ATOMISTIC MODELING OF DIFFUSION AND PHASE TRANSFORMATIONS IN METALS AND ALLOYS

by

Ganga Prasad Purja Pun
A Dissertation Submitted to the Graduate Faculty of George Mason University in Partial Fulfillment of The Requirements for the Degree of Doctor of Philosophy Physics

Committee:

Dr. Yuri Mishin, Dissertation Director
Dr. Karen Sauer, Committee Member
Dr. John A. Schreifels, Committee Member
Dr. Maria Emelianenko, Committee Member
Dr. Michael E. Summers, Department Chair
Dr. Timothy L. Born, Associate Dean for Student and Academic Affairs, College of Science
Dr. Vikas Chandhoke, Dean, College of Science

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By

Ganga Prasad Purja Pun
Master of Science
Minnesota State University, 2003
Bachelor of Science
Tribhuvan University, 1995

Director: Dr. Yuri Mishin, Professor
School of Physics, Astronomy and Computational Science

Fall Semester 2011
George Mason University
Fairfax, VA
Dedication

To my wife Shanti, daughters Usha and Shunibha, mother Bhabisa and father Nanda Bahadur who are my sources of inspiration. I would also like to dedicate this to my brothers Yam, Sewanta and Chhetra for their constant support and encouragement throughout my study.
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<tr>
<td>$D_{eff}$</td>
<td>effective diffusion coefficient</td>
</tr>
<tr>
<td>$D_b$</td>
<td>bulk diffusion coefficient</td>
</tr>
<tr>
<td>$D_d$</td>
<td>coefficient of dislocation diffusion</td>
</tr>
<tr>
<td>$D, \overline{D}$</td>
<td>general diffusion coefficient</td>
</tr>
<tr>
<td>$a, a_0$</td>
<td>lattice constant</td>
</tr>
<tr>
<td>$D_0, D_{0d}, D_{d0}^0$</td>
<td>pre-exponential factor</td>
</tr>
<tr>
<td>$P_d$</td>
<td>integrated dislocation diffusion flux</td>
</tr>
<tr>
<td>$A_d$</td>
<td>area of dislocation core</td>
</tr>
<tr>
<td>$\tau_d$</td>
<td>radius of dislocation core</td>
</tr>
<tr>
<td>$\tau_d^v$</td>
<td>radius of dislocation core with a pre-existing vacancy</td>
</tr>
<tr>
<td>$\tau_d^i$</td>
<td>radius of dislocation core with a pre-existing interstitial</td>
</tr>
<tr>
<td>$\tau_d^d$</td>
<td>radius of dislocation core without any point defects</td>
</tr>
<tr>
<td>$E$</td>
<td>activation energy of lattice diffusion</td>
</tr>
<tr>
<td>$E_d$</td>
<td>activation energy of dislocation diffusion</td>
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<td>$\delta$</td>
<td>width of grain boundary</td>
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<td>$D_v$</td>
<td>diffusivity of vacancy</td>
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<td>$E_i$</td>
<td>impurity formation energy</td>
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<td>$c_0$</td>
<td>bulk impurity concentration</td>
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<td>total energy</td>
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<td>$F_{si}$</td>
<td>embedding energy of atom $i$ of chemical sort $s_i$</td>
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<tr>
<td>$\rho_i$</td>
<td>host electron density at the site $i$ induced by all other atoms</td>
</tr>
<tr>
<td>$\rho_{sj}$</td>
<td>atomic electron density of chemical sort $s_j$</td>
</tr>
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<td>$\tau_{ij}$</td>
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<td>$V_{ss}, V_{s's'}, V_{ss'}$</td>
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<td>$f_i$</td>
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<td>$r_i$</td>
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Abstract

ATOMISTIC MODELING OF DIFFUSION AND PHASE TRANSFORMATIONS IN METALS AND ALLOYS
Ganga Prasad Purja Pun, PhD
George Mason University, 2011
Dissertation Director: Dr. Yuri Mishin

Dissertation consists of multiple works. The first part is devoted to self-diffusion along dislocation cores in aluminum followed by the development of embedded atom method potentials for Co, NiAl, CoAl and CoNi systems. The last part focuses on martensitic phase transformation (MPT) in Ni$_x$Al$_{1-x}$ and Al$_x$Co$_y$Ni$_{1-x-y}$ alloys.

New calculation methods were developed to predict diffusion coefficients in metal as functions of temperature. Self-diffusion along screw and edge dislocations in aluminum was studied by molecular dynamic (MD) simulations. Three types of simulations were performed with and without (intrinsic) pre-existing vacancies and interstitials in the dislocation core. We found that the diffusion along the screw dislocation was dominated by the intrinsic mechanism, whereas the diffusion along the edge dislocation was dominated by the vacancy mechanism. The diffusion along the screw dislocation was found to be significantly faster than the diffusion along the edge dislocation, and the both diffusivities were in reasonable agreement with experimental data. The intrinsic diffusion mechanism can be associated with the formation of dynamic Frenkel pairs, possibly activated by thermal jogs and/or kinks. The simulations show that at high temperatures the dislocation core becomes an
The NiAl potential accurately reproduces a variety of physical properties of the B2-NiAl and L1$_2$-Ni$_3$Al phases. The potential is expected to be especially suitable for simulations of hetero-phase interfaces and mechanical behavior of NiAl alloys.

Apart from properties of the HCP Co, the new Co potential is accurate enough to reproduce several properties of the FCC Co which were not included in the potential fit. It shows good transferability property. The CoAl potential was fitted to the properties of B2-CoAl phase as in the NiAl fitting where as the NiCo potential was fitted to the $ab$ initio formation energies of some imaginary phases and structures.

Effect of chemical composition and uniaxial mechanical stresses was studied on the martensitic phase transformation in B2 type Ni-rich NiAl and AlCoNi alloys. The martensitic phase has a tetragonal crystal structure and can contain multiple twins arranged in domains and plates. The twinned martensites were always formed under the uniaxial compression where as the single variant martensites were the results of the uniaxial tension. The transformation was reversible and characterized by a significant temperature hysteresis. The magnitude of the hysteresis depends on the chemical composition and stress.
Chapter 1: Introduction

The dissertation consists of three parts related to dislocation, development of interatomic potentials and martensitic phase transformation. They are unified by the same atomistic methodology and emphasis on defects, in particularly dislocations, in material processes and the martensitic phase transformation.

Dislocation diffusion plays crucial role in many material processes. In fact it is fundamentally the least understood phenomena in materials science. Experimental data are rare and measurements are very difficult and expensive even in pure metal such as aluminum. Aluminum is widely used in industries and nickel-aluminum superalloy is the backbone of aircraft grade materials \[17\][18]. Today, if one needs an experimental value of the dislocation diffusion coefficient in a particular metal or alloy at a particular temperature, such data are unlikely to be found in the literature. For a few metals (e.g., Ag, Al, Au, Fe and Ni) the measurements of the 1960s–1970s can be extrapolated to the desired temperature. For Al, direct measurements have never been made due to the lack of a suitable radio tracer. An isotope of Al, $^{26}$Al, has a half-life of $7.4 \times 10^5$ yrs which does not give desired level of counts \[19\]. Only the indirect measurements of 1971 \[5\] are available. No reliable experimental data on dislocation diffusion in Al alloys can be found in the literature, except for a few rather crude indirect estimates of the activation energy from internal friction \[20\].

Interaction between atoms plays crucial role in any molecular dynamic (MD) simulations where outcomes always depend on the accuracy of the potentials used. There have been several methods proposed in the past to describe the interaction between the atoms. The most often used methods are embedded atom method (EAM) and Finnis-Sinclair potentials. They are semi-empirical in nature because they use analytical functions fitted to some \textit{ab initio} and experimental data.
Over the past 25 years, EAM and Finnis-Sinclair potentials have been applied for atomistic simulations of interfaces, dislocations, fracture, diffusion, phase transformations, deposition and many other processes. These potential forms have been proved to be capable of giving very reasonable values of elastic moduli, phonon dispersion relations, thermal expansion, melting properties, stacking fault energies, point-defect formation and migration energies, surface and interface energies and many other properties of metallic materials. For binary systems, simple phase diagrams can be reproduced in semi-quantitative agreement with experiment [2,21].

Early EAM and Finnis-Sinclair potentials were developed by fitting to a few experimental numbers. The current trend is to include a significant amount of \textit{ab initio} information [1,2,21–29], essentially turning potentials into parameterizations of \textit{ab initio} calculations. The \textit{ab initio} data drastically improve the reliability of potentials by sampling large areas of configuration space, including configurations far away from areas sampled by experimental data. The \textit{ab initio} information can be included in the form of energies or forces for real or artificial crystal structures, or forces in snapshots drawn from \textit{ab initio} MD simulations [22].

There has been significant progress in improving the potential fitting methods [23,30,31], including approaches based on neural networks [32,33] and genetic algorithms [34,35]. Although the development of accurate and reliable potentials remains similar to art [36], new algorithms and rigorous statistical methods begin to play an increasingly important role.

Shape memory alloys are technologically important materials due to their ability to change shapes. They have been used in actuators, sensors, micro-devices and large structures like aircraft engines. Nickel based superalloys have high strength and corrosion resistance at high temperatures. The shape memory effect is caused by reversible martensitic phase transformation from high temperature B2 structure to low temperature L1_0 structure with significant hysteresis of temperature. This effect can also be induced by external stresses. Molecular dynamics (MD) and Monte Carlo simulations were recently used to
study mechanisms of the martensitic transformation in NiAl alloys \cite{37,44}. Experimental observations of the martensitic transformations in some alloys were reported by several investigators such as \cite{45,58}. The martensitic phase transformation in AlCoNi alloys have been experimentally investigated by \cite{51,53,57,64}. However, direct simulation of the martensitic phase transformation in AlCoNi alloys has not been done to date and there exists no credible EAM potential for this system.

For the atomistic simulation of diffusion we chose aluminum with a dislocation as a model and focused on the diffusion along the core of the dislocation. The Ni-rich NiAl and AlCoNi alloys were taken as the models to simulate the phase transformations. This work has three folds: (i) dislocation diffusion in aluminum, (ii) EAM potential developments of several systems and (iii) martensitic phase transformations in B2 type Ni-rich NiAl and AlCoNi alloys. They are divided into several chapters. First two chapters deal with introduction, motivation and methodologies used in the work followed by actual work on self-diffusion in dislocation cores of screw and edge dislocations in aluminum. The last two chapters covers applications of recently developed EAM potentials of NiAl, and AlCoNi systems.

1.1 Dislocation diffusion

Kinetics of many material processes such as phase transformations, microstructure evolution, high-temperature modes of plastic deformation and fracture, oxidation, corrosion, and many others are controlled by mass transport as a result of atomic diffusion \cite{65}. It has been established that fast atomic diffusion can occur along core regions of extended defects, such as surfaces, grain boundaries \cite{66,67} and dislocations \cite{66,68,69} (so-called “short-circuit” diffusion). The early indication of this fact can be traced back to a work by Zener \cite{70}. Theoretically, the entropy of activation for diffusion can have both negative and positive values but a negative value is highly improbable. Zener \cite{70} interpreted all cases of negative experimental values in terms of inhomogeneities in structure that yield rapid diffusion paths. This work indicated possible influence of dislocation on mass transport along cores
of dislocations.

Dislocations not only serve as preferred sites for phase nucleation \[71\], but also the kinetics of particle growth are often controlled by the mass transport along dislocations. The nucleation and growth constitute the main mechanism of plasticity effect on phase transformations \[72\]. The particle size distribution is found to be governed to some extent by dislocation diffusion as the total mass flow to particles (or from the particles) includes the volume or matrix flow and flow along dislocation cores \[73\]. Al alloys often exhibit precipitation induced and accelerated by the dislocation diffusion \[74\]–\[76\]. For example, \(\text{Al}_2\text{Li}(\delta^-)\) particles nucleate on dislocations, preferentially at compressive regions of edge dislocations without destroying their core structure \[77\]. The dislocation assisted diffusion model was proposed by Cai et al. for the transformation of bismuth cuprate 2212 to -2223\[78\]. The Ostwald ripening of multicomponent MC-type (Metal Carbon) carbides in high-strength low-alloy steels was suggested to be influenced by dislocation diffusion \[79\]. Although their growth kinetics are mainly controlled by bulk diffusion, dislocation diffusivity is responsible for understanding full account of growth kinetics \[80\] if a material contains such a defect. In fact, effect of dislocations on microstructure evolution and mechanical properties strongly depends on alloy types and aging.

The origin of dynamic strain aging (DSA) lies in the resistance to dislocation motion due to the diffusion of solute atoms at arrested dislocations \[81\]–\[82\] from forest of dislocations, precipitates, and other obstacles. The solute segregation occurs during the arrest time of dislocations. An increase in strain rate shortens the arrest time and lowers the solute segregation level, which in turn reduces the resistance to slip. When the arrest time is comparable to the segregation time, strain rate sensitivity (SRS) becomes negative, which signifies instability of flow stress \[83\]–\[85\]. The segregation kinetics can be controlled either by diffusion from the bulk or diffusion along the cores of the mobile and/or forest dislocations \[86\]–\[88\]. The deviation from the strain rate exponent, \(n = 2/3\), and different activation energies strongly suggest the significance of dislocation diffusion in the DSA processes \[87\].

Kinetics of solute segregation at surfaces and grain boundaries are often enhanced by
the dislocation diffusion with some variations on types of dislocations \[89\, \text{91}\]. Dislocations ending at interfaces could serve as easy paths for solute atoms to diffuse through. The impact of dislocation diffusion can be either beneficial or detrimental, depending on the effect of the segregation on material’s properties. In cases of severely embrittling impurities, dislocation diffusion essentially controls the service life of the material.

Dislocations can contribute to the mass transport involved in different mechanisms of creep, including dislocation climb and the Orowan loop bowing \[92\]. The dislocation diffusion is found to play a significant role in the creep of steels \[93\, \text{94}\], Ni base super-alloys \[95\], particle-reinforced Ti alloys \[96\], Sn alloys \[97\], and Al alloys \[98\, \text{99}\]. The deviation from the power law of creep is often attributed to the dislocation diffusion \[93\, \text{94}\]. The creep behavior of Sn-3.5Ag solder/Cu couple was studied to characterize the behavior of solder balls in electronics devices and found to be correlated to dislocation core diffusion at low temperatures \[97\].

Coarsening kinetics in particle-strengthened alloys are often influenced or even controlled by diffusion along dislocations. This effect is strongest in nanometer-scale structures, where dislocation lines can directly connect the growing particles. It is through this effect that plastic deformation can have a tremendous impact on coarsening kinetics. Besides dislocations produced by slip in the matrix, diffusion along misfit dislocation at the particle/matrix interface can also be important. For example, diffusion along misfit dislocations at \(\gamma/\gamma'\) interfaces contributes to the \(\gamma'\) coarsening and rafting kinetics and affects creep resistance of super-alloys \[95\]. The plasticity-induced dissolution is another effect of transport along dislocations \[72\].

Inter-diffusion of particles during ball milling can occur by atomic diffusion along the cores of dislocations terminating at the interfaces \[100\]. For example, dislocation diffusion is known to enhance sintering rates during the ball milling of Fe powders \[101\]. (Care should be exercised in separating dislocation diffusion from the so-called “ballistic effects” accompanying ball milling \[72\, \text{102}\].) Although surface and grain-boundary diffusion play the dominant role \[66\], the overall rate of sintering may depend on the supply of a particular
alloy component from the bulk or other sources. The rate of this mass transport can be influenced or limited by dislocation diffusion. As an example, sintering of beta Ti is found to be dominated by mass transport along dislocation cores [103].

Almost all rate equations governing material processes involve diffusivity, which often has a significant contribution from diffusion along cores of dislocations. Thus, in general the effective diffusivity may be written

$$D^{eff} = (1 - f)D_b + fD_d,$$

(1.1)

where $f$ is the volume fraction of total dislocation volume defined as the dislocation density times the area of the dislocation core, which is dimensionless quantity. $D_b$ and $D_d$ denote diffusion coefficients in undisturbed lattice and extended defects respectively. The dislocation density is defined as the ratio of total length of the dislocation line to the total volume. Thus, the typical unit of the dislocation density is $m^{-2}$. The temperature dependence of the diffusion coefficient generally follows the Arrhenius law:

$$D = D_0 \exp(-E/kT)$$

(1.2)

where $D_0$ and $E$ denote the pre-exponential factor and activation energy respectively. In general, one can expect the diffusion coefficient $D_d$ to depend on the character of the dislocations, but there exists no consensus on which type of dislocation, screw, edge or mixed dominates over the other in a given material. On top of this, there still remains a question of the driving mechanisms for the dislocation diffusion. The generally accepted mechanisms involve migration of vacancies (mono vacancies, divacancies and higher order vacancy clusters) or interstitials (single interstitials, dumbbell interstitials, interstitialcies, and crowdions). Also, intuitively, a single mechanism may not work for all types of dislocations and in all materials. In the first place, apart from these issues, how can we directly or indirectly determine self-diffusion along dislocations $D_d$ for the given material, for example, aluminum?
1.1.1 Experimental measurements

Experimental measurements of dislocation diffusion coefficients are rare and hence, reliable data are scarce. A comprehensive summary of early measurements was given in [66,68]. In direct experimental measurements, the diffusion coefficient is deduced from the penetration profile of radioactive-tracer or impurity atoms diffused into either a deformed single crystal or a polycrystal containing low-angle grain boundaries. In the radio tracer technique, the concentration profile is deduced from radioactivity measurements of thin layers. To interpret the profile, each dislocation is approximated by a pipe of a radius \( r_d \) with a high diffusivity \( D_d \). The diffusivity \( D \) outside the pipe is assumed to be the same as in undisturbed lattice. There are several continuum solutions of this diffusion problem [66], all assuming that the dislocations are (1) normal to the surface; (2) equally spaced within a wall or form a periodic (e.g., hexagonal) array; and (3) isolated from each other. Of course, such conditions cannot be exactly met in experiments. The experimental penetration profile is fitted to a model solution that gives the integrated diffusion flux \( P_d = D_d A_d \), where \( A_d = \pi r_d^2 \) is the cross-sectional area of the dislocation pipe. To estimate \( D_d \) separately, a reasonable assumption about \( r_d \) is made, usually \( r_d = 0.5 \text{ nm} \), which is somewhat arbitrary and may depend on the crystal structure. Note that it is actually the quantity \( P_d \) that appears in all models of diffusion-controlled processes, not \( D_d \) separately. Table 1.1 summarizes the experimental results obtained in the past for aluminum.

Impurity diffusion along dislocations can be studied by SIMS (secondary ion mass spectrometry) measurements [115], which are less accurate than radio-tracers but more affordable. However, such measurements are also very rare [115,116]. The pipe diffusion was observed over the temperature range of 1424 – 1636°C using \(^{18}\text{O} \) isotopes and SIMS.

Besides direct measurements, \( P_d \) can be evaluated by indirect methods, such as internal friction, dislocation climb rate, dislocation loop shrinkage, growth kinetics of \( \delta' \) phase in Al-Li alloy [80], annihilation of dislocation dipoles [115,117], and others [68]. Essentially, it can be any process whose rate is assumed to be controlled by dislocation diffusion. By
Table 1.1: Summary of experimental data for the pre-exponential factor $D_0$ and activation energy $E$ of lattice diffusion, grain-boundary diffusion, and dislocation diffusion in Al. $\delta$ is the grain boundary width and $A_d$ is the cross-sectional area of the dislocation core. The dash indicates that data is unavailable.

<table>
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<tr>
<th></th>
<th>Lattice diffusion $D_0$ (m$^2$/s)</th>
<th>Boundary diffusion $E$ (eV)</th>
<th>$\delta D_0$ (m$^3$/s)</th>
<th>$E_b$ (eV)</th>
<th>$A_d D_0$ (m$^4$/s)</th>
<th>$E_d$ (eV)</th>
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<tr>
<td>Lundy et al. [6]</td>
<td>1.71 x 10^{-4}</td>
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<td>0.85</td>
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<td>Engardt [104]</td>
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<td>1.3</td>
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<td>Spokas et al. [105]</td>
<td>3.5 x 10^{-6}</td>
<td>1.25</td>
<td>—</td>
<td>1.7 x 10^{-4}</td>
<td>1.9 x 10^{-14}</td>
<td>0.62</td>
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<td>DeSorbo et al. [106]</td>
<td>0.02 x 10^{-1}</td>
<td>1.22</td>
<td>—</td>
<td>2.3 x 10^{-22}</td>
<td>—</td>
<td>0.55</td>
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<td>Fradin et al. [107]</td>
<td>1.7 x 10^{-4}</td>
<td>1.48</td>
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<td>Stoebe et al. [108]</td>
<td>0.2 x 10^{-4}</td>
<td>1.33</td>
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<td>Huer et al. [109]</td>
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<td>1.76 x 10^{-5}</td>
<td>1.31</td>
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<td>Gangulee et al. [110]</td>
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<td>Levenson et al. [111]</td>
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<td>Federighi et al. [112]</td>
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<td>Volin et al. [113]</td>
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<td>Haruyama et al. [114]</td>
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<td>Stoebe et al. [108]</td>
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$1.9 \times 10^{-5}$ m$^2$ s$^{-1}$ multiplied by $\delta = 1.0$ nm.
measuring the process rate, \( P_d \) can be back-calculated using a suitable model of the process. Unfortunately, such models often rely on rather crude approximations and contain other parameters whose values are not known either. As a consequence, indirect measurements are only accurate up to an order of magnitude at best and have poor reproducibility. Volin et al. [5] measured mass transport along individual dislocations in aluminum using void shrinkage rates for range of temperatures from 50–180\( ^{\circ} \)C. Voids were introduced in thin film specimens (200–400 Å diameters) and connected to individual dislocations ending at the surface of the specimens with Burgers vector \( \frac{a}{2}(110) \). The dislocation diffusivity was found much higher than self-diffusion in aluminum [114]. The pipe diffusion in undoped and Magnesia(MgO)-doped sapphire was also determined from the annihilation of dislocation dipoles [117]. Self-diffusion of Oxygen by pipe diffusion in deformed sapphire single crystals (\( \alpha \)-\( \text{Al}_2\text{O}_3 \) sapphire) with a high density of unidirectional basal dislocations was deduced from the annihilation of dislocation dipoles [115].

According to experimental data available, the activation energy of dislocation diffusion \( E_d \) along dislocations with the Burgers vector \( \frac{a}{2}(110) \) is roughly 0.6–0.7 of the activation energy of bulk diffusion \( E \), while the pre-exponential factor is close to typical bulk values [68]. The diffusion coefficients tend to increase with the magnitude of the Burgers vector and decrease with the dissociation width into Shockley partials in FCC (Face Centered Cubic) metals. Diffusion along edge dislocations appears to be faster than along screw dislocations. It is generally assumed that dislocation diffusion is mediated by atomic exchanges with single vacancies, but there is no convincing experimental evidence for this mechanism. In fact, except for the analogy with lattice diffusion, there is no fundamental reason why vacancy diffusion in dislocations must always dominate over interstitial diffusion or any other mechanism.

1.1.2 Computer simulation and modeling

Early atomistic simulations performed with pair potentials confirmed that atomic mobility in dislocation cores is larger than in the lattice, and that typically \( E_d \approx 0.6 – 0.7 \) \( E \) [118,120].
In dissociated dislocations, diffusion was found to occur not only along the partial dislocation cores but also along the stacking-fault ribbon, thus making the effective cross-sectional area of diffusion larger.

Recently, more accurate simulations employing embedded-atom method (EAM) potentials have been performed for dislocations in Au [121], Al [122,124], Cu [119,120,125], Al-Mg [124] and Al-Cu [126] alloys. A similar method was also used in [127] to compute self-diffusion in Aluminum by the vacancy mechanism. In agreement with previous work, the rate of vacancy jumps along the dislocation core was found to depend on the character of the dislocation (edge, screw or mixed). Diffusion within the stacking fault region was confirmed to be faster than in the bulk. Only diffusion by the vacancy mechanism was addressed in the previous works. The activation energy obtained from separate calculations of defect formation and migration energies, which were deduced from jump rates or mean-squared displacements from very short simulations.

Nevertheless, the methodology of the simulations has been brought to a brand new level. While the earlier pair-potential work was relevant to a generic solid, the use of accurate embedded-atom potentials has afforded simulations specific to a particular material (e.g. Al or AlMg alloys). Accurate vacancy jump barriers can now be calculated routinely using the nudged elastic band (NEB) method [122,124]; the vacancy diffusion coefficient can be computed by the kinetic Monte Carlo method [122]; molecular dynamics (MD) can be run on relatively large systems for nanoseconds or longer; even the hyper dynamics method [128] has been applied to study vacancy diffusion in the core of an Al edge dislocation [123].

Despite these methodological advances, the recent work [121–124,126] has not led to significantly new physical insights into dislocation diffusion. The current knowledge of atomic mechanisms of dislocation diffusion remains rudimental, if existent. It is noteworthy to mention that although Gunther et al. [129] derived an exact solution to diffusion by the vacancy mechanism for 2D-lattice, different jump frequencies and correlation factors involved in the solution make it difficult to comprehend.

Indeed, as a vacancy migrates along the dislocation core with a diffusion coefficient $D_v$, it
displaces and intermixes atoms, thus causing their diffusion with a coefficient $D_d$. The latter depends not only on $D_v$ but also on the vacancy occupation probabilities (concentrations) at various core sites, as well as on the partial jump-correlation factors.

In the case of impurity diffusion, simply placing an impurity atom at various core sites and treating its exchanges with neighboring vacancies with an equal weight for every site is inconsistent with thermodynamics. For a proper calculation, the thermodynamically equilibrium distribution of impurity atoms over the core sites must be known, depending on the temperature and the bulk composition. This distribution can be estimated in the dilute-solution approximation by placing a single impurity atom at various core sites $i$ and calculating the difference $E_i$ between the relaxed energy and the energy of a reference system containing a single impurity in the lattice. The impurity occupation probability at site $i$ can be estimated as $c_0 \exp(-E_i/kT)$, $c_0$ being the bulk impurity concentration. Note that this calculation neglects the vibrational free energy contribution. More importantly, even for a dilute solution in the bulk, the impurity concentration in the atmosphere around the dislocation can be so high that neglecting impurity-impurity interactions can be a very crude approximation. The time to achieve the equilibrium impurity distribution by means of atomic diffusion is far beyond the time scale of MD simulations. One way to address this problem would be to implement grand-canonical Monte Carlo simulations prior to diffusion calculations.

Another important aspect of dislocation diffusion is the critical role of jump-correlation effects. Given the complex structure and quasi-1D confinement of the dislocation core, an accurate description of jump-correlation effects is a very difficult task.

There is a theorem of random-walk theory which states that the correlation factor of vacancy diffusion in 1D systems is exactly zero. In other words, there is no atomic diffusion in 1D even if the vacancy jump rate is very high. This happens because after each exchange with a particular atom, the vacancy is bound to return to it and induce its jump in the opposite direction. Thus, each atom hops back and forth between two sites and does not contribute to long-range diffusion. If a structure contains isolated “fast-diffusion
paths” with a high vacancy jump rate, their contribution to the overall atomic transport is exactly zero. It is only when there are “cross-links” between such paths, which break their 1D confinement, that atomic diffusion becomes possible. But then it is the rate of “cross link” jumps that controls the effective diffusivity and not the jump rate along the paths. Unfortunately, this important fact is often overlooked and dislocation diffusion is attributed to a particular path of easy vacancy jumps. For impurity diffusion along dislocations, jump-correlation effects are even more important than for self-diffusion and are much less understood. Correlation effects associated with non-vacancy diffusion mechanisms in dislocations have not been even discussed in the literature. Clearly, a rigorous theoretical treatment of jump correlations in dislocation diffusion must be developed in the future. This is necessary not only for raising the dislocation diffusion theory to a higher intellectual level, but also for the pragmatic goal of making predictive calculations of dislocation diffusion coefficients.

1.2 Embedded Atom Method (EAM)

Atomic-level computer simulations offer a powerful tool for gaining fundamental knowledge of materials processes and properties. Many simulations involve large ensembles of atoms or require statistical averaging over multiple atomic events. Examples include dislocation motion, crack propagation, multicomponent diffusion, melting, crystallization and many other processes. Due to computational limitations, such large-scale simulations are presently far beyond the capabilities of first-principles (ab initio) methods. They are afforded by the use of semi-empirical interatomic potentials, which parameterize the configuration space of the material and express its energy as a relatively simple function of configuration point. The energy calculations become very fast and have an order-$N$ scaling with the number of atoms $N$. The potential functions depend on adjustable parameters, which are fitted to give desired properties of the material known from experiment or computed by ab initio methods. The basic assumption underlying this approach is that a potential fit to energies or forces for a certain set of configuration points will also give
reasonable results for configurations between and beyond those points. This property of potentials is called “transferability” and is the most important measure of their quality.

For metallic systems, the most common potential forms are those of the Finnis-Sinclair method (FS) \([137]\) and the embedded atom method (EAM) \([138]\). The detail of the theory is discussed elsewhere \([28,138–142]\). The embedded atom method (EAM) potentials are semi-empirical many body interatomic potentials which have been successfully applied to many materials systems especially metallic unary and binary systems \([1,23–25,27,121,143–152]\). In both the EAM and F-S methods, the total energy \(U\) has the form

\[
U = \frac{1}{2} \sum_{i,j}(j \neq i) V_{s_is_j}(r_{ij}) + \sum_i F_{s_i}(\bar{\rho}_i),
\]  

(1.3)

where the first term is the sum of pair interactions \(V_{s_is_j}(r_{ij})\) between atom \(i\) and \(j\) with chemical species \(s_i\) and \(s_j\). The second term is the sum of embedding energies \(F_{s_i}\) of atoms \(i\) into the host electron density \(\bar{\rho}_i\) induced by all other atoms. In EAM, the host electron density is given by the sum of contributions \(\rho_{s_j}(r)\) from all neighboring atoms \(j\),

\[
\bar{\rho}_i = \sum_{j \neq i} \rho_{s_j}(r_{ij}).
\]  

(1.4)

where \(r_{ij}\) is the distance between atom \(i\) and \(j\).

In the Finnis-Sinclair formalism, \(\bar{\rho}_i\) is represented by a sum of pairwise functions \(\Phi_{s_is_j}(r_{ij})\) whereas \(F_{s_i}(\bar{\rho}_i)\) is taken as a negative of the square root of \(\bar{\rho}_i\). Although originally derived from different physical approximations (density-functional theory \([138,139]\) or second-moment tight-binding \([137]\), the EAM and Finnis-Sinclair potential forms are formally similar. There are other potential forms used in simulations such as angular dependent potential (ADP) \([28]\), embedded defect method (EDM) \([153]\), Stillinger-Weber (SW) \([154]\) and modified embedded atom method (MEAM) \([145]\). They are all based on decomposition of terms on the right hand side of Eq. (1.3). The EAM formalism is much simpler, central
in nature compared to other types of potentials which include bond order.

The pair interaction and electron density are usually expressed in terms of some analytical functions but they can also be splines. For n-component system we need:

- \( \frac{n(n + 1)}{2} \) pair interaction functions \( V_{ss'}(r) \),
- \( n \) electron density functions \( \rho_s(r) \),
- \( n \) embedding functions \( F_s(\bar{\rho}) \) (\( s = 1, ..., n \)).

As an example, a ternary system requires 13 functions: \( V_{AA}, V_{BB}, V_{CC}, V_{AB}, V_{AC}, V_{BC}, \rho_A(r), \rho_B(r), \rho_C(r), F_A(\bar{\rho}), F_B(\bar{\rho}) \) and \( F_C(\bar{\rho}) \).

