DISLOCATION SLIP AND TWINNING STRESS IN SHAPE MEMORY ALLOYS -
THEORY AND EXPERIMENTS

BY

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DISSENTATION

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Abstract

Slip and twinning are two important deformation mechanisms governing Shape Memory Alloys (SMAs) plasticity, which results in affecting their pseudoelasticity and shape memory performance. Precisely determining Peierls stress in dislocation slip and critical twin nucleation stress in twinning is essential to facilitate the design of new transforming alloys. This thesis presents an advanced energetic approach to investigate the attributes of phase transformation, slip and twinning in SMAs utilizing Density Functional Theory based ab initio calculations, and the role of energy barrier is characterized. Through different length scales incorporating atomistic simulations into dislocation-based mechanics, an extended Peierls-Nabarro (P-N) model is developed to establish flow stresses in SMAs and the predicted Peierls stresses are in excellent agreement with experiments. In addition, a twin nucleation model based on P-N formulation is proposed to determine the critical twin nucleation stresses in SMAs, and the validity of the model is confirmed by determining twinning stresses from experiments.

The first part of the thesis presents an energetic approach to comprehend a better understanding of phase stability, martensitic transformation path and dislocation slip in SMAs utilizing first principle simulations. In particular, we discovered energy barriers in transformation path from austenite B2 to martensite B19' and B33 of NiTi, and studied phase stability of B19' and B33 under effect of hydrostatic pressure. The results provide a more authoritative explanation regarding the discrepancy between the experimental observations and theoretical studies. In addition, we calculated energy barriers associated with martensitic transformation from austenite L2₁ to modulated martensite 10M of Ni₂FeGa incorporating shear and shuffle and slip resistance in [111] direction as well as in [001] direction of austenite L2₁. The results show that the unstable stacking fault energy barriers for slip by far exceeded the transformation transition state barrier permitting transformation to occur with little irreversibility. This explains the experimentally observed low martensitic transformation stress and high reversible strain in Ni₂FeGa. Furthermore, we established the energetic pathway and calculated the theoretical shear strength of several slip systems in B2 NiTi. The results show the smallest and second smallest energy barriers and theoretical shear strength for the (011)[100] and the (011)[1\bar{1}1] cases, respectively, which are consistent with the experimental observations. This study presents a
quantitative understanding of plastic deformation mechanism in B2 NiTi, and the methodology can be applied for consideration of a better understanding of SMAs.

In the second part of the thesis, we developed an extended P-N model to precisely predict dislocation slip stress in SMAs utilizing atomistic simulations and mesomechanics. We validated our model by conducting experiments and the results show that this model provides precise and rapid results compared to traditional experiments. This extended P-N model with Generalized Stacking Fault Energy curves provides an excellent basis for a theoretical study of the dislocation structure and operative slip modes, and an understanding to discovery of new compositions avoiding the trial-by-trial approach in SMAs. Further, we developed a twin nucleation model based on the P-N formulation to precisely predict twin nucleation stress in SMAs. We classified different twin modes that are operative in different crystal structures and developed a methodology by establishing the Generalized Planar Fault Energy to predict the twinning stress. This new model provides a science-based understanding of the twin stress for developing SMAs.
To my wonderful family
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Chapter 1 Introduction

1.1 Background

Compared to regular metals, shape memory alloys (SMAs) exhibit large deformations and remember their original shape upon unloading; thus SMAs are similar to rubber but have alloy properties [1]. Given this, SMAs have invaluable applications in numerous industries, ranging from actuators and sensors, vibration control systems, medical devices, and aerospace systems [2]. However, because the fundamental behavior of SMAs is not fully understood and the engineering aspects of these materials are accordingly in flux, the application of SMAs is therefore limited in industries and academia. Designing new SMAs that exhibit superior transformation characteristics remains a growing challenge due to: (1) phase change involving complex transformation paths, such that the energy barrier levels corresponding to the transition are not well established; and (2) dislocation slip and twinning, the important plastic deformation mechanisms, limit the transformation strains in SMAs.

In this thesis, we present an energetic methodology to comprehend a better understanding of phase transformation, energy landscape associated with dislocation slip and twinning in SMAs. Based on the accurate prediction of energies, we extended the Peierls-Nabarro (P-N) formulation with atomistic simulations to determine the slip stress, and developed a twin nucleation model based on P-N formulation to predict twin nucleation stress in SMAs. These new models provide a precise, rapid and inexpensive approach to predict the slip and twin stress in SMAs, which can be used to better understand and design new SMAs.

1.1.1 Phase transformation in SMAs-the Ni$_2$FeGa example

SMAs have two phases with different crystal structures and therefore different properties [3, 4]. One is the high temperature phase called austenite and the other is the low temperature phase called martensite. Austenite has a crystal structure with a high symmetry (generally cubic);
while martensite has a crystal structure with a low symmetry (tetragonal, orthorhombic, monoclinic and modulated monoclinic). Generally, the transformation from austenite to martensite and vice versa occurs by shear lattice distortion, not by diffusion of atoms [2, 5]. There are two approaches to induce the phase transformation from austenite (parent phase) to martensite (product phase) and vice versa. The first one is the stress-induced phase transformation, which leads to strain generation during loading and subsequent strain recovery upon unloading at temperatures above $A_f$ ($A_f$ is the austenite finish temperature, so the transformation starts from the stable austenite). This SMAs behaviour is called pseudoelasticity and will be described in details later using $Ni_2FeGa$ as an example. The second approach to induce the phase transformation is called thermally induced phase transformation [2]. When the material at austenite is cooled below the $M_f$ ($M_f$ is the martensite finish temperature) in the absence of an applied load, the crystal structure changes from austenite to martensite, which is termed the forward transformation. When the material at martensite is heated above the $A_f$, the crystal structure changes from martensite to austenite, which is termed the reverse transformation [2, 3, 6]. In this thesis, we focus on the stress-induced transformation and study the deformation associated with the dislocation slip and twin.

The $Ni_2FeGa$ alloys are new class of SMAs and have received recent attention because of high transformation strains and potential for magnetic actuation [7]. These alloys are proposed to be a good alternative to the currently studied ferromagnetic SMAs, $Ni_2MnGa$, due to their superior ductility in tension and transformation strains exceeding 10% [8, 9]. According to the experiments reported by researchers [8, 10, 11], there are several crystal structures identified in $Ni_2FeGa$, which exhibits the martensitic transformation from the austenite $L2_1$ (cubic) to intermartensite $10M/14M$ (modulated monoclinic), and martensite $L1_0$ (tetragonal) phases [9, 12-14]. Figure 1.1 [8, 14, 15] shows a schematic of the stress-strain curve of $Ni_2FeGa$ at room temperature. The initial phase of $Ni_2FeGa$ is the austenite $L2_1$ and it transforms to intermartensite $10M/14M$ as the loading reaches a critical transformation stress approximately 40 MPa. With further deformation, the martensite $L1_0$ is obtained at nearly 80 MPa and the second plateau takes place. During unloading, the reverse phase transformation occurs and the pseudoelasticity is observed as the total recovery of deformation [8]. The details of phase transformation from $L2_1$ to $10M$ and the associated energies are described in Chapter 3.
Figure 1.1 Schematic of the pseudoelastic stress-strain curve of Ni$_2$FeGa at room temperature showing the martensitic transformation from the L$_2$$_1$ cubic austenite to the 10M/14M modulated monoclinic intermartensite, and the L$_1$$_0$ tetragonal martensite [8, 15].

1.1.2 Dislocation slip in shape memory alloys

A similar stress vs. temperature correlation is experimentally observed [8, 16-18] for determination of dislocation slip stress in austenite SMAs (Figure 1.2). The critical stress for martensitic transformation increases with temperature above A$_f$ and the critical stress for dislocation slip of austenite decreases with temperature. When these two values cross at the temperature M$_d$, the stress-induced martensitic transformation is no longer possible, but only the dislocation slip of austenite. The critical austenite slip stress at M$_d$ is considered as the experimental data for austenite slip [6] and compared to the present theory in this thesis (Chapter 5).
Figure 1.2 Schematic of critical stress vs. temperature for SMAs. The critical stress represents the stress-induced martensitic transformation below temperature $M_d$ (red straight line) and the dislocation slip of the austenite phase above $M_d$ (blue straight line). $A_t$ is the austenite finish temperature, and the $M_d$ is the temperature above which the martensite cannot form under deformation.

Figure 1.3 shows the determination of dislocation slip stress in martensite SMAs. At the temperature above austenite finish temperature $A_t$, the material is fully austenitic. After elastic deformation of the austenite, a stress-induced martensitic transformation occurs. When the critical stress, $\sigma_{\text{slip}}$, for martensite yield is reached, slip of oriented martensite is observed. Upon unloading, the martensitic single crystal undergoes elastic deformation followed by pseudoelastic behavior and reverse martensite to austenite transformation occurs. The details of experimental evidence of the dislocation slip and measurement of the slip stress in martensite SMAs are described in Chapter 5. Figure 1.4 shows the TEM image of the martensite phase L1$_0$ with $<112>|{111}|$ dislocation slip in a Ni$_{54}$Fe$_{19}$Ga$_{27}$ (at %) single crystal.
Figure 1.3 Schematic of determination of dislocation slip stress in martensite SMAs.

Figure 1.4 TEM image displays the martensite phase $L1_0$ with $<112>\{111\}$ dislocation slip in a Ni$_{54}$Fe$_{19}$Ga$_{27}$ (at %) single crystal.
1.1.3 Twinning in shape memory alloys

Twinning in SMAs is of paramount importance, which exists in two main characteristics of SMAs. In the first case, when the alloy in the austenitic state is cooled below the martensite finish temperature with no external stress, the internally twinned martensite is formed. If the twinned martensite is subsequently deformed, the twin variants that are oriented favorably to the external stress grow in expense of others. The growth of the twin is a process of advancement of twin interfaces and requires overcoming an energy barrier called the 'unstable twin fault energy'. Upon further deformation, the internally twinned martensite detwins completely into a single martensite crystal. After unloading, the twinning-induced deformation remains. If the material is heated over the austenite finish temperature, then martensite to austenite transformation occurs and the material reverts back to austenite. Hence, the heating and cooling changes can make the material behave as an actuator, which is called 'shape memory effect'. A schematic of the shape memory effect is shown in Figure 1.5. Figure 1.6 shows a schematic and experimental evidence of $<112\{111>$ twinning in $\text{L1}_0$ martensite $\text{Ni}_2\text{FeGa}$.

![Shape Memory Effect](image)

**Figure 1.5** Schematic of shape memory effect in SMAs.
In the second case, when the SMAs undergo isothermally stress-induced transformation from austenite to martensite (Figure 1.1), the martensite undergoes detwinning and this contributes to the overall recoverable strain. Upon unloading, the martensite reverts back to austenite, and this called ‘pseudoleasticity’. The magnitude of the lattice strain is of the order of 5% in NiTi while the shear associated with detwinning is also nearly 5% making the total near 10% [19, 20]. In the case of Ni$_2$FeGa, the magnitude of the strains are higher (near 12%) [8, 21, 22], and the process of twinning plays a considerable role.

Therefore, the phenomenon of twinning or detwinning either during shape memory or during pseudoelasticity relies on the atomic movements in the martensitic crystal. It influences the recoverability, the transformation stress levels, hence both the shape memory effect/pseudoelasticity response. For shape memory, the martensite is deformed first and then heated to the austenitic phase for full recovery. Martensite undergoes twinning during deformation at relatively low stress levels. If slip occurs during martensite deformation, this would curtail full recoverability. On the other hand, during pseudoelasticity, austenite

Figure 1.6 (a) Schematic and (b) Experimental evidence of $\langle 112 \rangle \{111\}$ twinning in L1$_0$ martensite Ni$_2$FeGa.
transformation to martensite takes place upon loading. If slip resistance is low, then austenite and martensite domains can deform plastically inhibiting full recoverability upon unloading. Despite the significant importance of twinning in SMAs, there has been no attempt to develop models to predict their twinning mechanism. Thus, a fundamental understanding of twin nucleation is essential to capture the mechanical response of SMAs.

1.2 Methodology

In this thesis, we considered different length scales associated with the plastic deformation of SMAs (Figure 1.7). In the material science and meso-continuum mechanics field, coupling the various length scales involved in order to understand the plastic deformation still remains a major challenge [23]. At the dislocation core scale, quantum mechanics describe the atomic level interactions and the forces exerted on atoms; while at the mesoscale level, elastic strain fields of defects address the interactions [24]. The ensemble of dislocations and their interactions with the microstructure define the continuum behavior. With atomistic simulations one can gain a better understanding of the energy associated with deformation. Therefore, atomistic simulations in this case will provide additional insight into material’s behavior and the deformation mechanisms [20].

Figure 1.7 Schematic of the multi-scale methodology for modeling of deformation in SMAs.
At the atomic level, the first-principles total-energy calculations were carried out using the Vienna ab initio Simulations Package (VASP) with the projector augmented wave (PAW) method and the generalized gradient approximation (GGA) [25, 26]. In our calculations, Monkhorst Pack k-point meshes were used for the Brillouin-zone integration. A sufficiently dense mesh of integration points is crucial for the convergence of results. Therefore, the mesh sizes were chosen depending on the particular supercell and calculation systems. The energy cutoff of 500 eV was used for the plane-wave basis set. The total energy was converged to less than $10^{-5}$ eV per atom. Periodic boundary conditions across the supercell were used to represent bulk material. More details for the DFT setting are described in the subsequent chapters.

The Peierls-Nabarro (P-N) model represents a mesoscale level integration of atomistic and elasticity theory considerations. It accounts for the dislocation cores on one hand and lattice resistance to flow by applying continuum concepts to elastic deformation at atomic scale [24]. The model has stood the test of time over many years, and its main contribution is that the P-N stress level for dislocation glide are much lower than ideal stress calculations [27-30]. The calculations for P-N stress represent the breakaway of atoms within the core region of the dislocation. In this thesis, the P-N model with modifications will be utilized to study the slip resistance and twin nucleation. The details of utilizing P-N formulation to develop dislocation slip and twin nucleation models in SMAs are described in Chapters 5 and 6.

Finally, we conducted experiments to measure the dislocation slip stress and twinning stress, and compared the predicted values from our models to the experimental data. The agreement is excellent considering the complexity of real microstructures and the idealizations adopted in theoretical models.

**1.3 Thesis Organization**

In the next three Chapters of this thesis (Chapters 2-4) we present an energetic approach to quantitatively comprehend the characteristics of phase stability, martensitic phase transformation and dislocation slip in SMAs (NiTi and Ni$_2$FeGa). The results provide an important insight of the role of energy barriers in SMAs. In the Chapters 5 and 6, we extended
Peierls-Nabarro formulation incorporated with atomistic simulations to determine Peierls stress in SMAs; we proposed a twin nucleation model based on P-N formulation utilizing first principle simulations to predict twin nucleation stress in SMAs. These theoretical results are in a good agreement with experimental measurements. These models provide a rapid, inexpensive and precise approach to predict stress associated with plastic deformation (slip and twinning) in SMAs. In Chapter 7, we summarized the studies in the thesis and discussed the future work.

In Chapter 2, we make quantitative advances towards understanding of a quandary associated with the martensitic phase stability of NiTi. Utilizing first principles calculations with high resolution shear steps, we show unequivocally that a significant energy barrier exists between the martensitic B19' and B33. We also present an analysis how hydrostatic pressure alter this energy barrier and the phase stability of martensite NiTi. This study provides an authoritative rationalization of why B19' (monoclinic lattice) has been experimentally observed while B33 (base-centered orthorhombic lattice) has been proposed on theoretical grounds to have a lower energy.

In Chapter 3, we address the mechanism of low martensitic transformation stress and high reversible strains in Ni$_2$FeGa utilizing first principle simulations and conducting experiments. We establish the energy barriers associated with the transformation from austenite L2$_1$ to modulated martensite 10M incorporating shear and shuffle and slip resistance in [111] direction as well as in [001] direction. The results show that the unstable stacking fault energy barriers for slip by far exceeded the transformation transition state barrier permitting transformation to occur with little irreversibility. Experiments at the mesoscale on single crystals and transmission electron microscopy provide further proof of the pseudoelastic behavior. This provides design of new SMAs that possess low energy barriers for transformation coupled with high barriers for dislocation slip.

In Chapter 4, we studied dislocation slip in B2 NiTi with atomistic simulations in conjunction with transmission electron microscopy. We examine the generalized stacking fault energy (GSFE) curves for five potential slip systems: {011}, {211} and {001} slip planes with <100>, <111> and <011> slip directions. The results show the smallest and second smallest energy barriers for the (011)[100] and the (011)[1$ar{T}$1] cases, respectively, which are consistent
with the experimental observations of dislocation slip reported in this study. Furthermore, we calculated the ideal shear stress for these five slip systems and discussed the rationale for slip resistance in austenite NiTi. This study represents a methodology for consideration of a better understanding of SMAs.

In Chapter 5, we provide an extended Peierls-Nabarro formulation with a sinusoidal series representation of GSFE to establish flow stress in several important SMAs. We predicted the Peierls stress in L1\textsubscript{0} Ni\textsubscript{2}FeGa as an example to show the extended formulation. Utilizing atomistic simulations, we determined the GSFE landscapes with stacking fault energies in L1\textsubscript{0} Ni\textsubscript{2}FeGa. The smallest energy barrier was determined as 168 mJ/m\textsuperscript{2} corresponding to a Peierls stress of 1.1 GPa. We conducted experiments on single crystals of Ni\textsubscript{2}FeGa under compression to determine the L1\textsubscript{0} slip stress (0.75 GPa), which was much closer to the P-N stress predictions (1.1 GPa) compared to the theoretical slip stress levels (3.65 GPa). This extended P-N model with GSFE curves provides an excellent basis for a theoretical study of the dislocation structure and operative slip modes SMAs.

In Chapter 6, we present a twin nucleation model based on the Peierls-Nabarro (P-N) formulation utilizing first-principles atomistic simulations. We investigate twinning in several important SMAs starting with Ni\textsubscript{2}FeGa to illustrate the methodology, and predict their twin stress in excellent agreement with experiments. We calculated and minimized the total energy involved in the twin nucleation process, and led to determination of the twinning stress accounting for twinning energy landscape (GPFE) in the presence of interacting multiple twin dislocations and disregistry profiles at the dislocation core. This study provides a rapid, inexpensive and precise methodology to predict twin nucleation stress in SMAs.

