 406 55
[12] Rautiainen T T and Sutton A P 1999 Phys. Rev. B 59 13681
[13] Soisson F 2006 J. Nucl. Mater. 349 235
[14] Pareige C, Roussel M, Novy S, Kuksenko V, Olsson P, Domain C and Pareige P 2011 Acta. Mater. 59 2404
[15] Vincent E, Becquart C S, Pareige C, Pareige P and Domain C 2008 J. Nucl. Mater. 373 387
[16] Levesque M, Martinez E, Fu C C, Nastar M and Soisson F 2011 Phys. Rev. B 84 184205
[17] Martinez E, Senninger O, Fu C-C, Soisson F 2012 Phys. Rev. B 86 224109
[18] Trushin O, Karim A, Kara A and Rahman T S 2005 Phys. Rev. B 72 115401
[19] Henkelman G and Jonsson H 2001 J. Chem. Phys. 115 9657
[20] Nandipati G, Shim Y, Amar J G, Karim A, Kara A, Rahman T S and Trushin O 2009 J. Phys.: Condens. Matter 21 084214
[21] Shah S I, Nandipati G, Kara A and Rahman T S 2012 J. Phys.: Condens. Matter 24 354004
[22] Nandipati G, Shah S I, Kara A and Rahman T S 2012 J. Comput. Phys. 231 3548
[23] Kara A, Trushin O, Yildirim H and Rahman T 2009 J. Phys.: Condens. Matter 21 084213
[24] Bortz A B, Kalos M H and Lebowitz J L 1975 J. Comput. Phys. 17 10
[25] Nandipati G and Kara A 2012 private communication
[26] Henkelman G, Uberuaga B P and Jonsson H 2000 J. Chem. Phys. 113 9901
[27] Plimpton S 1995 J. Comput. Phys. 117 1
[28] Lee B J and Baskes M I 2000 Phys. Rev. B 62 8564
[29] Lee B J, Baskes M I, Kim H and Cho Y K 2001 Phys. Rev. B 64 184102
[30] Kim Y M, Kim N J and Lee B J 2009 Calphad 33 650
[31] Ganeshan S, Hector L G Jr and Liu Z K 2010 Comput. Mater. Sci. 50 301
[32] Peterson N L 1978 J. Nucl. Mater. 69–70 3
[33] Mehrer H 2007 Diffusion in Solids (Berlin: Springer)
[34] Combronde J and Brebec G 1971 Acta Metall. 19 1393
[35] Mantina M 2008 First-principles methodology for diffusion coefficients in metals and dilute alloys PhD Thesis Pennsylvania State University
[36] Einstein A 1905 Ann. Phys. 17 549
[37] Ganeshan S, Hector L G Jr and Liu Z K 2011 Acta. Mater. 59 3214
[38] Zhou B C, Shang S L, Wang Y and Liu Z K 2016 Acta Metall. 103 573
[39] Das S K, Kim Y M, Ha T K, Gauvin R and Jung I H 2013 Metall. Mater. Trans. A 44 2593
[40] Das S K, Kim Y M, Ha T K, Gauvin R and Jung I H 2013 Metall. Mater. Trans. A 44 3420
[41] Kammerer C C, Kulkarni N S, Warmack R J and Sohn Y H 2014 J. Alloys Compounds 617 968
[42] Brennan S, Warren A P, Coffey K R, Kulkarni N, Todd P, Kilmove M and Sohn Y H 2012 J. Phase Equilib. Diffus. 33 121
[43] Brennan S, Bermudez K, Kulkarni N and Sohn Y H 2012 Metall. Mater. Trans. A 43A 4043
[44] Wagner C 1969 Acta Metall. 17 99
[45] Boltzmann L 1894 Ann. Phys. Chem. 53 959
[46] Matano C 1935 Japan. J. Phys. 8 109
[47] Hall L D 1953 J. Chem. Phys. 21
[48] Ghate P B 1964 Phys. Rev. 133 A1167
[49] Allnatt A R, Belova I V and Murch G E 2014 Phil. Mag. 22 2487
[50] Stukowski A 2009 Modelling Simul. Mater. Sci. Eng. 18 015012