In order to construct the embedding function, \( F(\bar{\rho}) \), the total energy in Eq. (1.3) is expressed as an empirical relation between binding energy per unit atom and a characteristic size of lattice constant, which was originally proposed by Rose \textit{et al.} [155], given by

\[
E(a^*) = E_0 \left(1 + a^*\right) e^{-a^*} \tag{1.5}
\]

where

\[
a^* = \frac{a}{a_0} - 1 - \frac{1}{2} \left( \frac{E_0}{9BV_0} \right)^{1/2}.
\]

Here \( E_0, B, V_0 \) and \( a_0 \) are binding energy per atom, bulk modulus, volume per atom and lattice constant respectively at absolute zero. Eq. (1.5) may be simplified further by introducing a constant, \( \alpha = (9BV_0/E_0)^{1/2} \), which yields

\[
E(x) = E_0 \left(1 + \alpha x\right) e^{-\alpha x} \tag{1.6}
\]
where \( x = \frac{a}{a_0} - 1 \). We may modify Eq. (1.6) as

\[
E(x) = E_0 \left( 1 + \alpha x + \beta x^3 \right) e^{-\alpha x},
\]

(1.7)

without changing \( \alpha \). This adds one more fitting parameter \( \beta \) which gives a freedom to change the shape of the equation of state away from the minimum.

It can be readily proved that potential functions are invariant under the following sets of transformations:

\[
(i) \quad \begin{align*}
\rho_s(r) & \rightarrow \lambda_s \rho_s(r) \\
\rho_s'(r) & \rightarrow \lambda_s' \rho_s'(r) \\
F_s(\rho) & \rightarrow F_s(\rho/\lambda_s) \\
F_s'(\rho) & \rightarrow F_s'(\rho/\lambda_s'),
\end{align*}
\]

(1.8)

\[
(ii) \quad \begin{align*}
F_s(\rho) & \rightarrow F_s(\rho) + g_s \rho \\
F_s'(\rho) & \rightarrow F_s'(\rho) + g_s' \rho \\
V_{ss}(r) & \rightarrow V_{ss}(r) - 2g_s \rho_s(r) \\
V_{ss'}(r) & \rightarrow V_{ss'}(r) - 2g_s' \rho_s'(r) \\
V_{ss'}(r) & \rightarrow V_{ss'}(r) - g_s \rho_s' - g_s' \rho_s(r),
\end{align*}
\]

(1.9)

These transformations do not alter any properties of pure \( s \) or \( s' \) but change the shape of the cross-interaction function, \( V_{ss'}(r) \), during the fitting process \[156\]. The transformation coefficients \( \lambda_s, \lambda_s', g_s \) and \( g_s' \) are additional fitting parameters. In addition to the transformation coefficients, potential functions have their own parameters.
1.3 Martensitic phase transformation (MPT)

Nickel based super alloys and transition metal (TM) aluminides such as FeAl, NiAl and CoAl have drawn considerable attention because of their high oxidation and corrosion resistance, high strength to weight ratio and wide ranges of applications in shape memory devices and high temperature structure materials even though they are very brittle. Shape memory alloys are novel and special materials which have been used in many applications such as micro-electrochemical system (MEMS), biomedical devices and civil structures. The shape memory effect was discovered in AuCd and CuZn alloys in the 1930s [157]. After three decades later it was accidentally discovered in NiTi alloys at the US Naval Ordinance Laboratory, which was commercialized under the brand name “NiTinol”.

![Figure 1.1: Lattices of (a) B2 and (b) L1\textsubscript{0} structures. B2 structure transforms to L1\textsubscript{0} when c becomes $\sqrt{2}a_{bcc}$. (color online)](image)

The shape memory effect occurs due to a martensitic phase transformation (MPT) from a cubic B2 structure (CsCl prototype) at high temperatures to a tetragonal L1\textsubscript{0} structure (CuAu prototype) at low temperatures which is a tetragonal distortion of the face center
cubic (FCC) structure (see Fig. 1.1). Upon cooling, the high-temperature phase called austenite transforms to the low-temperature phase called martensite. Austenite was named after the UK metallurgist Sir W. C. Roberts-Austen (1843 – 1902) and martensite was named after the German metallurgist Adolf Martens (1850 – 1914). This transformation is often referred to as diffusionless or displacive because it occurs by relatively small and highly correlated atomic displacements that do not involve diffusion. The transformation can be induced by stress or/and temperature. The martensitic phase transformation is first order and exhibits a significant temperature hysteresis whose magnitude depends on the heating and cooling rates, the microstructures in the samples and other factors. The hysteresis loop is usually characterized by the difference between the martensite-start temperature $M_s$ determined during the cooling and the austenite-finish temperature $A_f$ during the inverse transformation upon heating. The martensite usually has a heavily twinned structure composed of multiple plates [158]. This twinned structure is sometimes interpreted as a crystallographically distinct 7R structure [159,160], although this interpretation of diffraction patterns is considered misleading [45].

In NiAl alloys this transformation is experimentally observed only in Ni-rich compositions $\text{Ni}_x\text{Al}_{1-x}$ with $x = 0.62 – 0.69$ at.%. Noda et al. [46] studied the transformation in $\text{Ni}_{62.5}\text{Al}_{37.5}$ alloy and found a seven-layered monoclinic unit cell (7M) martensite and on the basis of this experiment Yamada et al. [161] proposed a transformation theory. The experiments on $\text{Ni}_x\text{Al}_{1-x}$ alloys for $x = 0.50, 0.58, 62.5$, and $63.9$ at.% revealed a tweed structure as a precursor of martensite [162].

The martensitic phase transformation occurs not only in the binary alloys; it has been demonstrated in multi-component alloys such as Al-Co-Ni [51,53,57,64], Ni-Co-Mn-Sn [163], Ni-Mn-Ga [164], Ti-Ni-Hf [165], Co-Ni-Ga and Ni-Fe-Ga-Co [166].
1.4 Motivation

Aluminum and its alloys are important technological materials widely used in industries. Most of the diffusion data for aluminum available today were measured in the 1960s–1970s (see Table 1.1). Presently, radio-tracer diffusion measurements are only made in a few laboratories in the world and mostly for lattice and grain boundary diffusion [167]. Despite numerous works [6, 19, 105–108, 168, 169] on impurity and self-diffusion in Aluminum, for dislocation self-diffusion in metals, our literature search indicates that the recent papers on ultra high purity iron [170] and rapid mass transport along dislocations in aluminum [5] might be the only works published in the past decade. Reuther et al. [171] studied dislocation diffusion in Niobium (Columbium) single crystals from the penetration profile using $^{95}$Nb tracer at 1000°C ($0.46T_m$). It is interesting to quote that self-diffusion in aluminum is still controversial [19, 172] in the sense that it might not follow the Arrhenius relation. There is a considerable controversy on mechanisms of self-diffusion in Al [19].

By contrast to the common assumption, Huang et al. [119,120] found that vacancies and interstitials can make comparable contributions to dislocation diffusion. Only diffusion by the vacancy mechanism was addressed in the recent works; the earlier indications of the role of interstitials [119,121] were neglected. Except for the evaluation of the ring mechanism in [124] (which turned out to be unfavorable), no alternatives to the vacancy mechanism have been considered. These studies obtained the activation energy from separate calculations of defect formation energy and migration energy, which were deduced from jump rates or mean-squared displacements from very short simulations.

While the vacancy diffusion coefficients $D_v$ have been calculated in a few studies [120–123], the atomic diffusion coefficient $D_d$ has only been estimated [120,124,126] but never determined by direct simulations. Note that it is the atomic diffusion coefficient that controls the mass flux along the dislocation core and enters all models of diffusion-controlled processes, not the point-defect diffusion coefficients. For impurity diffusion, the impurity occupation probabilities at different sites and impurity-vacancy binding energies in different
configurations within the core region must also be known for a proper calculation of $D_d$. More generally, the diffusion coefficient of the point defect responsible for diffusion is only one ingredient required for the calculation of the atomic diffusion coefficient. For multiple diffusion mechanisms operating concurrently, the diffusion coefficients of different point defects must be properly combined with other relevant quantities to give the atomic diffusion coefficient. Alternatively, $D_d$ could be computed by direct MD simulations, in which case it is the mean-squared atomic displacements in the core region that should be analyzed, not the mean-squared displacements of the defect. This was the approach in this work.

The nickel based alloys are important technological materials. Much of the experiments were done on Ni-rich NiAl alloys. Simulation wise it is the most quoted alloy in the literature. However it lacks a systematic study of martensitic phase transformation under uniaxial stresses and with defects. Similarly our literature search found only one instant of ternary potential for AlCoNi system [173] which was used to simulate aluminum diffusion in three different decorations of decagonal quasicrystals of the AlCoNi system. The martensitic transformation in several alloys of AlCoNi system have been experimentally studied in the past [51, 53, 58, 62–64] but the systematic study of the MPT behavior in AlCoNi alloys with direct simulation has not been done yet.

The purpose of the dissertation is

- to study self-diffusion in the cores of a screw and an edge dislocations in aluminum with new proposed method.
- to study relative importance of three mechanisms: (i) without any pre-existing defect, “intrinsic”, (ii) with a vacancy and (iii) with an interstitial.
- to develop EAM potential for AlCoNi ternary system.
- to investigate the martensitic phase transformation in several alloys of AlCoNi system using MD simulation.

Aluminum with pure edge and screw dislocations were chosen as a model system for the
dislocation diffusion. Similarly, NiAl and AlCoNi alloys with B2 structure were chosen to model the martensitic transformations.
Chapter 2: Methodology

2.1 Potential fit

The problem of potential fit is related to a global optimization of parameters in a large configuration space. Simulated annealing method is one of several other methods used to solve multidimensional optimization. It readily finds a best local minimum (not necessarily global minimum). The simulated annealing technique along with the modified downhill simplex method were implemented in the fitting code. The details of the methods and the codes are described here [174]. The simulated annealing is based on thermodynamics. The probability of finding a system in a particular state $E$ is given by the Boltzmann's distribution

$$ P(E) \sim \exp\left(-\frac{E}{kT}\right) $$

where $E$ is an objective function that has to be minimized but not necessarily an energy and $T$ is the temperature. This indicates that even at low temperature there is a chance (small probability) of being in a higher state of $E$. Thus it ensures that there is a chance to get out of a unfavorable local minimum by going uphill sometime and crossing a energy barrier to a deeper minimum. Within the problem of potential fit, we defined the objective function as the sum of squares of errors given by

$$ E(x) = \sum_{i=1}^{n} w_i (y_i(x) - Y_i)^2, $$

(2.1)

where $y_i(x)$ is a function of $N$-dimensional vector of fitting parameters, $x$. $Y_i$ is the target value and $w_i$ is the weight associated with the target $i$. We seek the minimum of $E(x)$,
among other local minima, which satisfies our requirement.

In general the simulated annealing requires (i) an objective function, \( f(x) \) of \( N \)-dimensional vector \( x \) (\( N \) being the number of fitting parameters), (ii) \( N + 1 \) vectors in \( N \) dimensions to construct a simplex, (iii) method to change the configuration, \( x = x_0 + \Delta e \), and (iv) the control parameter \( T \) and an annealing schedule. \( x_0 \) is the initial configuration and \( e \) is the unit vector in \( N \) dimensions. A simplex is the geometrical object bounded by \( N + 1 \) points (or vertices) in \( N \) dimensions.

### 2.2 Molecular dynamics

Molecular dynamics is based on classical mechanics through Newton’s equation of motion \( ma = F \) where \( F \) is the force acting on mass \( m \). For a system of \( N \) particles the equation of motion can be written as

\[
f_i = m_i \frac{d^2 r_i(t)}{dt^2} = -\nabla_i U(r), \quad i = 1, ..., N
\]

where \( r_i \) the position vector of \( i \)th particle. \( U(r) \) is only a function of distance that describes the interaction between particles. Using the Verlet algorithm we can compute the new position of a particle after time \( t + \Delta t \) as

\[
r(t + \Delta t) = 2r(t) - r(t - \Delta t) + \frac{f(t)}{m} \Delta t^2 + O(\Delta t^4)
\]

and the new velocity as

\[
v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t} + O(\Delta t^2).
\]
The new position and velocity are only accurate to order $\Delta t^4$ and $\Delta t^2$ respectively. The errors can be improved by using other Verlet like algorithms. Molecular dynamic simulations are run with (i) micro-canonical (constant – $NVE$), (ii) canonical (constant – $NVT$) and (iii) isobaric-isothermal (constant – $NPT$) ensembles where $N$, $V$, $E$, $T$ and $P$ denote number of particles, volume, energy, temperature and pressure of the system. The $NVE$ ensemble is the conventional molecular dynamics equivalent to adiabatic process in which no heat enters or leaves the system. The $NVT$ ensemble requires a heat bath whose temperature can be controlled by different thermostats such as the velocity rescaling, the Andersen, the Nose-Hoover, and the Berendsen. The Nose-Hoover thermostat is based on the Lagrangian of the extended system [175]. In addition to the thermostat the $NPT$ ensemble requires a barostat to control its pressure such as the Andersen barostat which is also based on the extended Lagrangian.

In this work the ITAP molecular dynamics (IMD) code was used which implements the $NVE$, the $NVT$ and the $NPT$ ensembles [176, 177]. The change in the simulation block in the $NPT$ ensemble can be isotropic ($NPT_{ISO}$) where the shape does not change or anisotropic ($NPT_{AXIAL}$) where the shape changes. We used the $NVT$ ensemble to simulate the diffusion process. The simulations of the martensitic phase transformations were performed with the $NPT$ ensemble where as the $NVE$ ensemble was used in the simulations of melting processes.

2.3 Monte Carlo simulation

The Monte Carlo (MC) simulation is based on stochastic technique. It has been used in many fields of science. It is very much suited in atomistic simulations where we want to achieve an equilibrated system at a given temperature.

The MC method uses the Metropolis scheme [178] to decide a transition from configuration $o$ to $n$. In order to do this we need to find a transition probability, $w(o \rightarrow n)$ (say). In equilibrium, the average number of accepted trial moves leaving the state $o$ must be equal
to the average number of accepted trial moves from all other states \( n \) to state \( o \). Thus we need to have a balance condition:

\[
N(o)w(o \rightarrow n) = N(n)w(n \rightarrow o),
\]

(2.2)

where \( N(o) \) is the probability density of state \( o \) which is proportional to the Boltzmann’s factor \( \exp[-\beta \mathcal{H}(o)] \). Here, \( \mathcal{H}(o) \) is the Hamiltonian in the \( o \)-space and \( 1/\beta = kT \).

From Eq. (2.2) follows

\[
\frac{w(o \rightarrow n)}{w(n \rightarrow o)} = \frac{N(n)}{N(o)} = \exp[-\beta(\mathcal{H}(n) - \mathcal{H}(o))].
\]

(2.3)

This equation is satisfied by a number of choices. According to the Metropolis

\[
w(o \rightarrow n) = \frac{N(n)}{N(o)} \quad \text{if} \quad N(n) < N(o)
\]

\[= 1 \quad \text{if} \quad N(n) \geq N(o).\]

(2.4)

We may write Eq. (2.4) in terms of the Hamiltonian as

\[
w(o \rightarrow n) = \exp[-\beta \Delta \mathcal{H}] \quad \text{if} \quad \Delta \mathcal{H} > 0
\]

\[= 1 \quad \text{if} \quad \Delta \mathcal{H} \leq 0.\]

(2.5)

Here, the use has been made of \( \Delta \mathcal{H} = \mathcal{H}(n) - \mathcal{H}(o) \). Thus, the Metropolis algorithm follows:

1. Select a particle at random in state \( o \)

2. Make a trial move from state \( o \) to a neighboring state \( n \) at random

3. Calculate \( \Delta \mathcal{H} \)

4. If \( \Delta \mathcal{H} < 0 \), accept the move unconditionally
5. If $\Delta \mathcal{H} > 0$

   (a) Generate a random number $R \in [0, 1)$

   (b) Accept the move if $R \leq \exp[-\beta \Delta \mathcal{H}]$; otherwise reject it

6. If the move is accepted, the new state becomes $o$

7. Go to 1

Even if the initial state of a system may be far away from equilibrium, in time the system attains the equilibrium. Therefore, we can determine thermodynamic average of any physical quantity $\mathcal{A}(s)$ by simply averaging over a large number of states of the system as

$$\langle \mathcal{A} \rangle = \frac{1}{K} \sum_{i=1}^{K} \mathcal{A}_i,$$

where $K$ is the number of MC steps used for averaging and $\mathcal{A}_i$ is the value of $\mathcal{A}$ in state $i$. In fact, the thermodynamic average is given by

$$\langle \mathcal{A} \rangle = \int \mathcal{A}(s)w(s)ds.$$

The MC method simply performs the integration by distributing integration points with probability $w(s)$, which is a procedure known as Importance sampling.

From the thermodynamic we can derive an appropriate Hamiltonian for the MC simulation,

$$h = E(x) - \sum_i \mu_i N_i - kTN \ln V - \frac{3}{2} kT \sum_i \ln m_i.$$  \hspace{1cm} (2.7)

Here $E$ is the potential energy of the system which is a function of $3N$-vector of the Cartesian coordinates of all $N$ atoms, $x$, present in the volume $V$. $\mu_i$, $N_i$ and $m_i$ are the chemical
potentials, the number of atoms and the atomic masses of the species present in the system. The configuration space is described by \( s = \{x, V, N_1, \ldots, N_n\} \).

Equation (2.7) can be manipulated further to describe different processes. If the system is closed (no exchange of particles with the environment) and the volume is fixed, the difference between the Hamiltonian of two states becomes \( \Delta h = \Delta E \). In this case we perform random walk over the \( x \)-space. Thus, we accept and reject a trial move depending on sign of \( \Delta E \).

Suppose the external pressure is zero so that the volume can fluctuate and the system is closed. Then, the trial moves include the random displacements of particles and the random changes in the volume. If the volume changes by the amount \( \Delta V \), we get the Hamiltonian

\[
\Delta h = \Delta E - N kT \ln(1 + \epsilon),
\]

where \( \epsilon = \Delta V/V \), the relative volume change.

Next in addition to the random displacements and the changes in volume we can also vary their number and chemical sorts by keeping chemical potentials constant. This corresponds to a grand-canonical ensemble. If we limit the total number of atoms constant and change only chemical sorts, the process is so-called restricted grand canonical ensemble. For a binary alloy of chemical sorts \( A \) and \( B \), if we replace an atom \( A \) by atom \( B \) the change in the Hamiltonian is

\[
\Delta h = \Delta E - N kT \ln(1 + \epsilon) + \mu_A - \mu_B - \frac{3}{2} kT \ln \left( \frac{m_B}{m_A} \right).
\]

Similarly if an atom \( B \) is replaced by \( A \) the change in the Hamiltonian becomes

\[
\Delta h = \Delta E - N kT \ln(1 + \epsilon) + \mu_B - \mu_A - \frac{3}{2} kT \ln \left( \frac{m_A}{m_B} \right).
\]

Thus, a simulation of a binary alloy needs only the difference in the chemical potentials but not their absolute values. The MC method is implemented in the “SOLD” code (http:}
This code has been used extensively throughout the research.

### 2.4 Structural stability

Relative stability of two structures, FCC and HCP (say), can be established by using Gibbs free energy. In order to compute the Gibbs free energy enthalpy must be known at a given temperature which may be computed as

\[
H(T) = \bar{E}_p + \frac{3}{2}kT
\]  

(2.11)

where \( \bar{E}_p \) is the average potential energy per atom.

The change in the enthalpies of the structures can be expressed as

\[
\Delta H(T) = H_{fcc}(T) - H_{hcp}(T) = H_0 + AT + BT^2
\]  

(2.12)

where \( H_0, A \) and \( B \) are constants to be determined by fitting to the data. From the thermodynamics the Gibbs equation reads

\[
\left[ \frac{\partial (\Delta G(T)/T)}{\partial T} \right] = -\frac{\Delta H(T)}{T^2}
\]  

(2.13)

where \( \Delta G(T) \) is the Gibbs free energy change between the structures at a given temperature. Integration of Eq. (2.13) yields

\[
\Delta G(T) = \Delta G_0 \frac{T}{T_0} + H_0 \left(1 - \frac{T}{T_0}\right) - BT(T - T_0) - AT \ln \left(\frac{T}{T_0}\right)
\]  

(2.14)

where \( \Delta G_0 \) is the integration constant which has the meaning of the free energy at \( T = T_0 \). It is the quantity \( G_0^{fcc} - G_0^{hcp} \). The Gibbs free energies \( G_0^{fcc} \) and \( G_0^{hcp} \) may be computed

2.5 Energy calculations

The formation energy \( E_f \) of a compound \( A_nB_m \) is defined by

\[
E_f = \frac{E_0(A_nB_m) - nE_0(A) - mE_0(B)}{n + m}, \tag{2.15}
\]

where \( E_0 \) are cohesive energies of the respective elements or compounds.

The formation energy \( E_{f,1,v} \) of a single vacancy may be defined by

\[
E_{f,1,v} = E_{d_n} - (n - 1)E_0 = \Delta E_{vn} + E_0 \tag{2.16}
\]

where \( \Delta E_{vn} = E_{d_{n-1}} - nE_0 \) is the energy difference between the relaxed block with a vacancy and the initial relaxed block with \( n \) number of atoms.

The formation energy \( E_{f,n',i} \) of \( n' \) interstitials is defined by

\[
E_{f,n',i} = E_{d_{n+n'}} - (n + n')E_0 = \Delta E_{in} - n'E_0 \tag{2.17}
\]

where \( n \) and \( n' \) are the initial number of atoms and the number of interstitials introduced; \( \Delta E_{in} = E_{d_{n+n'}} - nE_0 \) is the energy difference between the relaxed block with \( n' \) interstitials and the initial relaxed block.

The formation energy of a defect can be computed by relaxing either at constant pressure or constant volume. In both the cases the formation energy depends on the initial number of atoms. The formation energy as a function of inverse \( n \) is usually fitted to a straight line and the energy at \( 1/n = 0 \) gives the required energy. The vacancy jump barriers (migration energies) can be accurately calculated using the nudged elastic band (NEB).
method \cite{122,124}. All static relaxations and the NEB calculations were performed with the “SOLD” code.

2.6 Computation of dislocation diffusion

We proposed a new computational method to compute the dislocation diffusivity with and without a pre-existing point defect such as a vacancy or an interstitial. The diffusion along a dislocation core is basically a 1D problem in which mean squared displacement \( \langle z^2(t) \rangle \) at a given temperature follows the Einstein formula

\[
\langle z^2(t) \rangle = 2D_d t, \tag{2.18}
\]

where the constant \( D_d \) is called the coefficient of dislocation diffusion. The approximate dependency of the diffusion coefficient on temperature can be described by the Arrhenius law

\[
D_b = D_d^0 \exp \left( -\frac{E_d}{k_B T} \right), \tag{2.19}
\]

where \( k_B \) being the Boltzmann constant and \( T \) temperature. \( E_d \) represents the activation energy of the dislocation diffusion. If the diffusion is assisted by point defects such as vacancies and interstitials, \( E_d \) can be decomposed into (i) formation and (ii) migration of a defect as

\[
E_d = E_d^f + E_d^m,
\]

where \( E_d^f \) and \( E_d^m \) are the formation and the migration energies of a defect respectively.

In this work we assumed that the dislocation core has a finite extent like a pipe within which the diffusion is fast and constant but outside the core the diffusion slows down drastically. The finite region of the core is characterized by the dislocation core radius \( r_d \). With this analogy the dislocation diffusion is sometimes referred to as a pipe diffusion.

We can construct an imaginary cylinder around the dislocation core with a radius \( R \) and
compute the diffusivity $\overline{D}(R)$ at a given temperature $T$. The diffusivity data may be fitted to a Gaussian function

$$
\overline{D}(R) = A \exp\left(-\frac{R^2}{r_d^2}\right) + B,
$$

(2.20)

where $A$, $B$ and $r_d$ are the parameters of best fit. Accordingly, we can compute an effective dislocation diffusivity without any point defects (intrinsic) as

$$
D_{d}^{I} \equiv \overline{D}(R = r_d) = A/e + B.
$$

(2.21)

The superscript $I$ denotes the intrinsic case. While in an infinitely large system $B$ would be zero, in a finite-size system it is small but finite due to the effect of boundary conditions. To a good approximation, $D_{d}^{I}$ can be evaluated as simply $D_{d}^{I} \sim A/e$.

In the presence of a vacancy, the diffusivity may be computed as above

$$
D_{d}^{v,\text{raw}} \equiv \overline{D}(R = r_d^v) = A/e + B,
$$

(2.22)

where $r_d^v$ is the effective radius of the dislocation core when there is a pre-existing vacancy. The “raw” value of $D_{d}^{v,\text{raw}}$ overestimates the actual vacancy contribution to the dislocation diffusivity by a factor of $1/N_v$ where

$$
N_v = \sum_{n=1}^{N} \exp\left(-\frac{E_{vn}^f}{k_B T}\right)
$$

(2.23)

is the equilibrium number of vacancies that would be found in the simulation block. $E_{vn}^f$ is the vacancy formation energy at site $n$. Assuming that the intrinsic diffusion mechanism continues to operate in the presence of a vacancy, it can also contribute to $D_{d}^{v,\text{raw}}$. Thus, the
true dislocation diffusivity \( D_d^v \) in the presence of equilibrium vacancies can be calculated by

\[
D_d^v = D_d^I + N_v (D_d^{v,\text{raw}} - D_d^I),
\]

(2.24)

where the second term represents the vacancy contribution.

With an interstitial we would write the diffusivity as

\[
D_d^{i,\text{raw}} \equiv \mathcal{D}(R = r_d^i) = A/e + B,
\]

(2.25)

where \( r_d^i \) has the meaning of an effective radius of the dislocation core in the presence of an interstitial. Similarly, the true dislocation diffusivity \( D_d^i \) in the presence of equilibrium interstitials is computed from

\[
D_d^i = D_d^I + N_i (D_d^{i,\text{raw}} - D_d^I),
\]

(2.26)

where \( N_i \) is the equilibrium number of interstitials that would be present in the simulation block. It can be evaluated from

\[
N_i = \sum_{n=1}^{K} \exp \left( -\frac{E_{in}^I}{k_B T} \right),
\]

(2.27)

where the summation is over \( K \) stable interstitial configurations in and around the dislocation core region and \( E_{in}^I \) is the formation energy of an interstitial at site \( n \).

In order to compare with experimental results, which are usually expressed in terms of integrated flux, we can compute the integrated flux by adding the contribution of different mechanisms as

\[
P_d = D_d^v A_d^v + D_d^i A_d^i + D_d^{I} A_d^{I},
\]

(2.28)

where \( A_d^v, A_d^i \) and \( A_d^{I} \) are the cross-sectional areas corresponding to the core radii \( r_d^v, r_d^i \).
and $r_d^f$.

2.7 Visualization and characterization of defects

Characterization of structural defects is necessary in order to distinguish between perfect crystal atoms (i.e. BCC, FCC, HCP), atoms in HCP local environment (stacking fault, twin boundary) and the defected (disordered) atoms in the dislocation cores and grain boundaries (GBs). Among several structural characterization methods, common neighbor analysis (CNA) proposed by Honeycutt and Andersen [179] is widely used where as central symmetry (CS) parameter can be handy for defects like vacancies, vacancy-clusters, stacking faults, planar defects and dislocations. The central symmetry method does not distinguish between structural types such as BCC, FCC, HCP, icosahedral etc. but is capable of describing local ordered and disordered environments. It is well defined only in a centrosymmetry crystal such as FCC and BCC. The common neighbor analysis (CNA) [179, 182] is used to classify crystal structures, interfaces (stacking faults, twin boundaries, GBs), and defects (vacancies, dislocations, planar defects). The following sections describes briefly the methods.

2.7.1 Common neighbor analysis (CNA)

The common neighbor analysis is a classification of atoms based on their local environment [179, 182]. A set of four indices $ijkl$ is assigned to characterize a pair of atoms (root pair) which have common nearest neighbor atoms. The nearest neighbor atoms are defined by a cutoff distance which is the first minimum from radial distribution function. The first index, $i$, is either 1 or 2, describing the root pair, that is whether or not the root atoms are the nearest neighbor atoms. The second index, $j$, represents the number of common nearest neighbor atoms shared by the root pair. The third index, $k$, represents the number of bonds between the common nearest neighbor atoms where bonded atoms are nearest neighbor atoms. The fourth index, $l$, is assigned to the number of bonds in the longest continuous chain formed by the $k$ bonds between common nearest neighbors.
Based on this description the perfect FCC structure has only 1421 bonded pairs (see Fig. 2.1(a)). The perfect BCC structure consists of six pairs of type 1666 (or 1661) and eight pairs of type 1444 (or 1441) [181, 182]. The ideal HCP structure has twelve nearest neighbors; half of them form 1421 while the other half form 1422 types (see Fig. 2.1(b) and 2.1(c)). The presence of pairs of 1555 type is the signature of icosahedral [181].

### 2.7.2 Central symmetry parameter (CSP)

This method was originally proposed by Kelchner, Plimpton and Hamilton [7]. It helps us to quantify the local environment around an atom. It has meaning only in a centrosymmetry structure in which, in undistorted case, each atom has equal number of equal and opposite nearest neighbor vectors. The resultant of each pair of equal and opposite nearest neighbor vectors is always zero. For any homogeneous elastic deformation, this sense of equal and opposite is preserved even after a deformation but this will not be true if there is a defect near by. Thus the central symmetry or centrosymmetry parameter is zero for any centrosymmetry structures. According to Kelchner and co-workers [7] the centrosymmetry
parameter is defined as:

\[ P = \sum_{i=1,6} |\mathbf{R}_i + \mathbf{R}_{i+6}|^2 \]  \hspace{1cm} (2.29)

where \( \mathbf{R}_i \) and \( \mathbf{R}_{i+6} \) are position vectors of six pairs of equal and opposite nearest neighbors relative to the chosen atom in the FCC lattice. The calculation is trivial in a perfect crystal structure. In a deformed structure 12 nearest neighbor vectors, \( \mathbf{R}_i \), for each atom must be determined. Each almost equal and opposite vectors are added and sum of square of six resulting vectors is computed. The CSP in Eq. (2.29) has units of Å².

An alternative definition of CSP was proposed by Li [183] and implemented in a program “AtomEye”. It is defined as

\[ c_i = \frac{\sum_{k=1}^{m_i/2} D_k}{\sum_j |\mathbf{R}_j|^2} \]

where \( c_i \) is the central symmetry parameter of \( i^{th} \) atom; \( D_k = |\mathbf{R}_k + \mathbf{R}_{k'}|^2 \); \( m_i \) is the number of nearest neighbors; \( \mathbf{R}_j \) is the bond vector. By definition this parameter is dimensionless quantity. For each bond vector \( \mathbf{R}_k \) we look for another bond vector \( \mathbf{R}_{k'} \) from the set of \( m_i \) vectors, which minimizes \( D_k \). The pair of bond vectors which minimizes \( D_k \) is removed from the set and the procedure is repeated until the set is exhausted.
Chapter 3: Self-diffusion in the cores of screw and edge dislocations in aluminum

3.1 Introduction

The mobility of atoms in core regions of lattice dislocations can be orders of magnitude higher than in surrounding lattice regions. For historic reasons, this phenomenon is often referred to as “pipe diffusion”, although it should properly be called “dislocation diffusion” for consistency with the well-established terms of grain boundary diffusion and surface diffusion [66, 68, 184].

The fast atomic transport along dislocations can play a significant role in the kinetics of many processes in materials [185]. Dislocation diffusion can contribute to creep mechanisms, including dislocation climb and Orowan loop bowing [92]. Deviations from the power law of creep can be attributed to dislocation diffusion [93, 94]. Diffusion of solute atoms along arrested dislocations is one of the proposed mechanisms of dynamics strain aging in alloys exhibiting flow instabilities [81, 82, 87]. The kinetics of solute segregation to surfaces and grain boundaries can be enhanced by diffusion along dislocations terminating at the interfaces [89, 91]. Coarsening kinetics in precipitation-strengthened alloys are often influenced or even controlled by dislocation diffusion, especially in nanometer-scale structures in which dislocation lines can directly connect the growing particles. Diffusion along misfit dislocations at γ/γ′ interfaces can contribute to the γ'-phase coarsening and rafting kinetics, affecting the creep resistance of superalloys [95]. Dislocation diffusion can influence sintering processes [100, 101, 103], oxidation, corrosion, recovery of radiation damage, and electromigration damage in microelectronic devices [69].