Conclusions and future work is summarized in Chapter 7.
Chapter 2 Resolving Quandaries Surrounding NiTi


2.1 Abstract

We address a quandary associated with the phase stability of NiTi. The $B19'$ (monoclinic lattice) has been experimentally observed while $B33$ (base-centered orthorhombic lattice) has been proposed on theoretical grounds to have a lower energy. With high-resolution shearing steps, we show unequivocally that a significant energy barrier exists between the martensitic $B19'$ and $B33$ which is dependent on pressure. The transition state designated as $B19^i$ has an energy level 25 meV/atom higher compared to $B19'$. We note that the formation of $B33$ can be suppressed because of the presence of the $B19^i$ high energy barrier which increases considerably under tensile hydrostatic stress.

2.2 Introduction

Equiatomic NiTi has been the most widely studied shape memory alloy (SMA) owing to its superior shape memory characteristics [31]. Experimental investigations have revealed that the $B19'$ structure (Figure 2.1a) is the martensitic phase in NiTi [32-34]. However, recent DFT calculations [4, 35-38] suggested that the $B19'$ structure is unstable compared to a higher-symmetry base-centered orthorhombic (BCO) structure (also termed $B33$ with monoclinic angle $\gamma \approx 107^\circ$) (Figure 2.1b). Some of these investigations proposed barrierless transformation paths between the $B2$ (Figure 2.1c) and $B19'$ as well as from the $B19'$ to $B33$ lattices [4, 36, 37]. But the question remains, why is $B19'$ experimentally observed? Two major explanations have been proposed in the literature: (1) the $B19'$ structure is stabilized by internal (or residual) stresses which exist within the microstructure [4, 38], and the $B33$ structure may be formed in certain conditions when the internal stresses are minimized [36]; (2) it has been proposed that the
presence of (nano) twins, often experimentally observed [39-42], can lower the B19' energy [43, 44]. In addition, we also note that the energy of the self-accommodated (internally twinned) B19' structure is lower compared to its detwinned counterpart [31]. Another point is that the B33 structure corresponds to a rather high (10.1%) elongation of the largest lattice parameter (compared to 3% [36] for B19') hence there is a corresponding higher elastic strain energy.

Figure 2.1 Crystal structures of NiTi. (a) Crystal structure of B19' (b) Crystal structure of B33 (c) Crystal structure of B2.

In this study, we provide a more authoritative explanation of the occurrence of B19' that has been overlooked: there are two energy barriers in the martensitic phase transformation path
from the B19' to B33, and the magnitude of the highest barrier is in the range of 8 to 25 meV/atom depending on the applied pressure.

We utilized DFT to investigate the phase stability and the corresponding energy barriers over the entire path, which is accomplished by an atomic bilayer shear distortion in the \{011\} basal plane along the <100> slip direction with structural optimization for all lattice parameters, angles, and internal atomic coordinates [36, 37]. The first-principles total-energy calculations were carried out using the Vienna ab initio Simulations Package (VASP) [25, 26] with the projector augmented wave (PAW) method and the generalized gradient approximation (GGA). PAW is an efficient all-electron method which achieves high accuracy when transition elements such as Ti are considered. In our calculation, Monkhorst-Pack 9×9×9 \(k\)-point meshes were used for the Brillouin-zone integration. Ionic relaxation was performed by a conjugate gradient algorithm and stopped when absolute values of internal forces were smaller than \(5 \times 10^{-3}\) eV/Å. The energy cut-off of 500 eV was used for the plane-wave basis set. The total energy was converged to less than \(10^{-5}\) eV per atom. The equilibrium structures for all phases were obtained by minimizing total energies at zero temperature. Furthermore, to simulate the effect of internal stresses, we calculated structural total energies and energy barriers under several hydrostatic stresses in the range of -14 GPa to 14 GPa.

2.3 Results and Discussion

The computed lattice parameters, monoclinic angles, volumes, total energies relative to the B2 phase (considered as the reference state) and energy barriers in the transformation are summarized in Table 2.1 (for the 0 GPa and 10 GPa cases).
Table 2.1 VASP-PAW-GGA calculated lattice parameters (Å), monoclinic angle (degree), volume (Å³ per formula unit), total energies (meV per atom) relative to B2 austenite phase considered as reference state and energy barriers (meV per atom) in the phase transformation of NiTi for two cases: zero pressure, hydrostatic tension at 10 GPa.

| Structures | Zero pressure | | | | | | Hydrostatic tension 10 GPa | | | |
|------------|---------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|            | $a$           | $b$              | $c$              | $\gamma$        | $V$              | $E\cdot E_{ref}$ | Energy barrier | $a$              | $b$              | $c$              | $\gamma$        | $E\cdot E_{ref}$ | Energy barrier |
| B2         | 3.004         | 4.25             | 4.25             | 90              | 27.1             | 0                | B2 $\rightarrow$ B2$'^i$ $\rightarrow$ B2$'$ | 3.07             | 4.35             | 4.35             | 90              | 0                | B2 $\rightarrow$ B2$'^i$ $\rightarrow$ B2$'$ |
| B2$'$      | 2.91          | 4.32             | 4.31             | 90.5            | 27.11            | -4.38            | 0.53            | 2.97             | 4.43             | 4.42             | 90.71           | -0.64            | 1.76            |
| B2$'^i$    | 2.93          | 4.31             | 4.27             | 90.7            | 26.88            | -2.48            | B2$'$ $\rightarrow$ B2$'^i$ $\rightarrow$ B19$'$ | 3.07             | 4.35             | 4.34             | 91.52           | 1.83             | B2$'$ $\rightarrow$ B2$'^i$ $\rightarrow$ B19$'$ |
| B19$'$     | 2.91          | 4.64             | 4.06             | 97.3            | 27.18            | -44.1            | 2               | 3.03             | 4.77             | 4.08             | 101.2           | -49.6            | 2.47            |
| B19$'^i$   | 2.88          | 4.58             | 4.11             | 90.9            | 27.24            | -36.14           | 2.99            | 4.74             | 4.16             | 96.34           | 90.52           | -24.5            |
| B19$''$    | 2.94          | 4.76             | 3.99             | 101.7           | 27.44            | -51.37           | 8               | 3.04             | 4.87             | 4.07             | 102             | -43.1            | 25              |
| B33        | 2.93          | 4.91             | 4.00             | 107.38          | 27.51            | -52.4            | B19$''$ $\rightarrow$ B19$''$ $\rightarrow$ B33 | 3.05             | 5.02             | 4.08             | 107.7           | -39.3           | B19$''$ $\rightarrow$ B33 |

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The present results (B2, B19' and B33 at zero pressure) are compared with previous theoretical [36, 38, 45, 46] and experimental findings [32, 34, 47], and they are in excellent agreement. However, we point to several metastable structures and transition states which have not been discovered before. In this letter, the most important transition state is defined as B19'' (Figure 2.2). Our first principles calculations confirm that the B19' has higher energy relative to the B33 at zero pressure, while at 10 GPa hydrostatic tension B19' has the lowest energy. We discovered the energy barrier of 8 meV/atom (corresponding to B19'') between the B19' and B33 as the most significant in Fig. 2 (and Table 2.1) which is raised to 25 meV/atom at 10 GPa. We note that all lattice parameters change abruptly after the shear displacement reaches $\frac{u}{a_0} = 0.21$ corresponding to B19'' (see Table 2.1). The decrease of the lattice parameters $a$ (in-plane Ni-Ni interatomic distance between two adjacent {100} layers) and $b$ (in-plane Ni-Ni interatomic distance between two adjacent {011} layers) significantly affects the arrangement of atoms that get closer to each other, which causes excessive interatomic repulsive forces during the shear transformation. As $\frac{u}{a_0} = 0.21$ is approached, the interatomic distances in these layers will increase as shear proceeds and the total energies will decrease until the B19'' is formed. The metastable structure B19'' results in a very small energy barrier less than 0.4 meV/atom.
Figure 2.2 Total energies variation with the transformation displacement from the B2 to the B33 of NiTi. The B19' is composed of two monoclinic lattices with 8 atoms (a double-monoclinic-hybrid structure, see Figure 2.3 for details). The B33 can be represented in a 4-atom monoclinic unit cell with an angle 107.38° or in an 8-atom base center orthorhombic unit cell (red dash line) related to two equivalent monoclinic unit cells. The blue and grey spheres correspond to Ni and Ti atoms respectively. The large spheres represent atoms in the plane, and small spheres are located out of plane (one layer below or above) of the unit cells.

A schematic of the bilayer shear transformation from the B2 to B19' in the {011} basal plane along the <100> slip direction is given in Figure 2.3. We note that the B19' is composed of two monoclinic lattices with different monoclinic angles, $\gamma^{(1)} = 90.9^\circ$ and $\gamma^{(2)} = 96.69^\circ$, and different largest lattice parameters, $b^{(1)} = 4.58$ Å and $b^{(2)} = 4.67$ Å, i.e., a double-monoclinic-hybrid structure. As a non-equilibrium state in the transformation path from the B19' to B33, this double-monoclinic-hybrid structure connected through a coherent interface is formed by
allowing full relaxation of the lattice parameters, monoclinic angles and atomic positions in the DFT calculation. The full relaxation approach, during the imposed bilayer \{011\}<100> shear, results in a shuffle of the atomic positions and lowers the structural energy during the phase transformation [36, 37]. However, the B19\textsuperscript{th} hybrid structure still constitutes an important energetic barrier which makes the transition to B33 difficult.

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**Figure 2.3** Schematic of the bilayer shear transformation from B2 to B19\textsuperscript{th}. (a) The initial B2 structure with lattice parameters $a_0$, $b_0$ and $c_0$. The green and red color planes are the \{011\}
basal planes, which form the sheared bilayers. The red arrows show the alternating shear direction with normalized magnitude $\frac{u}{2a_o}$ in the $\{011\}$ basal planes. (b) The B19$^d$ structure is formed after relative shear displacement of $\frac{u}{a_o} = 0.21$. It is a double-monoclinic-hybrid structure with different monoclinic angles, $\gamma^{(1)} = 90.9^\circ$ and $\gamma^{(2)} = 96.69^\circ$, and different largest lattice parameters, $b^{(1)} = 4.58$ Å and $b^{(2)} = 4.67$ Å.

The B19$^d$ plays a key role in the phase transformation from the B19$'$ to B33 as at this transition state we found a significantly high energy barrier of around 8 meV/atom above the B19$'$ (this is the globally highest cubic-monoclinic energy barrier). Since the energy barriers between the B2 and B2$'$ (0.53 meV/atom) as well as the B2$'$ and the B19$'$ (2 meV/atom) are rather low, the stress required to induce B19$'$ from B2 is not high. In contrary, the stress required for B19$'$ to B33 change will be much higher owing to the large energy barrier between them. So even if the B33 is energetically preferred, the transformation from the B2 to the B19$'$ overcomes a much lower barrier and the system will be stabilized at the B19$'$ phase.

The effect of hydrostatic tension and compression at 8 GPa on the structural total energies and energy barriers is shown in Figure 2.4, where four structures B2, B19$'$, B19$^d$ and B33 are indicated. Compared to the result at zero pressure in Figure 2.2, the position of the shear levels corresponding to the transformation steps and energy barriers are altered dramatically by pressure. Three major pressure effects are evident: (1) the energy barrier between the B19$'$ and B33 increases from 8 meV/atom at zero pressure to 18 meV/atom (tension) and decreases to 1 meV/atom (compression) at 8 GPa; (2) the B19$'$ has very close energy (tension) and much higher energy (compression) compared to B33, which indicates that the B19$'$ becomes more stable under hydrostatic tension, but less stable at hydrostatic compression; (3) the B19$'$ occurs at a smaller transformation displacement, $\frac{u}{a_o}$, permitting a smaller shear strain to achieve the transformation from B2 to B19$'$. 

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Figure 2.4 Total energies variation with the transformation displacement from the B2 to the B33 of NiTi under hydrostatic tension (brown curve) and compression (green curve) at 8 GPa. The schematic of crystal structures of B19', B19'' and B33 are inserted and indicated in the transformation path.

Based on the above results, we also calculated the effect of hydrostatic tension at higher pressure of 10 GPa on the structural total energies and energy barriers (Figure 2.5). Compared to the result at zero pressure in Figure 2.2 and at pressure of 8 GPa in Figure 2.4, we note that (1) the energy barrier between the B19' and B33 increases from 8 meV/atom at zero pressure to 25 meV/atom at 10 GPa; (2) the B19' has lower energy than B33 and becomes the global minimum energy structure, which indicates that the B19' is more stable than the B33 under hydrostatic tension. Overall, the results point to the presence of an energy barrier that is a strong function of applied pressure in NiTi, and the B19' may become energetically stable relative to the B33 under high hydrostatic tension.
**Figure 2.5** Effects of hydrostatic tension at 10 GPa on total energies in the phase transformation of NiTi. The energy barrier between the B19' and B33 is much higher as 25 meV/atom. The B19' is the global minimum energy structure and the B33 becomes a transition state in the transformation path.

To examine the phase stability of the B19' relative to B33 at various hydrostatic stresses (negative hydrostatic stress corresponds to positive pressure), we calculated the total energy difference between them as shown in Table 2.2. We note that the total energy difference favors B19' as the stable structure at 10 GPa of tensile hydrostatic stress.

**Table 2.2** Total energy difference between the B19' and B33 under hydrostatic stress.

<table>
<thead>
<tr>
<th>Hydrostatic Stress (GPa)</th>
<th>-8</th>
<th>0</th>
<th>4</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>B19' - B33 (meV/atom)</td>
<td>16.9</td>
<td>8.3</td>
<td>3.4</td>
<td>3.2</td>
<td>-10.3</td>
</tr>
</tbody>
</table>

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2.4 Summary

We conclude that the presence of energy barriers and their magnitude in the martensitic phase transformation of NiTi is central to understanding the stabilization of the observed B19' structure. The hydrostatic stress influences the structural energies; especially the high hydrostatic tension can significantly contribute to stabilize the B19' structure in martensite.
Chapter 3 Transformation and Slip Behavior of Ni$_2$FeGa


3.1 Abstract

Ni$_2$FeGa is a relatively new shape memory alloy (SMA) and exhibits superior characteristics compared to other SMAs. Its favorable properties include low transformation stress, high reversible strains and small hysteresis. The first stage of stress-induced martensitic transformation is from a cubic to a modulated monoclinic phase. The energy barriers associated with the transformation from L2$_1$ (cubic) to modulated martensite (10M-martensitic) incorporating shear and shuffle are established via atomistic simulations. In addition, the slip resistance in the [111] direction and the dissociation of the full dislocation into partials as well as slip in [001] direction are studied. The unstable stacking fault energy barriers for slip by far exceeded the transformation transition state barrier permitting transformation to occur with little irreversibility. Experiments at the meso-scale on single crystals and transmission electron microscopy were conducted to provide further proof of the pseudoelastic (reversible) behavior and the presence of anti-phase boundaries. The results have implications for design of new shape memory alloys that possess low energy barriers for transformation coupled with high barriers for dislocation slip.

3.2 Introduction

3.2.1 Challenges in Designing Shape Memory Alloys

Designing new shape memory materials that exhibit superior transformation characteristics remains a challenge. There needs to be a better fundamental basis for describing how reversible transformation (shape memory) works in the first place. Specifically, two aspects
remain uncertain. The first is that the phase changes involve complex transformation paths with shear and shuffle [1] and the energy barrier levels corresponding to the transition are not well established. The second issue is that the determination of dislocation slip resistance [2], which decides the reversibility of transformation of shape memory alloys, is very important and requires further study. Thus, this paper is geared towards establishing both the energy barriers in the phase changing of Ni$_2$FeGa and the fault energies associated with dislocation slip for the same material.

Thermo-elastic phase transformation refers to a change in lattice structure upon exposure to stress or temperature and return of the lattice to the original state upon removal of stress or temperature [3]. Modern understanding of shape memory transforming materials has relied on the phenomenological theory of martensite transformation [4], which does not deal with the presence of dislocation slip. The presence of slip has been observed in experimental work at micro- and meso-scales [5, 6], and incorporated in some of the continuum modeling approaches [7] A low transformation stress [8] and high slip resistance [9] are precursors to reversible martensitic transformation. Recently, theoretical developments at atomic length scales have been utilized [10-12] bringing into light the magnitude of energies of different phases and defect fault energies in NiTi.

NiTi is the most well known shape memory alloy that meets the requirement of excellent slip resistance in both martensite [13] and in austenite [14-18]. The recent interest in the austenite slip behavior of NiTi is well founded because it is a key factor that influences the shape memory response. We note that some of the other shape memory alloys of the Cu- variety [19-23] and the Fe-based [24-28] alloys possess large transformation strains but are susceptible to plastic deformation by slip. Plastic deformation has been incorporated into continuum energy formulations where the interaction of plastic strains and the transformation improves the prediction of overall mechanical response [29-31]. All these previous works point to the importance of dislocation slip resistance in shape memory alloys.

The Ni$_2$FeGa alloys have large recoverable strains [32-34] and can potentially find some important applications like NiTi. In the case of Ni$_2$FeGa alloys, stress-induced transformation to modulated martensite [35-39] and the slip deformation of austenite [32, 33] are two factors that dictate shape memory performance. The phase change in Ni$_2$FeGa occurs primarily upon shape
strains (Bain strain) in combination with shuffles to create a 'modulated' martensitic structure. The 'modulated' monoclinic structure has a lower energy than the 'non-modulated' lattice, and hence is preferred. We focus on atomic movements and the energy landscapes for transformation of L2$_1$ austenite to a 10M modulated martensite structure and establish the barrier for this change. We then investigate the dislocation slip barriers in [111] and [001] directions.

It is important to assess the transformation paths and energies associated with the austenite to martensite transformation simultaneously with dislocation slip behavior because the external shear stress that can trigger transformation can also result in dislocation slip. What we show is that the order strengthened Ni$_2$FeGa alloy requires elevated stress levels for dislocation slip while undergoing transformation nucleation at much lower stress magnitudes (with lower energy barriers).