Despite its importance, the phenomenon of dislocation diffusion is not well understood
on the fundamental level. The amount of reliable experimental information is rather limited \[66, 68, 184\]. According to experimental data available, the coefficient \(D_d\) of dislocation diffusion approximately follows the Arrhenius law Eq. (2.19). The activation energy of dislocation diffusion, \(E_d\), is approximately 0.6 – 0.7 of the activation energy of lattice diffusion \(E\), whereas the pre-exponential factor \(D_0^d\) is close to typical values for lattice diffusion \[68\]. Dislocation diffusion coefficients tend to increase with the magnitude of the Burgers vector and decrease with the dissociation width into Shockley partials in FCC metals. It is assumed that dislocation diffusion is mediated by atomic exchanges with single vacancies, although there is no convincing experimental evidence for this mechanism. In fact, except for the analogy with lattice diffusion, there is no fundamental reason why vacancy diffusion must necessarily dominate over interstitial diffusion or other possible diffusion mechanisms.

Experimental measurements of dislocation diffusion are difficult and can be divided in two categories. In direct measurements, the diffusion coefficient is extracted from the penetration profile (concentration versus depth) of radioactive tracer or impurity atoms diffused into a deformed single crystal or a polycrystal containing low-angle grain boundaries. The penetration profile is analyzed in terms of continuum models, in which the dislocations are represented by high-diffusivity “pipes” of some radius \(r_d\) whose diffusion coefficient \(D_d\) is much larger than the lattice diffusivity \(D\). Several mathematical solutions of this diffusion problem have been developed \[66\], all assuming that the dislocations are normal to the surface and arranged in a wall or another (e.g., hexagonal) periodic array. By fitting a model solution to the experimental profile, the so-called integrated diffusion flux \(P_d = D_d A_d\) is extracted, where \(A_d = \pi r_d^2\) is the cross-sectional area of the dislocation “pipe”. To estimate \(D_d\) separately, an assumption about \(r_d\) must be made, which is usually \(r_d = 0.5\) nm. This uncertainty of \(r_d\) does not affect applications since it is only the quantity \(P_d\) that appears in all models of diffusion-controlled processes in materials, not \(D_d\) separately. Most of the dislocation diffusion coefficients available today were measured in the 1960s – 1970s. Very few direct measurements are made these days, see \[170\] (radio-tracer self-diffusion in Fe) and \[115, 116\] (secondary-ion mass spectrometry for oxides) as some recent examples.
In indirect methods, $P_d$ is back-calculated from the rate of a particular diffusion-controlled process, such as internal friction, dislocation climb, dislocation loop shrinkage, phase growth kinetics \[69\] \[80\], or annihilation of dislocation dipoles \[68\] \[115\] \[117\]. Essentially, it can be any process whose rate is assumed to be controlled by dislocation diffusion and for which a model containing $P_d$ is available. Unfortunately, such models often rely on crude approximations and contain other unknown parameters. Indirect measurements are only accurate up to an order of magnitude at best and have a poor reproducibility.

As one example relevant to this work, Table 1.1 summarizes experimental data for Al self-diffusion. For dislocation diffusion, only indirect measurements from void-shrinkage kinetics are available \[5\]. For dislocation diffusion in Al alloys, only crude estimates of the activation energy from internal friction experiments \[20\] exist in the literature.

The enhanced atomic mobility along dislocations and the correlation $E_d \approx 0.6–0.7E$ were confirmed by early atomistic simulations with pair potentials \[118\] \[120\]. Contrary to the common assumption, Huang et al. \[119\] \[120\] found that vacancies and interstitials could make comparable contributions to dislocation diffusion. More accurate simulations employing embedded-atom method (EAM) potentials have recently been performed for dislocations in Au \[121\], Al \[122\] \[124\] \[127\] \[185\] and Cu \[119\] \[121\], as well as Al-Mg \[124\] and Al-Cu \[126\] alloys. The rates of vacancy jumps along the core were found to depend on the dislocation character (edge, screw or mixed). However, except for \[121\] \[185\], only diffusion by the vacancy mechanism was analyzed. Furthermore, while the diffusion coefficient of vacancies, $D_v$, was calculated in several studies \[120\] \[123\], the atomic diffusion coefficient $D_d$ was only estimated in \[120\] \[124\] \[126\] and determined by direct simulations only in \[185\]. We emphasize that it is $D_d$, not the point-defect diffusion coefficient, that controls the mass flux along the dislocation core and appears in all models of diffusion-controlled processes. The point-defect diffusion coefficient constitutes only one ingredient of the diffusion process, which must be combined with point-defect concentrations, jump-correlation factors and other ingredients to obtain $D_d$ \[186\]. For impurity diffusion, the equilibrium segregation and impurity-defect binding energies at different sites should also be known \[82\] \[126\].
An alternative and more straightforward approach adopted in [185] is to extract $D_d$ from mean-squared atomic displacements computed by direct molecular dynamics (MD) simulations. An additional advantage of this approach is that information about diffusion mechanisms can be inferred from MD results, instead of postulating particular mechanisms as it is done in other methods. Recent simulation studies of grain boundary diffusion [187–192] have revealed a large variety of possible diffusion mechanisms, some of which cannot operate in the lattice. A similar multiplicity and complexity of diffusion mechanism might exist in dislocation cores.

The goal of this work is to study the effect of the dislocation character on diffusion, and to evaluate the relative importance of vacancies and interstitials. We analyze the limiting cases of the edge and screw dislocations in Al, applying MD simulations to extract the diffusion coefficients in both dislocations.

### 3.2 Methodology

The atomic interactions are modeled with the EAM potential for Al developed in [23]. This potential is accurately fit to experimental and *ab initio* data and reproduces a number of properties of Al, including elastic constants, phonon frequencies, the intrinsic stacking fault energy, and point-defect formation and migration energies. The melting temperature $T_m$ of Al predicted by this potential is 1042 K [193], which is about 10% above the experimental value. The predicted activation energy of bulk diffusion in Al is 1.33 eV [23] in good agreement with experiment [194,195].

A cylindrical model is used with a periodic boundary condition along the cylinder axis $z$. For the screw dislocation, the $z$ axis is parallel to the crystallographic direction [110], whereas the $x$ and $y$ axes are aligned with [112] and [111], respectively. The length of the cylinder is 47 Å and its initial diameter is about 150 Å. To create a dislocation, all atoms are displaced from their initially perfect lattice positions according to the anisotropic linear elasticity solution for a straight screw dislocation [196] with the Burgers vector $\frac{1}{2}[110]$. The
elastic center is placed between atomic rows so that to avoid the singularity. After the displacements, a smaller cylinder is cut out of the large one, containing only 7,344 atoms and having the same length but a smaller diameter of 58 Å. Atoms within a 6 Å thick outer layer of this smaller cylinder are fixed and all other atoms are relaxed by minimizing the total potential energy with respect to atomic positions. The relaxed structure of the dislocation core is found to be slightly dissociated into Shockley partials on a \{111\} plane. This dissociation is very narrow but can be readily resolved by the Nye tensor method (see Fig. 3 in [197]) or other visualization techniques [198]. For a diffusion study, more atoms of this relaxed configuration are fixed, leaving only \( N = 2064 \) atoms free to move during the subsequent MD simulations. These free atoms are located within a cylinder of \( d = 30 \) Å in diameter centered at a midpoint between the partials. The goal of this step is to create a model with a relatively small number of dynamic atoms that would permit long MD runs.

A similar procedure has been applied to create an edge dislocation. In this case, the cylinder axis \( z \) is parallel to [112], whereas the \( x \) and \( y \) directions are aligned with [1\( \bar{1} \)0] and [11\( \bar{1} \)], respectively. The cylinder has the diameter and length of 100 Å and 50 Å, respectively, and contains 23,450 atoms. The Burgers vector \( \frac{1}{2}[110] \) of the edge dislocation is parallel to \( x \) and the splitting of the partials is slightly larger than for the screw dislocation. For diffusion simulations, only \( N = 4570 \) atoms are left free to move, while all other atoms are fixed. The free atoms are located within a cylinder of \( d = 44 \) Å in diameter.

Dislocation diffusion has been studied at several temperatures from 750 K to 1000 K, the highest temperature being 42 K below the melting point with this potential. The MD simulations employed the ITAP Molecular Dynamics (IMD) code [177], with the integration time step of 2 fs. The \( NVT \) ensemble (see Section 2.2) was implemented, with the temperature controlled by a Nose-Hoover thermostat. To minimize thermal stresses that might arise at high temperatures, the simulation block is expanded uniformly by the thermal expansion factor at the chosen temperature prior to the MD simulations. The thermal expansion factors predicted by this potential were computed earlier [193]. In each MD
run, the temperature is ramped up to the target value during the first 2 ns, followed by isothermal annealing for at least 30 ns.

At the post-processing stage, the isothermal anneal time is divided into several equal intervals from 3 to 7 ns each, depending on the temperature. For each time interval, we identify all dynamic atoms located within an imaginary cylinder of a chosen radius $R < d/2$ in the beginning and at the end of the time interval. The mean-squared displacement $\langle z^2(t) \rangle$ of all such atoms parallel to the dislocation line is calculated as a function of time $t$. The functions $\langle z^2(t) \rangle$ computed for individual time intervals are then averaged over all intervals. This calculation is repeated for several values of $R$, producing a function $\langle z^2(t) \rangle(R)$ used for extracting the dislocation diffusion coefficients as will be discussed in Section 3.3.

Due to the periodic boundary condition in the $z$ direction, an atom attempting to leave the block during the MD simulations is automatically translated back by the repeat period of the block and reappears on its opposite side. By examining MD snapshots saved every 0.2 ns during the simulation run, all such translations across the block are identified and the atoms are moved back before using their coordinates for the calculation of $\langle z^2(t) \rangle$. We emphasize that this “unwrapping” procedure is implemented at the post-processing stage and by no means affects the actual MD simulations.

Three different types of simulations have been performed: when a single vacancy is created inside the dislocation core prior to the MD run, when a single self-interstitial is created, and when no point defects are introduced. The latter case will be referred to as intrinsic diffusion.

As will be discussed later, calculations of the diffusion coefficient after the introduction of a vacancy require the knowledge of the average number $N_v$ of vacancies that would be found in the simulation block under equilibrium conditions at the given temperature. This number can be evaluated by Eq. (2.23). The values of $E_{vn}^f$ were obtained by separate calculations, in which a single vacancy was created at various sites and the block was relaxed statically at 0 K. From the energy difference $\Delta E_{vn}$ between the relaxed block with a vacancy and the initial relaxed block without a vacancy, $E_{vn}^f$ was obtained from Eq. (2.16),
where $E_0 = -3.36 \text{ eV}$ is the equilibrium cohesive energy of the perfect crystal $^{23}$. These calculations were simplified by the fact that the $E_{vn}^f$ values in each atomic row running parallel to $z$ are identical, therefore only one $E_{vn}^f$ per row needed to be computed.

A similar procedure was applied to determine the equilibrium number $N_i$ of interstitial atoms that would be found in the simulation block (see Eq. (2.27)). The formation energy of bulk interstitials is so high that only a limited number of interstitial configurations in a narrow vicinity of the core make non-negligible contributions to Eq. (2.27). The interstitial formation energy is given by Eq. (2.17).

### 3.3 Results

#### 3.3.1 Point defect energies in dislocation cores

For lattice vacancies, the EAM potential employed in this work gives the formation energy $E_{v}^f = 0.68 \text{ eV}$ and the migration energy $E_{v}^m = 0.65 \text{ eV} ^{23}$. Thus, the activation energy of vacancy-mediated self-diffusion is predicted to be $E = E_{v}^f + E_{v}^m = 1.33 \text{ eV}$. The lattice self-interstitial formation energy is much higher, $2.59 \text{ eV}$, even for the most stable ([001] split dumbbell) configuration.

The vacancy formation energies $E_{vn}^f$ calculated for different sites $n$ within the simulation block range from 0.51 eV to 0.71 eV for the screw dislocation and from 0.52 eV to 0.75 eV for the edge dislocation. The lowest values are found in the dislocation core region while the highest values near the boundary between the dynamic atoms and the fixed region (due to image forces). Our range of $E_{vn}^f$ values is comparable to that computed by Hoagland et al. $^{122}$ using a different EAM potential. Figure 3.1 displays contour plots of $E_{vn}^f$ for both dislocations. For the screw dislocation, the contours clearly reveal the core splitting on the $(1\bar{1}1)$ plane, with minima of $E_{vn}^f$ in the partial core regions (Fig. 3.1(a)). For the edge dislocation, the exact positions of the partials are not revealed by the contours but the splitting is clearly seen. The vacancy formation energy is reduced relative to its bulk
value in the compression region above the glide plane (Fig. 3.1(b)).

The interstitial formation energy varies between 1.04 and 2.72 eV for the screw dislocation and between 0.89 and 2.84 eV for the edge dislocation. Again, the energies slightly exceeding the ideal bulk value (2.59 eV) are found near the fixed region. The lowest formation energies occur inside the dislocation core and rapidly increase to the bulk value at short distances away from the core.

### 3.3.2 Intrinsic diffusion along dislocation cores

An important finding of this work is the existence of the intrinsic diffusivity along the dislocation cores. Specifically, even without any pre-existing point defects, atoms are found to migrate along the screw dislocation core at all temperatures studied here and along the edge
dislocation core at high temperatures. While intrinsic diffusion at high temperatures can be explained by the increasingly disordered core structure that becomes capable of generating point defects, the existence of intrinsic diffusion at low temperatures is an interesting and unexpected phenomenon. Before quantifying this effect, Fig. 3.2 gives its qualitative demonstration for the screw dislocation at 900 K. An arbitrary MD snapshot was taken, atoms located within a slice of material normal to the dislocation line were selected, and their motion was tracked through subsequent snapshots. In the figure the bounding box represents the dimensions of the cylindrical simulation block viewed from a side. The dislocation line is marked by a horizontal dashed line. Atoms initially located in a slice normal to the dislocation line were selected and their new positions after a 2 ns long MD run are shown in this plot. All other atoms remain invisible. The observed random scattering of the labeled atoms in both directions parallel to the dislocation line gives direct evidence of diffusive motion in the core region.

Figure 3.2: Demonstration of atomic diffusion along the screw dislocation at 900 K in the absence of pre-existing point defects (intrinsic diffusion).
Typical time dependencies of mean-squared displacements of atoms are displayed in Fig. 3.3(a). These plots were obtained for the screw dislocation with $R = 7 \AA$, but they look qualitatively similar for the edge dislocation and for other values of $R$. It is seen that the plots accurately follow a linear relation expected from the Einstein formula, Eq. (2.18), confirming that our simulations have properly sampled the diffusion kinetics. The slope $S$ of the least-squares linear fit to such plots gives the diffusion coefficient $D = S/2$ averaged over the cylindrical region of the chosen radius $R$. In the continuum models of dislocation diffusion (Section 3.1), the diffusion coefficient is assumed to be discontinuous and have a high value $D_d$ inside a “pipe” of a radius $r_d$ and a much smaller value outside the “pipe”. In reality the diffusivity is continuous but can still be expected to have a sharp maximum in the core region. Accordingly, the diffusivity averaged over a cylindrical region of radius $R$, considered as a function of $R$, should also have a maximum in the core and fall off to zero at infinitely large $R$. The exact form of this function was unknown a priori, but after trying several analytical forms we found that our simulation data is best described by a Gaussian function (Eq. (2.20)) with adjustable parameters $A$, $B$ and $r_d$. Examples of fit with this equation are given in Fig. 3.4(a). The absence of data points below a certain value of $R$ is explained by limited statistics collected when the probing cylinder contains too few atoms. In addition, at small $R$ the results begin to depend on the exact placement of the axis of the probing cylinder. Parameter $r_d$ in Eq. (2.20) has the obvious meaning of the dislocation core radius.

The intrinsic diffusivities obtained in Eq. (2.21) for the screw dislocation approximately follow the Arrhenius law (Eq. (2.19)) (Fig. 3.5(a)) with the activation energy and pre-exponential factor given in Table 3.1. For the edge dislocation, we were able to determine the intrinsic diffusion coefficients only at temperatures 925 K and higher (Fig. 3.5(b)). They were found to be more than an order of magnitude smaller than for the screw dislocation. At lower temperatures, the intrinsic diffusivity of the edge dislocation is below the detection capabilities of our method and was not calculated. Comparison of these results with diffusion by other mechanisms and with experimental data will be discussed later (Section 3.4).
Figure 3.3: Mean-squared atomic displacements along the core of the screw (a,b) and edge (c,d) dislocations as functions of time at selected temperatures: (a) in the absence of point defects (intrinsic diffusion), (b,d) in the presence of a single vacancy, (c) in the presence of a single interstitial. The displacements are averaged over a cylinder of radius $R = 7\, \text{Å}$ in (a,b,c) and $8\, \text{Å}$ in (d).
3.3.3 Vacancy diffusion in dislocation cores

When a single vacancy is introduced into the dislocation core prior to the MD simulations, the plots of $\langle z^2(t) \rangle$ versus $t$ remain linear but their slopes increase relative to the intrinsic
Figure 3.5: Arrhenius plots of calculated diffusion coefficients in (a) the screw dislocation core and (b) the edge dislocation core. The lines show Arrhenius fits in the selected temperature intervals.

Table 3.1: Arrhenius parameters of diffusion along the screw and edge dislocations in Al computed in this work. The diffusion radius of the core $r_d$ is also indicated. The error bars are represented by standard deviations.

<table>
<thead>
<tr>
<th></th>
<th>Intrinsic</th>
<th>With vacancy</th>
<th>With interstitial</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Screw dislocation:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_d$ (eV)</td>
<td>0.64 ± 0.10</td>
<td>0.70 ± 0.07</td>
<td>0.64 ± 0.10</td>
</tr>
<tr>
<td>log $D_{od}$ (m²/s)</td>
<td>−7.16 ± 0.57</td>
<td>−6.71 ± 0.40</td>
<td>−7.15 ± 0.57</td>
</tr>
<tr>
<td>$r_d$ (nm)</td>
<td>0.59 ± 0.001</td>
<td>0.61 ± 0.006</td>
<td>0.60 ± 0.003</td>
</tr>
<tr>
<td><strong>Edge dislocation:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_d$ (eV)</td>
<td>—</td>
<td>1.19 ± 0.14</td>
<td>1.13 ± 0.04</td>
</tr>
<tr>
<td>log $D_{od}$ (m²/s)</td>
<td>—</td>
<td>−5.65 ± 0.89</td>
<td>−7.21 ± 0.24</td>
</tr>
<tr>
<td>$r_d$ (nm)</td>
<td>—</td>
<td>1.16 ± 0.13</td>
<td>0.89 ± 0.04</td>
</tr>
</tbody>
</table>

case (Fig. 3.3(b,d)), indicating an enhancement of diffusion by the vacancy. The average core diffusivity $\bar{D}(R)$ can again be fitted by Eq. (2.20), where parameter $B$ represents the vacancy-mediated bulk diffusivity distorted by the boundary conditions (Fig. 3.4(b,d)). As in the intrinsic case, the quantity $D_{d}^{e,raw} = A/e + B$ can be taken as the effective dislocation
core diffusivity. However, this “raw” value needs to be corrected for the equilibrium vacancy concentration.

Indeed, in the MD simulations, the dynamic region of the simulation block contains exactly one vacancy at all temperatures. This single vacancy spends most of its time in the core (where it diffuses fast along the \(z\) direction) and a small fraction of the time in surrounding lattice regions (where it diffuses relatively slowly). The fixed boundaries prevent the vacancy from escaping and it remains confined to the dynamic region. Under real equilibrium conditions, however, the dynamic region would contain on average \(N_v\) vacancies, where \(N_v\) is given by Eq. (2.23). This number depends on temperature and, at most temperatures studied here, remains smaller than one. Thus, the “raw” value \(D_{d}^{v,raw}\) overestimates the actual vacancy contribution to the dislocation diffusivity by a factor of \(1/N_v\). Assuming that the intrinsic diffusion mechanism continues to operate in the presence of the vacancy, it can also contribute to \(D_{d}^{v,raw}\). Thus, the true dislocation diffusivity \(D_{d}^{v}\) in the presence of equilibrium vacancies can be calculated by Eq. (2.24).

For the screw dislocation, the diffusivities \(D_{d}^{v}\) computed from Eq. (2.24) are only slightly larger than the intrinsic diffusivities (Fig. 3.5(a)), indicating that the second term in Eq. (2.24) is relatively small. Accordingly, the Arrhenius parameters obtained in the presence of vacancies are close to those for intrinsic diffusion (Table 3.1). In other words, although the introduction of a single vacancy produces a large enhancement of the core diffusivity, the recalculation to the equilibrium vacancy concentration reduces the vacancy contribution to a small correction.

Similar calculations have been performed for the edge dislocation. In this case, however, the situation is very different. At temperatures below 950 K the contribution of the intrinsic diffusivity is negligibly small and Eq. (2.24) can be applied in the approximate form \(D_{d}^{v} = N_v D_{d}^{v,raw}\). At higher temperatures, where the rapidly increasing intrinsic diffusivity becomes large, the \(D_{d}^{v}\) values computed from Eq. (2.24) come close to \(D_{d}^{I}\). At these temperatures, the edge dislocation core is capable of generating its own point defects and
the addition of a vacancy does not produce any significant effect. The diffusion coefficients calculated for the edge dislocation are shown in Fig. 3.5(b). Considering the different roles of the added vacancy at low and high temperatures, the Arrhenius parameters (Table 3.1) were computed by fitting to the diffusion coefficients obtained only at temperatures below 950 K.

### 3.3.4 Interstitial diffusion in dislocation cores

Due to the high mobility of interstitials, the difference between $D_i^{\text{raw}}$ and $D_i^I$ is greater than in the vacancy case and at low temperatures easily reaches an order of magnitude. This fact offers an opportunity to cross-check our methodology. Indeed, since we kept only one interstitial in the simulation block at all temperatures, the Arrhenius fit to $D_i^{\text{raw}}$ should give us an effective interstitial migration energy $E_{im}$ in the core region. For the screw dislocation, assuming that at $T \leq 900$ K the intrinsic contribution to $D_i^{\text{raw}}$ can be neglected, the Arrhenius fit gives $E_{im} = 0.14 \pm 0.04$ eV. This number compares well with the migration energy of bulk interstitials computed with this EAM potential (0.15 eV) and the migration energy measured experimentally (0.1 eV). Equally encouraging results have been obtained for the edge dislocation.

The true dislocation diffusivity $D_i^d$ in the presence of equilibrium interstitials is computed from Eq. (2.26). For the screw dislocation, the obtained $D_i^d$ values are almost identical to $D_i^I$ due to the very small magnitude of $N_i$. Although $D_i^{\text{raw}}$ is much larger than $D_i^I$, typical values of $N_i$ are on the order of $10^{-3} - 10^{-4}$, making the second term in Eq. (2.26) negligibly small. Thus, interstitials are predicted to give practically no contribution to the diffusivity in the screw dislocation in comparison with intrinsic diffusion (Fig. 3.5(a)), leading to $E_i^d \approx E_i^I \approx 0.64 \pm 0.10$ eV (Table 3.1).

By contrast, in the edge dislocation the intrinsic diffusivity is so small that it can be completely neglected at all temperatures below 925 K. The Arrhenius plot of $D_i^d$ at these temperatures (Fig. 3.5(b)) was used to extract the activation energy and pre-factor listed in...
Table 3.1 At higher temperatures, the situation changes as the rapidly increasing intrinsic diffusivity reaches and then exceeds the interstitial contribution. This temperature range is dominated by a different diffusion regime and was not included in the Arrhenius fit.

3.4 Discussion and conclusions

Figure 3.5 and Table 3.1 summarize the main findings of this work. Self-diffusion coefficients have been computed for the screw and edge dislocations in Al in the presence of vacancies, interstitials and without any pre-existing defects (intrinsic diffusion) over a range of temperatures. We find that diffusion along the screw dislocation is dominated by the intrinsic mechanism, with vacancies and interstitials making only minor contributions. In contrast, intrinsic diffusion in the edge dislocation is very slow at all temperatures below 950 K, and the core diffusivity is dominated by vacancies. At high temperatures (> 950 K), the core of the edge dislocation becomes increasingly disordered and begins to operate as an effective source of point defects. As a result, the core diffusivity remains high even when no point defects are introduced prior to the MD simulations, and when such defects are introduced, they produce little effect on the core diffusivity. Overall, diffusion along the screw dislocation is found to be significantly faster than diffusion along the edge dislocation. These results demonstrate that diffusion rates and diffusion mechanisms strongly depend on the dislocation type.

The diffusion radius of the dislocation core is about 0.6nm of the screw dislocation and about 1nm for the edge dislocation. Both numbers are physically reasonable and validate the assumption $r_d = 0.5$nm commonly accepted in the continuum models of dislocation diffusion [66]. No temperature dependence of $r_d$ was detected within the error bars of the simulations.

The only experimental data that can be used for comparison with our simulations was obtained by indirect measurements based on void shrinkage kinetics in thin films [5]. Such measurements give only the integrated flux $P_d = D_d A_d$, $A_d$ being the cross-sectional area of the core. To enable comparison with this experiment, we have computed the integrated
flux from Eq. (2.28).

Because our EAM potential overestimates the experimental melting point, homologous temperatures \( T/T_m \) are used as a common basis for comparison. The computed and experimental fluxes are plotted on the Arrhenius diagram in Fig. 3.6. Since these two sets of data were obtained in very different temperature intervals, extrapolation across a wide range of temperatures is made. Nevertheless, we observe that the experimental Arrhenius line extrapolates to the same range of \( P_d \) values at high temperatures as obtained by our simulations. Furthermore, the experimental measurements represent an average diffusivity over different types of dislocations present in the experimental samples. It is, therefore, encouraging to see that the extrapolated experimental values of \( P_d \) lie between our calculations for the limiting cases of the screw and edge dislocations. Considering all the uncertainties involved in this comparison, the agreement between the experiment [5] and simulation is quite satisfactory.

Table 3.2 summarizes the effective Arrhenius parameters for the screw and edge dislocations obtained by fitting to the fluxes \( P_d \). As expected from Fig. 3.6, the experimental activation energy for an “average” dislocation lies between the computed activation energies for the screw and edge dislocations. Furthermore, the computed ratios of the dislocation to lattice activation energies are, respectively, on the lower and higher sides of the experimental range 0.6–0.7 [68]. Our finding that the Arrhenius characteristics of dislocation diffusion depend on the dislocation type is also in agreement with experimental data [66, 68, 184].

Table 3.2: Arrhenius parameters of dislocation diffusion obtained from Fig. 3.6

<table>
<thead>
<tr>
<th>Property</th>
<th>Screw</th>
<th>Edge</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_d ) (eV)</td>
<td>0.68±0.08</td>
<td>1.19±0.14</td>
<td>0.85</td>
</tr>
<tr>
<td>( \log P_{0d} ) (m^4/s)</td>
<td>-24.54±0.47</td>
<td>-23.01±0.85</td>
<td>-24.15</td>
</tr>
<tr>
<td>( E_d/E )</td>
<td>0.51</td>
<td>0.89</td>
<td>0.64</td>
</tr>
</tbody>
</table>
To put the obtained dislocation diffusivities in perspective, Fig. 3.6 includes data for lattice self-diffusion. The lattice self-diffusion coefficients were calculated by standard methods \cite{172,186} based on the transition state theory, with the vacancy formation and migration energies computed by molecular statics (Table 3.3). To enable plotting in the same coordinates, the computed and experimental diffusion coefficients were multiplied by $\pi r_d^2$ with $r_d = 0.5\,\text{nm}$. The most reliable experimental data is represented by direct radio-tracer measurements by Lundy and Murdock \cite{6}. Two conclusions can be drawn from this comparison.

\footnote{This calculation of the lattice diffusivity is correct only in the limit of low temperatures and can give errors when extrapolated to high temperatures. This approximation is used here only for the purpose of putting the dislocation diffusivities in perspective with lattice diffusion.}
First, the reasonable agreement between the calculated and experimental lattice diffusivities is a reassurance of accuracy of our methodology. Second, this comparison confirms that dislocation diffusion remains faster than lattice diffusion even at temperatures approaching the melting point. At \(0.5T_m\), the difference between the two types of diffusivity reaches 2–3 orders of magnitude.

Table 3.3: Calculated vacancy formation energy \(E_{vf}\), formation entropy \(S_{vf}\), migration energy \(E_{vm}\), attempt frequency \(\nu\) and lattice constant \(a\) used for the calculation of the lattice self-diffusion coefficient in Al.

<table>
<thead>
<tr>
<th>(E_{vf}) (eV)</th>
<th>(S_{vf}/k_B)</th>
<th>(E_{vm}) (eV)</th>
<th>(\nu) (Hz)</th>
<th>(a) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.675</td>
<td>-0.360</td>
<td>0.630</td>
<td>6.00 \times 10^{12}</td>
<td>4.05</td>
</tr>
</tbody>
</table>

We now discuss atomic mechanisms of dislocation diffusion. Two mechanisms have been identified in this work as most important: the intrinsic diffusion and the vacancy-mediated diffusion. The role of interstitials is relatively small; although their mobility is very high, the formation energy is too large resulting in extremely small concentrations and thus insignificant contributions to diffusion.

The intrinsic diffusion mechanism is a rather intriguing phenomenon that does not occur in lattice diffusion under normal conditions. Although we have not been able to achieve a full understanding of the underlying atomic mechanism, the following observations might give some clue.

Firstly, the intrinsic simulations at temperatures above 800 K reveal rare events in which a vacancy is injected from the core into nearby lattice regions. The vacancy makes several jumps in the lattice and quickly returns to the core. Evidence of such events is obtained by plotting atomic trajectories between sequential MD snapshots, as shown in Fig. 3.7(a) for the screw dislocation at 850 K. A chain of arrows connecting lattice sites shows a trace of a vacancy walk through those sites. A snapshot containing an injected vacancy that is still in the lattice would contain a chain of arrows originating from a lattice site (which would
indicate the current vacancy position) and ending in the core. A set of arrows forming a loop starting and ending in the core indicates a vacancy excursion into the lattice and back into the core. Such loops were indeed frequently observed at high temperatures, with the exit point of the vacancy being generally different from the reentry point into the core. At all temperatures below 950 K, none of our snapshots contained a vacancy in the lattice, suggesting that the vacancy excursions were much shorter than 0.2 ns. Note that when a vacancy is injected into the lattice, an interstitial is left in the core, which is free to migrate along the core until the vacancy returns and recombines with it.

Figure 3.7: Typical cross-sectional views of the simulation block showing vacancy migration paths without any pre-existing point defects in the dislocation core (intrinsic case) (a) Screw dislocation at 850 K. (b) Edge dislocation at 1000 K. The dislocation line is normal to the page. The small black circles show projections of dynamic atoms. The red arrows indicate atomic displacements between two snapshots separated by 0.2 ns. The blue arrow shows the location of a vacancy generated by the dislocation core.

Based on these observations we suggest the following mechanism of intrinsic diffusion. Once in a while, a Frenkel defect (vacancy-interstitial pair) spontaneously forms in the core by thermal fluctuations. The two defects briefly separate and migrate along the core
independently, producing self-diffusion before they recombine and restore the defect-free structure. Because the interstitial formation energy in the lattice is very high, it always stays in the core during this process. The vacancy, on the other hand, has a finite probability of making a few jumps into adjacent lattice regions and returning into the core, giving rise to chains of atomic displacements seen in our simulations. Thus, the intrinsic diffusion can be attributed to the existence of dynamic Frenkel pairs in the dislocation core.

The second clue is that the screw dislocation core is seen to form dynamic jogs at relatively high temperatures (Fig. 3.8). The jogs typically nucleate by pairs, spread along the core and recombine with their periodic images. As a result, the dislocation line fluctuates around an average position. By contrast, no thermal jogs or kinks were found at the edge dislocation in our simulations. Given that the intrinsic diffusion is dominant in the screw core and negligibly small in the edge core, we hypothesize that the thermal jogs might be involved in the Frenkel pair formation. It seems possible that the jogs create local atomic configurations that facilitate Frenkel pair nucleation, but this connection between the two processes would need to be tested in future studies. In this work we tried but have not been able to confirm a correlation between the jog formation and vacancy excursions around the core.

At temperatures 950 K and above, the intrinsic diffusion mechanism changes. We begin to see vacancies frequently abandoning the core and performing relatively long walks (0.6 ns or longer) in the surrounding lattice. Such vacancies are readily revealed by arrow plots, as demonstrated in Fig. 3.7(b) for the edge dislocation. Some of the snapshots contained more than one vacancy path and/or more than one vacancy present in the lattice simultaneously. Together with significant structural distortions observed in the core region, these findings suggest that the core apparently becomes an effective supplier of point defects.

Finally, when a single vacancy is introduced into the core prior to the MD simulations, the arrow plots reveal its occasional excursions into the lattice. Their frequency is larger and the duration much longer than in the intrinsic case, and both increase with temperature. However, only one vacancy is always present in the simulation block. It is only at
Figure 3.8: Typical configurations of the screw dislocation core at 750 K without any pre-existing point defects, showing the formation of thermal jogs. (a) Straight dislocation; (b,c) Double jogs with screw segments in parallel glide planes; (d) Multiple jogs with some of the screw segments in intersecting glide planes. The edge segments are usually as short as one Burgers vector. The core structure is visualized using the centrosymmetry parameter $^7$.

high temperatures approaching $T_m$ that the core acquires the ability to generate additional vacancies, which is illustrated in Fig. 3.7(b).

The part of this work was published in [185, 199]. This work was supported by the US Air Force Office of Scientific Research, Structural Mechanics Program.
Chapter 4: EAM potential for Ni-Al system

4.1 Introduction

In this work we propose a new potential for the Ni-Al system based on the EAM formalism. Several potentials have been developed for this system in the past, including the Finnis-Sinclair potential of Yan et al. [200] and the EAM potentials by Foiles and Daw [201], Voter and Chen [156], Ludwig and Gumbsch [202] and one of the present authors [1,2]. However, most of these potentials were developed for one particular phase, either NiAl or Ni$_3$Al, and do not give accurate results (if tested at all) when applied to other phases of the Ni-Al system. Although the most recent potentials [1,2] have a significant degree of transferability, they leave room for further improvements.

Indeed, the potential developed in [1], which we will call EAM-2002, has a strong focus on the B2-NiAl phase. It accurately reproduces many properties on this phase, including the formation of structural Ni vacancies on the Al side of the stoichiometry. But this potential is less accurate for Ni$_3$Al and even less accurate for other phases. Furthermore, the pure Ni and Al functions were fitted as part of the development of the binary potential, and because the main focus was on NiAl, these function are not intended for simulations of pure Ni or Al. On the other hand, the potential proposed in [2], which will be referred to as the EAM-2004 potential, was based on accurate Ni and Al potentials and the focus was shifted to Ni$_3$Al. Again, the potential reproduces many properties of Ni$_3$Al in good agreement with experiment and ab initio data. The Ni-rich part of the phase diagram was computed with this potential and was found to be in reasonable agreement with experiment [2]. However, the elastic constants and other properties of B2-NiAl predicted by this potential are not accurate.
The goal of developing yet another Ni-Al potential is twofold. First, this is an attempt to create a more “universal” potential for this system that would be equally accurate for NiAl, Ni$_3$Al, as well as pure Ni and Al. Second, this gives us an opportunity to further explore the limits of accuracy and transferability achievable by semi-empirical potentials for binary systems. In Section 4.2 of this paper we describe the potential development methodology, followed by its testing for properties of NiAl (Section 4.3) and Ni$_3$Al (Section 4.4). Through the testing process, we compare the properties calculated with the new potential with experimental data, \textit{ab initio} results, and predictions of the EAM-2002 and EAM-2004 potentials. In Sections 4.5 and 4.6 we discuss the transferability of the new potential to different structures, chemical compositions and temperatures. Our conclusions will be summarized in Section 4.7.

4.2 Potential development

The potential was constructed based on existing functions for pure Ni \cite{2} and pure Al \cite{23}. Properties of Ni and Al predicted by these two potentials have been reported in detail \cite{2,23} and will not be repeated here. Note that the EAM-2004 potential \cite{2} was based on the same Ni but a different Al potential. In this work we chose a better established Al potential \cite{23} which was used in many previous studies of mechanical behavior of this metal.

Only the cross-interaction function $V_{NiAl}(r)$ was fitted in this work. It was postulated as the following combination of the existing elemental pair-interaction functions $V_{NiNi}(r)$ and $V_{AlAl}(r)$:

$$V_{NiAl}(r) = \psi \left( \frac{r - r_c}{h} \right) \left[ a_1 e^{-b_1(r)} V_{NiNi}(c_1 (r - r_1)) + a_2 e^{-b_2(r)} V_{AlAl}(c_2 (r - r_2)) + \delta \right], \quad (4.1)$$

where $\psi(x)$ is a cutoff function defined as
\[
\psi(x) = \begin{cases} 
    x^4 & \text{if } x < 0, \\
    1 + x^4 & \text{if } x \geq 0
\end{cases}
\]  

(4.2)

This function guarantees that \( V_{NiAl}(r) \) turns smoothly to zero at a cutoff distance \( r_c \). Eq. (4.1) contains 10 fitting parameters \( a_1, a_2, b_1, b_2, c_1, c_2, r_1, r_2, \delta, r_c \) and \( h \). In addition, the potential functions were subject to the following sets of transformations based on Eq. (1.8) and Eq. (1.9)

(i) \[
\begin{align*}
\rho_{Al}(r) &\rightarrow s_{Al}\rho_{Al}(r), \\
F_{Al}(\vec{\rho}) &\rightarrow F_{Al}(\vec{\rho}/s_{Al}),
\end{align*}
\]

and (ii) \[
\begin{align*}
F_{Ni}(\vec{\rho}) &\rightarrow F_{Ni}(\vec{\rho}) + g_{Ni}\vec{\rho}, \\
F_{Al}(\vec{\rho}) &\rightarrow F_{Al}(\vec{\rho}) + g_{Al}\vec{\rho}, \\
V_{NiNi}(r) &\rightarrow V_{NiNi}(r) - 2g_{Ni}\rho_{Ni}(r), \\
V_{AlAl}(r) &\rightarrow V_{AlAl}(r) - 2g_{Al}\rho_{Al}(r).
\end{align*}
\]

These transformations do not alter any properties of pure Ni or Al but change the shape of the cross-interaction function during the fitting process [156]. The transformation coefficients \( s_{Al}, g_{Ni} \) and \( g_{Al} \) were used as additional fitting parameters, bringing the total number of parameters to 13.

The fitting database included the experimental values of the lattice parameter \( a_0 \), formation energy \( E_f \) and elastic constants \( c_{ij} \) of the B2 structure of NiAl. The \textit{ab initio} part of the database included the formation energies \( E_f \) of the following nine ordered structures of the Ni-Al system: L1_2-Ni_3Al, D0_22-Ni_3Al, D0_3-Ni_3Al, B1-NiAl, L1_0-NiAl, L1_1-NiAl, B32-NiAl, 40-NiAl (NbP prototype) and L1_2-Al_3Ni. The formation energy \( E_f \) of a compound
Ni\textsubscript{n}Al\textsubscript{m} was computed using Eq. (2.15).

The \textit{ab initio} data used in this work were computed in [1]. Note that by contrast to the previous potentials [1, 2] where energy-volume relations of the structures were included in the fit, in this work we used only the minimum-energy values obtained from such relations. Thus, the potential was not “informed” about the equilibrium lattice parameters or bulk moduli of those nine structures. The smaller database used in this work was commensurate with the smaller number of fitting parameters in comparison with the previous potentials [1, 2].

![Pair-interaction functions of the new EAM potential not in the effective pair format.](image)

Figure 4.1: Pair-interaction functions of the new EAM potential not in the effective pair format.

The potential function (4.1) was optimized by minimizing the weighted mean-squared deviation of properties from their target values using the simulated annealing method. The fitted values of the parameters are shown in Table 4.1. Figure 4.1 shows the obtained potential functions which are not in the effective-pair format [141]. Tabulated forms of the potential functions are available for download from [http://www.ctcms.nist.gov/potentials/](http://www.ctcms.nist.gov/potentials/)
or from the authors by request.

Table 4.1: Optimized values of the fitting parameters used in the cross pair interaction, $V_{NiAl}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_c$ (Å)</td>
<td>0.5666557e+01</td>
</tr>
<tr>
<td>$h$ (Å)</td>
<td>0.3967462e+00</td>
</tr>
<tr>
<td>$a_1$ (eV)</td>
<td>0.4419079e+01</td>
</tr>
<tr>
<td>$b_1$ (Å⁻¹)</td>
<td>0.5924268e+00</td>
</tr>
<tr>
<td>$a_2$ (eV)</td>
<td>0.2385638e−01</td>
</tr>
<tr>
<td>$b_2$ (Å⁻¹)</td>
<td>−0.737822e+00</td>
</tr>
<tr>
<td>$c_1$</td>
<td>0.7881069e+00</td>
</tr>
<tr>
<td>$c_2$</td>
<td>0.1065580e+01</td>
</tr>
<tr>
<td>$r_1$ (Å)</td>
<td>−0.5788568e+00</td>
</tr>
<tr>
<td>$r_2$ (Å)</td>
<td>−0.1741778e+00</td>
</tr>
<tr>
<td>$\delta$ (eV)</td>
<td>−0.1673671e−01</td>
</tr>
<tr>
<td>$s_{Al}$</td>
<td>0.1281900e+01</td>
</tr>
<tr>
<td>$g_{Ni}$ (eV)</td>
<td>0.3055408e+00</td>
</tr>
<tr>
<td>$g_{Al}$ (eV)</td>
<td>−0.2576234e+00</td>
</tr>
</tbody>
</table>

4.3 Properties of B2-NiAl

4.3.1 Lattice properties and structural stability

The potential reproduces the lattice parameter, cohesive energy and elastic constants of B2-NiAl in good agreement with experiment and on the level of accuracy of the EAM-2002 potential (Table 4.2). These properties were included in the potential fit.

The phonon dispersion curves computed with the new potential are shown in Fig. 4.2. The agreement with experiment (inelastic neutron scattering at room temperature) is very good at low frequencies, with a trend to overestimate the frequencies of optical phonons. The EAM-2002 potential was also accurate at low frequencies but the discrepancy at high frequencies was larger than with the new potential. The phonon frequencies for the selected branches are listed in Table 4.3. The new potential is almost 50% improvement over the
Table 4.2: Lattice properties of B2-NiAl calculated with the new EAM potential in comparison with the EAM-2002 potential \cite{1} and experimental data. These properties were included in the potential fit.

<table>
<thead>
<tr>
<th>Property</th>
<th>Experiment</th>
<th>EAM (present)</th>
<th>EAM-2002$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (Å)</td>
<td>2.88$^a$</td>
<td>2.83</td>
<td>2.86</td>
</tr>
<tr>
<td>$E_0$ (eV)</td>
<td>-4.50$^b$</td>
<td>-4.51</td>
<td>-4.47</td>
</tr>
<tr>
<td>$c_{11}$ (GPa)</td>
<td>199$^c$</td>
<td>191</td>
<td>200</td>
</tr>
<tr>
<td>$c_{12}$ (GPa)</td>
<td>137$^c$</td>
<td>143</td>
<td>140</td>
</tr>
<tr>
<td>$c_{44}$ (GPa)</td>
<td>116$^c$</td>
<td>121</td>
<td>120</td>
</tr>
</tbody>
</table>

$^\dagger$Ref. \cite{1}; $^a$Ref. \cite{203}; $^b$Ref. \cite{204}; $^c$Ref. \cite{205}

EAM-2002 potential based on the experiment.

Thermal expansion factors of NiAl were computed by NPT Monte Carlo simulations and were found to be in excellent agreement with experiment at all temperatures 293 K to

![Figure 4.2: Phonon dispersion relations in B2-NiAl calculated with the new EAM potential (lines) in comparison with experimental data (points) \cite{8}](image-url)
Table 4.3: Phonon frequencies (in THz) in B2-NiAl calculated with the new EAM potential in comparison with the EAM-2002 potential [1], experimental and *ab initio* data. These properties were not included in the potential fit. The numbers typeset in bold are closest to the experiment.

<table>
<thead>
<tr>
<th>Point</th>
<th>Branch</th>
<th>Experiment(^a)</th>
<th>EAM(present)</th>
<th>EAM(^b)</th>
<th><em>Ab initio</em>(^c)</th>
<th><em>Ab initio</em>(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma = [000])</td>
<td>LO</td>
<td>8.60</td>
<td><strong>9.66</strong></td>
<td>10.67</td>
<td>9.353</td>
<td>8.074</td>
</tr>
<tr>
<td>(X = \frac{1}{2}[001])</td>
<td>TA</td>
<td>4.78</td>
<td>5.71</td>
<td><strong>5.43</strong></td>
<td>5.317</td>
<td>4.699</td>
</tr>
<tr>
<td></td>
<td>LA</td>
<td>6.05</td>
<td>6.39</td>
<td><strong>6.08</strong></td>
<td>6.472</td>
<td>5.648</td>
</tr>
<tr>
<td></td>
<td>TO</td>
<td>7.72</td>
<td><strong>8.21</strong></td>
<td>8.61</td>
<td>8.345</td>
<td>7.354</td>
</tr>
<tr>
<td></td>
<td>LO</td>
<td>10.10</td>
<td><strong>11.10</strong></td>
<td>12.23</td>
<td>11.599</td>
<td>10.181</td>
</tr>
<tr>
<td>(M = \frac{1}{2}[011])</td>
<td>LA=T1A</td>
<td>4.00</td>
<td><strong>3.43</strong></td>
<td>3.30</td>
<td>4.052</td>
<td>3.554</td>
</tr>
<tr>
<td></td>
<td>T2A</td>
<td>5.60</td>
<td>6.25</td>
<td><strong>6.10</strong></td>
<td>6.014</td>
<td>5.270</td>
</tr>
<tr>
<td></td>
<td>T2O</td>
<td>7.82</td>
<td><strong>8.23</strong></td>
<td>8.30</td>
<td>8.118</td>
<td>7.173</td>
</tr>
<tr>
<td></td>
<td>LO=T1O</td>
<td>10.50</td>
<td><strong>11.90</strong></td>
<td>13.11</td>
<td>11.059</td>
<td>9.566</td>
</tr>
<tr>
<td>(R = \frac{1}{2}[111])</td>
<td>LA=TA</td>
<td>4.96</td>
<td>5.97</td>
<td><strong>5.82</strong></td>
<td>5.290</td>
<td>4.439</td>
</tr>
<tr>
<td></td>
<td>LO</td>
<td>9.80</td>
<td><strong>10.27</strong></td>
<td>12.25</td>
<td>10.479</td>
<td>9.239</td>
</tr>
</tbody>
</table>

\(^a\)Ref. [8]; \(^b\)Ref. [1]; \(^c\)Ref. [206]

the melting point (Fig. 4.4). In fact, the agreement is significantly better than with the EAM-2002 potential, even though the latter was fit to thermal expansion factors while the new potential was not. The deviations from the experimental data at low temperatures are due to the quantum effects in vibrations, which are not captured by the classical Monte Carlo method.

Table 4.4 summarizes the formation energies of NiAl compounds with different crystalline structures. The new potential is in significantly better agreement with *ab initio* calculations than the previous potentials [1, 2]. This improved agreement with respect to phase stability is important for asserting the transferability of the potential. The phase diagram is shown in Fig. 4.3.

To further evaluate the transferability of the potential to regions of configuration space that are far away from equilibrium, energy along two homogeneous deformation paths was computed and compared with *ab initio* calculations. For the Bain deformation path (Fig. 4.5)
the initially equilibrium B2 structure was elongated or compressed along a [001] direction with a simultaneous compression or elongation in two other cubic directions so that to preserve the atomic volume. When the tetragonal distortion $c/a$ reaches $\sqrt{2}$, the B2 structure transforms into ideal L$_1^0$ structure. Fig. 4.5 demonstrates that the new potential is in slightly better agreement with ab initio results than the EAM-2002 potential under compression but is slightly less accurate under tension. Overall, however, both potential are in good agreement with ab initio calculations. Note that the L$_1^0$ structure does not produce any energy minimum, indicating its instability with respect to tetragonal distortions at this atomic volume. Calculations show that even if the volume is allowed to vary, the L$_1^0$ structure is still mechanically unstable.
Figure 4.4: Linear thermal expansion (%) of B2-NiAl relative to room temperature (293 K) computed with the new EAM potential in comparison with the EAM-2002 potential [1] and experimental data [10].

For the trigonal deformation path (Fig. 4.6), the B2 structure was stretched along the [111] direction and simultaneously compressed in normal directions to preserve the volume. The degree of the trigonal distortion is characterized by the angle \( \theta \) between the lattice translation vectors with \( \theta = 90^\circ \) for the B2 structure. The angles \( \theta = 60^\circ \) and \( \theta = 33.6^\circ \) produce the B1 and L1\(_1\) structures, respectively. The new potential demonstrates a significant improvement of the agreement with \textit{ab initio} data in comparison with the EAM-2002 potential. We emphasize that this better agreement resulted without any fitting, pointing to an improved transferability of the potential.
Table 4.4: Formation energies (eV/atom) of selected crystal structures of the NiAl and Ni$_3$Al compounds calculated with the new EAM potential in comparison with the EAM-2002 [1] and EAM-2004 [2] potentials and with ab initio (LAPW) results [1] when available. The structures marked by an asterisk were not included in the fit of the new potential. The numbers typeset in bold are in closest agreement with ab initio data.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Ab initio</th>
<th>EAM</th>
<th>EAM-2002</th>
<th>EAM-2004</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Al</td>
<td>L$\text{l}_2$</td>
<td>-0.4680</td>
<td>\textbf{-0.4540}</td>
<td>-0.3837</td>
<td>-0.4486</td>
</tr>
<tr>
<td></td>
<td>D0$_{22}$</td>
<td>-0.4305</td>
<td>-0.4474</td>
<td>-0.3745</td>
<td>\textbf{-0.4318}</td>
</tr>
<tr>
<td></td>
<td>D0$_3$</td>
<td>-0.4093</td>
<td>\textbf{-0.4213}</td>
<td>-0.3245</td>
<td>-0.4356</td>
</tr>
<tr>
<td></td>
<td>D0$_{11}$*</td>
<td>\textbf{-0.0827}</td>
<td>-0.0464</td>
<td>-0.0147</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D0$_{23}$*</td>
<td>-0.4520</td>
<td>-0.3793</td>
<td>-0.4401</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D0$_{19}$*</td>
<td>-0.4503</td>
<td>-0.3681</td>
<td>-0.4392</td>
<td></td>
</tr>
<tr>
<td>NiAl</td>
<td>B2</td>
<td>-0.7041</td>
<td>\textbf{-0.6059}</td>
<td>-0.5337</td>
<td>-0.5918</td>
</tr>
<tr>
<td></td>
<td>B1</td>
<td>-0.0335</td>
<td>\textbf{-0.0337}</td>
<td>-0.0564</td>
<td>-0.0596</td>
</tr>
<tr>
<td></td>
<td>L1$_0$</td>
<td>-0.5469</td>
<td>-0.4811</td>
<td>-0.3615</td>
<td>\textbf{-0.5139}</td>
</tr>
<tr>
<td></td>
<td>L1$_1$</td>
<td>-0.3251</td>
<td>\textbf{-0.3343}</td>
<td>-0.1509</td>
<td>-0.3590</td>
</tr>
<tr>
<td></td>
<td>B32</td>
<td>-0.3544</td>
<td>\textbf{-0.3736}</td>
<td>-0.1634</td>
<td>-0.4721</td>
</tr>
<tr>
<td></td>
<td>“40” (NbP)</td>
<td>-0.5435</td>
<td>-0.4728</td>
<td>-0.3368</td>
<td>\textbf{-0.4762}</td>
</tr>
<tr>
<td></td>
<td>B20*</td>
<td>-0.4901</td>
<td>-0.4035</td>
<td>-0.4283</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.5: Energy along the volume-conserving Bain path of B2-NiAl computed with the new EAM potential in comparison with the EAM-2002 potential [1] and ab initio (LAPW) calculations [1]. The energies are given relative to the equilibrium B2-NiAl phase.
Figure 4.6: Energy along the volume-conserving trigonal deformation path of B2-NiAl computed with the new EAM potential in comparison with the EAM-2002 potential [1] and ab initio (LAPW) calculations [1]. θ is the angle between the initial ⟨100⟩ directions in the B2 structure. This angle is varied to obtain the B1 and L1_1 structures. The energies are given relative to the equilibrium B2-NiAl phase.

Table 4.5: Surface, anti-phase boundary (APB) and unstable stacking fault energies (J/m^2) in B2-NiAl calculated with the new EAM potential in comparison with the EAM-2002 potential [1], experimental and ab initio data. The (100) and (111) surface energies represent average values over the Ni and Al terminations. These properties were not included in the potential fit.

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>Ab initio</th>
<th>EAM (present)</th>
<th>EAM-2002†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>(100)</td>
<td>2.85^a, 2.75^b</td>
<td>2.12, 1.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(110)</td>
<td>2.05^c, 1.87^c, 1.79^d, 1.37^d</td>
<td>1.89, 1.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>2.20, 1.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>APB</td>
<td>(110)</td>
<td>&gt; 0.50^e</td>
<td>0.88^f, 0.81^g</td>
<td>0.65, 0.55</td>
</tr>
<tr>
<td></td>
<td>(211)</td>
<td>&gt; 0.75^e</td>
<td>0.89^f, 0.99^g</td>
<td>0.73, 0.72</td>
</tr>
<tr>
<td>Unstable fault</td>
<td>(100)(001)</td>
<td>1.3^a, 3.35^h</td>
<td>1.56, 1.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(110)(001)</td>
<td>2.85^h</td>
<td>1.12, 0.83</td>
<td></td>
</tr>
</tbody>
</table>

†Ref. [1]; ^Ref. [207]; †Ref. [208]; †Ref. [209]; †Ref. [205]; †Ref. [210]; †Ref. [211]; †Ref. [212]; †Unrelaxed energy, Ref. [213]
4.3.2 Surfaces and stacking faults

The EAM-2002 potential tended to underestimate the surface energies of B2-NiAl (Table 4.5). As indicated in Table 4.5, the new potential predicts significantly higher surface energies, which are in a much better agreement with *ab initio* calculations. Again, this improvement was achieved without any fitting. The improved surface energies are important because they make the potential more suitable for simulations of fracture, ensuring the correct balance between the energies of the newly formed surfaces and the unstable stacking fault energy [214].

To assess the suitability of the potential for simulations of plastic deformation of NiAl, γ-surfaces on different crystal planes were calculated. The γ-surface is a plot of a generalized stacking fault energy γ as a function of displacement along different directions in the fault plane [215]. The fault energy is calculated by minimizing the total energy with respect to atomic displacements in the direction normal to the fault plane while prohibiting displacements in parallel directions. Minima and maxima of the γ-surface correspond to stable and unstable planar faults. Vectors connecting energy minima give Burgers vectors of possible dislocations, while the unstable stacking fault energies give the barriers for the formation of stable faults. Thus, γ-surfaces are useful for predicting possible dislocation reactions, core dissociations and other properties relevant to mechanical behavior.

Fig. 4.7 shows [111] sections of γ-surfaces on the (110) and (211) planes of B2-NiAl. The minimum on each curve corresponds to the formation of a stable anti-phase boundary (APB) on the respective crystal plane. From these plots, it can be predicted that a perfect [111] dislocation will dissociate into $\frac{1}{2}[111]$ super-partial separated by an APB on the (110) or (210) plane. In reality, the APB energies are so large that the core splitting is beyond the resolution of transmission electron microscopy. From this experimental fact, the lower bounds of the APB energies were estimated to be 0.5 J/m$^2$ for the (110) plane and 0.75 J/m$^2$ for the (211) plane [210]. *Ab initio* calculations [211, 212] give value consistent with these bounds (Table 4.5). Both the new and the EAM-2002 potentials predict (110) APB energies
above the experimental lower bound but below the *ab initio* calculations, with the new potential being in a better agreement with the *ab initio* results. For the (211) APB, both potentials give energies close to the experimental lower bound but significantly below the *ab initio* calculations. It should be noted that the APB energies listed in Table 4.5 are fully relaxed and thus slightly lower than the values on the γ-surfaces. We also emphasize that the (110) APB energy was included in the fitting of the EAM-2002 potential but not in the fitting of the new potential. The (211) APB energy was not in the fit for either potential.

Considering that the preferred slip in NiAl is with the Burgers vector [001] [216], we have also computed [001] cross-sections of γ-surfaces on (100) and (110) planes (Fig. 4.8). The single energy maximum observed in both cross-sections indicates that the [001] dislocation should have a compact core, which is consistent with transmission electron microscopy observations [217]. The height of the energy maximum represents the unstable stacking
fault energy, whose values for the (100) and (110) planes are given in Table 4.5. Both potentials are in agreement with *ab initio* data (note that the fault energies reported in [213] are unrelaxed and should be considered as upper bounds of the true energies) and are consistent with the easiest slip on the (110)[001] system observed experimentally [216].

![Graph](image.png)

**Figure 4.8:** Sections of γ-surfaces of B2-NiAl on the (100) and (110) planes in the [001] direction computed with the new EAM potential. The energy maxima give the unstable stacking fault energies.

### 4.3.3 Point defects

The new potential has been tested for point-defect properties of B2-NiAl. The results are compared with *ab initio* data in Table 4.6. Before making conclusions from this comparison, an explanation should be given of the quantities appearing in this Table.

The B2-NiAl compound contains two sub-lattices and supports four types of point defects: vacancies on the Ni and Al sub-lattices (V\textsubscript{Ni} and V\textsubscript{Al}) and antisite defects Al\textsubscript{Ni} (Al
atom on the Ni sub-lattice) and NiAl (Ni atom on the Al sub-lattice). These defects can have a strong impact on thermodynamic properties and diffusion in this compound, especially near the stoichiometric composition. Furthermore, B2-NiAl displays the so-called triple-defect mechanism of compositional disorder, in which derivations from the exact stoichiometry on the Al-rich side are accommodated predominantly by vacancies on the Ni sub-lattice, whereas on the Ni-rich side they are accommodated by antisite defects on the Al sub-lattice (NiAl). The majority of other inter-metallic compounds form antisites on both sides of the stoichiometry. The triple-defect mechanism of compositional disorder observed in B2-NiAl has been verified both experimentally \cite{218, 219} and by \emph{ab initio} calculations \cite{220, 222}, and it was built into the development of the EAM-2002 potential.

Table 4.6: Energies (in eV) of composition-conserving point-defect complexes in B2-NiAl calculated with the new EAM potential in comparison with the EAM-2002 potential \cite{1} and \emph{ab initio} data. $\varepsilon_d$ denotes the “raw” formation energy of defect $d$. All other notations are explained in the text. These energies were not included in the potential fit.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Equation</th>
<th>$Ab\ initio$</th>
<th>EAM (present)</th>
<th>EAM-2002$^\ddagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchange</td>
<td>$\varepsilon_{NiAl} + \varepsilon_{AlNi}$</td>
<td>3.15$^a$, 3.10$^b$, 3.63$^c$, 2.65$^d$</td>
<td>2.075</td>
<td>2.765</td>
</tr>
<tr>
<td>Divacancy</td>
<td>$\varepsilon_{V_{Ni}} + \varepsilon_{V_{Al}} + 2E_0$</td>
<td>3.07$^a$, 2.71$^b$, 2.53$^c$, 2.18$^d$</td>
<td>2.569</td>
<td>2.396</td>
</tr>
<tr>
<td>Triple-Ni</td>
<td>$2\varepsilon_{V_{Ni}} + \varepsilon_{NiAl} + 2E_0$</td>
<td>2.83$^a$, 2.22$^b$, 2.36$^c$, 1.58$^d$</td>
<td>2.807</td>
<td>2.281</td>
</tr>
<tr>
<td>Triple-Al</td>
<td>$2\varepsilon_{V_{Al}} + \varepsilon_{AlNi} + 2E_0$</td>
<td>6.46$^a$, 6.30$^b$, 6.32$^c$, 5.44$^d$</td>
<td>4.406</td>
<td>5.276</td>
</tr>
<tr>
<td>Interbranch-Ni</td>
<td>$2\varepsilon_{V_{Al}} - \varepsilon_{NiAl} + 2E_0$</td>
<td>3.31$^a$, 3.20$^b$, 2.69$^c$, 2.78$^d$</td>
<td>2.331</td>
<td>2.511</td>
</tr>
<tr>
<td>Interbranch-Al</td>
<td>$\varepsilon_{AlNi} - 2\varepsilon_{V_{Ni}} - 2E_0$</td>
<td>0.32$^a$, 0.88$^b$, 1.28$^c$, 1.07$^d$</td>
<td>-0.732</td>
<td>0.484</td>
</tr>
</tbody>
</table>

$^\ddagger$Ref. \cite{1}; $^a$Ref. \cite{223}; $^b$Ref. \cite{224}; $^c$Ref. \cite{220}; $^d$Ref. \cite{222}

The condition that Al-rich compositions on B2-NiAl favor the formation of Ni structural vacancies over Al$_{Ni}$ antisites can be formulated as a certain relation between point-defect energies. Specifically, the so-called interbranch-Al energy \cite{220} that will be defined below must be positive. This energy at zero Kelvin predicted by \emph{ab initio} calculations \cite{220, 222, 224} ranges widely from 0.32 eV \cite{223} to as high as 1.28 eV \cite{220}, depending on computational details. During the development of the EAM-2002 potential \cite{1}, a positive value of the interbranch-Al energy was enforced. The value actually achieved by the fit was 0.48 eV,
which compares well with *ab initio* predictions.

It should be pointed out that point-defect calculations in ordered compounds are not as straightforward as in elemental solids. One can readily calculate the so-called “raw” formation energy of a defect, which is defined as the energy difference between a simulation block with a single point defect and the same block without any defects [225]. However, this difference depends on reference constants involved in the energy calculations. “Raw” energies of point defects can have very different values in *ab initio*, EAM and other calculation methods. Since the equilibrium point defect concentrations are independent of any reference constants, they can only depend on such combinations of “raw” energies in which the reference constants cancel out. To meet this requirement, it was proposed to express point defect concentrations through formation energies of so-called composition-conserving defect complexes [220, 222, 226]. Such complexes can be considered as thermal excitations that automatically preserve the chemical composition. It can be shown [220, 222, 226] that the knowledge of formation energies of any three of such complexes is sufficient for computing all point defect concentrations.

Examples of composition-conserving defect complexes include the interbranch-Al defect which creates an antisite on the Ni sub-lattice instead of two Ni vacancies (Al$_{Ni} - 2V_{Ni}$), and the interbranch-Ni defect which creates two Al vacancies and eliminates an antisite on the Al sub-lattice (2$V_{Al} - Ni_{Al}$). Expressions for the energies of these and other complexes in terms of “raw” energies of individual point defects are given in Table 4.6. Since the complex energies are independent of reference constants, they are suitable for comparing calculations performed by different methods. Table 4.6 compares predictions of the new potential with *ab initio* results and calculations with the EAM-2002 potential. The important observation is that the new potential unfortunately gives a negative interbranch-Al energy, which is in disagreement with the predominance of Ni structural vacancies in Al-rich compositions. For all other energies, both potentials are in about the same good agreement with *ab initio* calculations.
4.4 Properties of L12-Ni3Al

Testing the potential for Ni3Al properties was especially important because the only quantity related to this compound that was included in the potential fit was its formation energy. Thus, all comparisons between predictions of this potential and available experimental or ab initio data are essentially tests of its transferability.