3.2.2 Energetics of Phase Transformation and Dislocation Slip

A schematic of pseudoelastic stress-strain response at constant temperature is given in Figure 3.1. We note that the initial crystal structure at zero strain is that of austenite. Upon deformation, the crystal undergoes a phase transformation to a modulated martensitic structure. In the case of Ni$_2$FeGa, the structures of austenite and martensite are cubic and monoclinic, respectively. Over the plateau stress region, austenite and martensite phases can coexist. In the vicinity of austenite to martensite interfaces, high internal stresses are generated to satisfy compatibility. Hence, slip deformation can occur in the austenite domains as illustrated in the schematic. Once the transformation is complete, the deformation of the martensitic phase occurs with an upward curvature. Upon unloading, the martensite reverts back to austenite as shown in the schematic. The strain recovers at the macroscale, but at the micro-scale residual slip deformation could remain as shown with TEM studies.
Figure 3.1 Schematic of stress-strain curve displaying the modulated martensite and dislocation slip in austenite over the plateau region during pseudoelasticity.

We capture the energetics of the transformation through ab initio density functional theory (DFT) calculations. In Figure 3.2a, the initial lattice constant is $a_0$ and the monoclinic lattice constants are $a$, $b$ and $c$ with a monoclinic angle. We incorporate shears and shuffles for the case of transformation from L2$_1$ to 10M. A typical transformation path is described in Figure 3.2a. The martensite has lower energy than the austenite. To reach the martensitic state, there exists an energy barrier (corresponding to $\gamma_u^{A\rightarrow M}$ in Figure 3.2a) that needs to be overcome. This barrier is dictated by the energy at the transition state (TS) as shown in Figure 3.2a. A smaller barrier is desirable to allow transformation at stress levels well below dislocation mediated plasticity. Along the transformation path, we find a rather small energy barrier (8.5 mJ/m$^2$ for the L2$_1$ to 10M transformation in Ni$_2$FeGa).
Figure 3.2 (a) Schematic of transformation path showing the energy in the initial state, the final state and the transition state, (b) atomic arrangements of Ni$_2$FeGa with long range order (first configuration). The viewing direction is [110]. The (001) planes are made of all Ni atoms, and alternating Fe and Ga atoms. The dashed line represents the slip plane. The displacement $<111>/4$ creates nearest neighbor APBs (middle configuration) and the displacement $<111>/2$ results in next nearest neighbor APBs (third configuration). (c) generalized fault energy of austenite associated with full dislocation dissociation into partials in an ordered alloy.
Dislocation slip resistance in the L2₁ austenite can be understood by consideration of energetics of slip displacements in the [111] direction associated with the motion of the dissociated dislocations. Ribbons of anti-phase boundaries (APBs) form by dissociation of superdislocations in the L2₁ parent lattice. We compute the separation distance of the superpartials via equilibrium considerations and show the presence of these APBs from TEM observations. The energy barriers are manifested via generalized stacking fault energy curves (GSFE) and decide the slip resistance of the material. We check the GSFE curves in two possible dislocation slip systems and calculate theoretical resolved shear stress.

The fundamental descriptions of the APB formation in ordered cubic materials point to decomposition of full dislocations [40] [41]. For the Ni₂FeGa, as atoms are sheared over other atoms in neighboring planes the energy landscape indicates the decomposition of the full dislocation to four partials resulting in APBs. The partial dislocations are not zig zag type as in face centered cubic systems but are in the same direction as the full dislocation. This is illustrated in Figure 3.2b. It is easiest to see the APB formation with a [110] projection (Figure 3.2b). The x-axis is [001] and the y-axis is [1\bar{T}0] in this case. In this view atoms on only two planes (in-plane and out-of-plane) are noted (a different view will be illustrated later). Because we have twice as many Ni atoms then Fe and Ga, in the [1\bar{T}0] direction every second column has all Ni atoms. When slip occurs with vector 1/4[1\bar{T}1] the original ordering of the lattice no longer holds. The passage of the first partial 1/4[1\bar{T}1] results in disordering of the atomic order at near neighbors. The passage of the second partial restores the original stacking of next to near neighbor atoms. Upon a slip displacement of 1/2[1\bar{T}1] the columns with all Ni atoms are restored but other columns do not have the original ordering (Figure 3.2b). Upon displacement of [1\bar{T}1] the original lattice structure with long range order of the matrix is recovered. The fault energy barriers corresponding to Figure 3.2b have several minima (metastable equilibrium points) corresponding to the passages of the partial dislocations (Figure 3.2c). More details will be given later in the text. In Figure 3.2b \( \gamma_{us} \) refers to the unstable fault energy and \( \gamma_{NN} \) and \( \gamma_{NNN} \) describe the nearest-neighbor (NN) and next-nearest neighbor (NNN) APB energies respectively. The fault energy barriers are moderately high (>400 mJ/m² in Ni₂FeGa) and point to the considerable
slip resistance in Ni$_2$FeGa. We provide TEM evidence of the presence of APBs in the austenitic phase for samples that have undergone pseudoelastic cyclic deformation.

### 3.3 Cubic to Modulated (10M) Transformation in Ni$_2$FeGa

The martensitic structure is critical to the properties of ferro-magnetic shape memory alloys. Their tetragonality c/a, twinning stress and magnetocrystalline anisotropy constant determine the magnetic-field-induced strain (MFIS) [42, 43]. However, large MFIS originates mainly from the contribution of the modulated martensites[44]. Experiments have shown that the cubic structure (L2$_1$) undergoes the phase transformation to martensitic phases, designated modulated structure (10M/14M) and tetragonal structure (L1$_0$). The transformation from a cubic structure (L2$_1$) to a modulated 10M structure is an important one in shape memory alloys of the ferro-magnetic variety [32, 45-48]. The Ni$_2$FeGa alloys undergo such a transformation via a combination of shear (distortion) and shuffle. This is the first stage of multiple transformation steps resulting in the L1$_0$ structure. It is a very important step because it decides the transformation stress and the plateau stress for the shape memory alloy.

The first-principles total-energy calculations were carried out using the Vienna ab initio Simulations Package (VASP) with the projector augmented wave (PAW) method and the generalized gradient approximation (GGA). In our calculation, we used a 9×9×9 Monkhorst Pack k-point meshes for the Brillouin-zone integration to ensure the convergence of results. The energy cut-off of 500 eV was used for the plane-wave basis set. The total energy was converged to less than $10^{-5}$ eV per atom. Considering the effect of the number of layers on stacking fault energies [10], the present DFT calculation of GSFE for slip system (011)<111> is conducted using a 8 layer supercell having 12-atom per layer; while for slip system (011)<001>, a 8 layer supercell having 4-atom per layer is used. For every shear displacement, the relaxation perpendicular to the fault plane was allowed for minimizing the short-range repulsive energy between misfitted adjacent layers [70, 71]. We construct a supercell consisting of 40 atoms to model the 10M structure in order to incorporate the full period of modulation in the supercell [72, 73]. The relaxation by changing the supercell shape, volume and atomic positions were carried
The periodic boundary conditions are maintained across the supercell to represent bulk Ni$_2$FeGa material (no free surface). All supercells used in the study ensure the convergence of the calculation after careful testing.

The lattice parameters of L$_2$$_1$ and L$_1$$_0$ structures using DFT were calculated and compared with experimental measurements. They are in a good agreement. In order to obtain the 10M structure, the initial calculation parameters $a = 4.272$ Å, $b = 5.245$ Å, $c = 4.25$ Å and the monoclinic angle $\beta = 91.49^\circ$ [39] are estimated by assuming the lattice correspondence with the L$_1$$_0$ structure [74, 75]. The relaxation by changing the supercell shape, volume and atomic positions were carried out. By using this optimization method, the atoms in the supercell move from their initial positions after each relaxation step by local forces, and after numerous such iteration processes, the configuration will be finally converged where the forces are zero in the stable 10M structure.

Table 3.1 The L$_2$$_1$ structure lattice constants for austenitic Ni-Fe-Ga ($a_o$) and the lattice constants of the modulated monoclinic (10M) structure.

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>Theory (this study)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Austenite</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L$_2$$_1$</td>
<td>Lattice parameter, $a_o$ ($\text{Å}$), $5.76$ [39], $5.7405$[49]</td>
<td>Lattice parameter, $a_o$ ($\text{Å}$), $5.755$</td>
</tr>
<tr>
<td><strong>Cubic Structure</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Martensite</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10M</td>
<td>Lattice parameter ($\text{Å}$), $a=4.24$, $b=5.38$, $c=4.176$, $\text{[39]}$</td>
<td>Lattice parameter ($\text{Å}$), $a=4.203$, $b=5.434$, $c=4.1736$, Monoclinic angle=91.456$^\circ$</td>
</tr>
<tr>
<td><strong>Monoclinic Structure</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Energy Barrier (TS) $8.5 \text{ mJ/m}^2$</td>
</tr>
</tbody>
</table>
Figure 3.3 (a) Schematic of the L2\textsubscript{1} austenitic structure of Ni\textsubscript{2}FeGa, (b) the sublattice displaying the modulated and basal planes, (c) the 10M monoclinic modulated structure of Ni-Fe-Ga.
In Figure 3.3a, the L2₁ lattice of Ni-Fe-Ga is shown. We note that the distance \( a_0 \) represents repeating atom positions in the <001> directions. We refer to coordinates in the L2₁ structure with the larger cell noting that the small cell represents a B2 structure. The L2₁ unit cell contains eight cells of the B2 type. Upon transformation to martensite, the lattice structure becomes monoclinic (Figure 3.3b) characterized by three constants \( a, b, c \) and a monoclinic angle of 91.49°. In Figure 3.3b, the sublattice of L2₁ is displayed. The distortion plane can be viewed with atom layers A and B superimposed. The change in dimension is from length \( a_0 \sqrt{2} / 2 \) to length \( c \) for the modulation direction [110], and from \( a_0 \sqrt{2} / 2 \) to length \( a \) in the [1T0] direction. The lattice dimension in [001] is changed from \( a_0 \) to \( b \). The lattice constants are summarized in Table 3.1. The second column gives the experimental results, while the third and fourth columns provide the simulations. The agreement between experimental and theoretical lattice constants including the monoclinic angle is remarkable. The \textit{ab-initio} VASP code with GGA [50-53] is used in the simulations (see Appendix).

Because the transformation occurs first via L2₁→10M, we investigated the energy landscape associated with this important step. We note that the lattice parameters of the 10M are designated as \( a_1, b_1, c_1 \), while the L2₁ lattice is defined by \( a_0 \). Relative to the parent body 10M phase involves a volumetric distortion and local shuffle. The deformation gradient can be written in the following form to represent the volumetric distortion, where \( \varepsilon \) represents the extent of the Bain-type deformation with \( \varepsilon = 0 \) corresponding to the L2₁ and \( \varepsilon = 1 \) to the 10M end states. The Cauchy-Born rule was used in establishing the deformation gradient expression given below.

\[
F(\varepsilon) = \begin{bmatrix}
\frac{b_1(\varepsilon)}{\sqrt{2}a_0} & \frac{b_1(\varepsilon)}{\sqrt{2}a_0} & 0 \\
\frac{c_1(\varepsilon)}{\sqrt{2}a_0} & \frac{c_1(\varepsilon)}{\sqrt{2}a_0} & 0 \\
0 & 0 & \frac{a_1(\varepsilon)}{\sqrt{2}a_0}
\end{bmatrix}
\]

To account for the internal displacements associated with the shuffles, the strain energy density is minimized with respect to the shuffle displacements while \( F(\varepsilon) \) is held fixed. This is achieved with internal relaxations of the atoms to the local energy minimum. The normalized
shuffle parameter is defined as $\eta = \frac{s}{a}$ where $s$ is the absolute shuffle. The energy landscape is completed for the multiple pathways that could achieve $L2_1 \rightarrow 10M$ by exploring all combinations of distortion and shuffle for Ni$_2$FeGa. The transformation path to the 10M structure is rather complex as shown in Figures 3.4a and 3.4b and involves both shear (Bain strain) and shuffle. The energy contours shown in Figure 3.4b show that the non-modulated martensite (10NM) has a higher energy than the modulated 10M structure. The 10NM structure has the same lattice constants as 10M. The difference between the two is that 10M involves considerable shuffle that results in the modulation. The minimum energy path is indicated in Figure 3.4a. We note that there is a rather small barrier (8.5 mJ/m$^2$) at the early stages of combined shear and shuffle. This is the principal reason why the transformation stress is rather low (< 50MPa) in this alloy.

To obtain the Potential Energy Surface (PES) within reasonable computational time, we divided the shear and shuffle based computational domain primarily into $7 \times 7$ nodes. Additional nodes are added near the energetically significant positions such as the local minima and the saddle point. A symmetry-adapted “free energy” polynomial was fitted to our $\Delta E(\eta, \epsilon)$ data. For this fault energy functional $\Delta E(\eta, \epsilon)$, we chose a fourth order cosine-sine polynomial [54], which can appropriately represent the shear shuffle coupling, i.e.

$$\Delta E(\eta, \epsilon) = \sum_{m,n=-4}^{m+n \leq 4} a_{mn} [X(\eta)]^m [X(\epsilon)]^n [1 - \delta_{m0} \delta_{n0}] + \sum_{m,n=0}^{m+n \leq 4} b_{mn} [X(\eta)]^m [Y(\epsilon)]^n$$

where, $[X(x)] = [1 - \cos(\pi x)]$, $[Y(x)] = [\sin(\pi x)]$, and $\delta_{ij}$ represents Kronecker’s delta ( $\delta_{ij}$ is 1(0) if i is (not) equal to j). An additional constraint of $|d\Delta E(\eta, \epsilon)/dx|_{x=0,1} = 0$ was imposed to ensure local minima at (0, 0) and (1, 1) positions in the PES.
Figure 3.4 (a) The energy landscape associated with the L2₁ to 10M transformation. The transformation is comprised of a distortion and shuffle and the path is rather complex. (b) 3D view of the transformation surface showing that the energy of 10NM (non-modulated martensite) structure is higher than 10M (modulated). See Figure 3.3b for the lattices.

3.4 Dislocation Slip (GSFE) in Ni₂FeGa

3.4.1 The (011)<111> Case

The generalized stacking fault energy (GSFE), first introduced by Vitek [55], is a comprehensive definition of the fault energy associated with dislocation motion. In fcc alloys, a
single layer intrinsic stacking fault is formed by the passage of partial dislocations in the $<1\overline{1}2>$ direction on the $\{111\}$ plane. The fault energy of different sheared lattice configurations can be computed as a function of displacement $u_x$. The generalized stacking fault energy (GSFE) is represented by a surface ($\gamma$-surface) or a curve ($\gamma$-curve). The peak in fault energy was termed as the unstable SFE by Rice [56]. In the case of Ni$_2$FeGa, all fault energies are determined relative to the energy of the L2$_1$ structure.

Figure 3.5 (a) The austenite (L2$_1$) lattice showing the slip plane and slip direction, (b) The $\{112\}$ projection illustrating the atom positions on the $\{110\}$ plane and $<111>$ direction, note the stacking sequence in the $[111]$ direction, (c) Upon shearing in the $<111>$ direction the
dissociation of the superlattice dislocation \( a_o[111] \) to four partials, and the associated NNAPB and NNNAPB energies are noted.

We investigated slip in the \(<111>\) direction consistent with experiments [57]. In this case the slip plane is \{110\}. Figure 3.5a shows the L2_1 lattice with the slip plane (shaded) and the \(<111>\) direction, and Figure 3.5b the stacking in the [111] direction as ABCDEFGAB'CD'EF'.... This stacking is similar to the \(<111>\) direction in bcc metals, but the difference arises because of the presence of three elements in Ni_2FeGa. Because the normal plane is \{112\}, a total of 6 layers must be shown in this projection. The largest atom represents in-plane and the atom size becomes smaller as the out-of-plane is depicted. The smallest atom is in the fifth layer (out-of-plane) and the largest atom is in the zeroth layer (in-plane). Considerable attention should be placed on establishing the correct atom positions when multiple planes and binary or ternary alloys are considered. We utilize visualization softwares (particularly VMD) to check for accuracy of the coordinates.

We note that in the case of dislocation moving through an ordered lattice (such as D0_3 or L2_1) an antiphase boundary forms on the glide plane. The GSFE associated with the APB formation is given in Figure 3.5c. We note that the stable fault structure formed due to a shear displacement \( u_x = |b| \) (see Figure 3.5c corresponding to a local minimum, on the curve with fault energy intrinsic stacking fault (isf) (or APB)) where \( b=a_o/4[111] \) (the intrinsic stacking fault energy has been also referred as the APB energy and both terms have been used interchangeably). The equilibrium fault structure corresponds to the intrinsic stacking fault on the \{110\} plane. Further shear beyond the first minima on the \( \gamma \)-curve along \(<111>\) direction results in another stable structure at \( u_x = 2|b| \) (Figure 3.5c).

As stated earlier, the nearest neighbor (NN) and next nearest neighbor (NNN) bonds are altered in the glide plane via the passage of first partial. When the second dislocation travels in succession, it reorders the NN sites but there is a further change in the next nearest neighbor (NNN) sites. The passage of the third dislocation disorders the NN sites and results in another change of the NNN sites. The fourth dislocation reorders both the NN and NNN sites across the slip plane. If four dislocations travel in succession (as in the present case), the dislocations are
bound by two types of anti-phase boundaries. Then, the distances between dislocations 1 and 2 and 2 and 3 are dictated by the APB energies ($\gamma_{NN}$ and $\gamma_{NNN}$). We note that mechanical relaxation was allowed for deviation from the perfect crystallographic displacements and these displacements were found to be less than 1% of the Burgers vector [58, 59]. Although these displacements are small, the relaxation in all three directions permits higher accuracy in terms of the APB energy values (Figure 3.5c).

The position of the atoms corresponding to $b=a_0/4[111]$ is shown in Figure 3.6a. The ordering is incorrect across AD, BE, DC, DA ...... planes. We note that in Figure 3.6b the correct ordering has been restored connecting the atoms across AA, CC, and EE. Thus, the NNNAPB plane is subdivided periodically with all Ni atoms arranged in the original ordered positions along [110] direction, with the adjacent layers of Fe and Ga not conforming to the original order.

**Figure 3.6** (a) Atomic displacements for Ni$_2$FeGa along the [111] direction. The atoms across the slip plane with a basic displacement of 1/4[111] are no longer in the correct position, (b) Upon a displacement of 1/2[111] atoms AA, CC, EE across the slip plane (APB) are partially ordered.