Table 4.7: Lattice properties of Ni3Al predicted by the new EAM potential in comparison with the EAM-2004 potential \[2\] and experimental data. Only the cohesive energy \(E_0\) was included in the potential fit.

<table>
<thead>
<tr>
<th>Property</th>
<th>Experiment(^a)</th>
<th>EAM (present)</th>
<th>EAM-2004(^\ddagger)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_0) (Å)</td>
<td>3.57</td>
<td>3.533</td>
<td>3.571</td>
</tr>
<tr>
<td>(E_0) (eV)</td>
<td>-4.620</td>
<td>-4.631</td>
<td>-4.626</td>
</tr>
<tr>
<td>(c_{11}) (GPa)</td>
<td>230</td>
<td>238</td>
<td>236</td>
</tr>
<tr>
<td>(c_{12}) (GPa)</td>
<td>149</td>
<td>166</td>
<td>154</td>
</tr>
<tr>
<td>(c_{44}) (GPa)</td>
<td>132</td>
<td>130</td>
<td>127</td>
</tr>
</tbody>
</table>

\(^a\)Ref. \[227,228\]; \(^\ddagger\)Ref. \[2\]

4.4.1 Lattice properties

Table 4.7 demonstrates that the lattice parameter and elastic constants of Ni3Al predicted by the new potential are in about the same good agreement with experimental data as the EAM-2004 potential. The latter, however, was directly fitted to these properties, whereas the new potential was not.

The phonon dispersion relations computed at 0 K (Fig. 4.9) are in reasonable agreement with experimental results obtained by inelastic neutron scattering at room temperature \[11\]. The acoustic branches are reproduced with excellent accuracy, whereas the frequencies of the upper optical branches are somewhat overestimated. Nevertheless, even in the high-frequency range the agreement with experiment is better than with the EAM-2004 potential \[2\]. We emphasize that neither of the two potentials was fitted to phonon frequencies. For easy comparison, the phonon frequencies are presented in Table 4.8.
Figure 4.9: Phonon dispersion relations in Ni$_3$Al calculated with the new EAM potential (lines) in comparison with experimental data (points) [11].

The thermal expansion factors computed by NPT Monte Carlo simulations are in fair agreement with experimental data but are less accurate than with the EAM-2004 potential (Fig. 4.10). The discrepancies at low temperatures are caused by quantum effects which are not included in the Monte Carlo method.

The formation energies of several different compounds with the same Ni$_3$Al stoichiometry are listed in Table 4.4. The new potential is in significantly better agreement with ab initio calculations than the EAM-2002 potential and in slightly better agreement than the EAM-2004 potential. Note, however, that the ordering of the energies of the different structures is the same for all three potentials and matches the ab initio energies with only one exception: the EAM-2004 potential predicts the D0$_{22}$ structure to be slightly (0.004 eV) more stable than D0$_3$, which is in disagreement with ab initio data.
Table 4.8: Phonon frequencies (in THz) in Ni$_3$Al predicted by the new EAM potential in comparison with the EAM-2004 potential [2] and experimental data. The numbers typeset to bold are closest to the experiment.

<table>
<thead>
<tr>
<th>Point Branch</th>
<th>Experiment$^a$</th>
<th>EAM (present)</th>
<th>EAM-2004$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma = [000]$</td>
<td>O1 6.12</td>
<td><strong>6.47</strong></td>
<td>6.68</td>
</tr>
<tr>
<td></td>
<td>O2 6.83</td>
<td>8.04</td>
<td><strong>7.68</strong></td>
</tr>
<tr>
<td></td>
<td>O3 9.85</td>
<td><strong>11.18</strong></td>
<td>12.21</td>
</tr>
<tr>
<td>$X = \frac{1}{2}[001]$</td>
<td>TA 4.59</td>
<td><strong>4.72</strong></td>
<td>4.83</td>
</tr>
<tr>
<td></td>
<td>LA 6.11</td>
<td>6.56</td>
<td><strong>6.43</strong></td>
</tr>
<tr>
<td></td>
<td>LO1 5.82</td>
<td><strong>6.10</strong></td>
<td>6.57</td>
</tr>
<tr>
<td></td>
<td>TO1 5.22</td>
<td>5.51</td>
<td><strong>5.47</strong></td>
</tr>
<tr>
<td></td>
<td>LO2 6.59</td>
<td><strong>6.66</strong></td>
<td>6.73</td>
</tr>
<tr>
<td></td>
<td>TO2 7.29</td>
<td>8.27</td>
<td><strong>8.13</strong></td>
</tr>
<tr>
<td></td>
<td>LO3 9.45</td>
<td><strong>9.51</strong></td>
<td>9.79</td>
</tr>
<tr>
<td></td>
<td>TO3 9.68</td>
<td><strong>10.44</strong></td>
<td>11.46</td>
</tr>
<tr>
<td>$M = \frac{1}{2}[011]$</td>
<td>LA 4.70</td>
<td><strong>4.74</strong></td>
<td>4.75</td>
</tr>
<tr>
<td></td>
<td>T1A 5.70</td>
<td><strong>6.46</strong></td>
<td>6.55</td>
</tr>
<tr>
<td></td>
<td>T2A 3.98</td>
<td><strong>3.87</strong></td>
<td>4.37</td>
</tr>
<tr>
<td></td>
<td>LO1 7.55</td>
<td>8.11</td>
<td><strong>8.02</strong></td>
</tr>
<tr>
<td></td>
<td>T1O1 5.62</td>
<td><strong>6.46</strong></td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td>T2O1 4.48</td>
<td><strong>4.51</strong></td>
<td>4.66</td>
</tr>
<tr>
<td></td>
<td>LO2 7.55</td>
<td>8.43</td>
<td><strong>8.19</strong></td>
</tr>
<tr>
<td></td>
<td>T1O2 5.62</td>
<td><strong>6.46</strong></td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td>T2O2 4.70</td>
<td><strong>4.74</strong></td>
<td>4.75</td>
</tr>
<tr>
<td></td>
<td>LO3 9.80</td>
<td><strong>10.49</strong></td>
<td>10.98</td>
</tr>
<tr>
<td></td>
<td>T1O3 8.82</td>
<td><strong>9.75</strong></td>
<td>10.43</td>
</tr>
<tr>
<td></td>
<td>T2O3 9.70</td>
<td><strong>10.49</strong></td>
<td>10.98</td>
</tr>
<tr>
<td>$R = \frac{1}{2}[111]$</td>
<td>LA 5.77</td>
<td><strong>5.52</strong></td>
<td>5.24</td>
</tr>
<tr>
<td></td>
<td>TA 4.10</td>
<td><strong>3.94</strong></td>
<td>4.35</td>
</tr>
<tr>
<td></td>
<td>LO1 4.48</td>
<td><strong>4.57</strong></td>
<td>4.64</td>
</tr>
<tr>
<td></td>
<td>TO1 4.30</td>
<td>3.94</td>
<td><strong>4.64</strong></td>
</tr>
<tr>
<td></td>
<td>LO2 8.85</td>
<td>9.83</td>
<td><strong>9.38</strong></td>
</tr>
<tr>
<td></td>
<td>TO2 5.77</td>
<td><strong>5.52</strong></td>
<td>5.24</td>
</tr>
<tr>
<td></td>
<td>LO3 10.20</td>
<td><strong>11.37</strong></td>
<td>12.16</td>
</tr>
<tr>
<td></td>
<td>T3 10.20</td>
<td><strong>11.37</strong></td>
<td>12.16</td>
</tr>
</tbody>
</table>

$^a$Ref. [11]; $^b$Ref. [2]
Figure 4.10: Linear thermal expansion (%) of Ni$_3$Al relative to room temperature (293 K) computed with the new EAM potential in comparison with the EAM-2004 potential [1] and experimental data [10].

4.4.2 Planar defects

The energies of low-index surfaces of Ni$_3$Al are given in Table 4.9. We are not aware of any reliable experimental or *ab initio* data that could be used for comparison. However, it is known that EAM potentials tend to underestimate surface energies of metals and intermetallic compounds [141]. The fact that the surface energies predicted by the new potential are significantly higher than those predicted by the EAM-2004 potential may suggest that the new potential represents surface energies more accurately. This conjecture will need to be tested by future calculations or measurements.

For simulations of mechanical behavior of Ni$_3$Al, it is important for the potential to reproduce the energies of stacking faults on (111) and (001) crystal planes. Indeed, plastic
Table 4.9: Calculated and experimental energies (in mJ/m$^2$) of surfaces and planar faults in Ni$_3$Al predicted by the new EAM potential in comparison with the EAM-2004 potential [2], *ab initio* and experimental data. These properties were not included in the potential fit.

<table>
<thead>
<tr>
<th>Property</th>
<th>Experiment</th>
<th><em>Ab initio</em></th>
<th>EAM (present)</th>
<th>EAM-2004†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(100)</td>
<td></td>
<td>2150</td>
<td>1711</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td></td>
<td>2257</td>
<td>1847</td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td></td>
<td>1966</td>
<td>1483</td>
<td></td>
</tr>
<tr>
<td>Planar fault</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APB(111)</td>
<td>180$^a$, 175$^b$, 195$^c$, 188$^d$, 210$^e$, 172$^f$</td>
<td>180</td>
<td>252</td>
<td></td>
</tr>
<tr>
<td>CSF(111)</td>
<td>206$^a$, 235$^b$, 236$^c$, 225$^e$, 223$^f$</td>
<td>229</td>
<td>202</td>
<td></td>
</tr>
<tr>
<td>SISF(111)</td>
<td>6$^b$</td>
<td>80$^e$, 79$^f$</td>
<td>21</td>
<td>51</td>
</tr>
<tr>
<td>APB(100)</td>
<td>104$^b$, 160$^c$</td>
<td>121$^g$</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>

†Ref. [2]; $^a$Ref. [229]; $^b$Ref. [230]; $^c$Ref. [231]; $^d$Ref. [232]; $^e$Ref. [233]; $^f$Ref. [234]; $^g$Ref. [235]

deformation of this compound is influenced by the core structure of $\langle 110 \rangle$ screw super-dislocations. These dislocations can dissociate into super-partials by one of two different schemes. In one, the dislocation dissociates into $1/2\,\langle 110 \rangle$ super-partials separated by an APB on a (111) plane [236–239]. Each of the super-partials can dissociate into Shockley partials bounding a complex stacking fault (CSF). Alternatively, the dislocation can dissociate into $1/3\,\langle 211 \rangle$ Kear super-partials bounding a superlattice intrinsic stacking fault (SISF). Thus, the dislocation core structure and mobility depend on the energies of three planar faults on the (111) plane: APB, CSF and SISF. At high temperatures, the leading superpartial can cross-slip into a (001) plane and form a locked configuration. This lock includes a (001) APB, whose energy is assumed to be smaller than the energy of the (111) APB providing a driving force of the cross-slip. This cross-slip and the lock formation are responsible for the flow stress anomaly in Ni$_3$Al [236, 239].

The $\gamma$-surfaces on the (111) and (001) planes were computed using the methodology as discussed in [2]. The results are summarized in Table 4.9 and compared with *ab initio* calculations [232, 235] and experimental data obtained by transmission electron microscopy.
Both the new and the EAM-2004 potential demonstrate satisfactory agreement with experimental and \textit{ab initio} energies without any fitting. The lower energy of the (001) APB relative to the (111) APB is consistent with the existence of driving force for the cross-slip process, although the anisotropy of the APB energy is overestimated in comparison with both experiment and \textit{ab initio} results. The SISF energy predicted by both potentials is between the \textit{ab initio} and experimental values. The large gap between the \textit{ab initio} and experimental results for the SISF energy is still a mystery; see discussion in \cite{2}.

\subsection*{4.4.3 Point defects}

As in the case of B2-NiAl, the Ni$_3$Al compound supports four types of point defects: a vacancy and an antisite on each sub-lattice. As discussed in Section 4.3.3, the “raw” energies of individual point defects depend on reference constants and are useful only as input for calculations of point-defect concentrations \cite{2,148,225} from a lattice gas model \cite{148,220,222,224}. Exact solutions of the model can be obtained only numerically, but one can derive approximate analytical solutions for some limiting cases \cite{2,148}.

According to experimental data \cite{240} and \textit{ab initio} calculations \cite{241}, thermal disorder in Ni$_3$Al is dominated by antisite defects on either side of the stoichiometry, with vacancy concentrations being orders of magnitude smaller. Using this fact, approximate analytical expressions have been derived \cite{2} that express point-defect concentrations as Arrhenius exponentials of so-called effective formation energies. Table 4.10 gives expressions for the effective formation energies of point defects in stoichiometric Ni$_3$Al in terms their “raw” energies, along with results obtained with the new and EAM-2004 potentials. The new potential shows a better agreement with \textit{ab initio} energies for the Al vacancy but is somewhat less accurate for the Ni vacancy and the antisites. Overall, however, both potentials perform equally well. In particular, the significantly higher vacancy formation energies relative to the antisite energies are consistent with the predominantly antisite disorder mechanism, justifying the approximations underlying the analytical solutions.
4.5 Phase stability in the Ni-Al system

Table 4.11 summarizes the cohesive energies and lattice constants of different phases of the Ni-Al system computed with the new potential. The results predicted by the potential compare reasonably well with experimental data when available, including phases that were not included in the potential fit.

Another way of comparing the potential predictions with experiment is to plot the formation energies $E_f$ of different inter-metallic compounds versus their chemical composition. The formation energies were computed from Eq. (2.15). A convex-hull construction of this plot gives the set of structures that should be observed on the experimental phase diagram at low temperatures. The formation energies of all other structures must lie above the convex hull. Figure 4.11 shows this construction for the new potential. The inter-metallic phases predicted to be stable are $\text{Ni}_5\text{Al}_3$, $\text{Ni}_3\text{Al}$ and $\text{NiAl}$ with the crystal structures of $\text{Ga}_3\text{Pt}_5$, $\text{L1}_2$ and $\text{B2}$, respectively. These compounds with exactly these crystal structures are indeed observed on the experimental phase diagram [3]. All other crystal structures with these stoichiometries have energies above the tie lines, as they should. Furthermore, the $\text{Ni}_5\text{Al}_3$ formation energy is just slightly below the line connecting $\text{Ni}_3\text{Al}$ and $\text{NiAl}$, suggesting that this phase is barely stable and should form at significantly lower temperatures than other phases, which is again very consistent with the experimental phase diagram [3]. It should be noted that the EAM-2002 and EAM-2004 potentials give $\text{Ni}_5\text{Al}_3$ formation...
Table 4.11: Equilibrium lattice parameters ($a_0$) and cohesive energies ($E_0$) of selected phases of the Ni-Al system calculated with the new EAM potential in comparison with experimental data where available. For non-cubic structures, two or three lattice parameters are listed. The asterisk indicates structures which were not included in the potential fit.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Experiment $a_0$ (Å)</th>
<th>Experiment $E_0$ (eV)</th>
<th>EAM $a_0$ (Å)</th>
<th>EAM $E_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>A1</td>
<td>3.52$^a$</td>
<td>-4.45$^b$</td>
<td>3.52</td>
<td>-4.45</td>
</tr>
<tr>
<td>Ni$_3$Al</td>
<td>L$_{12}$</td>
<td>3.57$^c$</td>
<td>-4.57$^d$</td>
<td>3.5329</td>
<td>-4.6249</td>
</tr>
<tr>
<td></td>
<td>D$<em>{0</em>{22}}$</td>
<td></td>
<td></td>
<td>5.5425</td>
<td>-4.5988</td>
</tr>
<tr>
<td></td>
<td>D$_0$</td>
<td></td>
<td></td>
<td>6.0265, 7.0703, 4.4186</td>
<td>-4.2602</td>
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<tr>
<td></td>
<td>D$<em>{0</em>{11}}$</td>
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<td></td>
<td>3.5338</td>
<td>-4.6295</td>
</tr>
<tr>
<td></td>
<td>D$<em>{0</em>{19}}$</td>
<td></td>
<td></td>
<td>4.9910, 4.0645</td>
<td>-4.6278</td>
</tr>
<tr>
<td>NiAl</td>
<td>B2</td>
<td>2.88$^a$</td>
<td>-4.50$^d$</td>
<td>2.8320</td>
<td>-4.5109</td>
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<td></td>
<td>B1</td>
<td></td>
<td></td>
<td>4.7535</td>
<td>-3.9387</td>
</tr>
<tr>
<td></td>
<td>L$_{10}$</td>
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<td></td>
<td>3.6309</td>
<td>-4.3861</td>
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<tr>
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<td>3.6718</td>
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<tr>
<td></td>
<td>B$_{32}$</td>
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<td></td>
<td>4.9689</td>
<td>-4.2786</td>
</tr>
<tr>
<td></td>
<td>40(NbP)</td>
<td></td>
<td></td>
<td>3.4685</td>
<td>-4.3778</td>
</tr>
<tr>
<td></td>
<td>B$_{20}$</td>
<td></td>
<td></td>
<td>4.5815</td>
<td>-4.3951</td>
</tr>
<tr>
<td>Ni$_3$Al$_4$</td>
<td>Ni$_3$Ga$_4$</td>
<td>11.408$^e$</td>
<td>11.275</td>
<td>-4.2658</td>
<td></td>
</tr>
<tr>
<td>Ni$_2$Al$_3$</td>
<td>D$<em>{5</em>{19}}$</td>
<td>4.03, 4.88$^f$</td>
<td>4.38$^d$</td>
<td>3.9970, 4.8527</td>
<td>-4.1580</td>
</tr>
<tr>
<td>Ni$_5$Al$_3$</td>
<td>Ga$_3$Pt$_5$</td>
<td></td>
<td></td>
<td>7.181, 6.5256, 3.7077</td>
<td>-4.5782</td>
</tr>
<tr>
<td>NiAl$_3$</td>
<td>D$<em>{0</em>{11}}$</td>
<td>6.60, 7.35, 4.80$^f$</td>
<td>-4.02$^f$</td>
<td>6.4622, 7.5677, 4.8661</td>
<td>-3.8741</td>
</tr>
<tr>
<td></td>
<td>L$_{12}$</td>
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<tr>
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<td>D$_0$</td>
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</tr>
<tr>
<td></td>
<td>D$<em>{0</em>{22}}$</td>
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<td></td>
<td>3.7980</td>
<td>-3.8900</td>
</tr>
<tr>
<td></td>
<td>D$<em>{0</em>{23}}$</td>
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<td></td>
<td>3.7994</td>
<td>-3.8916</td>
</tr>
<tr>
<td></td>
<td>D$<em>{0</em>{19}}$</td>
<td></td>
<td></td>
<td>5.3720, 4.3517</td>
<td>-3.8970</td>
</tr>
<tr>
<td>Ni$_2$Al</td>
<td>C$_{11}$</td>
<td></td>
<td></td>
<td>2.8037, 8.4110</td>
<td>-4.5546</td>
</tr>
<tr>
<td>NiAl$_2$</td>
<td>C$_{11}$</td>
<td></td>
<td></td>
<td>2.9435, 8.8304</td>
<td>-4.1050</td>
</tr>
<tr>
<td>Al</td>
<td>A1</td>
<td>4.05$^a$</td>
<td>-3.36$^b$</td>
<td>4.05</td>
<td>-3.36</td>
</tr>
</tbody>
</table>

*Ref. 203; $^a$Ref. 242; $^b$Ref. 218 243
$^d$Ref. 204; $^e$Ref. 244; $^f$Ref. 218 245

energies lying above the Ni$_3$Al-NiAl tie line, in contradiction to the experimental phase diagram.

However, the formation energies of the Ni$_2$Al$_3$ and NiAl$_3$ compounds which appear on the experimental phase diagram lie above the NiAl-Ni line, indicating that the potential
Figure 4.11: Formation energy of experimentally observed or imaginary inter-metallic compounds of the Ni-Al system predicted by the new EAM potential. The compounds marked by an asterisk and labeled in the plot are observed on the experimental phase diagram.

Underestimates their binding. In addition, the potential predicts that the energy of the D0_{19} structure of NiAl_{3} is slightly below the experimentally observed D0_{11} structure, which is also incorrect. Again, the EAM-2002 and EAM-2004 potentials had similar problems in reproducing the Al-rich part of the phase diagram. It should be pointed out that this analysis of phase stability is based on 0 K energies. At finite temperatures, atomic vibrations can affect the free energies of the crystal structures and alter their relative stability. The energy differences between some of the competing structures discussed here are as small as a few meV.
4.6 Melting temperatures of the phases

The transferability of the potential to high temperatures was evaluated by computing the melting points of Ni, NiAl and Ni$_3$Al. We employed all-periodic simulations blocks consisting of solid and liquid phases separated by a (001) interface (see example for Ni$_3$Al in Fig. 4.12a). The blocks contained 9 to 16 thousand atoms and were 100 – 150 Å thick in the direction normal to the interface. The blocks were created by melting a half of an initially single-phase solid system, which in the case of NiAl and Ni$_3$Al had a perfectly stoichiometric chemical composition.

Table 4.12: Melting temperatures (in K) of selected phases of the Ni-Al system calculated with the new potential in comparison with experimental data [3,4].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ni</th>
<th>Ni$_3$Al</th>
<th>NiAl</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAM (present)</td>
<td>1701</td>
<td>1678</td>
<td>1780</td>
<td>1042</td>
</tr>
<tr>
<td>Experiment</td>
<td>1728</td>
<td>1645</td>
<td>1911</td>
<td>933</td>
</tr>
<tr>
<td>Discrepancy (%)</td>
<td>1.6</td>
<td>1.9</td>
<td>6.8</td>
<td>11.7</td>
</tr>
</tbody>
</table>

To calculate the melting temperature $T_m$, the system was first brought to mechanical equilibrium at some temperature close to the expected $T_m$ value by an $NPT$ MD run (fixed temperature, number of atoms and zero pressure). The MD ensemble was then switched to micro-canonical ($NVE$) and an additional 4 ns long run was performed. During this run, some partial melting or crystallization could occur, after which the temperature and pressure leveled out at new constant values. These values were determined by averaging over the last 2 ns of the $NVE$ run, giving a melting temperature and the corresponding pressure. Such simulations were repeated several times starting from different snapshots saved during the $NPT$ run, producing a plot of the melting temperature versus pressure. An example of such a plot is shown in Fig. 4.12b for pure Ni. The final value of $T_m$ was obtained by linear interpolation to zero pressure.
Figure 4.12: Examples of calculation of melting points. (a) Simulation block used for calculation of the melting temperature of Ni$_3$Al, with dark and bright points representing Ni and Al atoms. The solid-liquid interface orientation is (001). (b) Melting temperature versus pressure for pure Ni. The dotted vertical line corresponds to zero pressure and is shown as a guide to the eye. The linear fit (solid line) is used to calculate the melting point at zero pressure.

Table 4.12 summarizes the obtained melting temperatures in comparison with experimental data. The melting temperature of Al calculated by the same method elsewhere has been added for completeness. The melting points of Ni and Ni$_3$Al are in excellent agreement with experiment. The melting temperatures of NiAl and especially Al are less accurate but still reasonable. The main point of this comparison, however, is that none of these melting temperatures or any liquid properties, in fact not even any finite-temperature properties of the phases, were included in the potential fit. It is always possible to achieve

---

1B2-NiAl melts congruently. Experimental data for the melting point of Ni$_3$Al vary from 1645 to 1668 K. There is even a controversy about whether this compound melts congruently or via a $\gamma$-$\gamma'$ eutectic. We use the lower bound of 1645 K.
an accurate match to the experimental melting point by including it in the fitting process. That the four melting points listed in Table 4.12 have been predicted by the new potential at this level of accuracy, without any fit, speaks for its very good transferability to high temperatures.

4.7 Discussion and conclusions

The Ni-Al potential developed in this work accurately reproduces a variety of physical properties of both NiAl and Ni₃Al. In addition, it demonstrates a fairly good agreement with experimental and ab initio data for the formation energies of several other compounds of the Ni-Al system. The overwhelming majority of the properties reproduced by this potential were not included in the fitting database. This excellent transferability of the potential was achieved by fitting to ab initio formation energies of several real or imaginary compounds with different crystalline structures and chemical compositions across the phase diagram. During the fitting process, the weights of formation energies of different compounds were kept comparable to each other, thus spreading the fitting errors nearly uniformly over the database. This is in contrast to previous potentials [1,2], which were developed by putting heavy weights on particular properties of either NiAl or Ni₃Al.

Thus, the strategy of giving a high priority to the “global” fit over insisting on particular properties of particular compounds has paid off by producing a highly transferable, “universal” potential for the Ni-Al system. This potential is nearly as accurate as the previously developed specialized potentials [1,2] for most of the properties tested in this work. In fact, for a number of properties the new potential is superior to the specialized potentials [1,2], most notably for phonon frequencies, surface energies and some of the planar fault energies.

One flaw of the new potential is its failure to reproduce the stability of Ni structural vacancies in Al-rich compositions of B2-NiAl. Ab initio calculations and experimental measurements proving or allegedly disproving the existence of such vacancies have an interesting history that was discussed in Ref. [1,151,226] and references therein. Presently, the compositional disorder of NiAl accompanied by the formation of Ni structural vacancies can be
taken as an established fact. The criterion of stability of such vacancies is the positive sign and a significant magnitude (0.5 – 1.0 eV) of the interbranch-Al energy discussed in Section 4.3.3. Examination of existing semi-empirical potentials for the Ni-Al system indicates that (i) this criterion is not satisfied by potentials automatically without specifically fitting to it, and (ii) this criterion is only satisfied by the EAM-2002 potential [1] where it was strongly enforced. In the latter case, the fit was achieved at a large expense in accuracy of some other properties. Other potentials give either a negative interbranch-Al energy [2,156,201], or positive but too small to ensure the stability of structural vacancies [200,202].

The difficulty in reproducing the structural vacancies in NiAl is likely to be an intrinsic limitation of the EAM/Finnis-Sinclair formalism. It may have an electronic origin that is yet to be understood. It would be interesting to check if potentials reaching beyond EAM and Finnis-Sinclair framework, for example by including angle-dependent interactions [27,144,246], can reproduce the structural vacancies more easily. In the meantime, the EAM potential developed in here can be used for simulations that do not involve the formation of structural vacancies. If they do, then the EAM-2002 potential would present a better choice.

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Chapter 5: EAM potential for HCP Cobalt

5.1 Introduction

Cobalt is one of the 3d electron transition metals which is widely used in many magnetic shape memory alloys [44, 52, 53, 57, 59, 61, 63, 163, 166, 247–250]. The cobalt and its alloys are used in wear-resistant, corrosion-resistant and thermal-resistant applications. It is ferromagnetic until $T_c$ ($\sim 1393$ K) [251]; slightly different value was reported in [252]. It is also allotropic with the HCP and the FCC phases like other technologically relevant metals: Ti, Fe, Zr, Sn and U. The HCP phase is the low temperature phase with transition temperature around $\sim 700$K and enthalpy of transition, $\Delta H_{hcp\rightarrow fcc}$, 0.004 eV/atom as reported in [251, 252]. Although the transition temperature is well above the room temperature a thick film of FCC Co may be obtained at the room temperature with an epitaxial growth on Cu(110) surface [253]. A new metastable phase, the BCC Co, was first grown epitaxially on GaAs substrate by Prinz et al. [254] which is the thickest sample with thickness 357 Å ever made to date. It is a ferromagnetic metal similar to $\alpha$-Fe and the lattice constant was measured $a_0=2.827$ Å. A recent paper by O’Shea et al. [255] pointed out the existence of another metastable phase, $\epsilon$, which is a cubic structure (space group P4132) and contains 20 cobalt atoms in a unit cell. Its cohesive energy was reported slightly larger than that of the magnetic FCC Co indicating possible transformations into the HCP or the FCC structures.

The elastic constants of the HCP and the FCC phases of cobalt are reported in several experimental works. The earliest experimental measurement of the elastic moduli in a single crystal cobalt at the room temperature (25°C) was reported by McSkimin et al. [256]. Antonangeli et al. [257] determined the elastic constants and their pressure derivatives in a single crystal HCP Co by the inelastic x-ray scattering (IXS) up to 39 GPa pressure in
the helium and the neon environments from which zero pressure moduli were deduced. The same group also studied elastic properties of polycrystalline cobalt under high pressure up to 99 GPa [258]. Another high pressure study up to 79 GPa was performed by Fujihisa et al.

Theoretical calculations of the elastic moduli of pure cobalt are rare. For example, Steinle-Neumann et al. [259] computed the elastic constants of the pure HCP Co at high pressure with the first principle calculations.

Several elements and compounds exhibiting martensitic phase transformation have been studied by using inelastic neutron scattering in order to investigate the origins and the mechanisms of the transformations. Frey et al. [260] and Strauss et al. [261] did not find softening of the T[ζζ0] and the T[ζζζ] branches of the phonon dispersion in the cobalt at and around the transition temperature. In fact, no precursor effect was observed during the transition [260]. Another interesting experiment revealed that the FCC→HCP transition did not happen in fine particles of the FCC Co synthesized at the ambient temperature during slow heating and cooling processes between the temperature range, 28–293 K [262].

A nice theory of the martensitic transformation has been presented in [263].

A number of embedded-atom method (EAM) and modified embedded atom method (MEAM) potentials for the HCP metals have been developed in the past [264–267]. Igarashi et al. developed Finnis-Sinclair (F-S) type many-body potentials for the HCP metals such as Co, Zr, Ti, Ru, Hf, Zn, Mg and Be and applied to calculations of the stacking fault energy and the phonon dispersion relation [268]. The modified embedded atom method (MEAM) has been successfully applied to a number of HCP metals including those with a negative Cauchy pressure [269].

In terms of the computer simulation of the martensitic transformation in the cobalt there are not many articles related to the subject. Jiang et al. performed the molecular dynamic (MD) simulations of the phase transformation in the cobalt by introducing a Shockley dislocation and an intrinsic stacking fault in the perfect closed pack (FCC) structures and with the two-phase (the FCC and the HCP phases) configuration using the EAM potential.
For notational convenience the HCP, FCC and BCC cobalts are referred by $\epsilon$-Co, $\alpha$-Co and $\beta$-Co respectively. The purpose of this work was to develop an EAM potential for pure Co which is required to construct the EAM potentials for the CoAl and the CoNi binaries. These binaries with NiAl would constitute an EAM potential for the NiAlCo ternary system.

### 5.2 Methodology

The EAM method was employed to describe the interaction between the cobalt atoms. The detail of the theory is discussed in section 1.2 and elsewhere [28, 138–142].

The pair interaction term was formulated as the generalized Lenard-Jones type:

$$V(r) = \psi\left(\frac{r - r_c}{h}\right) \left[ \frac{V_0}{b_2 - b_1} \left( \frac{b_2}{z^{b_1}} - \frac{b_1}{z^{b_2}} \right) + \delta \right]$$

where $z = r/r_1$; $r_c$, $h$, $V_0$, $b_1$, $b_2$, $\delta$ and $r_1$ are the fitting parameters; $\psi(x)$ is the cutoff function defined in Eq. (4.2).

The empirical form of the electron density function was chosen to be

$$\rho(r) = \psi\left(\frac{r - r_c}{h}\right) \left[ A_0 z^y e^{-\gamma z} (1 + B_0 e^{-\gamma z}) + C_0 \right]$$

where $z = r - r_0$; $A_0$, $y$, $\gamma$, $B_0$, $C_0$ and $r_0$ are also the fitting parameters as well.

The total energy was expressed in a form resembling the Rose’s equation of state given in Eq. (1.6). The embedding function was obtained by inverting Eq. (1.3); therefore it effectively eliminated a search for a specific analytical form for the embedding energy function.

In this approach there are altogether 13 model parameters to be determined. The fitting algorithm was based on the simulated annealing with the modified downhill simplex method [174]. The experimental data of the $\epsilon$-Co in conjunction with the ab initio calculations, such as the lattice constants, elastic moduli, cohesive energy and vacancy formation energy were
used to fit the parameters. The energies of other alternate structures (metastable/unstable) either from the experiments or the first principle calculations were also included in the fit. Table 5.1 summarizes the fitting data.