The superdislocation splitting into four superpartials with two NN APBs and one NNN APB can be described as,
\[
[111] = \frac{1}{4}[111] + \text{NNAPB} + \frac{1}{4}[111] + \text{NNAPB} + \frac{1}{4}[111] + \text{NNAPB} + \frac{1}{4}[111]
\]

where, the lattice constant is omitted in the expression. The APBs pull the partials together while their elastic interaction results in repulsion. There is equilibrium spacing for the APB boundaries. Ribbons of APB formed by dislocation glide are visible as bands in transmission electron microscopy of deformed samples which we discuss below.

The separations of the partial dislocations \(d_1\) and \(d_2\) can be calculated using force balance [60, 61] for each partial leading to the following equations:

\[
\begin{align*}
\gamma_{\text{NN}} & = K \left\{ \frac{1}{d_1} + \frac{1}{d_1 + d_2} + \frac{1}{2d_1 + d_2} \right\} \\
\gamma_{\text{NNN}} - \gamma_{\text{NN}} & = K \left\{ \frac{1}{d_2} + \frac{1}{d_1 + d_2} - \frac{1}{d_1} \right\}
\end{align*}
\]

These equations can be solved for the separation distances giving the energy levels and the other material constants as input. The factor \(K\) is given as \(K = \frac{\mu b_p^2}{2\pi}\) where \(\mu = 19\,\text{GPa}\) (obtained from our simulations), \(b_p = \frac{\sqrt{3}}{4}a_0\) and \(a_0 = 5.755\,\text{Å}\) as noted earlier. This results in \(d_1 = 1.73\,\text{nm}, d_2 = 2.41\,\text{nm}\), hence the width of the entire fault is of the order of \(10a_0\). We note that if the shear modulus is not known from simulations one can determine the value of \(K\) above from the cubic constants using a formula provided by Head [62].

### 3.4.2 The (011) <001> Case

We conducted simulations to determine the energy barriers (GSFE) for the (011) <111> dislocation slip. The (011) <111> dislocation slip system has been observed experimentally for CuZnAl alloys as mentioned earlier. As the ionic character of the bonding changes there is a transition to <100> slip as noted for NiTi [63]. Therefore, it is important to check the GSFE behavior and compare the results to the <111> case.
Figure 3.7 (a) Atomic configuration for the (011) <100> slip (b) the GSFE curve for the (011) <100> case.

The atomic configuration for our simulations is shown in Figure 3.7a. The GSFE results are given in Figure 3.7b. We note the stacking fault energy is near 250 mJ/m². Most importantly, the unstable energy barrier is very high near 1400 mJ/m². The full dislocation dissociated to $\frac{1}{2}[001]$ in this case. The stress level required to overcome the unstable barrier is rather high in this case, hence this slip system would require very high stress magnitudes to be activated in Ni$_2$FeGa.

3.5 Experimental Results

Single crystal Ni$_{54}$Fe$_{19}$Ga$_{27}$ with [0 0 1] orientation was utilized in this work. After single crystal growth, the samples were heat treated at 900 °C for 3 h and subsequently water quenched. The details of the processing and heat treatment are described in our previous work [46]. The Ni$_2$FeGa is characterized by the forward and reverse transformation temperatures obtained via differential scanning calorimetry. The reverse transformation temperature (martensite to
austenite) for the Ni-Fe-Ga alloy is 16°C. Our experiments were conducted at room temperature (25 °C). The material is in the austenitic state at the beginning of the experiment and undergoes a stress-induced transformation. In the first step the transformation is from $L_2_1$ to 10M with a transformation strain of 4%, then transformation to 14M results in additional 2% strain. Finally, the transformation to $L_1_0$ (tetragonal) results in a transformation strain as high as 12%. Single crystals (of [001] direction) were used in the experiments to facilitate the interpretation of results and maximize the transformation strains. The samples were deformed to a strain of 12% and then unloaded to zero strain. This process was repeated and pseudoelastic behavior was established cycle after cycle. The stress-strain response is shown in Figure 3.8a.

Digital image correlation results (DIC) providing for the strain fields are given in Figure 3.8a. The initial transformation stress represents the $L_2_1$ to 10M transformation. The details of the DIC technique for measuring the displacement fields by tracking features on the specimen surface can be found in [64]. The DIC local strain measurement images are shown at selected points along the curve for the Ni$_2$FeGa alloy. Each image in the figure corresponds to a marker point indicated on the stress-strain curve. Note that the loading axis for all images is vertical, and the color contours represent magnitudes of axial strain based on the inset common scale. With proper choice of magnification, nuances of martensite nucleation and strain gradients at austenite/martensite interfaces can be resolved.

As the loading reaches a critical transformation stress, one can establish the instant of martensite nucleation and the corresponding stress precisely. In the third image of the sequence (left to right), the 10M phase appears as the blue region and this 10M band propagates along the specimen length. This shows that it is possible to identify intermediate transformations not evident in the macroscale stress-strain response. With further deformation, a critical transformation stress for the $L_1_0$ phase is achieved at approximately 80 MPa and followed by a second plateau.

Under suitable composition and annealing conditions, second-phase ($\gamma$-phase) particles with a FCC structure can be precipitated in the $L_2_1$ austenite of Ni$_2$FeGa. Based on the Fe content determined by Energy-dispersive X-ray (EDX), this phase does not undergo a martensitic transformation, but plastic accommodation [33, 38]. In Figure 3.8b, the TEM results
are shown clearly displaying the presence of APBs in this alloy. The TEM samples were extracted from samples that have undergone pseudoelastic cycling as described above. The dislocations were retained after the cycling sequence. The APBs appear as series of lines and are extended across the specimen width. Considering some deviations because of magnetic rotation between diffraction patterns and the actual image, the trace of the image was found to be close to the {110} type plane.

![Image](image_url)

**Figure 3.8** (a) Pseudoelasticity experiments (at room temperature) [45] (b) TEM results displaying APBs in the austenite domains.

### 3.6 Implication of Results

Based on the GSFE results the ideal stress levels for dislocation slip were calculated for <111> and <001> directions and the magnitudes are shown in Table 2. We note that the stress magnitudes for slip nucleation, \(\tau_{\text{shear}}\), are rather high precluding significant slip within austenite. However, the stresses at the austenite-martensite interfaces can be sufficiently high to generate dislocation slip in the austenite domains. Furthermore, Fisher [65] made a first
order estimate of the additional stress associated with the dislocation motion creating a change in order within the crystal. The increase in energy of the interface needs to be balanced by the extra applied shear stress to move the dislocations. Upon utilizing 200 mJ/m² (corresponding to the lower value of $\gamma_{NN}$) we calculate the Fisher strengthening near 1 GPa for both cases as shown in Table 3.2.

**Table 3.2** Calculated fault energies, Burgers vector, (ideal) critical stress for slip nucleation and Fisher stress for movement of APBs.

<table>
<thead>
<tr>
<th>Slip Plane</th>
<th>Slip Direction</th>
<th>b (Å)</th>
<th>Fault Energy, $\gamma$ (mJ/m²)</th>
<th>$(\tau_{\text{shear}})_{\text{max}}$ (GPa)</th>
<th>$(\tau_{\text{shear}})_{F} = \frac{\gamma}{b}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>[111]</td>
<td>2.5</td>
<td>200</td>
<td>3.7</td>
<td>0.8</td>
</tr>
<tr>
<td>(110)</td>
<td>[001]</td>
<td>2.88</td>
<td>263</td>
<td>9.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

We finally note that the calculated separation distances for partials within the APBs are consistent with the experiments reported in this study. The precise width of the APBs can be further resolved by experiment utilizing high resolution methods, which are outside the scope of the present work. Even though the experimental measurement of separation distances is not available because they are only several nanometers, the experiments clearly show the presence of APBs. An example of high density of APB formation in Ni-Fe-Ga has also been reported by Chumlyakov [34] and the images are in agreement to those presented in this study.

We make a comparison between the current results and the work on CuZnAl alloys where the fault energies were of the order of 45 mJ/m², which resulted in prediction of Fisher strengthening near 330 MPa [66]. Similarly, if we are to consider dislocation glide in Ni₂FeGa
and use Fisher’s formula \( (\tau_{\text{shear}})_c \) we find the magnitude of extra shear stress to drag the APBs to be near 0.8 to 0.9 GPa. This magnitude is still significantly higher than the transformation stresses (less than 0.2 GPa) observed experimentally for Ni\(_2\)FeGa. Taking into account the temperature dependence in the phase transformation and plasticity behavior, we note that the critical stresses for the initial martensitic transformation and slip nucleation in Ni\(_2\)FeGa will be modified with increasing temperatures. However, the present results are insightful because they represent the energies associated with displacements to render the transformation or plasticity at a reference temperature (0K). Consequently, there is mounting evidence of the potential for Ni\(_2\)FeGa as a shape memory alloy with favorable characteristics. To our knowledge, this is the first time the transformation path for L\(_2\)\(_1\) to 10M for Ni\(_2\)FeGa has been determined and the GSFE in <111> and <001> directions are computed for the same alloy. Also, we present experimental evidence of APBs on samples that have undergone pseudoelastic cycling.

There are a number of reasons why a transformation is reversible versus irreversible. Reversibility is favored when the energy barriers for forward and reverse transformations are small compared to the energy barriers for dislocation slip. The absence of long range ordering results in rather large hysteresis levels in martensite transformations. For example, the Fe-C or Fe-Ni steels exhibit very large thermal hysteresis of the order of 400 °C, and the FeNiCoTi and FeMnSi fcc shape memory alloys (which do not have long-range ordering) also exhibit high hysteresis levels (200 °C). On the other hand, the Fe-Pt shape memory alloys, which can be ordered [67], exhibit hysteresis levels as low as 10 °C. In Ni based alloys (also of the shape memory variety) such as NiTi, NiTiX (X = Cu,Fe), where long-range ordered B2 to monoclinic martensite transformation has been observed, the hysteresis levels are typically of the order of 10 °C to 20 °C. In Ni\(_2\)FeGa, where the austenite phase is long-range ordered cubic L\(_2\)\(_1\) and the martensite is monoclinic 10M, the thermal hysteresis can be as low as 1 °C [32] generating new possibilities for applications [68]. It is shown that the transformation barrier is rather low in Ni\(_2\)FeGa (8.5 mJ/m\(^2\)), hence the critical stress levels for forward and reverse transformation are much lower than for dislocation slip.

There has been previous discussion of the slip systems in L\(_2\)\(_1\) shape memory alloys of the CuZnAl type. The <111> glide planes have been observed with APB formation for the L\(_2\)\(_1\) CuZnAl alloys as well [66, 69]. It is known that when the APB energies are low, <111> slip
dominates. As APB energies become higher with increasing ionic character, <100> slip is favored as noted by Rachinger and Cottrell [63]. The present results show that the unstable energies for the <001> case are exceedingly high precluding its occurrence unless the stress magnitudes exceed a few GPa.

Finally, we summarize what primarily influences the transformation reversibility of Ni$_2$FeGa alloys. The increase in elastic accommodation of the transformation with an increase in plastic slip resistance leads to the reversible transformations. We show that the slip resistance in long-ranged ordered Ni$_2$FeGa is high with total dislocations decomposing to partials connected with anti-phase boundaries.
Chapter 4 Plastic Deformation of NiTi Shape Memory Alloys

[The material in this chapter is published as T. Ezaz, J Wang, H. Sehitoglu, H.J. Maier, Acta Materialia, vol 61, 2012. This work is started by Dr. Ezaz]

4.1 Abstract

Dislocation slip in B2 NiTi is studied with atomistic simulations in conjunction with transmission electron microscopy. The atomistic simulations examine the generalized stacking fault energy (GSFE) curves for the \{011\}, \{211\} and \{001\} planes. The slip directions considered are \langle100\rangle, \langle111\rangle and \langle011\rangle. The results show smallest energy barriers for the \langle011\rangle[100] case, which is consistent with the experimental observations of dislocation slip reported in this study. To our knowledge, slip on the \langle011\rangle[1\overline{1}1] system is illustrated for the first time in our TEM findings, and atomistic simulations confirm that this system has the second lowest energy barrier. Specimens that underwent thermal cycling and pseudoelasticity show dislocation slip primarily in the austenite domains while the bulk of martensite domains does not display dislocations. The results are discussed via calculation of the ideal slip nucleation stress levels for the five potential slip systems in austenite.

4.2 Introduction

The shape memory alloy NiTi has considerable technological relevance and has also been scientifically perplexing. For some time, the plastic deformation of austenite via dislocation slip has not been fully understood, although it is very important as it limits the shape memory performance [48-53]. The role of slip in austenite has drawn significant attention recently [54-57].
The understanding of NiTi has been empowered with recent atomistic simulations. The simulations provide the energy levels for the different phases [4, 58, 59], the lattice parameters [38], the elastic constants [36] and the energy barriers for martensite twinning [20, 31]. Beyond these advances, a detailed consideration of the dislocation slip behavior via simulations is urgently needed to compare with the experimental findings of active slip systems. Upon establishing the GSFE (Generalized Stacking Fault Energy) curves in the austenitic (B2) phase, we study the propensity of five potential slip systems, and note the formation of anti-phase boundaries (APBs) in certain cases. Consequently, we assess the magnitude of ideal stresses needed to activate slip in these different systems. We find the (011)[100] system to be the most likely one consistent with experiments. The occurrence of (011)[111] slip is reported in our experimental findings in Section 4.3.1, which has not been reported earlier to our knowledge. This is the second most likely slip system after [100] slip.

To gain a better appreciation of the role of slip on shape memory behavior we show two results in Figure 4.1 for NiTi. In the first case, the temperature is cycled at a constant stress (Figure 4.1a). The range of temperature is 100 to -100 °C which is typical for application of NiTi. It is evident that as the stress magnitudes exceed 150 MPa, the strain upon heating is not fully recoverable. A small plastic strain remains and this is primarily due to residual dislocations in the B2 matrix. In Figure 4.1b the experiment is conducted at a constant temperature. The sample is deformed and austenite to martensite transformation occurs, with austenite domains primarily undergoing dislocation slip to accommodate the transformation strains (see Section 4.3.2 for further details). Upon unloading, a small but finite amount of plastic strain remains. The plastic strains become noticeable at the macroscale at stress levels exceeding 600 MPa for the solutionized 50.1%Ni NiTi. The small plastic strains can accumulate over many cycles and deteriorate the shape memory effect. Apart from the residual strain that is produced, the presence of plasticity reduces the maximum transformation strain and increases the stress hysteresis, two other measures of shape memory performance. This will be discussed further in Section 2.3.
Figure 4.1 Shape memory and pseudoelasticity experiments on solutionized 50.1%Ni-Ti, (a) The development of macroscopic plastic (residual) strain upon temperature cycling (100 °C to -100 °C) under constant stress [60] (b) The plastic (residual) strain under pseudoelasticity at constant temperature (T = 28°C).

Under fatigue loading, the NiTi alloys exhibit gradual degradation of pseudoelasticity with cycles, and this deterioration has been attributed to slip deformation [50, 51]. As stated above, the domains that undergo slip curtail the reversibility of transformation. Therefore, a higher slip resistance is desirable to achieve pseudoelasticity over many cycles in NiTi. Based on this background, it is extremely worthwhile to develop a quantitative understanding of dislocation slip; specifically, it’s crucial to determine the energy barriers (GSFE curves) for the most important slip systems. In this study, the simulation results (in Sections 4.4 and 4.5) are aimed towards building a framework for a better comprehension of shape memory alloys.

The glide planes and directions of possible slip systems in austenitic NiTi are shown as Figure 4.2. We note that there are multiple planes within the same family of slip systems, and only one of the planes is shown in Figure 4.2 for clarity. The potential slip planes are {011}, {211} and {001}. In the studies of Chumlyakov et al [7] and Tyumentsev et al. [61], NiTi is
deformed at high temperatures (>473K) where slip dominates. The slip systems were identified as {110}<010> and {100}<010>. The {110}<010> system was proposed by Moberly et al. [62]. More recently, Simon et al. [55], and Norfleet et al. [9] provided details of ‘transformation-induced plasticity’ and indexed the {101}<010> slip system. The ‘transformation-induced plasticity’ refers to the nucleation and buildup of slip in austenite to accommodate the rather high transformation strains [60, 63, 64] upon traversing martensite interfaces [64]. Recently, Delville et al. [65] argued the source of the irreversibility in shape memory alloys as primarily slip deformation; we note that residual martensite can also prevail, and contribute to the irreversibility.

Figure 4.2 Glide planes and directions of different possible slip systems in austenitic NiTi. The shaded ‘violet’ area points to the glide plane and the ‘orange’ arrow shows the glide direction in (a) (011)[100] (b) (011)[111] (c) (011)[011] (d) (211)[111] (e) (001)[010] systems respectively.
NiTi alloys exhibit considerable ductility. This high ductility behavior is viewed as unusual since B2 intermetallic alloys are expected to exhibit limited ductility [66]. As discussed above, the \{011\}<100> permits glide only in three independent slip systems. The presence of only three independent systems for the \{011\}<100> case was discussed in the textbook by Kelly, Groves and Kidd (p. 196) [67] and the recently in a paper on NiTi by Pelton et al. [10]. If loading was applied along any of the cube axis the cube is not able to deform because the resolved shear stress is zero for all possible \(<100>\) directions, hence certain orientations produce no glide if there are less than five independent slip systems. Given that at least five independent slip systems are required for dislocations to accommodate arbitrary deformations [68], additional slip systems must be present in B2 NiTi contributing to the enhanced plasticity. In B2 alloys, the potentially operative \{110\}<111> slip provides additional nine deformation modes that can contribute significantly to the superior ductility. The slip system \{110\}<111>, though observed in a few ordered intermetallic alloys of B2 type such as \(\beta\)-CuZn [69] and FeCo [70], has, however, not been reported for NiTi to our knowledge. Rachinger and Cottrell [71] classified the B2 type intermetallic compounds to two categories; (i) those of ionic binding with slip direction in \(<100>\) and (ii) those dominated by metallic binding with slip direction \(<111>\). In the present article, we report experimental evidence with transmission electron micrographs of \{110\}<111> slip in B2 NiTi in Section 4.3, and provide an energetic rationale in comparison to the other possible B2 slip modes such as \((011)[0\bar{1}1]\), \((001)[010]\) and \((\Sigma_{11})[111]\) in Section 4.5.

The underlying basis of dislocation motion in a certain glide plane and direction is described by the generalized stacking fault energy curve (GSFE) [72]. Simulations incorporating electronic structure are capable of predicting which systems are most likely. We also discuss dislocation dissociation scenarios for the \(<111>\) slip system in Section 5, uncovering the energetic basis (GSFE) of the super partials formed via dissociations with lower energy barriers.

Specifically, we focus on the \((011)[100]\) , \((011)[1\bar{1}1]\) , \((001)[010]\) , \((011)[0\bar{1}1]\) and \((\Sigma_{11})[111]\) dislocation slip cases. This information is critical for micro-mechanical models at higher length scales that can be used to predict the mechanical response during service as well as during processing. We also report transmission electron micrographs providing evidence of \((011)[1\bar{1}1]\) glide in conjunction with \((011)[100]\) slip from experiments under numerous
experimental conditions. Our quantitative GSFE calculations provide an underlying rationale for these observations and will be discussed in detail in the present article.

4.3 Experimental Results

4.3.1 Experimental Evidence of \{011\}<100> and (011)<111> Slip

To determine the slip planes and slip directions, experiments were conducted under compression at room temperature (28°C) on solutionized single crystals of 50.1%Ni NiTi. The solutionized (SL) samples underwent heating to 940°C for 24 hours and then quenching. In this case, the austenite finish temperature is 10 °C while the martensite finish temperature is near -40 °C. In Reference [73], the DSC curves for other heat treatments are provided.

The mechanical response of the deformed sample was presented as Figure 4.1b. In the case examined in this work, the specimen is subjected to compression in the [001] direction to strain levels of 5% and unloaded to zero stress. A very small residual plastic strain is present upon unloading and does not recover upon heating (Figure 4.1b). The overall behavior is pseudoleastic at the macroscale; however, dislocations are observed at the microscale.

The deformed samples are interrogated with transmission electron microscopy (TEM) upon conclusion of the pseudoleastic deformation response. Figure 4.3 shows TEM micrographs of dislocation arrangements observed at the same spot in the specimen deformed at room temperature. The Burgers vector of dislocations marked with the letter ‘A’ (colored white) in Figure 4.3a is identified to be [010] from \(g.b\) analysis. By contrast, the dislocations marked with the letter ‘B’ (colored white) in Figure 4.3b have a Burgers vector [1\(\overline{1}\)1]. These dislocations tangle each other, which is a cause of high strain hardening observed during deformation. To our knowledge, this is the first evidence of the presence of the [1\(\overline{1}\)1] dislocations in NiTi. We note that these dislocations are not inherited from martensite as the corresponding plane in martensite ((001)\(M\) plane) is not a slip plane [17].
Figure 4.3 (a) Transmission electron micrographs of dislocations in the specimen deformed at room temperature imaged with different g-vectors. The white arrow labeled with white letter ‘A’ points to dislocations of the \langle100\rangle type and (b) shows dislocations of the \langle1\bar{1}1\rangle type (labeled with white letter ‘B’).

4.3.2 Further Evidence of Dislocation Slip in Thermal Cycling and Pseudoelasticity Experiments at Microscale

Strong evidence of slip is noted in NiTi alloys of different compositions in early work which is summarized in Reference [60]. Typical Ni rich compositions studied in our work on single crystals are in the range 50.1 to 50.8% Ni. A series of strain-temperature responses were given in [60] and they conform to the pattern shown in Figure 4.1a. TEM results from these experiments under temperature cycling (under stress) are shown in Figures 4.4a through 4.4f. In all cases, the slip activity in the austenite phase is noted. When austenite to martensite interfaces are shown, it is noted that the dislocations exist primarily in the austenitic phase. In the case of 50.1% and 50.4%Ni NiTi compositions the temperature is cycled from RT→100°C→100°C→RT under stress. In Figure 4.4a the martensite and austenite domains are marked; in Figure 4.4b, the lower half of the image shows the transformation-induced dislocations in the austenitic phase, and the upper half shows the martensite. In Figures 4.4(c)-4.4(e) the dislocation configurations in the austenite away from the austenite-martensite interface
are shown. In the case of solutionized 50.8% Ni and higher Ni compositions the martensite start and finish temperatures are all below -100°C, hence the deformation is conducted in the pseudoelastic regime above austenite finish temperature as noted in Figure 4.4f.

![Figure 4.4](image)

(a) and (b) TEM images of a solutionized Ti-50.4at%Ni [123] single crystal taken at room temperature. Thermal-mechanically tested under constant uniaxial tensile load while the temperature was cycled from RT→100°C→100°C→RT. The load was increased in 25 MPa increments from 0 MPa to 100 MPa in successive tests (c) TEM image from single crystal of [111] 50.1%Ni orientation thermally cycled under constant load (1 cycle at each +10 MPa increment from +100 MPa to +170 MPa) showing dislocations within austenite, (d) TEM image from thermal cycling of 50.4%Ni NiTi in [123] orientation 1 cycle at each +25 MPa increments from +0 MPa to +100 MPa with RT→-100°C→100°C→RT, (e) TEM image from thermal
cycling of solutionized 50.4% Ni NiTi [001] orientation with the following history 1 Cycle at +125 MPa, +140 MPa, +170 MPa, +185 MPa, +215 MPa, +230 MPa, +245 MPa, +260 MPa; 2 Cycles at +200 MPa; 3 Cycles at +155 MPa (f) dislocation slip at room temperature of a solutionized Ti-50.8at%Ni [001] single crystal. Prior to TEM, the specimen was strained to 10% at room temperature (≈25°C).

4.3.3 Plasticity Mediated Transformation Strains and Residual Strains under Thermal Cycling at Macroscale

The results of differential scanning calorimetry for NiTi are shown in Figure 4.5a and the shape memory strains via temperature cycling under stress are shown in Figure 4.5b for 50.1%Ni. The strain for the correspondent variant pair CVP formation and CVP + detwinning strain from theory are marked in Figure 4.5b. This experiment is conducted on a single crystal with the loading axis in [123] direction. The detwinning strain in tension is appreciable and increases the maximum transformation strains depending on the crystal orientation. The main reason why the theoretical strain levels (10.51%) are not reached is the occurrence of slip resulting in irreversibility. The plastic strain is noted at the maximum temperature end of the strain-temperature curves as the stress level exceeds 125 MPa.

![DSC and Shape Memory Strains](image)

**Figure 4.5** (a) Differential scanning calorimetry results for solutionized 50.1%Ni-Ti and 50.4%Ni-Ti, the dotted curve is for cooling, the hysteresis levels are also marked on the figures
(b) Strain-temperature curves under temperature cycling showing the buildup of plastic strain with increase in stress (adapted from [60]).

4.4 Simulation Methodology-GSFE Calculations

The energy barrier during dislocation motion in a glide system is established via generalized stacking fault energy (GSFE) [30]. Also referred to as the fault energy curve, GSFE is defined as the energy associated with a rigid shift of the upper elastic half surface with respect to the lower half on a given slip plane in a given slip direction. During a GSFE calculation, a complete landscape of fault energy is investigated, which requires a displacement of a repeating unit lattice in the respective shear direction. Hence, the total displacement magnitudes in [100] and [111] directions are $a$ and $a[1\bar{1}1]=\sqrt{3}a$ respectively. The GSFE for the slip system $[uvw](hkl)$ is plotted against the displacement in each layer, $u_x$, which is normalized by its respective displacement, $[uvw]$

We used spin-polarized, ab-initio calculation to properly determine the undeformed and deformed energy states of NiTi austenite during the shearing in a certain slip system. The ab-initio calculations were conducted via the density functional theory based Vienna ab-initio Simulation Package (VASP) [25] and the generalized gradient approximation (GGA) [75] is implemented on a projection-augmented wave (PAW). Monkhorst-Pack $9\times9\times9$ $k$-point meshes were used for Brillouin zone integration. The structural parameter of NiTi in B2 phase was calculated first and found to be 3.004 Å with a stable energy of -6.95 eV/atom. We have used an $L$-layer $(hkl)$-based cell to calculate defect energies and performed shear along the $[uvw]$ direction to generate the GSFE curve in that system. We assessed the convergence of the GSFE energies with respect to increasing $L$, which indicates that the fault energy interaction in adjacent cells due to periodic boundary conditions will be negligible. The convergence is ensured once the energy calculations for $L$ and $L+1$ layers yield the same GSFE.

During calculation of GSFE, the calculation was followed up by incorporating a displacement of known magnitude (as discussed above) and performing a full internal atom relaxation, including perpendicular direction to the glide planes, until the atomic forces were less
than ±0.020 eV/Å. Further details of the computational method can be obtained in earlier literature [76].

4.5 Simulation Results

4.5.1 The (011)[100] Case

This is the most observed slip system in austenitic NiTi. In the B2 NiTi crystal structure, in the [011] stacking direction, in plane Ni (Ti) and out of plane - Ni (Ti) atoms are periodically arranged (stacking sequence ABAB…..) as shown in Figure 4.6a. During shearing the atom positions are shown in Figures 4.6b and 4.6c. The maximum energy barrier in this system is found to be 142 mJ/m² (shown in Figure 4.6d). The dislocations need to glide a distance ‘\(a\)’ in the [100] direction to preserve the same stacking sequence. After a glide of a distance \(a/2[100]\), the in plane Ni and in plane Ti reach the shortest near neighbor distance, which is shown in Figure 4.6b. This point corresponds to ‘unstable fault energy’. After a sliding distance of \(a/4\) (\(u_x/a[100]=0.25\)) and a distance of \(3a/4\) (\(u_x/a[100]=0.75\)) (antiphase of \(a/4\) (\(u_x/a[100]=0.25\))), the atomic positions of the first shear layer (shown by green box in Figure 4.6c) are different, which results in an unsymmetrical shape for the GSFE. Specifically, for the \(u_x/a[100]=0.75\) case (Figure 4.6c) the Ni atoms are positioned over other nickel atoms (near neighbors) which raises the energy levels. On the other hand, at \(u_x/a[100]=0.25\) the Ni atoms are positioned over Ti atoms in the next layer and the corresponding energy level is lower.
Figure 4.6 (a) Crystal structure of B2 NiTi observed from the [100] direction (b) after a rigid displacement of $a/2$ ($u_x/a[100] = 0.5$), the near neighbor distance of two in-plane Ni or Ti atoms becomes shortest (shown by red parenthesis) (c) after displacements of $a/4$ ($u_x/a[100] = 0.25$) and $3a/4$ ($u_x/a[100] = 0.75$), the position of atoms of the first shear layer (shown by green box) with respect to the undeformed lower half is different (d) GSFE curve for (011)[100] system.
4.5.2 The (011)[1\overline{1}1] Case

The energetics of (011)[1\overline{1}1] slip system is calculated and shown in Figure 4.7. We reported the occurrence of slip in this system in this study in Figure 4.5b. The stacking sequence is ABAB….. where the cell repeats every two planes in the [1\overline{1}1] direction. In Figure 4.7a, we show all the atoms and designate the furthest out of plane layer as (6) and the layer on the plane of the paper as in-plane (1). Atoms between layers 1 and 6 are shown with various diameters to indicate their position with respect to layers 1 and 6. The atom positions at \sqrt{3}a/3 (u_x/a||[1 \overline{1} 1]| = 0.33) and 2\sqrt{3}a/3 (u_x/a||[1 \overline{1} 1]| = 0.67) are shown in Figures 4.7b and 4.7c respectively. During sliding of the upper block of atoms relative to the lower half, the fault energy curve follows the typical antiphase boundary (APB) energy profile and is symmetric at the midpoint, \frac{3}{2} (u_x/a||[1 \overline{1} 1]| = 0.5) (shown in Figure 4.7d). The fault energy reaches a maximum (660 mJ/m^2) after a sliding distance \sqrt{3}a/3 (u_x/a||[1 \overline{1} 1]| = 0.33) (shown in Figure 4.7d) and 2\sqrt{3}a/3 (u_x/a||[1 \overline{1} 1]| = 0.67). At this position, near neighbor distances of two similar atoms (Ni or Ti) become the shortest. At \frac{3}{2} (u_x/a|[\overline{1} 1]| = 0.5), a slightly lower peak of 515 mJ/m^2 is observed where the near neighbor distance of two dissimilar atoms becomes the shortest.
Figure 4.7 (a) Crystal structure of B2 NiTi observed from the [\overline{2}\overline{1}\overline{1}] direction. Stacking sequence in the [011] direction is shown as ABAB. (b) after a rigid displacement of $\frac{\sqrt{3}a}{2} (u_x/a [1 \overline{1} 1] = 0.33)$, near neighbor distance of two out of plane Ni or Ti atoms becomes shortest (shown by green parenthesis). (c) after a displacement of $\frac{\sqrt{3}a}{2} (u_x/a [1 \overline{1} 1] = 0.5)$, near neighbor distance of out of plane Ni (Ti) and Ti (Ni) atoms becomes shortest (shown by red parenthesis), and the anti-phase boundary induced by slip alters the stacking of Ni and Ti atoms. (d) GSFE curve for the (011)[\overline{1}\overline{1}] system.
4.5.3 The (011)[0\bar{1}1] Case

The (011)[0\bar{1}1] system has been analyzed and the atom positions and the GSFE curve are shown in Figure 4.8. In the B2 structure, Ni and Ti atoms are periodically arranged (stacking sequence is ABAB… as shown in Figure 4.8a). Therefore, dislocations need to glide a distance $\sqrt{2}a$ in [0\bar{1}1] direction to obtain the same stacking sequence. After a glide of a distance $\sqrt{2}a / 2$, the Ni or Ti atoms reach the shortest near neighbor distance shown in Figure 4.8b. The maximum barrier energy in this system is found very high to be 1545 mJ/m$^2$ (shown in Figure 4.8c). Based on these results, (011)[0\bar{1}1] slip can occur at very high stress levels as we discuss later.

![Figure 4.8](image)

**Figure 4.8** (a) Crystal structure of B2 NiTi observed from the [100] direction (b) after a rigid displacement of $\sqrt{2}a / 2 (u_x / a |[0\bar{1}1]|= 0.5)$, the near neighbor distance of two in-plane Ni or Ti atoms becomes shortest (shown by red parenthesis) (c) GSFE curve for system (011)[0\bar{1}1].
4.5.4 The $(\bar{2}11)[111]$ Case

The $(\bar{2}11)[111]$ is a possible slip system in body centered cubic metals. The GSFE curve for the $(\bar{2}11)$ plane in the [111] direction is calculated by shearing the $(\bar{2}11)$ top half elastic space relative to the bottom in the [111] direction, as shown in Figure 4.9a. The viewing direction is $[0\bar{1}1]$. The GSFE in this system is plotted in Figure 4.9d. The plot reveals two distinct features for this system (i) there is a meta-stable position at the midpoint of a displacement of $\sqrt{3}a/2 (u_x/a[11\bar{1}]=0.5)$ (ii) the energy barriers for dislocation glide in [111] and in $[\bar{1}\bar{1}\bar{1}]$ directions are unequal. The maximum energy barrier is calculated to be 847 mJ/m$^2$ at position $u_x/a[11\bar{1}]=0.33$. At this position the near neighbor distance between two Ni or Ti atoms becomes the shortest. A meta-stable position is observed at $u_x/a[11\bar{1}]=0.5$, which lowers the energy by 155 mJ/m$^2$ to 692 mJ/m$^2$. A second peak is observed at $u_x/a[11\bar{1}]=0.67$ with 795 mJ/m$^2$. 
Figure 4.9 (a) Crystal structure of B2 NiTi observed from the [0\bar{1}1] direction. The stacking sequence is ABCDEFA, where the cell repeats every 6 planes in the [\bar{2}11] direction, the dashed line denotes the slip plane (b) after a rigid displacement of $\sqrt{3}a/3 (u_x/a[111]=0.33)$, near neighbor distance of two in-plane Ni or Ti atoms is shortest (shown by red parenthesis) (c) after a rigid displacement of $2\sqrt{3}a/3 (u_x/a[111]=0.67)$, near neighbor distance of in-plane Ni and
out of plane Ti atoms is largest (shown by red parenthesis). (d) GSFE curve for the \(\{211\}{[111]}\) system.

### 4.5.5 The \((001)[010]\) Case

Another possible slip system for the body centered cubic structure is \((001)[010]\) and is also investigated for B2 NiTi. In the B2 structure, Ni and Ti atoms are symmetrically arranged in the \([001]\) and \([010]\) direction, which is shown in Figure 4.10a. During shearing in this system, in-plane Ni and out of plane Ti atoms get nearer only at a position \(a/2 (u_x/a|[010]|=0.5)\) (shown in Figure 4.10b). The GSFE curve shown in Figure 4.10c exhibits only one peak pointing out this position. The maximum energy barrier for atoms to glide in \((001)\) in \([100]\) direction is calculated to be 863 mJ/m².

![Figure 4.10](image)

**Figure 4.10** (a) Crystal structure of B2 NiTi observed from the \([100]\) direction (b) after a rigid displacement of \(a/2 (u_x/a|[010]|=0.5)\), near neighbor distance of in-plane Ni and out-of-plane Ti atoms becomes shortest (shown by red parenthesis). (c) GSFE curve for the \((001)[010]\) system.

### 4.6 Analysis and Discussion of Results

The importance of slip in influencing the shape memory alloy characteristics is well known and further illustrated based on the TEM images given in Figures 4.3 and 4.5. The
observation of (011)[1 11] slip in Figure 4.3b is particularly noteworthy (and first to our knowledge).

Although some of the shape memory materials have high theoretical transformation strains such as the Cu-based alloys [77] and Fe-based alloys [78, 79], their performance have not been as favorable because of the occurrence of plastic deformation. The NiTi alloys have been widely accepted as having superior performance characteristics because of their inherent resistance to slip. The present work explains the origins of the high resistance to slip in NiTi alloys. In B2 NiTi, slip systems such as (211)[1 11] or (011)[100] have significantly higher fault barrier energy as compared to the (011)[100] and (011)[1 11] systems. Thus, in B2 NiTi, dislocation glide is more likely in the (011)[100] and (011)[1 11] systems.