The first principle LAPW calculations predicted total energy difference between the BCC and the FCC phases of the cobalt, $E_{\text{bcc}} - E_{\text{fcc}}$, to be 8.9 mRy/atom (0.12 eV) \[271\] which is much larger than 0.014 eV obtained by \[272\]. The BCC phase of the Co does not exist in the nature.

Table 5.1: Fitting database for Co. The entries marked by asterisks are only for comparison purpose and were not included in the actual fitting.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Property</th>
<th>Ab initio</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCP:</td>
<td>$E_c$ (eV/atom)</td>
<td>-4.72$^e$ -5.49$^f$ -3.66$^i$</td>
<td>-4.39$^a$</td>
</tr>
<tr>
<td></td>
<td>a (Å)</td>
<td>2.476$^f$</td>
<td>2.507$^b$</td>
</tr>
<tr>
<td></td>
<td>c (Å)</td>
<td>3.997$^f$</td>
<td>4.07$^a$</td>
</tr>
<tr>
<td></td>
<td>c/a</td>
<td>1.614$^f$ 1.642$^i$</td>
<td>1.623$^b$</td>
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<tr>
<td></td>
<td>B (GPa)</td>
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</tr>
<tr>
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<td>$c_{11}$ (GPa)</td>
<td>319.50$^c$</td>
<td></td>
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<tr>
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<td>166.09$^c$</td>
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<td>$E_f$ (eV)</td>
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</tr>
<tr>
<td>FCC:</td>
<td>$E_c$ (eV/atom)</td>
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</tr>
<tr>
<td>diamond:</td>
<td>$E_c$ (eV/atom)</td>
<td>-3.00$^k$</td>
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</tr>
</tbody>
</table>

$a$ Ref \[273\]; $b$ Ref \[274\]; $c$ Ref \[275\]; $d$ Ref \[276\]; $e$ Ref \[277\]
$f$ $E_{\text{bcc}} - E_{\text{hcp}} = 0.038$ eV (http://alloy.phys.cmu.edu)
$g$ Ref \[278\]; $h$ $E_{\text{bcc}} - E_{\text{fcc}} = 0.12$ eV (Ref \[271\])
$i$ $E_{\text{sc}} - E_{\text{bcc}} = 0.65$ eV (private communication)
$j$ $E_{\text{diamond}} - E_{\text{sc}} = 0.58$ eV (private communication)
$k$ $E_{\text{diamond}} - E_{\text{sc}} = 0.58$ eV (private communication)
$l$ Ref \[255\]
5.3 Results and discussions

The shape of the pair interaction function is illustrated in Fig. 5.1(a) with effective-pair format \[141\]. It is qualitatively similar to one obtained by Pasianot et al. \[265\]; both of them have positive humps but at different positions.

The atomic electron density as a function of distance is shown in Fig. 5.1(b) which effectively goes to zero at large distances beyond the cutoff distance, \( r_c \). The embedding energy as a function of host electron density, \( \bar{\rho} \), in the effective pair format is presented in Fig. 5.1(c). It has a very shallow minimum at \( \bar{\rho} = 1.0 \). Similarly, Fig. 5.1(d) illustrates the equation of state of the \( \epsilon \)-Co which goes smoothly to zero at and beyond the cutoff distance. It should be noted that the pair interaction and the embedding energy functions are plotted in the effective-pair format \[141\].

Table 5.2: Optimized values of the fitting parameters of the new EAM potential for the cobalt.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_c ) (Å)</td>
<td>0.6499539e+01</td>
</tr>
<tr>
<td>( h ) (Å)</td>
<td>0.1427612e+01</td>
</tr>
<tr>
<td>( V_0 ) (eV)</td>
<td>-0.6150127e+00</td>
</tr>
<tr>
<td>( r_1 ) (Å)</td>
<td>0.2436873e+01</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>0.1173323e+02</td>
</tr>
<tr>
<td>( b_2 )</td>
<td>0.3498429e+01</td>
</tr>
<tr>
<td>( \delta ) (eV)</td>
<td>-0.2618860e+01</td>
</tr>
<tr>
<td>( A_0 )</td>
<td>0.1274313e+02</td>
</tr>
<tr>
<td>( y )</td>
<td>0.1100594e+00</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>0.1913083e+01</td>
</tr>
<tr>
<td>( B_0 )</td>
<td>0.3585129e+01</td>
</tr>
<tr>
<td>( C_0 )</td>
<td>0.2050327e+01</td>
</tr>
<tr>
<td>( r_0 )</td>
<td>-0.2160589e+01</td>
</tr>
</tbody>
</table>
5.3.1 Structural stability

The cohesive energies of the selected structures of pure Co were computed during the fitting process and separately in order to get the correct relative stability. The results
Structural changes were not observed during the energy minimization of HCP, FCC, SC and A15 Co structures, which consisted of local displacements of atoms and variations of block sizes in all three directions by uniform deformation. However, the BCC structure transformed into the FCC with $c/a = \sqrt{2}$ under the same minimization scheme. The diamond structure was also found mechanically unstable.

Table 5.3: Lattice properties of stable, metastable and unstable phases of Co. For the references to the first principle and the experimental values refer to Table 5.1.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Property</th>
<th>Ab initio</th>
<th>Experiment</th>
<th>EAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCP</td>
<td>$E_{coh}$ (eV)</td>
<td>-4.72 -5.49 -3.66</td>
<td>-4.39</td>
<td>-4.3910</td>
</tr>
<tr>
<td></td>
<td>a (Å)</td>
<td>2.476</td>
<td>2.507</td>
<td>2.5187</td>
</tr>
<tr>
<td></td>
<td>$c/a$</td>
<td>1.614 1.642</td>
<td>1.623</td>
<td>1.6103</td>
</tr>
<tr>
<td>FCC</td>
<td>$E_{coh}$ (eV)</td>
<td>-4.35 -5.48 -3.79</td>
<td>-3.568</td>
<td>-4.3849</td>
</tr>
<tr>
<td></td>
<td>a (Å)</td>
<td>3.54 3.518a 3.548a</td>
<td>3.5447</td>
<td>3.5642</td>
</tr>
<tr>
<td>BCC</td>
<td>$E_{coh}$ (eV)</td>
<td>-4.23</td>
<td>-4.3273</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a (Å)</td>
<td>2.74</td>
<td>2.82</td>
<td>2.815</td>
</tr>
<tr>
<td>A15</td>
<td>$E_{coh}$ (eV)</td>
<td></td>
<td>-4.2271</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a (Å)</td>
<td></td>
<td>4.5481</td>
<td></td>
</tr>
<tr>
<td>SC</td>
<td>$E_{coh}$ (eV)</td>
<td>-3.58</td>
<td>-3.7608</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a (Å)</td>
<td></td>
<td>2.3711</td>
<td></td>
</tr>
<tr>
<td>diamond</td>
<td>$E_{coh}$ (eV)</td>
<td>-3.00</td>
<td>-2.7275</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a (Å)</td>
<td></td>
<td>5.3436</td>
<td></td>
</tr>
</tbody>
</table>

$a$ Ref [255]

The total energy difference between the $\alpha$-Co and the $\epsilon$-Co, $(E^{hcp} - E^{fcc})$, is -0.0061 eV/atom at 0 K with this potential (see Table 5.4) while the experiment has -0.004 eV/atom at the transition temperature 695 K [252] similar to [251]. Again this may be compared to -0.007 eV/atom obtained by Pasianot et al. with their EAM potential [265]. This indicates that the present potential correctly represents the relative phase stabilities of the $\alpha$-Co and the $\epsilon$-Co below the transition temperature. Despite significant differences in the total energies between the phases based on the first principles data the potential predicts the
correct ordering of their relative stabilities.

Table 5.4: Properties of the $\epsilon$-Co computed with the present EAM potential in comparison with the first principle calculations and the experiments.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ab initio</th>
<th>Experiment</th>
<th>EAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c$ (eV/atom)</td>
<td>-4.72$^a$ -5.49$^r$ -3.66$^r$</td>
<td>-4.39$^b$</td>
<td>-4.3910</td>
</tr>
<tr>
<td>a (Å)</td>
<td>2.476$^c$</td>
<td>2.507$^d$</td>
<td>2.5187</td>
</tr>
<tr>
<td>c/a</td>
<td>1.614$^c$ 1.642$^r$</td>
<td>1.623$^d$</td>
<td>1.6103</td>
</tr>
<tr>
<td>B (GPa)</td>
<td></td>
<td>191.4$^b$</td>
<td>195.06</td>
</tr>
<tr>
<td>$c_{11}$ (GPa)</td>
<td>331$^n$, 297$^n$</td>
<td>319.50$^c$, 293$^m$, 307.1$^p$</td>
<td>311.88</td>
</tr>
<tr>
<td>$c_{12}$ (GPa)</td>
<td>161$^n$, 131$^n$</td>
<td>166.09$^c$, 143$^m$, 165.0$^p$</td>
<td>146.93</td>
</tr>
<tr>
<td>$c_{13}$ (GPa)</td>
<td>104.0$^n$, 82$^n$</td>
<td>102.09$^c$, 90$m$, 102.7$^p$</td>
<td>119.63</td>
</tr>
<tr>
<td>$c_{33}$ (GPa)</td>
<td>369$^n$, 342$^n$</td>
<td>373.60$^c$, 339$m$, 358.1$^p$</td>
<td>359.41</td>
</tr>
<tr>
<td>$c_{44}$ (GPa)</td>
<td>94$^n$, 96$^n$</td>
<td>82.41$^e$, 78$m$, 75.5$^p$</td>
<td>91.74</td>
</tr>
<tr>
<td>$\gamma_s$ (0001) (mJ/m$^2$)</td>
<td>2132$^f$</td>
<td>2550$^g$</td>
<td>2315</td>
</tr>
<tr>
<td>$\gamma_{I_2}$ (mJ/m$^2$)</td>
<td></td>
<td>27$^l$</td>
<td>39.8</td>
</tr>
<tr>
<td>$E_{f}^i$ (eV)</td>
<td>1.38$^h$</td>
<td></td>
<td>1.49</td>
</tr>
<tr>
<td>$E_{m}^i$ (eV)</td>
<td></td>
<td></td>
<td>0.98</td>
</tr>
<tr>
<td>$T^{hcp\rightarrow fcc}$ (K)</td>
<td>690$^i$, 695$^k$, 700$^p$</td>
<td></td>
<td>808</td>
</tr>
<tr>
<td>$T_m$ (K)</td>
<td></td>
<td></td>
<td>1890</td>
</tr>
<tr>
<td>$\Delta H^{fcc\rightarrow hcp}$ (eV)</td>
<td>-0.038$^j$</td>
<td>-0.004$^k$, -0.0048$^q$</td>
<td>-0.0061</td>
</tr>
</tbody>
</table>

$a$ Ref [277]; $b$ Ref [273]; $c$ http://alloy.phys.cmu.edu; $d$ Ref [274]; $e$ Ref [275]
$f$ private communication; $g$ Ref [279, 280]; $h$ Ref [276]; $i$ Ref [13]
http://alloy.physics.cmu.edu; $l$ Ref [281]
$m$ Ref [257]; $n$ Ref [257, 259]; $p$ Ref [256]; $q$ Ref [251]; $r$ Ref [255]

The computed cohesive energies and lattice parameters are consistent with the experiments for the most of the structures where the experimental values are available (see Table 5.3). For the $\epsilon$-Co the c/a ratio is close to the ab initio value.

The relative structural stability between the HCP and the FCC phases at temperatures above 0 K was obtained by computing the Gibbs free energy (see Eq. (2.14)). In order to compute the free energy, the enthalpy must be known at the given temperature. To compute the enthalpy, two separate FCC and HCP simulation blocks were created each with 4000 atoms and dimensions 35.64 Å×35.64 Å×35.64 Å and 25.19 Å×43.62 Å×40.56 Å.
respectively. The blocks were annealed at the temperatures from 50 K to 1200 K for at least 0.15 ns at each temperature by running the MD simulations with the NPT ensemble (pressure being zero and variation of block sizes in all direction). The temperatures were increased in step of 50 K in 0.01 ns. For each annealing stage the potential energies were averaged. The enthalpy was computed from Eq. (2.11). The enthalpy difference between the α-Co and the ε-Co, $\Delta H(T)$ was calculated using Eq. (2.12). Further more, the relative change in the Gibbs free energy was obtained from Eq. (2.14).

![Plot of differences in the enthalpy, $\Delta H(T)$, and the Gibbs free energy, $\Delta G(T)$, between FCC Co and HCP Co. The solid and the dashed lines represent $\Delta G(T)$ and the fit to $\Delta H(T)$ respectively.](image)

Figure 5.2: Plot of differences in the enthalpy, $\Delta H(T)$, and the Gibbs free energy, $\Delta G(T)$, between FCC Co and HCP Co. The solid and the dashed lines represent $\Delta G(T)$ and the fit to $\Delta H(T)$ respectively.

Fig. 5.2 shows the computed differences of the enthalpies and the free energies between
the $\alpha$-Co and the $\epsilon$-Co from the MD simulations as described above and the harmonic calculations. The latter calculations were performed on two separate blocks of HCP and FCC Co of sizes $20\,\text{Å} \times 22\,\text{Å} \times 20\,\text{Å}$ and $20\,\text{Å} \times 18\,\text{Å} \times 26\,\text{Å}$ with 800 and 864 atoms respectively. The classical statistics for the thermodynamic functions were used with the full harmonic calculations. The points represent the actual calculations corresponding to the given temperatures. The solid and the dashed lines correspond to the $\Delta G(T)$ and the fit to the $\Delta H(T)$ respectively. The comparison between the computed and the fitted free energies is for $T_0=300\,\text{K}$. The plot clearly shows crossing of the free energy at $717\,\text{K}$ which is the HCP→FCC transition temperature; the experimental transition temperature is around $700\,\text{K}$ [13,251,252]. This is an indirect proof which corroborates the fact that the only phase observed experimentally above the transition temperature is the $\alpha$-Co phase. It should be noted that the transition temperature may vary with the reference temperature used in the calculation of the free energy. The current work reflects the variation of the transition temperature roughly by $3\,\text{K}$ per $100\,\text{K}$ change in the reference temperature, $T_0$, in the temperature interval of $100\,\text{K} – 500\,\text{K}$.

In another indirect observation of the existence of the high temperature $\alpha$-Co phase, a perfect single crystal of FCC Co of dimensions $35.64\,\text{Å} \times 178.2\,\text{Å} \times 35.64\,\text{Å}$ with 20000 atoms and free surfaces (block faces of type $\{100\}$) normal to the longest dimension was completely melted by running a MD simulation with the isotropic-$NPT$ ensemble. This necessary so that the system would forget its history of the crystal structure upon melting. Then the melt was annealed with the anisotropic-$NPT$ ensemble (block sizes change independently) to a lower temperature so as to allow it to crystallize fairly quick since homogeneous nucleation is very difficult at temperatures close to the melting temperature. The annealing temperature was arbitrarily chosen $1500\,\text{K}$ which must be far from the HCP-FCC phase transition temperature. Finally the melt crystallized to two grains and the underlying crystal structures were analyzed with the CNA (Common Neighbor Analysis) [179,180]. The structure analysis revealed mostly the FCC phase in the grains with some amount of stacking faults (see Fig. 5.3). Thus, the melt first crystallized to the FCC crystal, the high
temperature phase of the cobalt.

Figure 5.3: Typical snapshots after annealing at 1500 K from complete melt.

5.3.2 Elastic moduli

In this work, the elastic constants of single crystal $\epsilon$-Co, $\alpha$-Co and $\beta$-Co were computed and compared to the theory and the experiments. For the $\epsilon$-Co, the results are listed in the Table 5.4. The elastic moduli of the $\epsilon$-Co were calculated with supercell size of 108 atoms by uniform straining of the lattice along appropriate directions before relaxing it. The relaxation of the block is necessary in order to take into account the lattice internal degrees of freedom due to two atoms per lattice site. Our calculations show maximum
discrepancy of 17% corresponding to $c_{13}$ compared to the data in \[275\]. Except for the $c_{13}$ and $c_{44}$, the elastic moduli computed with the present EAM potential are in good agreement (relative error < 5\%) with the experiments and the first principle results. The reported bulk modulus was computed using the Voigt average which is given by the expression

$$B = \frac{2}{9} \left( c_{11} + c_{12} + 2c_{13} + \frac{1}{2}c_{33} \right).$$

Since the FCC phase is stable at high temperature until $T_m$, it is intuitive to reproduce at least some of the important properties of it such as cohesive energy, lattice parameter, elastic constants and energies of the selected $\gamma$ surfaces. The elastic constants of the $\alpha$-Co are summarized in the Table 5.5. They are within the experimental range \([261, 283, 284]\) except for the $c_{11}$ which was over estimated by the present EAM potential. In fact, they were not explicitly included in the fit but computed only for sanity checks. This step is necessary because the FCC and the HCP phases are stable at high and low temperatures respectively; the experimental phase transition temperature is around $\sim 700$ K \([10, 251, 252]\).

The elastic properties of the $\beta$-Co were also computed with the present potential and are presented in the Table 5.6. The present potential under estimates the $c_{11}$ while it over estimates the $c_{12}$ and the $c_{44}$ as compared to the experiments \([290]\). The results are consistent with the observed values. In fact, the experimental values are from measurements on thin films of the $\beta$-Co synthesized on the GaAs substrate \([254, 290, 292]\). The thickest sample was measured 357 Å thick \([254]\). The properties of the $\alpha$-Co and the $\beta$-Co reproduced by the current potential speak themselves of the validity of the potential.

### 5.3.3 Point and Planar defects

Single vacancy formation and migration energies were computed with the static relaxation and the NEB (Nudge Elastic Band) method respectively. The vacancy formation energy in the $\epsilon$-Co is in good agreement with the experiment \([277]\), which was used in the fit. Although the first principle and experimental values of the vacancy migration energy in the
Table 5.5: Properties of the $\alpha$-Co computed with the present EAM potential in comparison with the first principle calculations and the experiments.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ab initio</th>
<th>Experiment</th>
<th>EAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c$ (eV/atom)</td>
<td>-4.35$^a$</td>
<td>-5.48$^p$</td>
<td>-3.79$^p$</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td>a (Å)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{11}$ (GPa)</td>
<td>325$^n$</td>
<td>260$^f$</td>
<td>225$^j$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{12}$ (GPa)</td>
<td>189$^n$</td>
<td>160$^f$</td>
<td>160$^j$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{44}$ (GPa)</td>
<td>156$^n$</td>
<td>110$^f$</td>
<td>92$^j$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_f^p$ (eV)</td>
<td>2.34$^d$</td>
<td>1.71$^d$</td>
<td>1.34–1.91$^g$</td>
</tr>
<tr>
<td>$E_m^p$ (eV)</td>
<td>1.19$^d$</td>
<td>0.98$^d$</td>
<td>0.95</td>
</tr>
<tr>
<td>$\gamma_s$ (100) (mJ/m$^2$)</td>
<td>2473$^h$</td>
<td>2470</td>
<td></td>
</tr>
<tr>
<td>$\gamma_s$ (110) (mJ/m$^2$)</td>
<td>2515$^h$</td>
<td>2604</td>
<td></td>
</tr>
<tr>
<td>$\gamma_s$ (111) (mJ/m$^2$)</td>
<td>2073$^h$</td>
<td>2333</td>
<td></td>
</tr>
<tr>
<td>$T_m$ (K)</td>
<td>1770$^i$</td>
<td>1768$^i$</td>
<td>1898</td>
</tr>
</tbody>
</table>

$E_{fcc}$ - $E_{hcp}$ = 0.038 eV (http://alloy.phys.cmu.edu/)

Table 5.6: Properties of the $\beta$-Co computed with the present EAM potential in comparison with the first principle calculations and the experiments.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ab initio</th>
<th>Experiment</th>
<th>EAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c$ (eV/atom)</td>
<td>-4.23$^a$</td>
<td>-4.3273</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-4.3273</td>
</tr>
<tr>
<td>$E_{bcc}$ - $E_{fcc}$ (eV)</td>
<td>0.12$^b$</td>
<td>0.0576</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>2.74$^b$</td>
<td>2.82$^g$</td>
<td>2.82$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.82$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.82$^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.82$^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.82$^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.815</td>
</tr>
<tr>
<td>$c_{11}$ (GPa)</td>
<td>193$^g$</td>
<td>193$^d$</td>
<td>212$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>180</td>
</tr>
<tr>
<td>$c_{12}$ (GPa)</td>
<td>241$^g$</td>
<td>170$^d$</td>
<td>165$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>190</td>
</tr>
<tr>
<td>$c_{44}$ (GPa)</td>
<td>131$^g$</td>
<td>48$^d$</td>
<td>53$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>174</td>
</tr>
</tbody>
</table>

$E_{bcc}$ - $E_{fcc}$ = 0.12 eV (Ref [271]; $E_{m, hcp} = 0.98$ eV and $E_{m, fcc} = 0.95$ eV. The former is the vacancy migration energy along the basal plane. The formation energy of a vacancy in the $\alpha$-Co are unavailable until now, the order of magnitude is not unreasonable as compared to one computed for the $\alpha$-Co; $E_{m, hcp} = 0.98$ eV and $E_{m, fcc} = 0.95$ eV. The former is the vacancy migration energy along the basal plane. The formation energy of a vacancy in the
α-Co is 1.56 eV which is within the range of experimentally observed values 1.34–1.91 eV \cite{279, 280}. For the same phase, the migration energy of a vacancy is 0.95 eV which is consistent with the \textit{ab initio} results \cite{285}. The formation and the migration energies of a single vacancy in the α-Co as well as the migration energy of the vacancy in the ϵ-Co were not included in the fit. These results show good transferability of the current potential.

As an another test, we computed energies of some well known surfaces and planar defects in the ϵ-Co and the α-Co (see Tables 5.4 and 5.5). The surface energy of basal plane, $\gamma_S(0001)$, of the ϵ-Co is in good agreement with the first principle and the experimental data, although there are few data available to compare with.

The energy of an intrinsic stacking fault of type, $\gamma_{1/2}$, in the ϵ-Co is 40 mJ/m$^2$, which is consistent with the experimentally observed value of 27 mJ/m$^2$ \cite{281} (see Table 5.4) and very close to 41 mJ/m$^2$ computed by Pasianot \textit{et al}. \cite{265}. It is 64 mJ/m$^2$ with the FS type potential developed in \cite{268}. This is another example of the tests of the present potential.

### 5.3.4 Lattice dynamics

The potential was evaluated for phonon frequencies of the ϵ-Co and the α-Co, which were not included in the fit. The phonon dispersion relations in the ϵ-Co and the α-Co were computed along the high symmetry directions: [100], [110] and [001] at 0 K, which are elaborated in Figures 5.4 and 5.5 respectively. The phonon dispersion of the ϵ-Co is very similar to those reproduced by \cite{268, 293, 294} and in qualitative agreement with the experimentally observed phonon dispersion by the neutron scattering experiment \cite{295}. The optical branches as well as high frequencies are poorly reproduced as compared to the experiment. Similar discrepancy was also observed in the calculations using the tight binding potentials \cite{296}. In the case of the α-Co the discrepancies between the experiment and the calculated phonon frequencies are significant at higher frequencies. However, the reported experimental phonon frequencies belong to a crystal of Co$_{0.92}$Fe$_{0.08}$ at room temperature \cite{297}.

The thermal expansion factors of the ϵ-Co and the α-Co were computed from the block sizes generated as a by product of the \textit{NPT} MD simulations used to compute the enthalpy,
Figure 5.4: Phonon frequencies of the HCP Co computed with the present EAM potential.

Figure 5.5: Phonon frequencies of the α-Co computed with the present EAM potential. The points represent experimental values from [12] which is described in the previous Section 5.3.1. They are in reasonable agreement with the experiment [13] at 300 K and above, although the discrepancies become large for the a-axis of the ε-Co as the temperature increases and reaches the computed phase transition.
5.3.5 Melting temperature of the FCC phase

The melting temperature of the $\alpha$-Co was determined to check the transferability of the potential to high temperatures. The $\alpha$-Co simulation block containing 20,000 atoms with solid and liquid phases separated by (010) interface was employed. The block was obtained by melting a half of the initial single solid phase with surface (010). The initial dimensions were $36 \, \text{Å} \times 178 \, \text{Å} \times 36 \, \text{Å}$ with the interface plane (010) normal to the y-direction.

To compute the melting temperature, blocks with the solid and the liquid phases were put into mechanical equilibrium by running MD simulations with $NPT$ (constant number of
Figure 5.7: Temperature as a function of pressure obtained from the MD simulations using micro-canonical ensemble for the FCC Co.

species, constant temperature and zero pressure) ensemble at the approximate melting temperature, \( T_m \), with all periodic boundary conditions. Then the simulations were switched to the micro-canonical ensemble (\( NVE \)) so that the system quickly attains equilibrium temperature and pressure after some partial melting or crystallization. The melting temperature may be estimated by fitting linearly the temperatures as a function of pressures for different micro-canonical configurations wherein it is identified by the temperature at the zero pressure. This potential gives the melting temperature of 1899 K (Fig. 5.7) for the \( \alpha \)-Co. The tight-binding potential gave melting temperature of 1950 K (\( \alpha \)-Co) [296].

An attempt to estimate the melting temperature of the \( \epsilon \)-Co was unsuccessful due to instability of the phase at high temperatures close to the melting temperature of the \( \alpha \)
5.4 Discussion and conclusions

The cobalt potential developed in this work reproduces most common physical properties of the $\epsilon$-Co and the $\alpha$-Co phases despite fitting to few properties of $\epsilon$-Co and formation energies of some alternate stable and imaginary phases and structures (see Table 5.1). This was achieved by distributing fitting errors uniformly over the database as far as possible. None of the properties of the $\alpha$-Co were involved in the fitting database except the cohesive energy.

Although the potential was not fitted to the phonon frequencies of both the phases of the cobalt, the dispersion relations are in qualitative agreement with the \textit{ab initio} \cite{268,293,294,296} and the experiments \cite{295,297}. The high frequencies are over estimated which reflects a general trend of the EAM and the first principle calculations unless they are implicitly or explicitly fitted or incorporated to. This is a drawback of the potential and a consequence of having high frequencies compared to the experiments has not been able to link to other properties that were looked into. In other words, the degree of correlation between the phonon frequencies and other properties has not been determined yet.

The biggest challenge in the development of the potential was to establish the phase transition between the HCP and the FCC phases and reasonable transition temperature. The transition behavior cannot be implemented in the fitting procedure at least in this work; a work around is to generate several potentials that reproduce accurately the properties included in the fitting database and quickly test the phase transition by computing the difference of free energies between the HCP and the FCC phases at several temperatures close to the experimental transition temperature.

The cobalt as a single material does not have any technological relevance but it is one of the main constituents of many shape memory alloys. As such the development of accurate cobalt potential is the fundamental step towards the development of potentials for binary and ternary systems. Based on the properties which were looked into this work, the current
EAM cobalt potential is suitable for crossing with other elemental potentials to produce desired binary and ternary alloys.

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Chapter 6: EAM potential for Al-Co system

6.1 Introduction

Experimentally only five intermediate phases of Al-Co system have been identified (see Fig. 6.1). The phase diagram is strikingly similar to the phase diagram of Ni-Al system (see Fig. 4.3). Al$_9$Co$_2$ has monoclinic structure \[298, 299\] while Al$_{13}$Co$_4$ has an orthorhombic structure (space group, \(Pmn2_1\); Pearson’s symbol, oP102) \[300\]. The growth of single crystals of Al$_{13}$Co$_4$ have been reported by Gille et al. using Czochralski method \[301\]. The high temperature Al$_3$Co is a crystalline approximant of decagonal quasicrystal (space group, \(C2/m\) (No. 12)) \[173, 302-305\]. Al$_5$Co$_2$ has an ordered hexagonal structure, D$_{8h}$ \[298\].

The stoichiometric B$_2$-CoAl alloy has high melting temperature and maintains the B$_2$ type structure in a wide range of concentration around the stoichiometric composition similar to the B$_2$-NiAl alloy. The martensitic phase transformation have been experimentally observed in the CoAl ferromagnetic alloys \[247, 249\]. Atomistic simulation of fracture in B$_2$-CoAl \[306\] has been performed with the EAM potentials developed by Vailhé et al. \[307\]. It was observed that B$_2$-CoAl has the lowest fracture resistance among three transition-metal aluminides: NiAl, CoAl and FeAl at room temperature \[308\].

This work was a part of the bigger scheme to develop an EAM potential of the AlCoNi system. Here we did not attempt to simulate the martensitic transformation in B$_2$ type CoAl alloys.
6.2 Methodology

The EAM potentials of pure Al from [2] and pure Co developed in Chapter 5 were mixed to construct the EAM potential for the Al-Co binary system. As usual mixed pair interaction between Al and Co is expressed as a Morse function

\[ V_{AlCo} = \left\{ E_0 \left[ e^{-q_b_1(r-r_1)} - q e^{-b_1(r-r_1)} \right] + \delta \right\} \psi \left( \frac{r-r_c}{\delta} \right) \quad (6.1) \]

where \( \psi(x) \) is the cutoff function defined in Eq. [4.2].

Figure 6.1: Phase diagram of Al-Co ([14])
The fitting parameters are $E_0$, $q$, $b_1$, $r_1$, $r_c$ and $h$. The input potentials were subject to the following sets of invariant transformations from Eq. (1.8) and Eq. (1.9):

(i) \[
\begin{align*}
\rho_{Co}(r) &\rightarrow s_{Co}\rho_{Co}(r), \\
F_{Co}(\bar{p}) &\rightarrow F_{Co}(\bar{p}/s_{Co}),
\end{align*}
\]

and (ii) \[
\begin{align*}
F_{Co}(\bar{p}) &\rightarrow F_{Co}(\bar{p}) + g_{Co}\rho, \\
F_{Al}(\bar{p}) &\rightarrow F_{Al}(\bar{p}) + g_{Al}\rho, \\
V_{CoCo}(r) &\rightarrow V_{CoCo}(r) - 2g_{Co}\rho_{Co}(r), \\
V_{AlAl}(r) &\rightarrow V_{AlAl}(r) - 2g_{Al}\rho_{Al}(r),
\end{align*}
\]

where $s_{Co}$, $g_{Al}$ and $g_{Co}$ are additional fitting parameters.

### 6.3 Results and discussions

The mixed pair interaction was fitted to several properties of B2-AlCo such as lattice parameter, formation energy and elastic moduli as well as formation energies of imaginary phase Al$_2$Co with structures CaF$_2$ and MoSi$_2$. The fitting database is presented in Table 6.1. Optimized values of the fitting parameters are given in Table 6.2.

Fig. 6.2 shows the potential functions obtained in this work. The mixed pair interaction, $V_{AlCo}$, could not be compared with the mixed pair interaction obtained by Vailhé et al. [307] since the later was in the effective-pair format but they show some resemblances.

The properties of B2-AlCo were computed with the present EAM potential (see Table 6.3). The present potential is accurate enough to reproduce lattice properties such as lattice constant and elastic moduli. The current potential out performed the existing potential by Vailhé et al. [307] in terms of cohesive energy and elastic moduli compared to the experiment. The formation energy of B2-AlCo is lower by $\sim 0.07$ eV/atom compared to the experiment but matches with the ab initio calculation. Energies of planar defects and
Table 6.1: Fitting database for Al-Co system. The base phase is the B2-AlCo.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Property</th>
<th>Ab initio</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td>a (Å)</td>
<td>2.863\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_f$ (eV/atom)</td>
<td>-0.6292\textsuperscript{b}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B (GPa)</td>
<td>157\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c_{11}$ (GPa)</td>
<td>257\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c_{12}$ (GPa)</td>
<td>107\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c_{44}$ (GPa)</td>
<td>130\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>C1 (CaF$_2$)</td>
<td>$E_f$ (eV/atom)</td>
<td>-0.46\textsuperscript{d}</td>
<td>-0.46\textsuperscript{d}</td>
</tr>
<tr>
<td>C11\textsubscript{b} (MoSi$_2$)</td>
<td>$E_f$ (eV/atom)</td>
<td>-0.4380\textsuperscript{e}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Ref 288
\textsuperscript{b,c} [http://alloy.phys.cmu.edu]
\textsuperscript{d} Ref 309; \textsuperscript{e} Ref 251

Table 6.2: Optimized values of the fitting parameters used in the cross pair interaction, $V_{\text{AlCo}}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_c$ (Å)</td>
<td>0.6297150e+01</td>
</tr>
<tr>
<td>$h$ (Å)</td>
<td>0.1069744e+01</td>
</tr>
<tr>
<td>$E_0$ (eV)</td>
<td>0.2363113e+00</td>
</tr>
<tr>
<td>$r_1$ (Å)</td>
<td>0.2527272e+01</td>
</tr>
<tr>
<td>$b_1$ (Å$^{-1}$)</td>
<td>0.3349737e+01</td>
</tr>
<tr>
<td>$g$</td>
<td>0.1442378e+01</td>
</tr>
<tr>
<td>$\delta$ (eV)</td>
<td>-0.1479785e+00</td>
</tr>
<tr>
<td>$s_{\text{Al}}$</td>
<td>0.1000000e+01</td>
</tr>
<tr>
<td>$s_{\text{Co}}$</td>
<td>0.114459e+01</td>
</tr>
<tr>
<td>$g_{\text{Al}}$ (eV)</td>
<td>0.1142000e+01</td>
</tr>
<tr>
<td>$g_{\text{Co}}$ (eV)</td>
<td>0.2734415e+01</td>
</tr>
</tbody>
</table>

dilute heats of solution were also computed with the present potential but they could not be compared effectively because of lack of available data. The present potential predicted the melting temperature of B2-AlCo to 1816 K using the method described in Section 4.6, the relative error was within 1%.

The surface energies of low index planes computed with the current potential were higher
than those of the B2-NiAl and B2-CoAl by Vailhé \textit{et al.} but their order, $\gamma_s(110) < \gamma_s(100) < \gamma_s(111)$, was preserved. It should be noted that the 3$d$ transition-metal aluminides NiAl, CoAl and FeAl are strikingly similar in terms of structure and other properties.

![Graphs of pair interaction, electron density, embedding energy, and equation of state of B2-AlCo](image)

**Figure 6.2:** Plots of (a) pair interaction, (b) electron density, (c) embedding energy and (d) equation of state of B2-AlCo.(color online)

Fig. 6.3 shows the sections of $\gamma$-surfaces of B2-AlCo in comparison with the B2-NiAl
Table 6.3: Properties of B2-AlCo computed with the current EAM potential. The asterisks indicate unstable faults.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ab initio</th>
<th>Experiment</th>
<th>EAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>2.799&lt;sup&gt;a&lt;/sup&gt; 2.9197&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.865&lt;sup&gt;d&lt;/sup&gt; 2.565&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.7968</td>
</tr>
<tr>
<td></td>
<td>2.80&lt;sup&gt;c&lt;/sup&gt; 2.862&lt;sup&gt;i&lt;/sup&gt;</td>
<td>2.861&lt;sup&gt;d&lt;/sup&gt; 2.863&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>$E_{coh}$ (eV/atom)</td>
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<td>-4.45&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-4.5149</td>
</tr>
<tr>
<td>$E_f$ (eV/atom)</td>
<td>-0.6292&lt;sup&gt;f&lt;/sup&gt; -0.75&lt;sup&gt;j&lt;/sup&gt;</td>
<td>-0.572&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-0.6394</td>
</tr>
<tr>
<td>B (GPa)</td>
<td>204&lt;sup&gt;a&lt;/sup&gt; 151&lt;sup&gt;c&lt;/sup&gt;</td>
<td>154.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>157&lt;sup&gt;h&lt;/sup&gt; 211&lt;sup&gt;i&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{11}$ (GPa)</td>
<td>256.3&lt;sup&gt;i&lt;/sup&gt; 251&lt;sup&gt;e&lt;/sup&gt; 257&lt;sup&gt;h&lt;/sup&gt;</td>
<td>269.1&lt;sup&gt;i&lt;/sup&gt;</td>
<td>255.22</td>
</tr>
<tr>
<td>$c_{12}$ (GPa)</td>
<td>107.3&lt;sup&gt;i&lt;/sup&gt; 101&lt;sup&gt;e&lt;/sup&gt; 107&lt;sup&gt;h&lt;/sup&gt;</td>
<td>107.3&lt;sup&gt;i&lt;/sup&gt;</td>
<td>104.73</td>
</tr>
<tr>
<td>$c_{44}$ (GPa)</td>
<td>129.8&lt;sup&gt;i&lt;/sup&gt; 134&lt;sup&gt;e&lt;/sup&gt; 130&lt;sup&gt;h&lt;/sup&gt;</td>
<td>139.4&lt;sup&gt;i&lt;/sup&gt;</td>
<td>130.94</td>
</tr>
<tr>
<td>$\gamma_s$ (100) (Jm&lt;sup&gt;-2&lt;/sup&gt;)</td>
<td></td>
<td>2.9309</td>
<td></td>
</tr>
<tr>
<td>$\gamma_s$ (110) (Jm&lt;sup&gt;-2&lt;/sup&gt;)</td>
<td></td>
<td>2.8383</td>
<td></td>
</tr>
<tr>
<td>$\gamma_s$ (111) (Jm&lt;sup&gt;-2&lt;/sup&gt;)</td>
<td></td>
<td>3.1424</td>
<td></td>
</tr>
<tr>
<td>(110)APB (Jm&lt;sup&gt;-2&lt;/sup&gt;)</td>
<td>1.6&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td>1.91&lt;sup&gt;*&lt;/sup&gt;</td>
</tr>
<tr>
<td>(211)APB (Jm&lt;sup&gt;-2&lt;/sup&gt;)</td>
<td></td>
<td>1.92&lt;sup&gt;*&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>$T_m$ (K)</td>
<td>191&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
<td>1816</td>
</tr>
</tbody>
</table>

Heat of solution

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al in HCP Co (eV)</td>
<td>-1.6911</td>
</tr>
<tr>
<td>Al in FCC Co (eV)</td>
<td>-1.7234</td>
</tr>
<tr>
<td>HCP Co in Al (eV)</td>
<td>-0.3323</td>
</tr>
<tr>
<td>FCC Co in Al (eV)</td>
<td>-0.3384</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ref [310]; <sup>b</sup> Ref [311]; <sup>c</sup> Ref [312]; <sup>d</sup> Ref [313]
<sup>e</sup> Ref [288]; <sup>f</sup> [http://alloy.phys.cmu.edu]; <sup>g</sup> Ref [251] @ 298K
<sup>h</sup> Ref [309]; <sup>i</sup> Ref [307] and references therein; <sup>j</sup> Ref [314]
predicted by the EAM potential of Ni-Al system developed also in this work. Energies of (110) and (211) APBs in B2-AlCo are much higher than those in the B2-NiAl and are unstable faults.

Table 6.4 lists formation energies of some imaginary and experimentally observed phases with simple structures of AlCo binary system computed with the current potential. The phase stability is illustrated in Fig. 6.4. The thin red line represents the convex hull predicted by the \textit{ab initio} calculation \cite{15}. Based on Ögüt \textit{et al.} work the Al-rich phases Al\textsubscript{13}Co\textsubscript{4} and Al\textsubscript{5}Co\textsubscript{2} were found lower than other phases Al\textsubscript{12}Co, Al\textsubscript{5}Co\textsubscript{2} and Al\textsubscript{3}Co\textsubscript{2}. Among the later phases, Al\textsubscript{5}Co\textsubscript{2} was the lowest phase. The present potential predicted the phase Al\textsubscript{3}Co\textsubscript{2} (D\textsubscript{519}) lower than the phase Al\textsubscript{5}Co\textsubscript{2} (D\textsubscript{811}). This was anticipated since none of these phases were included in the potential fit. The Al\textsubscript{5}Co\textsubscript{2} (D\textsubscript{811}) phase is the stable phase observed experimentally as well as in the \textit{ab initio} calculations. Another discrepancy
is that both the imaginary phases Al$_2$Co and AlCo$_2$ of type C11b were below the present tie line (blue line). Although Hultgren [251] mentioned about the Al$_2$Co phase with formation energy -0.4596 eV/atom, independent verifications could not be found and it does not exist in the phase diagram either (see Fig. 6.1).

![Figure 6.4: Formation energy of imaginary or experimentally observed inter-metallic compounds of Al and Co. Thin red line represents the ab initio convex hull obtained in [15]. (color online)](image-url)
Table 6.4: Formation energies of imaginary and experimentally observed phases of inter-metallic compounds of Al and Co computed with the present EAM potential in comparison with \textit{ab initio} and experiment.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Lattice parameters (a,b,c)(\r{\text{Å}})</th>
<th>Ab initio</th>
<th>Exp.</th>
<th>EAM</th>
<th>Ab initio</th>
<th>Exp.</th>
<th>EAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCo</td>
<td>B2</td>
<td>2.799\textsuperscript{d} 2.9197\textsuperscript{b} 2.80\textsuperscript{a}</td>
<td>2.863\textsuperscript{f}</td>
<td>2.7968</td>
<td>-0.6292\textsuperscript{e} -0.57\textsuperscript{e} -0.6394</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>L1\textsubscript{0}</td>
<td>2.6012 3.6786\textsuperscript{b}</td>
<td>2.4064 3.4032</td>
<td>4.5961</td>
<td>0.1187</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al\textsubscript{3}Co</td>
<td>A15</td>
<td>4.8791\textsuperscript{b}</td>
<td>3.8725\textsuperscript{b}</td>
<td>3.8598</td>
<td>0.001182</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>D0\textsubscript{22}</td>
<td>3.8725 7.451\textsuperscript{b}</td>
<td>4.1671 5.8931</td>
<td>5.8931</td>
<td>-0.05211</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>L1\textsubscript{2}</td>
<td>3.8725\textsuperscript{b}</td>
<td>3.8598</td>
<td>0.001182</td>
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<td></td>
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<tr>
<td></td>
<td>D0\textsubscript{3}</td>
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<td>-0.05211</td>
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<tr>
<td></td>
<td>D0\textsubscript{11}</td>
<td>6.76720 7.35106 4.62465\textsuperscript{c}</td>
<td>6.39851 7.48566 4.7454</td>
<td>-0.4336\textsuperscript{e} -0.43\textsuperscript{e} -0.1646</td>
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<tr>
<td>Al\textsubscript{5}Co\textsubscript{2}</td>
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<td>7.6644 7.56566</td>
<td>7.6581 7.6044</td>
<td>8.023 7.2694</td>
<td>-0.374\textsuperscript{g} -0.43\textsuperscript{e} -0.202</td>
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</tr>
<tr>
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<td>7.6560 7.5932\textsuperscript{f}</td>
<td>-0.4834\textsuperscript{c}</td>
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</tr>
<tr>
<td>Al\textsubscript{2}Co</td>
<td>C1</td>
<td>5.4951\textsuperscript{b}</td>
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</tr>
<tr>
<td></td>
<td>MoSi\textsubscript{2}</td>
<td>3.04190 8.31063\textsuperscript{c}</td>
<td>2.7189 10.2627</td>
<td>-0.4380\textsuperscript{c} -0.4678</td>
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</tr>
<tr>
<td>Al\textsubscript{12}Co</td>
<td>Al\textsubscript{12}W</td>
<td>7.4580\textsuperscript{b} 7.486\textsuperscript{c}</td>
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<td>-0.0948\textsuperscript{c} 0.0305</td>
<td></td>
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</tr>
<tr>
<td>Al\textsubscript{3}Co\textsubscript{2}</td>
<td>D5\textsubscript{19}</td>
<td>4.0129 4.7593\textsuperscript{b}</td>
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<td>-0.4870\textsuperscript{c} -0.3567</td>
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<tr>
<td></td>
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<td></td>
<td>4.01456 4.86485\textsuperscript{c}</td>
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<td>AlCo\textsubscript{3}</td>
<td>A15</td>
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<td>4.4429</td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>L1\textsubscript{2}</td>
<td>3.3961</td>
<td>3.3961</td>
<td>-0.3010</td>
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<tr>
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<td>5.5718</td>
<td>-0.2521</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>D0\textsubscript{11}</td>
<td>6.1216 7.1449 4.1865</td>
<td>6.1216 7.1449 4.1865</td>
<td>-0.2295</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlCo\textsubscript{2}</td>
<td>C1</td>
<td>5.3549</td>
<td>5.3549</td>
<td>-0.1026</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MoSi\textsubscript{2}</td>
<td>2.9127 7.6272</td>
<td>2.9127 7.6272</td>
<td>-0.5174</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlCo\textsubscript{12}</td>
<td>Al\textsubscript{12}W</td>
<td>6.6927</td>
<td>6.6927</td>
<td>-0.02426</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al\textsubscript{2}Co\textsubscript{3}</td>
<td>D5\textsubscript{19}</td>
<td>3.8954 4.7747</td>
<td>3.8954 4.7747</td>
<td>-0.3233</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ref \[309,312\]; \textsuperscript{b}Ref \[311\]; \textsuperscript{c}Ref \[http://alloy.phys.cmu.edu\]; \textsuperscript{d}Ref \[310\]; \textsuperscript{e}Ref \[251\]; \textsuperscript{f}Ref \[288\]; \textsuperscript{g}Ref \[315\].
6.4 Conclusion

Properties of B2-CoAl predicted by the present potential were in good agreement with the *ab initio* and the experiments. The melting temperature was predicted within 1% of the experimental value. The planar defect energies and dilute heats of solutions could not be validated because of lack of *ab initio* or/and experimental data. In this work properties of constitutional defects \[310, 316, 317\] were not explored since the purpose of the potential was to develop the AlCoNi ternary potential in which the AlCo potential constitutes one set of required binary potentials and ultimately test for the martensitic phase transformation in B2 type alloys of AlCoNi.

The present EAM potential of AlCo is best suited for properties of stoichiometric B2-AlCo. In the future it might be interesting to calculate self-diffusion coefficient of Co in B2 type inter-metallic compound of Al and Co which was performed experimentally by Nakamura and Iijima \[318\] for several concentrations of Al around the stoichiometric composition using \(^{57}\)Co isotope. It can be also tested for defect concentrations and energies against correlation model proposed by Semenova *et al.* \[319\]. Further more it may be tested for Co antisite segregation in the CoAl(111) surface \[320\].

This work was supported by the National Aeronautics and Space Administration through the Langley Research Center (NRA # NNX08AC07A).
Chapter 7: EAM potential for Co-Ni system

7.1 Introduction

Co-Ni alloys are used in corrosion resistance applications and high temperature structures in aircrafts \(^{321,322}\). Co-Ni system has simple phase diagram \(^{16,278,323}\) which is shown in Figure 7.1. The martensitic transformation, FCC $\leftrightarrow$ HCP, occurs in Co-Ni alloys with less than 35 at.% Ni. The high temperature phase is $\alpha$-Co and the low temperature phase is $\epsilon$-Co. The transformation behavior under stress has been studied on single crystal Co-32 wt.% Ni alloy by Yang et al. \(^{55}\). They found that this type of transformation do not preserve shape memory effect since the induced strains were in the same direction of the applied stresses for both the forward (FCC $\rightarrow$ HCP) and the reverse (HCP $\rightarrow$ FCC) transformations. This is a potential drawback to its shape memory application.

The purpose of this work was to develop EAM potential for Co-Ni binary system in view of completing EAM potential for Al-Co-Ni ternary system.

7.2 Methodology

The EAM potentials for Ni-Al and Al-Co binary systems have been developed in the previous works (see chapters 4 and 5). The original electron density of pure Ni was fixed and only the electron density of pure Al was scaled during the fitting of the Ni-Al binary potential. Likewise, the electron density of pure Co was scaled but fixed the electron density of pure Al in the Al-Co potential. Since the aluminum is common to both the systems, the ratio of scaling factors of the electron densities of pure Ni and pure Co is constrained to

$$
\frac{s_{Ni}}{s_{Co}} = k_1 k_2,
$$

(7.1)
which is illustrated in Figure 7.2. This reduces the number of fitting parameters by one.

The mixed pair interaction is represented by a Morse function,

\[
V_{\text{CoNi}} = \left\{ E_0 \left[ e^{-q b_1 (r-r_1)} - q e^{-b_1 (r-r_1)} \right] + \delta \right\} \psi \left( \frac{r - r_c}{h} \right) \quad (7.2)
\]

where \( \psi(x) \) is the cutoff function defined in Eq. (4.2).

\( E_0, q, b_1, r_1, r_c \) and \( h \) are fitting parameters. The input functions were subject to the
following sets of invariant transformations from Eq. (1.8) and Eq. (1.9):

\[
\begin{align*}
\text{(i)} & \quad \rho_{Ni}(r) \rightarrow s_{Ni} \rho_{Ni}(r), \\
& \quad F_{Ni}(\bar{p}) \rightarrow F_{Ni}(\bar{p}/s_{Ni}), \\
& \quad F_{Co}(\bar{p}) \rightarrow F_{Co}(\bar{p}) + g_{Co} \bar{p}, \\
\text{and (ii)} & \quad V_{NiNi}(r) \rightarrow V_{NiNi}(r) - 2g_{Ni} \rho_{Ni}(r), \\
& \quad V_{CoCo}(r) \rightarrow V_{CoCo}(r) - 2g_{Co} \rho_{Co}(r),
\end{align*}
\]

where \( g_{Al} \) and \( g_{Ni} \) are additional fitting parameters. Since the electron density of pure Co was not scaled \( (s_{Co} = 1.0) \), the electron density of pure Ni had to be scaled by a factor, \( k_1 k_2 = 0.6816253 \), according to Eq. (7.1) and was kept constant.


7.3 Results and discussions

The pair interaction was fitted to a number of imaginary phases and structures (see Table 7.2). Figure 7.3 shows optimized potential functions which are not in the effective-pair format. It should be noted that these functions are based on current values of  \( s_{Ni} \),  \( g_{Al} \) and  \( g_{Ni} \) which are listed in Table 7.1 in addition to other fitting parameters.

Table 7.1: Optimized values of the fitting parameters used in the cross pair interaction,  \( V_{CoNi} \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_c (\text{Å}) )</td>
<td>0.6295825e+01</td>
</tr>
<tr>
<td>( h (\text{Å}) )</td>
<td>0.3381617e+00</td>
</tr>
<tr>
<td>( E_0 (\text{eV}) )</td>
<td>0.1813642e+00</td>
</tr>
<tr>
<td>( r_1 (\text{Å}) )</td>
<td>0.2829389e+01</td>
</tr>
<tr>
<td>( b_1 (\text{Å}^{-1}) )</td>
<td>0.2123638e+01</td>
</tr>
<tr>
<td>( q )</td>
<td>0.1590563e+01</td>
</tr>
<tr>
<td>( \delta (\text{eV}) )</td>
<td>-0.3593848e-01</td>
</tr>
<tr>
<td>( s_{Ni} )</td>
<td>0.6816253e+00</td>
</tr>
<tr>
<td>( g_{Co} (\text{eV}) )</td>
<td>0.1664360e+00</td>
</tr>
<tr>
<td>( g_{Ni} (\text{eV}) )</td>
<td>0.9293709e-01</td>
</tr>
</tbody>
</table>

Table 7.2 summarizes lattice properties of some imaginary phases of Co-Ni binary system computed with the present EAM potential. The relaxed formation energies were computed using Eq. (2.15). The lattice parameters and the formation energies are in reasonable agreement with the *ab initio* even though the lattice parameters were not included in the potential fit.

Several versions of Co-Ni potentials were generated and indirectly tested for an imaginary phase Al\(_8\)Co\(_4\)Ni\(_4\) (Al\(_2\)CoNi.cF16) \( \text{[http://alloy.phys.cmu.edu](http://alloy.phys.cmu.edu)} \). It has an ordered cubic structure with lattice parameter 5.73519 Å and formation energy -0.6188 eV/atom. The present EAM potential gives the lattice parameter 5.69473 Å and the formation energy -0.63886 eV/atom of this phase.

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Figure 7.3: Plots of functions of (a) pair interaction, (b) electron density, (c) embedding energy and (d) typical equation of state of L1\textsubscript{2}-Co\textsubscript{3}Ni.(color online)

### 7.4 EAM potential for Al-Co-Ni system

The EAM potential for Al-Co-Ni system was constructed by applying appropriate reverse transformations of type Eq. (1.8) and Eq. (1.9) on Ni-Al, Al-Co and Co-Ni potential functions. The original transformation parameters are listed in Table 7.3 for each binary group.
Table 7.2: Lattice properties of some imaginary phases and structures obtained with the present EAM potential in comparison with \textit{ab initio} (http://alloy.phys.cmu.edu). The data marked with asterisks were used in the potential fit.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Lattice parameter (a,c) Å</th>
<th>Formation energy (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ab initio</td>
<td>EAM</td>
</tr>
<tr>
<td>CoNi</td>
<td>B1</td>
<td>5.04267</td>
<td>4.91311</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>2.79175</td>
<td>2.92241</td>
</tr>
<tr>
<td></td>
<td>HCP</td>
<td>2.47514 4.03298</td>
<td>2.43983 4.3795</td>
</tr>
<tr>
<td></td>
<td>L1\textsubscript{0}</td>
<td>3.56891 3.46130</td>
<td>3.69074 3.58706</td>
</tr>
<tr>
<td>CoNi\textsubscript{3}</td>
<td>L1\textsubscript{2}</td>
<td>3.49765</td>
<td>3.60925</td>
</tr>
<tr>
<td>Co\textsubscript{3}Ni</td>
<td>L1\textsubscript{2}</td>
<td>3.49699*</td>
<td>3.62163</td>
</tr>
</tbody>
</table>

In the potential fit we applied Eq. (1.8) first then Eq. (1.9). Therefore in order to get the original functions we need to apply the steps in reverse order with signs of $g$s reversed.

Table 7.3: Transformation parameters (original) in Ni-Al, Al-Co and Co-Ni systems as obtained from the fits.

<table>
<thead>
<tr>
<th>Ni-Al</th>
<th>Al-Co</th>
<th>Co-Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_{Ni} = 1.0$</td>
<td>$s_{Al} = 1.2819$</td>
<td>$s_{Co} = 1.0$</td>
</tr>
<tr>
<td>$s_{Al} = 1.0$</td>
<td>$s_{Co} = 1.144459$</td>
<td>$s_{Ni} = 0.6816253$</td>
</tr>
<tr>
<td>$g_{Ni} = 0.3055408$</td>
<td>$g_{Al} = 1.142$</td>
<td>$g_{Co} = 0.1664360$</td>
</tr>
<tr>
<td>$g_{Al} = -0.2576234$</td>
<td>$g_{Co} = 2.734415$</td>
<td>$g_{Ni} = -0.09293709$</td>
</tr>
</tbody>
</table>

The following transformation steps were required to achieve meaningful construction of the ternary EAM potential.

1. In the Ni-Al and the Al-Co potentials Al is common. Thus the potential functions of pure Al had to be made identical in both the groups as well as the electron density of Ni from the Ni-Al group must be scaled accordingly. In the Ni-Al group the following
steps would do this:

STEP 1

\[
\begin{align*}
F_{Al}(\bar{p}) & \to F_{Al}(\bar{p}) + g'_{Al}\bar{p} \\
V_{AlAl}(r) & \to V_{AlAl}(r) - 2g'_{Al}\rho_{Al}(r) \\
V_{NiAl}(r) & \to V_{NiAl}(r) - g'_{Al}\rho_{Ni}(r) - g'_{Ni}\rho_{Al}(r)
\end{align*}
\]

STEP 2

\[
\begin{align*}
\rho_{Al}(r) & \to s'_{Al}\rho_{Al}(r) \\
F_{Al}(\bar{p}) & \to F_{Al}(\bar{p}/s'_{Al}) \\
\rho_{Ni}(r) & \to s'_{Ni}\rho_{Al}(r) \\
F_{Ni}(\bar{p}) & \to F_{Ni}(\bar{p}/s'_{Ni})
\end{align*}
\]

where \( s'_{Al} = s'_{Ni} = 1/s_{Al} \), \( g'_{Al} = -g_{Al} \) and \( g'_{Ni} = 0 \) should be from the same group.

2. The following transformations were sufficient for the Al-Co functions:

STEP 1

\[
\begin{align*}
F_{Al}(\bar{p}) & \to F_{Al}(\bar{p}) + g'_{Al}\bar{p} \\
V_{AlAl}(r) & \to V_{AlAl}(r) - 2g'_{Al}\rho_{Al}(r) \\
V_{AlCo}(r) & \to V_{AlCo}(r) - g'_{Al}\rho_{Co}(r) - g'_{Co}\rho_{Al}(r)
\end{align*}
\]

where \( g'_{Al} = -g_{Al} \) and \( g'_{Co} = 0 \).

3. In the Co-Ni potential, the potential functions were transformed to match the potential functions of Ni and Co in the Ni-Al and the Al-Co potentials respectively. This
required the following transformations:

\[
\begin{align*}
\text{STEP 1} & \quad \begin{cases} 
F_{Ni}(\bar{p}) & \rightarrow F_{Ni}(\bar{p}) + g'_{Ni}\bar{p} \\
F_{Co}(\bar{p}) & \rightarrow F_{Co}(\bar{p}) + g'_{Co}\bar{p}
\end{cases} \\
& \quad \begin{cases} 
\rho_{Ni}(r) & \rightarrow s_{Co}^{AlCo} \rho_{Ni}(r), \\
\rho_{Co}(r) & \rightarrow s_{Co}^{AlCo} \rho_{Co}(r), \\
F_{Ni}(\bar{p}) & \rightarrow F_{Ni}(\bar{p}/s_{Co}^{AlCo}), \\
F_{Co}(\bar{p}) & \rightarrow F_{Co}(\bar{p}/s_{Co}^{AlCo}),
\end{cases}
\end{align*}
\]

\[
\begin{align*}
\text{STEP 2} & \quad \begin{cases} 
F_{Ni}(\bar{p}) & \rightarrow F_{Ni}(\bar{p}) + g''_{Ni}\bar{p}, \\
F_{Co}(\bar{p}) & \rightarrow F_{Co}(\bar{p}) + g_{Co}^{AlCo}\bar{p}, \\
V_{NiNi}(r) & \rightarrow V_{NiNi}(r) - 2g''_{Ni} \rho_{Ni}(r), \\
V_{CoCo}(r) & \rightarrow V_{CoCo}(r) - 2g_{Co}^{AlCo} \rho_{Co}(r), \\
V_{CoNi}(r) & \rightarrow V_{CoNi}(r) - g_{Co}^{AlCo} \rho_{Ni}(r) - g''_{Ni} \rho_{Co}(r).
\end{cases}
\end{align*}
\]

where \( g'_{Ni} = -g_{Ni} \) and \( g'_{Co} = -g_{Co} \); \( s_{Co}^{AlCo} \) and \( g_{Co}^{AlCo} \) are \( s_{Co} \) and \( g_{Co} \) respectively from the Al-Co potential. We found that \( g''_{Ni} \) should be equal to the product of \( g_{Ni} \) and \( s_{Al} \) from the Ni-Al potential.

Figure 7.4 shows all the pair interaction functions from the EAM potential of Al-Co-Ni ternary system after all these transformations. They are well behaved analytical functions within the range of interest. Similarly the electron density and the embedding functions of Al, Co and Ni are shown in Fig. 7.5.
Figure 7.4: Plot of pair interaction energy as a function of distance between a pair of atoms for all pairs in the Al-Co-Ni system obtained from the fit. (color online)
Figure 7.5: Plots of (a) electron density functions and (b) embedding functions of Al, Co and Ni. (color online)
7.5 Conclusions

The EAM potential for the Co-Ni system was constructed by fitting to the formation energies of few imaginary phases and structures. The formation energies and the lattice constants are in reasonable agreement with the first principle data even though the lattice constants were not included in the fit except for L12:Co3Ni. Finally, the EAM potential of Al-Co-Ni ternary system was constructed by transforming the potential functions from the Ni-Al, Al-Co and Co-Ni binary potentials with the help of the invariant transformations. The present Co-Ni potential may be tested for the martensitic phase transformation in the range of 0 at.% to 35 at.% of Ni (see Fig. 7.1).

This work was supported by the National Aeronautics and Space Administration through the Langley Research Center (NRA # NNX08AC07A).
Chapter 8: Computer simulation of martensitic phase transformation in Ni$_x$Al$_{1-x}$ alloys

8.1 Introduction

NiAl alloys are technologically important materials due to their high strength and oxidation resistance at high temperatures. In addition, NiAl alloys display the shape-memory effect due to a martensitic phase transformation from the cubic B2 structure (CsCl prototype) at high temperatures to a tetragonal L1$_0$ structure (CuAu prototype) at low temperatures. This transformation is experimentally observed only in Ni-rich compositions Ni$_x$Al$_{1-x}$ with $x = 0.62 - 0.69$.

Several authors applied molecular dynamics (MD) and Monte Carlo simulations to study mechanisms of the martensitic transformation in NiAl, see for example [38–40, 42–44, 324]. These studies have demonstrated the reversibility of the transformation, the temperature hysteresis and the effect of applied stresses. They have also revealed a strong effect of free surfaces, grain boundaries, dislocations and other elements of microstructure on the phase nucleation and growth during the transformation. It is known, however, that reliability of atomistic simulations depends on accuracy of semi-empirical interatomic potentials used in the simulations [141]. We developed an accurate and reliable interatomic potential for the Ni-Al system based on a large database of experimental as well as first-principles data [152] (see Chapter 4). Although the potential reproduces the phase stability behavior across the Ni-Al system, it has not been tested for the ability to reproduce the martensitic transformation in NiAl.

The goal of this work is to demonstrate that the potential of [152] reproduces the martensitic transformation in NiAl, and to perform a systematic study of the effect of chemical composition and applied uniaxial stresses on the transformation temperatures. We also
verify the formation of twinned martensite, including martensite plates, and demonstrate
the effect of lattice defects on the transformation temperature due to heterogeneous phase
nucleation in defected regions.

8.2 Methodology

Atomic interactions in the Ni-Al system were modeled with the embedded-atom potential
developed in [152]. The potential was fitted to a set of experimental and \textit{ab initio} data for
B2-NiAl and formation energies of several alternate crystalline structures with the NiAl,
Ni$_3$Al and NiAl$_3$ compositions. The potential accurately reproduces a number of physical
properties of B2-NiAl and L1$_2$-Ni$_3$Al that were not used during the fitting process, including
phonon frequencies, surface energies, stacking fault energies, thermal expansion and melting
temperatures of the phases.

The starting configuration of our simulations was a rectangular block containing per-
fectly stoichiometric B2-NiAl with periodic boundary conditions in all directions. The block
contained 6000 atoms and had the crystallographic directions [110], [1$\bar{1}$0] and [001] aligned
parallel to the $x$, $y$ and $z$ coordinate axes, respectively. To produce off-stoichiometric
samples, the initial block was subject to semi-grand canonical off-lattice Monte Carlo sim-
ulations at 1200 K with zero-stress boundary conditions in all directions. By adjusting
the imposed chemical potential difference between Ni and Al, several equilibrium Ni-rich
compositions were created. From the set of snapshots saved during the Monte Carlo sim-
ulations, samples with the following chemical compositions were selected for subsequent
MD simulations: 50.02, 60.00, 62.50, 65.08, 66.96 and 69.50 at.% Ni. For brevity, these
samples will be referred to as Ni50, Ni60, Ni63, Ni65, Ni67 and Ni69, respectively. Note
that this sample preparation procedure captures the long-range as well as short-range order
in the austenitic phase, by contrast to the random distribution of extra Ni atoms on the Al
sub-lattice implemented in previous studies [37, 39, 40, 42, 324, 325].