The [1 11] dislocation can dissociate into partial dislocations with smaller Burgers vectors. According to the Frank’s energy criteria, a \( a[1 \bar{1} 1] \) dislocation can dissociate into two \( \frac{a}{2}[1 \bar{1} 1] \) partial dislocations.

\[
a[1 \bar{1} 1] \rightarrow \frac{a}{2}[1 \bar{1} 1] + \frac{a}{2}[1 \bar{1} 1] \tag{1}
\]

This kind of dissociation has been reported for FeAl or CuZn [80]. In the ordered NiTi, an energy well is present in the (011)[1 11] GSFE curve at \( u_x/a[1 \bar{1} 1] = 0.5 \) (Figure 4.7(d)) confirming the presence of an APB. Hence, dislocations present in (011)[1 11] system can dissociate into partial dislocations with a stable equilibrium distance. We note that the separation distance would be rather small in view of the high APB energy and the resolved stress required would need to be rather high to move these dislocations.

The [1 11] dislocations can decompose into perfect dislocations on the (011) plane. Hence, as illustrated in Figure 4.11, a \( a[1 \bar{1} 1] \) dislocation dissociates according to (2). In Figure 11, \( b_2, b_3 \) represent the dissociated dislocations.
\[ a[1\bar{1}1] \rightarrow a[100] + a[0\bar{1}1] \]  
\[ b_1 \rightarrow b_2 + b_3 \]  

The \( b_3 \) dislocation may further decompose to yield additional <100> type perfect dislocations

\[ a[0\bar{1}1] \rightarrow a[0\bar{1}0] + a[001] \]

Based on the simple Frank's rule, there is no change in elastic energy associated with (2) and (3) as noted first by Nabarro [81]. And, a resolved stress that acts favorably on the \( a[100] \) can move this dislocation independently of others. This is particularly true in view of the lower GSFE magnitudes for the \( a[001] \) case. Therefore, the \([1\bar{1}1]\) or even \([0\bar{1}1]\) dislocations could exist in the crystal, but they do not dominate the dislocation slip process because they decompose, under sufficient stress, to yield <100> dislocations.

**Figure 4.11** Decomposition of \([1\bar{1}1]\) slip \( (b_1) \) along \([0\bar{1}1]\) \( (b_3) \) and \([100]\) \( (b_2) \) directions. The slip plane shown is \((011)\). Ni atoms are denoted by the dark shading in this schematic.

In the case of austenitic NiTi, <111> or <100> slip are identified as noted in Figure 4.3. Two factors are noteworthy. The first is that the B2 NiTi maintains a strong directionality in its Ni-Ni, Ti-Ti and Ni-Ti bonds; hence, a covalent bonding nature is observed in its deformation characteristics [82]. This covalent nature influences the energy levels observed during the entire simulations. The second factor is that the interplanar distance between \{112\} plane is measured to be 1.23 Å, whereas between \{011\}, this is calculated to be 2.13 Å. Shearing of covalent bonds
with smaller interplanar distance requires higher stresses and is manifested by a higher maximum fault energy.

The magnitude of maximum fault energy indicates the most energetically favorable system for dislocation nucleation\[83, 84\] and the slope of the GSFE curve equivalently measures the slip nucleation stress as follows, \( (\tau_{\text{SLIP}})_{\text{ideal}} = \frac{\partial \gamma}{\partial \delta u} \bigg|_{\max} \) \[85, 86\]. Hence, in a cubic system, with a single family of slip systems, the maximum energy barrier and ideal slip nucleation stress has a one to one correlation with each other and unstable stacking fault energy \( \gamma_{\text{us}} \) can be utilized to point out the active slip systems. In the case of a cubic system with multiple slip systems, the slip vector needs to be accounted for the calculation of ideal stress as well. The results shown in Table 4.1 utilize both the \( \gamma_{\text{us}} \) values and the corresponding Burgers vector for different slip systems in calculation of ideal stress. Also, we note that ideal slip nucleation stress calculated from the GSFE of particular system accounts the anisotropy of system and a measure without any continuum approximation. However, ideal nucleation stress differs from actual since energy associated with creation of surface during dislocation emission and effects related to reconstruction of the dislocation core are neglected which contributes to actual Peierls stress. These approximations may affect the exact number, but we expect the qualitative picture to remain the same.

Table 4.1 Maximum fault energy, shear modulus and elastic energy in different possible slip systems in B2 NiTi. The fault energy (computational) tolerance is less than 0.17 mJ/m\(^2\).

<table>
<thead>
<tr>
<th>Slip Plane</th>
<th>Burgers Vector</th>
<th>Maximum fault energy (mJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(011)</td>
<td>[100]</td>
<td>142</td>
</tr>
<tr>
<td>(011)</td>
<td>[111]</td>
<td>660</td>
</tr>
<tr>
<td>(011)</td>
<td>[011]</td>
<td>1545</td>
</tr>
<tr>
<td>(211)</td>
<td>[111]</td>
<td>847</td>
</tr>
<tr>
<td>(100)</td>
<td>[010]</td>
<td>863</td>
</tr>
</tbody>
</table>
It is important to point that the unstable stacking fault energy for the (011)[100]is 142 mJ/m$^2$ which is significantly lower than for pure metals and B19' martensite [76]. Consequently, slip in the B2 system is favored compared to martensite (B19') slip as noted in Figures 4.3a and 4.3b and Figures 4.5. The (011)[100] system will be activated at 2.6 GPa and the (011)[1 T1] system is expected to be activated at ideal stresses exceeding 5 GPa (Table 4.2). These levels represent ideal stresses and in experiments, local stresses in the vicinity of martensites [87], or near precipitates can be significant in mediating dislocation slip plasticity. In the analysis of Norfleet, the most stressed slip systems upon stress-induced transformation exceeded 2500 MPa, triggering local slip in austenite [56]. Also, experiments on nanopillars confirm that plastic deformation initiated in austenite at stress levels exceeding 2.5 GPa [88].

<table>
<thead>
<tr>
<th>Slip Plane</th>
<th>Slip Direction</th>
<th>$(\tau_{shear})<em>{ideal} = \frac{\delta y}{\delta u_x}</em>{\text{max}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(011)</td>
<td>[100]</td>
<td>2667</td>
</tr>
<tr>
<td>(011)</td>
<td>[1 T1]</td>
<td>5561</td>
</tr>
<tr>
<td>(011)</td>
<td>[0 T1]</td>
<td>12847</td>
</tr>
<tr>
<td>(211)</td>
<td>[111]</td>
<td>7430</td>
</tr>
<tr>
<td>(100)</td>
<td>[010]</td>
<td>9320</td>
</tr>
</tbody>
</table>

Returning to the GSFE of the (211)[111] system, as noted earlier, the energetic barrier for dislocation glide is higher than for (011)[1 T1] or (011)[100]. Hence, in B2 NiTi, dislocation glide in this system is possible only when the Schmid factor associated with internal stresses provides a large contribution. A metastable position is observed at $u_x / a ||[111]| = 0.5$ in this system. However, to nucleate any $\frac{a}{2}[111]$ superpartial, the atoms have to overcome an energy barrier of 847 mJ/m$^2$ with a shear of 2.12. However, the energetic profile of (211)[111] is
important since twinning glide can occur in this system. A perfect [111] dislocation can
dissociate into three $\frac{a}{3}[111]$ super partials that glide in three consecutive planes and generate a
three layer twin [54, 89]. The energy barrier during (112) twinning has recently been calculated [90].

The study sheds light into whether to- and -fro APB dragging can be a possible mechanism for shape memory. The concept is intriguing, under stress or temperature changes, the (011)[1\bar{1}1] dislocation motion could undergo reversible motion. Such a mechanism could potentially explain cases where the material undergoes nearly complete recovery despite the presence of dislocations in the micrographs. We note the need for further research in this particular area.

4.7 Summary

Further advances towards a quantitative understanding of slip in austenitic NiTi have been achieved. The results explain, in light of the generalized stacking fault energy curves (GSFE), why mainly (011)[100] and (011)[1\bar{1}1] systems are observed in experiments, and we provide a rationale for slip resistance in NiTi austenite with our predictions.

As shown in Table 4.2, the magnitude of ideal stress required for dislocation slip is determined to exceed 2 GPa. The reversible transformation can occur without dislocation build up provided that transformation stress magnitudes are limited levels less than that to activate slip. This is indeed the case for the NiTi alloys; and further improvement of slip resistance is important because the TEM evidence points to activation of slip in pseudoelastic and shape memory cases. The present results emphasize the importance of understanding of the atomic displacements and metastable positions (APBs) in most important slip systems. Overall, the study represents a methodology for consideration of a better understanding of shape memory alloys.
Chapter 5  Dislocation Slip Stress Prediction in Shape Memory Alloys


5.1 Abstract

We provide an extended Peierls-Nabarro (P-N) formulation with a sinusoidal series representation of generalized stacking fault energy (GSFE) to establish flow stress in a Ni$_2$FeGa shape memory alloy. The resultant martensite structure in Ni$_2$FeGa is L1$_0$ tetragonal. The atomistic simulations allowed determination of the GSFE landscapes for the (111) slip plane and \( \frac{1}{2}[\bar{1}01], \frac{1}{2}[\bar{1}10], \frac{1}{6}[\bar{2}11] \) and \( \frac{1}{6}[1\bar{1}2] \) slip vectors. The energy barriers in the (111) plane were associated with superlattice intrinsic stacking faults, complex stacking faults and anti-phase boundaries. The smallest energy barrier was determined as 168 mJ/m$^2$ corresponding to a Peierls stress of 1.1 GPa for the \( \frac{1}{6}[1\bar{1}2](111) \) slip system. Experiments on single crystals of Ni$_2$FeGa were conducted under tension where the specimen underwent austenite to martensite transformation followed by elasto-plastic martensite deformation. The experimentally determined martensite slip stress (0.75 GPa) was much closer to the P-N stress predictions (1.1 GPa) compared to the theoretical slip stress levels (3.65 GPa). The evidence of dislocation slip in Ni$_2$FeGa martensite was also identified with transformation electron microscopy observations. We also investigated dislocation slip in several important shape memory alloys and predicted Peierls stresses in Ni$_2$FeGa, NiTi, Co$_2$NiGa, Co$_2$NiAl, CuZn and Ni$_2$TiHf austenite in excellent agreement with experiments.
5.2. Introduction

5.2.1 Background

Shape memory alloys with high temperature [7-10, 91-95] and magnetic actuation capabilities [96-102] have generated considerable recent interest. The development of such alloys has traditionally relied on processing of different chemical compositions, making polycrystalline ingots, and then taking the expensive route of making single crystals. Then, the alloys have been tested under temperature or stress cycling, and in the case of ferromagnetic shape memory alloys under applied magnetic fields [103]. Additional tests may be necessary to establish the elastic constants, lattice constants and to determine the twinning stress and the slip stress of the austenite and martensite phases. There are numerous advantages to establishing the material performance in advance of the lengthy experimental procedures with simulations to accelerate the understanding of these alloys and to establish a number of key properties. Therefore, rapid assessment of potential alloys can be ascertained via determination of twinning, slip and phase transformation barriers, the stability of different phases (austenite and martensite), their respective elastic constants, and lattice constants. In this paper we focus on the slip stress determination with simulations and compare the results to experiments. We combine the ab-initio calculations with a modified mesoscale Peierls-Nabarro based formulation to determine stress levels for slip in close agreement with experiments.

We utilize the Ni$_2$FeGa as an example system to illustrate our methodology and then show its applicability to the most important SMAs. The Ni$_2$FeGa alloys are a new class of shape memory alloys (SMAs) and have received significant attention because of high transformation strains (>12% in tension and >6% in compression) and low temperature hysteresis. They also have the potential for magnetic actuation and high temperature shape memory [7, 8]. The magnetic actuation requires twinning at low stress magnitudes, and high temperature shape memory can only occur in the presence of considerable slip resistance. These alloys are proposed to be a good alternative to the currently studied ferromagnetic Ni$_2$MnGa-based SMAs due to their superior ductility in tension [9, 104-106]. There are several crystal structures identified in Ni$_2$FeGa [8, 10, 11], which exhibits martensitic transformations from L2$_1$ cubic austenite to intermediate 10M/14M modulated monoclinic martensites, and finally to the L1$_0$ tetragonal
martensite [9, 12-14]. However, one can get a single stage transformation from L2₁ to L1₀ as temperature is increased [8], also in the case of nano-pillars [107], and upon aging treatment [108]. Therefore, a study on the L1₀ martensite is both scientifically interesting and technologically relevant. The phase transformation of Ni₂FeGa has been experimentally observed and theoretically investigated using atomistic simulations [10, 14, 15, 109, 110]. The results show that the L2₁ austenite requires much high stress levels for dislocation slip while undergoing transformation nucleation at much lower stress magnitudes [15]. However, the plastic deformation of L1₀ martensite via dislocation slip has not been fully understood, although it is very important in understanding the shape memory performance.

Figure 5.1 shows a schematic of the stress-strain curve of Ni₂FeGa at temperatures in the range 75°C to 300°C where L2₁ can directly transform to L1₀. These temperatures are significantly above the austenite finish temperature. The initial phase of Ni₂FeGa is L2₁ and it transforms to L1₀ when the stress level reaches the transformation stress. The transformation occurs at a near plateau stress followed by elastic deformation of martensite. With further deformation, dislocation slip (of L1₀) takes place at a critical stress designated as σ_{slip}. This stress is much higher than the transformation stress. During unloading, the reverse phase transformation occurs with plastic (residual) strain remaining in Ni₂FeGa as part of the deformation cannot be recovered.
Figure 5.1 Schematic illustration of the stress-strain curve showing the martensitic transformation from L2₁ to L1₀, and the dislocation slip in L1₀ of Ni₂FeGa at elevated temperature. After unloading, plastic (residual) strain is observed in the material as deformation cannot be fully recovered.

It is well known that plastic deformation occurs via dislocation glide; and at the atomic level, dislocation glide occurs upon shear of atomic layers relative to one another in the lattice. At the dislocation core scale, quantum mechanics describe the atomic level interactions and the forces exerted on atoms; while at the mesoscale level, elastic strain fields of defects address the interactions [24]. The ensemble of dislocations and their interactions with the microstructure define the continuum behavior.

With atomistic simulations one can gain a better understanding of the lattice parameters and the unstable fault energies of L1₀. Therefore, atomistic simulations in this case will provide additional insight into material’s behavior and the deformation mechanisms [20]. Figure 5.2 shows the different length scales associated with plasticity of transforming Ni₂FeGa alloys. The
generalized stacking fault energy (GSFE) surface (γ-surface) at the atomic level (via atomistic simulations using density functional theory (DFT)) is shown at the lowest length scale. Of particular interest is the (111) plane, and from the entire γ-surface the propensity of slip in multiple directions can be established. The energy landscape for slip that is calculated is rather complex for the case of ordered shape memory alloys resulting in complex faults and anti-phase boundaries.

In the material science and meso-continuum mechanics field, coupling the various length scales involved in order to understand the plastic deformation still remains a major challenge [23]. The Peierls-Nabarro (P-N) model represents a mesoscale level integration of atomistic and elasticity theory considerations. It accounts for the dislocation cores on one hand and lattice resistance to flow by applying continuum concepts to elastic deformation at atomic scale [24]. The model has stood the test of time over many years, and its main contribution is that the P-N stress level for dislocation glide are much lower than ideal stress calculations [27-30]. The calculations for P-N stress represent the breakaway of atoms within the core region of the dislocation. If the core is narrow the stress required to overcome the barrier is higher compared to the case of a wider core, and smaller Burgers vectors require lower stress for glide. Different slip systems in fcc, bcc and ordered crystals can be evaluated, and the most favorable planes and directions can be readily identified. Thus, the P-N model predicts stresses for dislocation slip more precisely than the theoretical shear strength obtained directly from atomistic simulations.

In this study, the P-N model with modifications will be utilized to study the slip resistance. In Figure 5.2, the disregistry above and below the slip plane is shown which will be explained later in the paper. This results in a solution for the slip distribution (disregistry) within the core that exhibits a non-monotonic variation as a function of core position. We have made observations of slip during experiments in this paper and also in pseudoelasticity experiments at constant temperature. The dislocation slip was identified upon heating-cooling within the TEM via in-situ observations. Finally, we compared the calculated slip stresses with experimental measurements of slip stress under compression loading to strain exceeding 6%. The agreement is excellent considering the complexity of real microstructures and the idealizations adopted in theoretical models.
The occurrence of dislocation slip is noted at macro-scale by observing non-closure of the strain-temperature curves in Figure 5.2. For example, upon cooling the austenite reverts to martensite and upon heating the reverse transformation occurs. If the entire process is reversible, the transformation strain in forward and reverse directions is identical. If plastic deformation develops, there is a residual strain upon heating to austenite. We are not attempting to predict the entire strain-temperature response at the continuum level (shown in Figure 5.2) because multiple slip-twin systems and multi-phase interactions are governing. Our purpose is to point out the complexity of an isolated mechanism, mainly the dislocation glide behavior that contributes to the irreversibility.

Figure 5.2 Schematic description of the different length scales associated with plasticity in Ni$_2$FeGa alloys.

5.2.2 Dislocation Slip Mechanism

So far, the investigation of L1$_0$Ni$_2$FeGa martensite has been mostly through experimental research. Its properties are not well understood although it is very important to establish its dislocation slip behavior. The L1$_0$Ni$_2$FeGa has a tetragonal structure with no modulation [9, 12]. The modulation refers to the internally sheared crystal structures with periodic displacements. As a fundamental deformation mechanism, dislocation slip plays a critical role in defining the mechanical properties of SMAs, especially their irreversibility of transformation [15, 111, 112].
It is likely that the material can exhibit different dislocation slip modes (planes and directions), which are activated at different stress levels. To quantitatively understand the experimentally observed dislocation slip, a detailed study via atomistic simulations is needed to determine active slip systems and compare with experimental findings. It is possible to investigate the dislocation slip via generalized stacking fault energy (GSFE) curves. GSFE is the interplanar potential energy determined by rigidly sliding one half of a crystal over the other half [27, 113]. It was first introduced by Vitek [72] and is a comprehensive definition of the fault energy associated with dislocation motion [15]. By taking the maximum slope of the GSFE curve, the theoretical shear strength of the lattice along the slip direction is obtained. This stress is the upper bound on the flow stress of materials [28, 114] and is a much larger value compared to the experiments.