Our MD simulations employed the IMD code [176, 177] implementing various boundary
conditions and statistical ensembles. The integration step was 2 femtoseconds. To study the
effect of temperature and stress on the transformation, we applied all-periodic boundary conditions and the $NPT$ ensemble imposing a fixed temperature and fixed stresses $\sigma_{ii}$ in directions of the coordinate axes. The initial configuration of the MD simulations was taken directly from the Monte Carlo simulations at 1200 K. This configuration was thermally equilibrated by a short MD run at 1200 K, cooled down to 0 K, and then heated up back to 1200 K. The heating and cooling rates were constant and equal to $10^{11} \text{K/s}$. During the heating-cooling cycle, a uniaxial tension or compression in the [001] direction was applied by imposing a constant stress $\sigma_{zz} \neq 0$ with $\sigma_{xx} = \sigma_{yy} = 0$. In several cases, more complex heating-cooling-loading protocols were used as will be discussed below. To test the effect of crystalline defects on the transformation, the 6000 atom block was multiplied in all directions to create a larger block containing up to 384,000 atoms. Defects were introduced in this large block and appropriate modifications of the boundary conditions were made (Section 8.3.3). The structures formed during the phase transformations were examined using visualization techniques based on common-neighbor analysis.

## 8.3 Simulation results

### 8.3.1 Bain path calculations

Before simulating the phase transformation directly, we found it useful to compute the energy along the so-called volume-relaxed Bain path between the austenite and martensite for different alloy compositions. To this end, a snapshot with an appropriate chemical composition was taken from the Monte Carlo simulations at 1200 K and quickly (within a few tens of picoseconds) cooled down to 0 K. During the cooling process, the volume of the simulation block was allowed to vary by isotropic compression or expansion while preserving the cubic shape of the block. The fixed cubic shape prevented the transformation from happening, resulting in single-crystalline B2 structure with the chosen chemical composition. The block was then deformed by small increments of either tension or compression in the [001] direction. After each increment of deformation, the block was relaxed by an $NPT$
MD run for 4 picoseconds at 10 K. During the relaxation, the volume was allowed to vary to achieve zero hydrostatic stress whereas the $c/a$ ratio remained fixed.

![Diagram](image)

Figure 8.1: Energy as a function of tetragonality ratio $c/a$ along the Bain path for several compositions of NiAl alloys. The energy is plotted relative to perfectly stoichiometric B2-NiAl ($c/a = 1$). The alloy compositions (atomic % of Ni) are shown in the legend.

Fig. 8.1 shows the average energy per atom plotted as a function of $c/a$ for six chemical compositions. For clarity, the energies are plotted relative to stoichiometric B2-NiAl ($c/a = 1$) at 0 K. The stoichiometric composition shows a single energy minimum at $c/a = 1$. As Ni concentration increases, the minimum becomes increasingly more shallow and the curve develops shoulders of either side of the B2 structure. For the Ni65 composition, the right shoulder transforms to a very shallow minimum at $c/a \approx 1.22$, signifying the formation of a metastable tetragonal structure halfway between the ideal B2 and ideal L1$_0$ structures. In the Ni67 and Ni69 alloys, the B2 structure becomes unstable (the energy has a maximum at $c/a = 1$ instead of a minimum) while two minima appear at $c/a \approx 0.92$ and $c/a \approx 1.25$.  

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the latter minimum being deeper than the former. Examination of the relaxed crystal structures reveals that the right-hand side minimum corresponds to a single-crystalline tetragonal phase. Although the tetragonality is smaller than the ideal $\sqrt{2}$, this non-ideal structure will be referred to for brevity as L1$_0$ or L1$_0$-type. The minimum on the left-hand side results from the formation of twinned L1$_0$ structure under uniaxial compression. Thus, this minimum does not represent a new phase.

The Bain path calculations displayed in Fig. 8.1 allow us to make the following predictions: (i) For compositions around 65%Ni and higher, B2-NiAl can form an L1$_0$-type martensitic structure under a sufficiently high tensile strain applied in the [001] direction. (ii) B2 compositions with 67%Ni and higher are mechanically unstable at 0 K; in the absence of imposed constraints, they must spontaneously transform to L1$_0$ martensite. (iii) If compression is applied in the [001] direction, the martensite is likely to form a twinned structure. These predictions will be tested by direct MD simulations below.

8.3.2 Uniaxial stress-induced martensitic transformation

Fig. 8.2 demonstrates typical temperature dependencies of the block dimensions and energy during the cooling and heating of the 67%Ni alloy under tension. During the cooling, all three dimensions suddenly change and the energy drops at a temperature of about 240 K. This temperature can be identified as the martensitic transformation point. During the continued cooling the block dimensions and energy continue to vary slowly until we reach 0 K. At the martensitic transformation point, the block size $L_z$ in the tensile direction abruptly increases by approximately 12% whereas the sizes in the perpendicular directions, $L_x$ and $L_y$, decrease by about 6%. This tetragonal deformation is consistent with the $c/a$ ratio of approximately 1.2 in the martensitic structure. Upon subsequent heating of the simulation block, its dimensions and energy retrace their cooling values and vary smoothly until about 490 K when they begin to change very rapidly. When the temperature reaches 500 K, which can be identified as the austenite-finish temperature, the block dimensions and energy recover their values on the cooling branch and stay on it as the heating continues.
The behavior of the block dimensions and energy shown in Fig. 8.2 clearly demonstrates (i) the existence of a hysteresis and (ii) full reversibility of the martensitic transformation. A similar behavior was observed for all other chemical compositions and tensile loads studied in this work. In some cases, the cooling did not produce a martensitic transformation and the austenite structure remained stable at 0 K.

To quantify the phase transformation temperatures, the rates of change of one of the block dimensions during the heating and cooling were computed numerically. When a transformation occurred, this rate displayed a sharp peak in the temperature interval of the
transformation. This peak was fitted by a Gaussian function with an adjustable position $T^*$, height $H$ and half-width $s$. The temperatures $T^* - 2s$ for cooling and $T^* + 2s$ for heating were taken as the $M_s$ and $A_f$ points, respectively. The magnitude of $2s$ was typically about 10 to 15 K.

The computed $M_s$ and $A_f$ temperatures are plotted as functions of stress in Fig. 8.3. As the magnitude of stress increases, both temperatures increase for both tension and compression. Simultaneously, the temperature hysteresis narrows until $M_s$ and $A_f$ merge into a single transformation temperature at high stresses. Note that the $M_s$ branches computed under tension and compression do not join at zero stress. Instead, the curves reach $T = 0$ at a positive and negative stresses, respectively. Thus, for the chosen chemical compositions and under the simulation constraints existing in this study (such as the relatively small block size and high cooling rate), the martensitic transformation was not observed during stress-free cooling of periodic simulation blocks. It was only observed when the magnitude of the applied stress reached a certain value. For the Ni65, Ni67 and Ni69 compositions, the martensitic structure produced by cooling under sufficiently high stresses remained stable after the stress was removed at 0 K.

The stability of stress-free martensite but inability to produce it directly by stress-free cooling can be explained by the existence of a significant energy barrier between the phases and by constraints imposed by the boundary conditions of the simulation block. The barrier of homogeneous nucleation cannot be overcome by thermal fluctuations at low temperatures, resulting in quenched austenite. The applied stresses reduce the barrier and assist the austenite in overcoming it. Once the martensite has formed, it remains stable even without stress. In such cases, the reverse (austenitic) transformation was readily observed by heating the martensite with or without stresses. This explains why the tensile and compressive branches of the computed $A_f$ values join at zero stress (Fig. 8.3).

By contrast, for the Ni63 composition, the martensite formed under stress was found to spontaneously transform back to austenite when the stress was removed at 0K. This shows mechanical instability of unstressed martensite at low Ni concentrations, which is in
Figure 8.3: Calculated martensite-start ($M_s$, □) and austenite-finish ($A_f$, ▽) temperatures as functions of applied stress for different chemical compositions of NiAl alloys. The vertical dotted line is the zero-stress marker. For the Ni$_{0.69}$Al$_{0.31}$ composition, the plot includes $M_s$ values for simulation blocks containing a free surface, an anti-phase boundary and a dislocation dipole.

agreement with our predictions based on the Bain path calculations (Section 8.3.1). As a consequence, there is a certain range of stresses around zero in which neither $M_s$ nor $A_f$
could be determined for the Ni63 composition.

Another interesting observation is that the martensite obtained under tension and compression has different structures and forms by different mechanisms. Tension produces a single-variant L1₀ structure with the c-axis aligned along the tensile direction [001]. The transformation occurs by homogeneous tetragonal distortion of the austenite along the Bain path. By contrast, compression always results in a twinned structure composed of two crystallographic variants of L1₀ (see example in Fig. 8.4). The twin boundary planes were found to be parallel to (110)\textsubscript{B₂} in some samples and (1\overline{1}0)\textsubscript{B₂} in others. Both orientations are equivalent by crystal symmetry and one of them is chosen by the system at random. By comparing atomic positions before and after the transformation, it was evident that the twinned structure formed by deformation and modulated shear displacements (shuffling) of parallel \{110\}\textsubscript{B₂} planes.

Figure 8.4: Twinned martensite obtained by cooling the Ni\textsubscript{0.65}Al\textsubscript{0.35} alloy under a compressive stress of 700 MPa. The visualization is based on common-neighbor analysis and reveals twin boundaries as yellow atomic layers. The Miller indices are given relative to austenite.
It is interesting to examine the crystallographic orientation across twin boundaries. It is expected that the angle between the former \{100\} planes of austenite on either side of the twin boundary must deviate from \(90^\circ\). This is explained in the schematic diagram of twin formation shown in Fig. 8.5(a). Two crystallographic variants of martensite form out of cubic austenite by tetragonal distortion \((c/a > 1)\) in different \(\langle100\rangle\) directions. In order to form a twin boundary on a \{110\} plane, these variants must rotate towards this plane by equal angles \(\alpha/2\) and close the gap of vacuum. Due to this rotation, the angle between the \{100\} planes becomes \(\beta = 90^\circ + \alpha\), i.e. larger than \(90^\circ\). Specifically,

\[
\beta = 180^\circ - \arctan \frac{a}{c}.
\]

Fig. 8.5(b) shows an example of a twin boundary in a Ni65 sample. Using the measured angle \(\beta = 101.3^\circ\) and solving Eq. (8.1) for the tetragonality ratio gives \(c/a = 1.22\). This number is in excellent agreement with the Bain path calculations (see Section 8.3.1 and Fig. 8.1). Similar measurements on other twin boundaries give equally encouraging agreement.

### 8.3.3 Effects of crystalline defects on the transformation

In order to assess the possible effect of open surfaces on the transformation, simulations were performed by cooling large Ni65 and Ni69 austenite samples with \{110\} surfaces exposed to vacuum. The simulation blocks contained approximately \(10^5\) atoms and were cooled at the same rate as the 6000-atom blocks discussed previously.

Fig. 8.6 shows an example of martensitic structure formed in a Ni65 sample containing 384,000 atoms. Two important features are observed. First, while unstressed austenite does not undergo a martensitic transformation in a periodic block (cf. Fig. 8.3(b)), it does clearly display a transformation in a stress-free block with an open surface. Furthermore, the transformation is initiated at the surface and propagates in the normal direction by rapid migration of a plane austenite/martensite interface. This observation confirms that, in a defect-free material, the transformation can be delayed or even suppressed by a large
Austenite (cubic)

Martensite (tetragonal)

Variant 1

Twin boundary

Variant 2

α

β

Figure 8.5: (a) Schematic showing (from top to bottom) the formation of twinned martensite. The cubic austenite forms two crystallographic variants of tetragonal martensite, which then join along a \{110\} plane to form a twin boundary. To close the gap of vacuum, the variants must rotate by an angle $\alpha$. As a result of this rotation, the former \{100\} planes of austenite make an angle $\beta$ larger than 90°. (b) Projected view of the twinned structure presented in Figure 8.4 showing the angle $\beta = 101.3^\circ$.

barrier of homogeneous nucleation. By contrast, heterogeneous nucleation at a free surface lowers the barrier and enables the transformation on the timescale of MD simulations.

Second, while the martensite formed in relatively small blocks contains only two crystallographic variants and one set of twin boundaries, simulations in larger blocks produce multiple domains (plates) of twinned martensite. The set of domains shown in Fig. 8.6 comprises all three possible variants and all six possible twin-boundary orientations. This demonstrates the significant effect of the system size on the microstructure formed during atomistic simulations of martensitic transformations. Other examples and discussions of this effect can be found in [39,40,42,326].

We have also performed simulations by introducing a [001] dislocation dipole or a \{110\}
anti-phase boundary in a large block with periodic boundaries. In both cases, the martensitic transformation occurred during stress-free cooling of the austenite. The martensitic phase nucleated in the dislocation core region or at the anti-phase boundary, confirming again the predominance of heterogeneous nucleation. The respective $M_s$ temperatures for the Ni69 composition are shown in Fig. 8.3(d). Note that a stress-free transformation was not observed in defect-free blocks with this composition.
8.4 Conclusions

This work demonstrates that the embedded-atom potential developed in [152] is very suitable for atomistic simulations of the martensitic transformation in NiAl and can be used in future work. We have applied this potential for a systematic study of the effect of chemical composition and uniaxial stresses on the transformation temperatures $M_s$ and $A_f$ (Fig. 8.3). It has been shown that the stresses narrow the hysteresis loop $A_f - M_s$ and can close it under sufficiently high tension or compression. At a fixed stress, decreasing the Ni concentration reduces both $M_s$ and $A_f$ and eventually suppresses the transformation.

We find that the martensite typically has a twinned structure with a high density of twin boundaries. This structure effectively accommodates the large transformation strain by alternating the shear directions from one twin to the next. The twinned regions form plates and other types of domains that further reduce the strain energy. The relation between the twin formation and the transformation strain is further confirmed by the excellent agreement between the $c/a$ ratio in the martensite and the plane misorientation angles across the twin boundaries (Fig. 8.5).

We observe that the microstructure formed as a result of the transformation is influenced by existing crystalline defects. Such defects serve as martensite nucleation sites and tend to reduce the transformation temperatures and stresses in comparison with defect-free material. The heterogeneous nucleation mechanism explains why we do not see the transformation in defect-free simulation blocks unless a sufficiently high stress is applied, even when stress-free martensite is more stable than austenite. Real experimental samples contain defects, internal stresses, and are likely to have a significant variability of local chemical composition. These factors favor the martensitic transformation. This can explain why this transformation is observed experimentally even in 62% Ni alloys, whereas observations of this transformation in atomistic simulations require larger Ni concentrations or significant stresses.

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Chapter 9: Computer simulation of martensitic phase transformation in $\text{Al}_x\text{Co}_y\text{Ni}_{1-x-y}$ alloys

9.1 Introduction

Shape memory alloys (SMA) have gained importance and application in the last decades because of their ability to change size and shape under external influences. Ni-Co-Al exhibits both thermal and magnetic shape memory effects. It has high martensitic phase transformation (MPT) temperature and good ductility. The shape memory effect can be thermally or mechanically induced. Alloy compositions from $x=35$ at.% to $x=39$ at.% in $\text{Al}_{29}\text{Co}_x\text{Ni}_{71-x}$ were studied by Meyer et al. [53] and Chatterjee et al. [64]. Scheerbaum et al. [58] investigated the MPT for several different alloy compositions: $\text{Al}_{27.0}\text{Co}_{37.8}\text{Ni}_{35.2}$, $\text{Al}_{28.0}\text{Co}_{39.5-x}\text{Ni}_{32.5+x}$ and $\text{Al}_{27.0}\text{Co}_{39.5-x}\text{Ni}_{33.5+x}$ ($x=0,0.5,1.0,1.5,2.0$ at.%). In addition to these experiments other investigations into the MPT are listed in Table 9.2.

9.2 Simulation setup

B2-NiAl block of 6000 atoms was used to run MC simulations at 1700 K in order to obtain the desired compositions of Al, Co and Ni. The crystallographic directions of the block axes: [1T0], [110] and [001] were orientated along x, y and z directions of the coordinate system respectively. The dimensions of the initial block were 40.05 Å by 40.05 Å by 42.48 Å. Three different alloys $\text{Al}_{33}\text{Co}_{33}\text{Ni}_{34}$, $\text{Al}_{33}\text{Co}_{38}\text{Ni}_{39}$ and $\text{Al}_{28}\text{Co}_{36}\text{Ni}_{36}$ were prepared with actual compositions $\{32.96 \text{ Al}, 33.17 \text{ Co}, 33.87 \text{ Ni}\}$, $\{32.95 \text{ Al}, 27.85 \text{ Co}, 39.20 \text{ Ni}\}$ and $\{28.15 \text{ Al}, 36.03 \text{ Co}, 35.82 \text{ Ni}\}$ (numbers in at.%) respectively using MC simulation. The MC simulations were run for at least 50,000 MC steps excluding 1000 MC steps for equilibration. The alloys were annealed at 1700K before cooling down to 0 K and heating back to 1700 K.
with the rate of $2.5 \times 10^{11} \text{ K/s}$ using MD simulation with the npt-axial ensemble. Uniaxial tensile and compressive stresses at a given temperature were also applied to the same simulation blocks along the z-direction, [001] with the rate of $0.5 \times 10^9 \text{ GPa/s}$.

### 9.2.1 Results and discussions

Figure 9.1 demonstrates a typical temperature dependencies of block dimensions and energy during the cooling and heating processes in a large Al$_{33}$Co$_{33}$Ni$_{34}$ alloy with 384000 atoms. It was clear that the transitions were instantaneous and they exhibited significant hysteresis and the reversibility of the martensitic transformation. The martensite was found heavily twinned (see Figure 9.2). The strains are approximately 3.5%, 2.0% and 5.8% for box sizes along x, y and z respectively which are consistent with the strain (up to 4.3%) reported by Canadinc et al. [62] in a single crystal alloy Al$_{27.4}$Co$_{41.4}$Ni$_{31.2}$ although the compositions were different. Similar strain was observed in single crystals of Al$_{29}$Co$_{38}$Ni$_{33}$ alloy [53] and Al$_{27}$Co$_{41}$Ni$_{32}$ [166]. The martensitic phase transformation was simulated with and without mechanical loading in three different alloys Al$_{33}$Co$_{33}$Ni$_{34}$, Al$_{33}$Co$_{28}$Ni$_{39}$ and Al$_{28}$Co$_{36}$Ni$_{36}$. Twinning was found to be the primary mechanism of the MPT in all alloys we studied as observed in single crystal Ni-Mn-Ga magnetic shape memory alloys by Chmielus et al. [164]. The martensite start temperatures were estimated which are summarized in Table 9.1. For the same ~33 at.% aluminum composition the results indicate that increase in cobalt concentration decreased the transformation temperatures with and without small uniaxial stresses. This finding is qualitatively consistent with the experiments (see Table 9.2 and [61] not included in the table). This fact is even supported by completely different alloys of Co-Ni-Ga where increase in cobalt concentration decreased the transformation temperatures at constant composition of gallium. In an another direction, the work of Tanaka et al. [59] revealed that the slight change in aluminum composition in Al-Co-Ni alloy resulted into almost constant transformation temperatures. It should be noted that the transformation temperatures depend on rate of cooling and heating.

The dependencies of the martensitic phase transformation temperatures ($M_s$ and $A_f$)
on the applied stresses are illustrated in Figures 9.3, 9.4 and 9.5. The dotted lines in the figures represent boundaries of instability of the austenite phase and they have minima. In other words the austenite phase is unstable out side the dotted line. The points on the left of the minimum (with respect to temperature) on the dotted line are the twin martensite (TM) start temperatures and those on the right are the single variant martensite (SVM) start temperatures. The martensitic phase transformation temperatures below stress free $M_s$ and closer to the minima were obtained by cooling the samples at constant stresses. Higher the cobalt composition deeper is the minimum.

Table 9.1: Martensite start temperature ($M_s$) for three different alloy compositions with and without loading.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Actual composition (at. %)</th>
<th>$M_s$ (K) (no stress)</th>
<th>$M_s$ (K) (small tension)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Al_{33}Co_{33}Ni_{34}$</td>
<td>32.96 33.17 33.87</td>
<td>260</td>
<td>115</td>
</tr>
<tr>
<td>$Al_{33}Co_{28}Ni_{39}$</td>
<td>32.95 27.85 39.20</td>
<td>415</td>
<td>345</td>
</tr>
<tr>
<td>$Al_{28}Co_{36}Ni_{36}$</td>
<td>28.15 36.03 35.82</td>
<td>855</td>
<td>835</td>
</tr>
</tbody>
</table>
Figure 9.1: Typical hysteresis of martensitic phase transformation in the $\text{Al}_{33}\text{Co}_{33}\text{Ni}_{34}$ alloy with 384000 atoms. Red and Blue represent heating and cooling processes between temperature range of 0 K and 1700 K respectively under zero stress. (color online)
Figure 9.2: Typical example of twin martensites (3D) in the \textit{Al}_{33}\textit{Co}_{33}\textit{Ni}_{34} alloy with 384000 atoms. (color online)
Figure 9.3: Transformation temperatures as a function of applied stresses in Al$_{33}$Co$_{33}$Ni$_{34}$ alloy. TM and SVM are twin-martensite and single variant martensite respectively. (color online)
Figure 9.4: Transformation temperatures as a function of applied stresses in Al$_{33}$Co$_{28}$Ni$_{39}$ alloy. TM and SVM are twin-martensite and single variant martensite respectively. (color online)
Figure 9.5: Transformation temperatures as a function of applied stresses in Al$_{28}$Co$_{36}$Ni$_{36}$ alloy. TM and SVM are twin-martensite and single variant martensite respectively. (color online)
Table 9.2: Experimental martensitic phase transformation in Al$_{x}$Co$_{y}$Ni$_{1-x-y}$ alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Loading</th>
<th>Transformation temperatures (K)</th>
<th>Slope (MPa/K)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$<em>{37.6}$Co$</em>{32.9}$Ni$_{29.5}$</td>
<td>compress.</td>
<td>230 216 230 247 2.47</td>
<td></td>
<td>polycrystalline; annealed @1623K</td>
</tr>
<tr>
<td>Al$<em>{27.4}$Co$</em>{41.4}$Ni$_{31.2}$</td>
<td>compress.</td>
<td>163 – – – 1.7</td>
<td></td>
<td>along [001]; single crystal; annealed @1623K</td>
</tr>
<tr>
<td></td>
<td>compress.</td>
<td>188 – – – 1.3</td>
<td></td>
<td>along [110]; single crystal; annealed @1623K</td>
</tr>
<tr>
<td>Al$<em>{29}$Co$</em>{x}$Ni$_{71-x}$</td>
<td>–</td>
<td>96(x=39) to 270(x=35)</td>
<td></td>
<td>x = 35 to 39; polycrystalline; annealed @1473K</td>
</tr>
<tr>
<td>AlCo$<em>{1.28}$Ni$</em>{1.17}$</td>
<td>–</td>
<td>175 119 – 202 –</td>
<td></td>
<td>polycrystalline; annealed @1473K; Resistivity measurement;</td>
</tr>
<tr>
<td>Al$<em>{27.0}$Co$</em>{37.8}$Ni$_{35.2}$</td>
<td>–</td>
<td>263 – 293 – –</td>
<td></td>
<td>bulk annealed @1573 K; DSC measurement;</td>
</tr>
<tr>
<td>Al$<em>{28.0}$Co$</em>{39.5-x}$Ni$_{32.5+x}$</td>
<td>–</td>
<td>213(x=0) to 233(x=0) to 293(x=2)</td>
<td>–</td>
<td>x=0,0.5,1.0,1.5,2.0 at%; particles annealed @1573 K; SQUID measurement;</td>
</tr>
<tr>
<td>Al$<em>{27.0}$Co$</em>{39.5-x}$Ni$_{33.5+x}$</td>
<td>–</td>
<td>193(x=0) to 293(x=0) to ≥363(x=2)</td>
<td>–</td>
<td>x=0,0.5,1.0,1.5,2.0 at%; bulk annealed @1573 K; SQUID measurement;</td>
</tr>
</tbody>
</table>

1 Ref [51]; 2 Ref [62]; 3 Ref [64]; 4 Ref [53]; 5 Ref [63]; 6 Ref [58]
9.3 Conclusions

The martensitic transformations were successfully demonstrated in three different alloys of Al-Co-Ni: $\text{Al}_{33}\text{Co}_{33}\text{Ni}_{34}$, $\text{Al}_{33}\text{Co}_{28}\text{Ni}_{39}$ and $\text{Al}_{28}\text{Co}_{36}\text{Ni}_{36}$. The observed strains from the hysteresis were consistent with the experiments. The results partially supported the fact that the increase in cobalt composition decreases the transformation temperatures at constant aluminum composition. This indicates that cobalt is the effective tuning factor for the transformation temperatures. The martensites under compressions and small tensions were always heavily twinned. Under uniaxial tension the martensites were always single variant.

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Chapter 10: Summary and future plans

This work consists of three parts related to dislocation, construction of potentials and martensitic phase transformation. They are unified by the same atomistic methodology and emphasis on defects, in particularly dislocations, in material processes and the martensitic phase transformation.

Dislocation diffusion is important because it can control or affect many material processes such as creep, mechanical alloying, sintering, coarsening, phase transformation, segregation, dynamic strain aging and many others. It is well known that almost all rate equations and growth kinetics involve diffusion coefficient as one of the model parameters. Its measurement is expensive, difficult and tedious. Direct measurements are more accurate than indirect measurements but they involve radioisotopes which are not readily available and are subjects of nuclear safety. Only few laboratories around the world are involved in such experiments nowadays.

We performed atomistic simulation of dislocation diffusion over the wide range of temperatures in aluminum with the pure screw and the pure edge dislocations of $\frac{1}{2}[110]$ type. Overall, self-diffusion in the screw dislocation was found to be much faster than in the edge dislocation. The activation energies of screw and edge dislocations were 0.68 eV and 1.19 eV respectively, which bracket the experimental value 0.85 eV from the low temperature void shrinkage method [5]. The newly discovered intrinsic mechanism and the vacancy mechanisms were found to be dominant over the interstitial mechanism in the screw dislocation. In fact the interstitial diffusion in the screw dislocation is negligible. In the edge dislocation, the diffusion by the intrinsic mechanism was insignificant compared to the other two mechanisms at 925 K and below.

The simulations revealed that the dislocation core can act as a sink and a source of Frenkel defects at high temperatures. Our results clearly indicate that the dislocation
diffusion depends on the type of dislocations. With all these results we demonstrated that the dislocation diffusion in metals can be computed using computer simulations. However, it should be noted that the interatomic potential used in the simulations must be accurate enough to avoid artifacts.

An interesting topic of future research would be to compare these results with dislocation diffusion in a low stacking fault energy metal such as copper. If the existence of the intrinsic diffusivity is confirmed as a generic effect, it might motivate a revision of the current understanding of the role of point defects in atomic transport along dislocations. Furthermore, this would warrant a re-examination of the models of materials processes that rely on the assumption of vacancy-mediated diffusion, particularly models that invoke changes in dislocation diffusion as a result of vacancy over- or under-saturation in the material.

We have successfully developed new EAM potentials for pure Co, NiAl, CoAl and CoNi systems. Together with the pure Ni and pure Al potentials, this constitutes a version of an EAM potential for the AlCoNi ternary system. Without this work it would have been impossible to demonstrate phase transformations in NiAl and AlCoNi alloys. The interaction of atoms is a key of any atomistic simulation. There are very few reliable interatomic potentials for metallic systems. Potentials for ternary systems are especially rare and require a lot of effort and time to develop.

The present EAM potential for the Ni-Al system is a major improvement over the previous potentials [1,2]. It accurately reproduces many properties of B2-NiAl and L12-Ni3Al. It is highly transferable. However, it did not produce the martensitic phase transformation in the Ni-rich Ni_xAl_{1-x} alloys for \( x = 0.62 - 0.69 \) at.\% under a thermal cycle without stresses. Therefore, the martensitic transformation was investigated in Ni50, Ni60, Ni63, Ni65, Ni67 and Ni69 Ni-rich alloys under uniaxial loading in \( \langle 100 \rangle \) direction. The effects of free surfaces, anti-phase boundary and dislocation dipole on the martensitic transformation temperatures were studied in the Ni69 alloy. Only Ni63, Ni65, Ni67 and Ni69 Ni-rich alloys showed reversible martensitic transformation under uniaxial stresses.
Another advantage of the new Ni-Al potential is that it includes well-established potentials for pure Al \cite{23} and Ni \cite{2}. This makes the potential well suited for simulations of heterophase interfaces or mechanical behavior of two-phase alloys that include the terminal solutions based on either Ni or Al. For example, it can be used for studies of the $\gamma/\gamma'$ system as a model of Ni-based superalloys. As another example, we are currently working on certain applications that involve B2-NiAl nano-particles embedded in Al matrix. The new potential should be suitable for simulations of mechanical behavior of such systems.

We have developed an accurate EAM potential for HCP cobalt which reproduces lattice properties of not only HCP but FCC and BCC structures. The properties of FCC and BCC structures were not included in the potential fit except for their formation energies. The transformation, HCP $\leftrightarrow$ FCC, was verified after the development of the potential through the change in Gibbs free energies of the structures. This potential may be used to construct other binary potentials involving cobalt.

The present EAM potential of B2-CoAl accurately reproduces a number of properties such as lattice constant, formation energy, bulk modulus, and elastic moduli in good agreement with \textit{ab initio} data. The potential may be tested for the martensitic transformation since B2 type alloys of CoAl and NiAl have qualitatively similar phase diagrams and other properties. Simulation of the martensitic transformation has not been done for CoAl alloys to date. This potential, along with pure Co and Al potentials can constitute one ingredient of other ternary systems in the future.

The EAM potential for CoNi system was constructed in order to complete the potential for the AlCoNi ternary system. It was tested against the lattice constant and the formation energy of an imaginary phase Al$_8$Co$_4$Ni$_4$ (Al$_2$CoNi.cF16) and the result was in good agreement with the \textit{ab initio} data \url{http://alloy.phys.cmu.edu}. In the future it can be tested for the MPT which occurs in alloys with Ni compositions from 0 at.% to 35 at.% (see Fig. 7.1).

We have investigated the martensitic transformations in three different alloys Al$_{33}$Co$_{33}$Ni$_{34}$, Al$_{33}$Co$_{28}$Ni$_{39}$ and Al$_{28}$Co$_{36}$Ni$_{36}$ using computer simulations with the new EAM potential.
of AlCoNi system developed in this work. They were subjected to thermal cycles at zero stress as well as uniaxial stress cycles at constant temperatures. The martensites were heavily twinned under uniaxial compressions and small tensions with cooling. Single variant martensites were observed under uniaxial tensions. We found that at constant aluminum composition, the martensitic temperature, $M_s$ decreases with the increase in cobalt composition, the trend observed in experiments.

A systematic study of phase transformations in AlCoNi alloys using computer simulation has not been done to date. This ternary potential may be used for a further study of the martensitic transformations in other ranges of alloy compositions. It can be also used to compute mechanical properties such as strength and ductility as a function of alloy compositions, which limit applications of these ternary alloys.
Bibliography
Bibliography


Curriculum Vitae

Ganga Prasad Purja Pun was born in 1968 in Doba, Nepal. He earned a M.Sc. degree in general physics from Tribhuvan University, Nepal in 1995. He taught at Kathmandu Valley Boarding High School in Kathmandu, Nepal, for a year and worked as a part time lecturer at three colleges in Kathmandu. He also earned a M.S. degree from Minnesota State University, Mankato, with a thesis in physics in 2003. The title of the thesis was “Characterization of Silicon Nitride thin films prepared with Mirrortron Sputtering (MTS)”. He worked as a graduate teaching assistant during his master program in physics at Minnesota State University, Mankato.

He enrolled in PhD program in physics at George Mason University, Fairfax, Virginia in 2004. He was also employed as a graduate research assistant there under supervision of Dr. Yuri Mishin for little more than 6 years.

He published the following papers during his research as a graduate student at George Mason University, Fairfax:


In addition, he attended some major conferences:

- TMS 2010 in Seattle, WA.
- TMS 2009 in San Francisco, CA.
- MS&T 2008 in Pittsburgh, PA.