The Peierls-Nabarro (P-N) model is essentially based on continuum mechanics applied to lower length scales and addresses the dislocation structure by applying the elasticity theory and energetics from atomistic simulations. This model calculates stresses for dislocation slip more precisely. The corresponding Peierls stress \( \tau_p \) is the minimum external stress required to move a dislocation irreversibly through a crystal and can be considered as the critical resolved shear stress at 0 K [115-117]. The slip system with lowest \( \tau_p \) will be the dominant system in the crystal [113, 118, 119]. Recently, there has been renewed interest in calculating Peierls stress of dislocation by applying the P-N model [113, 120]. This is motivated by the advance of reliable first-principles calculations using DFT to determine the GSFE (\( \gamma \) energy) landscapes. However, when the GSFE curve comprises of multiple minima corresponding to various fault configurations, it cannot be approximated well by a single sinusoidal function as used in the original P-N model. Therefore, the representation of the P-N model needs to be modified to consider this complexity, which is described in detail in this study and applied for the dislocation slip calculations in L10 Ni2FeGa.

### 5.2.3 Purpose and Scope

A fundamental understanding of the dislocation slip that plays a key role in the shape memory behavior of L10 Ni2FeGa is currently lacking, which is essential for understanding the
mechanical response. Four possible slip systems in L1₀ martensite, \( \frac{1}{2} < \bar{1} 01 \)(111), \( \frac{1}{2} < \bar{1} 10 \)(111), \( \frac{1}{6} < \bar{2}11 \)(111) and \( \frac{1}{6} < 11 \bar{2} \)(111) are considered in Ni₂FeGa. Three related types of planar defects, superlattice intrinsic stacking fault (SISF), complex stacking fault (CSF) and anti-phase boundary (APB), are analyzed. We note that due to the tetragonality of the L1₀ lattice of Ni₂FeGa, the dislocation behavior of \( \frac{1}{6} [11 \bar{2}] \) is different from \( \frac{1}{6} [\bar{2}11] \)(similarly, \( \frac{1}{2} [\bar{1}01] \) is different from \( \frac{1}{2} [\bar{1}10] \)), which results in different energy levels as reported in section 3.2. Thus, in this paper the Miller indices with mixed parentheses \( <uvw> \) and \( \{hkl\} \) are used in order to differentiate the first two equivalent indices (corresponding to the a and b axis in the L1₀ lattice) from the third (corresponding to the tetragonal c axis), which indicate that all permutations of the first two indices are allowed, whereas the third one is fixed [121]. The purpose of this paper is to investigate the possible slip systems existing in L1₀ Ni₂FeGa, and to determine the most likely one by calculating the Peierls stresses and compare it with experimental observations. The results indicate that the mobility of the \( \frac{1}{6} [11 \bar{2}] \) partial dislocation in the slip plane (111) is controlling the plasticity of L1₀ Ni₂FeGa.

5.3 DFT Calculation Setup

We utilized DFT to precisely determine the undeformed and deformed energy states of L1₀ Ni₂FeGa during shearing in certain slip systems. The first-principles total-energy calculations were carried out using the Vienna ab initio Simulations Package (VASP) with the projector augmented wave (PAW) method and the generalized gradient approximation (GGA) [25, 26]. Monkhorst Pack 9×9×9 k-point meshes were used for the Brillouin-zone integration to ensure the convergence of results. An energy cut-off of 500 eV was used for the plane-wave basis set. The total energy was converged to less than \( 10^{-5} \) eV per atom. We have used an n-layer based cell to calculate fault energies to generate GSFE curves in the different slip systems. We assessed the convergence of the GSFE energies with respect to increasing \( n \), which indicates
that the fault energy interaction in adjacent cells due to periodic boundary conditions will be negligible. The convergence is ensured once the energy calculations for \( n \) and \( n+1 \) layers yield the same GSFE. In the present work, \( n \) was taken as 10 in order to obtain the convergent results. For each shear displacement \( u \), a full internal atom relaxation, including perpendicular and parallel directions to the fault plane, was allowed for minimizing the short-range interaction between misfitted layers near to the fault plane. This relaxation process caused a small additional atomic displacement \( r = \sqrt{r_x^2 + r_y^2 + r_z^2} \) in magnitude within 1\% of the Burgers vector \( b \). Thus, the total fault displacement is not exactly equal to \( u \) but involves additional \( r \). The total energy of the deformed (faulted) crystal was minimized during this relaxation process through which atoms can avoid coming too close to each other during shear [85, 122, 123]. From the calculation results of dislocation slip, we note that the energy barrier after full relaxation was near 10\% lower than the barrier where the relaxation of only perpendicular to the fault plane was allowed.

### 5.4 Simulation Results and Discussion

#### 5.4.1 The L1\(_0\) Crystal Structure

We note that two different unit cells are used in literature to describe the L1\(_0\) crystal structure. One is directly derived from the L2\(_1\) body centered cubic (bcc) axes forming a body centered tetragonal (bct) structure (Figure 5.3a); the other one is constructed from the principal axes of L1\(_0\) forming the face centered tetragonal (fct) structure (shown in brown dashed lines in Figure 5.3a). We note that if \( 2c = \sqrt{2}a \), Figure 3a represents the L2\(_1\) cubic structure; while if \( 2c \neq \sqrt{2}a \), it is the L1\(_0\) tetragonal structure. In this paper, the L1\(_0\) fct structure is considered and its corresponding lattice parameters are shown in Figure 5.3b. Note that the tetragonal axis is \( 2c \), so the L1\(_0\) unit cell contains two fct unit cells.
Figure 5.3 L1\textsubscript{0} unit cell of Ni\textsubscript{2}FeGa. (a) The body centered tetragonal (bct) structure of L1\textsubscript{0} is constructed from eight bct unit cells and has lattice parameters $\sqrt{2}a$, $\sqrt{2}a$ and $2c$. The blue, red and green atoms correspond to Ni, Fe and Ga atoms, respectively. The Fe and Ga atoms are located at corners and Ni atoms are at the center. The fct structure shown in brown dashed lines is constructed from the principal axes of L1\textsubscript{0}. (b) The fct structure of L1\textsubscript{0} with lattice parameters $a$, $a$ and $2c$ contains two fct unit cells.

The lattice parameter of L2\textsubscript{1} cubic was calculated as $2a_{0} = 5.755$ Å in our previous study [15]. During the martensitic transformation from L2\textsubscript{1} cubic to L1\textsubscript{0} tetragonal in Ni\textsubscript{2}FeGa, the unit cell volume can be changed since the material is always energetically more stable with lower energy level. For a certain unit cell volume of L1\textsubscript{0} tetragonal, there are many combinations of parameters $c$ and $a$ (or tetragonal ratio $c/a$), and one of these ratios yields the structure with the minimum energy level. To compute the unit cell volume change $\Delta V$ during the martensitic transformation, we considered a series of values $\Delta V / V_{0}$ (-3% to 3%), where $V_{0}$ is the L2\textsubscript{1} unit cell volume as the reference. For any $\Delta V / V_{0}$, we changed the tetragonal ratio $c/a$ from 0.55 to 1.1 and found that the minimum crystal structural energy almost always remains at a $c/a$ ratio of 0.95. The crystal structural energy as a function of $c/a$ in varying $\Delta V / V_{0}$ was calculated and
shown in Figure 5.4a (only a part of the calculated curves for a series of $\Delta V / V_0$ is shown for clarity). The lowest energy level among a series of $\Delta V / V_0$ was found at a $\Delta V / V_0$ of -0.76% and the corresponding crystal structure was L1$_0$. Figure 5.4b is a high resolution plot of the red dashed lines in (a) showing the minimum energy lever at the c/a ratio of 0.95 in the volume change $\Delta V / V_0$ of -0.76%. This energy was lower than L2$_1$ by 12.4 meV/atom, which indicates that the L1$_0$ is energetically more stable. The L1$_0$ lattice parameters were calculated as a=b=3.68 Å, and c=3.49 Å in Table 1 and they were in a good agreement with experimental measurements [9]. We note that the alloy in the experiment is off stoichiometry (Ni$_{54}$Fe$_{19}$Ga$_{27}$) [2] compared to our simulations (Ni$_{50}$Fe$_{25}$Ga$_{25}$), which causes the slight difference of the lattice parameters. These precisely determined lattice parameters form the foundation of atomistic simulations in this study. In the following section, we establish GSFE curves based on these parameters.

**Figure 5.4** (a) Crystal structural energy variation with tetragonal ratio c/a for a series of unit cell volume changes $\Delta V / V_0$, where L2$_1$ is considered as the reference volume $V_0$. The L1$_0$ tetragonal structure was found at a c/a of 0.95 for $\Delta V / V_0$ of -0.76%. (b) High resolution plot corresponding to the red dashed lines in (a).
Table 5.1 VASP-PAW-GGA calculated L1₀ tetragonal lattice parameters, unit cell volume change $\Delta V / V_0$ and structural energy relative to L2₁ cubic in Ni₂FeGa compared with experimental data.

<table>
<thead>
<tr>
<th>L1₀ tetragonal structure</th>
<th>Experiment [9]</th>
<th>Theory (this study)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>3.81</td>
<td>3.68</td>
</tr>
<tr>
<td>c</td>
<td>3.27</td>
<td>3.49</td>
</tr>
<tr>
<td>Volume change $\Delta V / V_0$ (%)</td>
<td>-0.65</td>
<td>-0.76</td>
</tr>
<tr>
<td>Structural energy relative to L2₁ (meV/atom)</td>
<td>_</td>
<td>-12.4</td>
</tr>
</tbody>
</table>

The dash indicates that experimental data were not available for comparison.

5.4.2 Dislocation Slip of L1₀Ni₂FeGa

From the classical dislocation theory, the most favorable slip systems should contain the close-packed lattice planes and the Burgers vectors with shortest shear displacements. Thus, dislocation slip in the L1₀ fct structure favors the {111} planes along close or relatively close packed directions. The {111} planes are preferred planes as in fcc metals [121], but the favorable dislocations in these planes are not identified. It is well known that superdislocations of the L1₀ structure can split into different types of partial dislocations with smaller Burgers vectors and smaller planar fault energies [124-126]. Figure 5.5 shows a top view from the direction perpendicular to the (111) slip plane with three-layers of atoms stacking in L1₀ Ni₂FeGa. Four dislocations in this plane are presented: superdislocations $[\bar{1}10]$, $\frac{1}{2}[11 \bar{2}]$ and $[\bar{1}01]$, and partial dislocations, $\frac{1}{6} < \bar{2}11 >$. Three types of planar defects, SISF (superlattice intrinsic stacking fault), CSF (complex stacking fault) and APB (anti-phase boundary) are marked on certain positions. We note that due to the non-unity tetragonal ratio $c/a$ of 0.95, the $\frac{1}{6}[\bar{2}11]$ dislocation vector is
slightly larger (by 1.03) compared to $\frac{1}{6}[11\bar{2}]$. The superdislocation can split into the related Shockley partials, according to the dislocation scheme:

$$[\bar{1}10] = \frac{1}{6}[\bar{2}11] + \text{CSF} + \frac{1}{6}[\bar{1}2\bar{1}] + \text{APB} + \frac{1}{6}[\bar{2}11] + \text{CSF} + \frac{1}{6}[\bar{1}2\bar{1}]$$  \quad (1)$$

$$[\bar{1}01] = \frac{1}{6}[\bar{1}\bar{1}2] + \text{SISF} + \frac{1}{6}[\bar{2}11] + \text{APB} + \frac{1}{6}[\bar{1}\bar{1}2] + \text{CSF} + \frac{1}{6}[\bar{2}11]$$  \quad (2)$$

$$\frac{1}{2}[11\bar{2}] = \frac{1}{6}[11\bar{2}] + \text{SISF} + \frac{1}{6}[1\bar{2}\bar{1}] + \text{APB} + \frac{1}{6}[11\bar{2}] + \text{CSF} + \frac{1}{6}[2\bar{1}\bar{1}]$$  \quad (3)$$

The different colors in these equations correspond to Figure 5.5 and represent the different dislocations and fault energies. We note that the superdislocation $\frac{1}{2}[11\bar{2}]$ in Eq. (3) cannot be divided into three equal $\frac{1}{6}[11\bar{2}]$ partials due to a much high energy barrier as shown later.

Figure 5.5 Possible dislocations and atomic configurations of L1$_0$ Ni$_2$FeGa in the (111) plane. Different sizes of atoms represent three successive (111) layers from the top view. Dislocations
\([\overline{1}10], \frac{1}{2}[1\overline{1}2], [\overline{1}01]\) and \(\frac{1}{6} < \overline{2}11 > \) are shown in different colors corresponding to Eqs. (1)-(3).

Three types of planar defects, SISF, CSF and APB are marked on certain positions.

Similar to the dislocation dissociation in fcc metals [127], it is very unlikely to dissociate the superdislocation \(\frac{1}{2}[1\overline{1}2]\) into three \(\frac{1}{6}[1\overline{1}2]\) partial dislocations, due to the much higher energy barrier formed when the atoms in the same plane sliding past each other. We calculated the GSFE curve for the superdislocation \(\frac{1}{2}[1\overline{1}2]\) dissociated into three \(\frac{1}{6}[1\overline{1}2]\) partial dislocations in Figure 5.6. After shearing the displacement \(u = \frac{1}{6}[1\overline{1}2]\), a metastable structure is obtained at point S in the curve. Similar to fcc metals [127], further shear beyond point S along the \([1\overline{1}2]\) direction results in an unstable structure at point C (\(u = \frac{1}{3}[1\overline{1}2]\)). We note that this unstable stacking fault energy (global energy barrier) is 475 mJ/m², which is much higher than the energy barrier of 360 mJ/m² along the direction \(\frac{1}{6}[\overline{1}2\overline{1}]\) shown in Figure 5.13. Thus, it is impossible to dissociate the superdislocation \(\frac{1}{2}[1\overline{1}2]\) into three \(\frac{1}{6}[1\overline{1}2]\) partial dislocations; instead, it will dissociate into the combination of \(\frac{1}{6}[1\overline{1}2]\) and \(\frac{1}{6}[\overline{1}\overline{2}\overline{1}]\) shown in Eq. (3).
Figure 5. GSFE curve of the superdislocation $\frac{1}{2}[11\bar{2}]$ dissociated into three $\frac{1}{6}[11\bar{2}]$ partial dislocations on the (111) plane of L1$_0$ Ni$_2$FeGa. We note that in order to move atoms at position A to the position C along $[11\bar{2}]$ direction, a high stress is required due to the high energy barrier formed when atoms at A slide over atoms at B in the same plane.

The planar defects SISF, CSF and APB are defined by pure movement of one half of a crystal over the other half in the (111) plane. The movement forms metastable positions corresponding to local minimum energies, which govern the dislocation slip behavior of L1$_0$ Ni$_2$FeGa. Figure 5.7 shows a schematic of the construction of SISF, CSF and APB in the (111) plane due to atom movements along different directions. As denoted earlier, the three different atom sizes indicate three (111) layers of atoms stacking. A SISF is produced, when the in-plane atoms and all atoms above are shifted along the Burgers vector $\frac{1}{6}[11\bar{2}]$. This displacement results in a stacking sequence where the in-plane Ga atoms lie directly above the out-of-plane Ga atoms. A CSF is generated, when the in-plane atoms and all atoms above are shifted along the Burgers vector $\frac{1}{6}[\bar{1}2\bar{1}]$. This displacement results in a stacking sequence where the in-plane Ga
atoms lie directly above the out-of-plane Ni atoms. An APB is formed when the in-plane atoms and all atoms above are shifted along the Burgers vector $\frac{1}{2}[\overline{1}10]$ (or $\frac{1}{2}[01\overline{1}]$). This displacement results in a stacking sequence where the in-plane Ga atoms lie directly above the in-plane Fe (or Ni) atoms.

![Figure 5. 7 Schematic of construction of slip movements that result in SISF, CSF and APB in (111) plane.](image)

The slip plane and directions of possible slip systems in L1$_0$ Ni$_2$FeGa are shown in Figure 5.8. The slip plane (111) is shown in Figure 5.8a (shaded violet), which is the same as in fcc metals. We note that if the tetragonal axis is denoted as c, not 2c, the corresponding slip plane will be (112). Figure 5.8b shows four dislocations $\frac{1}{2}[\overline{1}01]$, $\frac{1}{2}[\overline{1}10]$, $\frac{1}{6}[\overline{2}11]$ and $\frac{1}{6}[1\overline{1}2]$ in the (111) plane with Burgers vectors 2.54 Å, 2.6 Å, 1.49 Å, and 1.45 Å, respectively. The non-unity tetragonal ratio c/a results in different Burgers vectors between $\frac{1}{2}[\overline{1}01]$ and $\frac{1}{2}[\overline{1}10]$, and $\frac{1}{6}[\overline{2}11]$ and $\frac{1}{6}[1\overline{1}2]$. 
Figure 5.8 Slip plane and dislocations of possible slip systems in L1₀ Ni₂FeGa. (a) The shaded violet area represents the slip plane (111) and (b) four dislocations \( \frac{1}{6}[11\bar{2}], \frac{1}{2}[\bar{1}01], \frac{1}{2}[\bar{1}10], \frac{1}{6}[\bar{2}11] \) and \( \frac{1}{6}[11\bar{2}] \) are shown in the (111) plane.

The dislocation slip energy barriers and the faults (SISF, CSF and APB) are all characterized by the GSFE curve, which is calculated while one elastic half crystal is translated relative to the other in the slip plane along the slip direction [20]. The \( \frac{1}{6}[11\bar{2}](111) \) case of L1₀ Ni₂FeGa is illustrated in Figure 5.9 showing the configuration of slip in the plane (111) with dislocation \( \frac{1}{6}[11\bar{2}] \). Figure 5.8a is the perfect L1₀ lattice before shear, while Figure 5.9b is the lattice after shear by one Burgers vector, \( u = \frac{1}{6}[11\bar{2}] \) (1.45 Å), in the slip plane.

All fault energies can be computed as a function of shear displacement \( u \) and are determined relative to the energy of the undeformed L1₀.
Figure 5. Dislocation slip in the (111) plane with dislocation $\frac{1}{6}[1\bar{1}2]$ of L1$_0$ Ni$_2$FeGa. (a) The perfect L1$_0$ lattice observed from the [110] direction. The slip plane (111) is marked with a brown dashed line. (b) The lattice after a rigid shear with dislocation $\frac{1}{6}[1\bar{1}2]$, $\mathbf{u}$, shown in a red arrow.

The calculated shear displacements for the slip systems $\frac{1}{2}[[\bar{1}01](111)$, $\frac{1}{2}[\bar{1}10](111)$, $\frac{1}{6}[[211](111)$ and $\frac{1}{6}[1\bar{1}2](111)$ were normalized by their respective Burgers vectors, and the corresponding GSFE curves are shown in Figure 5.10. We note that the dislocation $\frac{1}{2}[[\bar{1}01]$ possesses the highest energy barrier of 932 mJ/m$^2$ (APB, 316 mJ/m$^2$). For the other three dislocations, the energy barriers decrease in the sequence of $\frac{1}{2}[\bar{1}10]$, $\frac{1}{6}[\bar{2}11]$ and $\frac{1}{6}[1\bar{1}2]$, corresponding to 723 mJ/m$^2$ (APB, 179 mJ/m$^2$), 360 mJ/m$^2$ (CSF, 273 mJ/m$^2$) and 168 mJ/m$^2$ (SISF, 85 mJ/m$^2$), respectively.
Figure 5. GSFE curves (initial portion for one Burgers vector only) of $\frac{1}{2}[101]$, $\frac{1}{2}[110]$, $\frac{1}{6}[\overline{2}11]$ and $\frac{1}{6}[\overline{1}1\overline{2}]$ dislocations in the (111) plane of L1$_0$ Ni$_2$FeGa. The calculated shear displacement, $u$, was normalized by the respective Burgers vector, $b$.

The generalized stacking fault energy surface ($\gamma$ surface) describes the energy variation when one half of a crystal is rigidly shifted over the other half with different fault vectors lying in a given crystallographic plane. To determine the $\gamma$ surface corresponding to the DFT derived $\gamma$ curves shown in Figure 5.10, we chose a fourth order cosine-sine polynomial [128], which can appropriately represent the energy variation in the (111) plane, i.e.

$$\gamma(k_1, k_2) = \sum_{m,n=0}^{m+n=4} a_{mn} [X(k_1)]^m [X(k_2)]^n [1 - \delta_{m0} \delta_{n0}] + \sum_{m,n=1}^{m+n=4} b_{mn} [X(k_1)]^m [Y(k_2)]^n \quad (4)$$

where, $k_1$ and $k_2$ are coefficients for fault vectors $e$ in the (111) plane and $e = k_1 e_1 + k_2 e_2$, where $e_1 = \frac{1}{6}[\overline{2}11]$ and $e_2 = \frac{1}{2}[\overline{1}10]$ are unit vectors along the [112] and [\overline{1}10] directions,
respectively. \([X(x)] = [1 - \cos(\pi x)]\) and \([Y(x)] = [\sin(\pi x)]\). \(\delta_{ij}\) represents Kronecker’s delta (\(\delta_{ij}\) is 1(0) if \(i\) is (not) equal to \(j\)). Figure 5.11a shows the \(\gamma\) surface for the (111) plane of L10 \(\text{Ni}_2\text{FeGa}\) with the \(x\) axis along the [11\(\bar{2}\)] direction, and the \(y\) axis along [\(\bar{1}10\)]. Figure 5.11b is a two-dimensional projection of the \(\gamma\) surface in the (111) plane.

![Figure 5.11a: Generalized stacking fault energy surface \(\gamma\) surface for the (111) plane in L10 \(\text{Ni}_2\text{FeGa}\).](image1)

![Figure 5.11b: A two-dimensional projection of the \(\gamma\) surface in the (111) plane.](image2)

**Figure 5.11** (a) Generalized stacking fault energy surface (\(\gamma\) surface) for the (111) plane in L10 \(\text{Ni}_2\text{FeGa}\). (b) A two-dimensional projection of the \(\gamma\) surface in the (111) plane. The \(x\) axis is taken along the [11\(\bar{2}\)] direction, and \(y\) axis along [\(\bar{1}10\)].
5.4.3 Peierls-Nabarro Model for Dislocation Slip

The original P-N framework is based on a simple cubic crystal containing a dislocation with Burgers vector \( b \) shown in Figure 5.12a. Glide of the dislocation with this Burgers vector leaves behind a perfect crystal. This approach yields a variation in the GSFE with a periodicity of \( b \) and thus the \( \gamma \) energy can be approximated by using a single sinusoidal function as seen next. To calculate the Peierls stress for dislocation slip, a potential energy of displacement associated with the dislocation movement, misfit energy \( E^\gamma_\gamma(u) \), must be determined. This energy depends on the position of the dislocation line, \( u \), within a lattice cell and reflects the lattice periodicity, thus it is periodic [120, 129, 130] as shown in Figure 5.12b. The misfit energy \( E^\gamma_\gamma(u) \) across the glide plane is defined as the sum of misfit energies between pairs of atomic planes and can be obtained from the GSFE at the local disregistry. With obtained dislocation profiles and considering the lattice discreteness, the \( E^\gamma_\gamma(u) \) can be expressed as follows [85]:

\[
E^\gamma_\gamma(u) = \sum_{m=-\infty}^{\infty} \gamma(f(ma'-u))a'
\]

(5)

where \( a' \) is the periodicity of \( E^\gamma_\gamma(u) \) and defined as the shortest distance between two equivalent atomic rows in the direction of the dislocation’s displacement, \( f(x) \) is the disregistry function representing the relative displacement (disregistry) of the two half crystals in the slip plane along the \( x \) direction, and \( u \) is the position of the dislocation line [114, 131, 132].

By using the Frenkel expression [133], the \( \gamma[f(x)] \) from GSFE can be written as follows:

\[
\gamma[f(x)] = \frac{\gamma_{\text{max}}}{2} \left[ 1 - \cos \left( \frac{2\pi f(x)}{b} \right) \right]
\]

(6)

where \( \gamma_{\text{max}} \) is the unstable stacking fault energy for GSFE, and \( b \) is the dislocation Burgers vector. Figure 5.12c shows a schematic of \( \gamma[f(x)] \) as a single sinusoidal function of \( \frac{f(x)}{b} \).

The solution of the disregistry function \( f(x) \) in the dislocation core is assumed to be of the Peierls type [114]:
f(x) = \frac{b}{2} + \frac{b}{\pi} \arctan \left( \frac{x}{\zeta} \right) \quad (7)

where \( \zeta = \frac{h}{2(1-\nu)} \) is the half-width of the dislocation for an isotropic solid [129], \( h \) is the interspacing between two adjacent slip planes and \( \nu \) is Poisson’s ratio. Figure 5.12d shows the normalized \( \frac{f(x)}{b} \) variation with \( \frac{x}{\zeta} \).

After substituting Eq. (6) and Eq. (7) into Eq. (5), we have the following formula of \( E^s_{\gamma}(u) \):

\[
E^s_{\gamma}(u) = \sum_{m=-\infty}^{+\infty} \gamma [f(ma'-u)] a' = \sum_{m=-\infty}^{+\infty} \gamma_{\text{max}} \left\{ 1 + \cos \left[ 2 \tan^{-1} \left( \frac{ma'-u}{\zeta} \right) \right] \right\} a' \quad (8)
\]

The Peierls stress \( \tau_p \) is the maximum stress required to overcome the periodic barrier in \( E^s_{\gamma}(u) \) and defined as the maximum slope of \( E^s_{\gamma}(u) \) with respect to \( u \) (shown Figure 5.11d) as follows:

\[
\tau_p = \max \left\{ \frac{1}{b} \frac{dE^s_{\gamma}(u)}{du} \right\} \quad (9)
\]
Figure 5. Schematic illustration of Peierls-Nabarro model for dislocation slip. (a) A simple cubic crystal containing a dislocation with Burgers vector $b$. $h$ is the interspacing between adjacent two slip planes. The relative displacement of the two half crystals in the slip plane along $x$ direction, $x_A - x_B$, is defined as the disregistry function $f(x)$. (b) Schematic illustration showing the periodic misfit energy $E^*_\gamma(u)$ as a function of the position of the dislocation line, $u$. The Peierls stress $\tau_p$ is defined as the maximum slope of $E^*_\gamma(u)$ with respect to $u$. (c) Schematic showing the $\gamma[f(x)]$ energy (GSFE curve) as a single sinusoidal function of $\frac{f(x)}{b}$. (d) Schematic showing the normalized $\frac{f(x)}{b}$ variation with $\frac{x}{\zeta}$. 

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The Peierls stress $\tau_p$ is smaller than the theoretical shear strength $(\tau_{\text{shear}})_{\text{neu}}$ and predicts experimental values more precisely. This is due to the fact that $\tau_p$ is determined not only by the energy barrier from GSFE curves, but also by the character of the dislocation slip distribution [134]. In this study, Peierls stresses of dislocation slip in L1$_0$ Ni$_2$FeGa were calculated based on the above equations. However, for the slip case of superdislocations dissociated to partial dislocations, the disregistry function $f(x)$ in Eq. (7) needs to be modified to include these partial dislocations with separation distances. Additionally, when the GSFE curve involves local minimum energy locations representing stacking faults, a single sinusoidal function in Eq. (6) cannot approximate it well and must be revised by applying multiple sinusoidal functions to fit it. The details of these modifications are described in Section 5.4.4.

### 5.4.4 Peierls Stress Calculations of L1$_0$ Ni$_2$FeGa

To determine the Peierls stresses required to move the dislocations, the misfit energies $E^s_\gamma(u)$ derived from GSFE curves must be calculated based on the method described in Section 5.4.3. However, for the case of GSFE curve comprising SISF, CSF and APB, the $E^s_\gamma(u)$ description is more complex than for simple fcc or bcc metals as a single sinusoidal function cannot approximate the GSFE curve well. Thus, revising the misfit energy formulation considering multiple sinusoidal functions to fit GSFE curves is necessary. For the case of the [110] superdislocation dissociated into four partials with smaller Burgers vectors as given in Eq. (1), the GSFE curve is shown in Figure 5.13.
Figure 5. Upon shearing the superdislocation \([\bar{1}10]\), the dissociation into four partials and the associated CSF and APB energies are determined. The unstable stacking fault energies \(\gamma_{us1} = \gamma_{us2} = 360 \text{ mJ/m}^2\) (energy barriers); the stable stacking fault energies \(\gamma_{s1} = 273 \text{ mJ/m}^2\) (CSF) and \(\gamma_{s2} = 179 \text{ mJ/m}^2\) (APB).

The separations of the partial dislocations \(d_1=0.538 \text{ nm}\) and \(d_2=1.85 \text{ nm}\) are calculated by the condition that the force due to the surface tension of stacking faults balances the mutual repulsion of partials [15, 135-137]. The separations, \(d_1\) and \(d_2\), of partial dislocations can be calculated using the force balance between attraction due to fault energies and elastic repulsion of partial dislocations [135, 136]:

\[
\sum F = F_{\text{attraction}}(\gamma) - F_{\text{repulsion}}(K, d) = 0
\]

This leads to the following equations for the case of superdislocation \([\bar{1}10]\) splitting into four partials \(\frac{1}{6} < \bar{2}11\) as follows:
\[ \gamma_{\text{CSF}} = K \left\{ \frac{1}{d_1} + \frac{1}{d_1 + d_2} + \frac{1}{2d_1 + d_2} \right\} \]  

(11)

\[ \gamma_{\text{APB}} - \gamma_{\text{CSF}} = K \left\{ \frac{1}{d_2} + \frac{1}{d_1 + d_2} - \frac{1}{d_1} \right\} \]  

(12)

with \( \gamma \) and \( K/d \) representing the attraction and elastic repulsion force, respectively. These equations can be solved for the separation distances giving the energy levels and the other material constants as input. As noted earlier, \( \gamma_{\text{CSF}} = 273 \text{ mJ/m}^2 \) and \( \gamma_{\text{APB}} = 179 \text{ mJ/m}^2 \). The factor \( K \) is given as \( K = \frac{\mu b^2}{2\pi} \), where \( \mu = 29.5 \text{ GPa} \) (obtained from our simulations), \( b = 1.49 \text{ Å} \).

This results in \( d_1 = 0.538 \text{ nm} \) and \( d_2 = 1.85 \text{ nm} \) shown in Figure 5.14.

![Figure 5.14 Separations of partial dislocations for the superdislocation [110].](image)

The disregistry function \( f(x) \) can be described in Eq.(13) by considering the multiple partials, and Figure 5.15 shows the normalized \( \frac{f(x)}{b} \) variation with \( \frac{x}{\zeta} \). In Figure 5.15, \( d_1 \) and \( d_2 \) are the distances between partial dislocations, and their values depend on the CSF and APB.

\[
f(x) = \frac{b}{\pi} \left[ \arctan \left( \frac{x}{\zeta} \right) + \arctan \left( \frac{x-d_1}{\zeta} \right) + \arctan \left( \frac{x-(d_1+d_2)}{\zeta} \right) + \arctan \left( \frac{x-(2d_1+d_2)}{\zeta} \right) \right] + 2b \]  

(13)
The disregistry function $f(x)$ for the superdislocation $[\bar{1}10]$ dissociated into four partials $\frac{1}{6} < 2 \bar{1}1]$. The separation distances of the partial dislocations are indicated by $d_1$ and $d_2$.

We note that this GSFE curve does not fit a single sinusoidal relation; instead, it is approximated by a sinusoidal series function. Thus, the corresponding misfit energy is presented as the explicit form in Eq. (14), and Figure 5.16 shows the misfit energy $E_{\gamma}^x(u)$ variation with the lattice period $a'$. Two quantities $\left(E_{\gamma}^x\right)_{s/2}$ and $\left(E_{\gamma}^x\right)_p$ in the plot are denoted. The $\left(E_{\gamma}^x\right)_{s/2}$ represents the minimum of $E_{\gamma}^x(u)$ function and provides an estimate of the core energy of dislocations. The $\left(E_{\gamma}^x\right)_p$ is defined as the Peierls energy, which is the amplitude of the variation of $E_{\gamma}^x(u)$ and the barrier required to move dislocations [129].
\[
E^s_{\gamma}(u) = \sum_{n=1}^{6} \left( E^s_{\gamma} \right)_n(u) = \sum_{m=\infty}^{0} \gamma_{us1} \left[ 1 - \cos \frac{2\pi f(m\alpha' - u)}{b} \right] a' + \\
\sum_{m=1}^{\infty} \left\{ \frac{\gamma_{us1} - \gamma_{ls1}}{2} \left[ 1 - \cos \frac{2\pi f(m\alpha' - u)}{b} \right] \right\} a' + \sum_{m=\infty}^{0} \left\{ \frac{\gamma_{us2} - \left( \gamma_{ls1} + \gamma_{ls2} \right)}{2} \left[ 1 - \cos \frac{2\pi f(m\alpha' - u)}{b} \right] \right\} a' + \\
\sum_{m=1}^{\infty} \frac{\gamma_{us1} - \gamma_{ls1}}{2} \left[ 1 - \cos \frac{2\pi f(m\alpha' - u)}{b} \right] a' + \sum_{m=1}^{\infty} \left\{ \frac{\gamma_{us2} - \gamma_{ls2}}{2} \left[ 1 - \cos \frac{2\pi f(m\alpha' - u)}{b} \right] \right\} a'
\] (14)

**Figure 5.16** Misfit energy \( E^s_{\gamma}(u) \) for the superdislocation [110] dissociated into four partials \( \frac{1}{6} < 211 \).

Once the misfit energy is determined, the Peierls stress \( \tau_p \) can be calculated by the maximum of \( \frac{1}{b} \frac{dE^s_{\gamma}(u)}{du} \). As mentioned before, by taking the maximum slope of the GSFE curve,
the theoretical shear strength \((\tau_{\text{shear}})^{\text{nuc}}\) for each slip system is obtained. The corresponding shear modulus \(\mu\) can then be approximately determined as \(\mu = 2\pi (\tau_{\text{shear}})^{\text{nuc}}\) [138]. The calculated shear modulus \(\mu\), theoretical shear strength \((\tau_{\text{shear}})^{\text{nuc}}\) and Peierls stress \(\tau_p\) for the four slip systems of L1_0 Ni_2FeGa are shown in Table 5.2. We note that \(\tau_p\) is smaller than \((\tau_{\text{shear}})^{\text{nuc}}\) and predicts experimental values more precisely, as described in Section 5.4.3. However, the theoretical shear strength \((\tau_{\text{shear}})^{\text{nuc}}\) follows the trend of the Peierls stress \(\tau_p\) for these four slip systems.

Table 5.2 Calculated shear modulus, theoretical shear strength and Peierls stress for dislocation slip of L1_0 Ni_2FeGa.

<table>
<thead>
<tr>
<th>Slip plane</th>
<th>Burgers vector, (b)</th>
<th>Shear modulus (GPa) (\mu = 2\pi (\tau_{\text{shear}})^{\text{nuc}})</th>
<th>Theoretical Shear Stress (GPa) ((\tau_{\text{shear}})^{\text{nuc}} = \max \left{ \frac{\partial \gamma}{\partial u} \right})</th>
<th>Critical Shear Stress (theory)-This Study (GPa) (\tau_p = \max \left{ \frac{1}{b} \frac{E^s_\gamma}{\partial u} \right})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111) (\frac{1}{2}[1\bar{0}1])</td>
<td>61.3</td>
<td>9.76</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>(111) (\frac{1}{2}[\bar{1}10])</td>
<td>52.5</td>
<td>8.36</td>
<td>3.13</td>
<td></td>
</tr>
<tr>
<td>(111) (\frac{1}{6}[\bar{2}11])</td>
<td>29.5</td>
<td>4.7</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>(111) (\frac{1}{6}[11\bar{2}])</td>
<td>22.9</td>
<td>3.65</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

Combining the results of \((\tau_{\text{shear}})^{\text{nuc}}\) and \(\tau_p\), we note that the \(\frac{1}{6}[11\bar{2}]\) has the lowest stress levels and will be most likely the first to activate. Both of the \(\frac{1}{2}[1\bar{1}0]\) and \(\frac{1}{2}[\bar{1}01]\) dislocations...
possess significantly higher \((\tau_{\text{shear}})_{\text{nuc}}\) and \(\tau_p\) values than \(\frac{1}{6}[\bar{2}11]\) and \(\frac{1}{6}[11\bar{2}]\), so these superdislocations will split into \(\frac{1}{6}<211>\) partials and planar defects left between them as shown in Eqs. (1) and (2). However, when the Schmid factor associated with internal shear stresses provides a larger contribution, the glide of \(\frac{1}{2}[\bar{1}01]\) and \(\frac{1}{2}[\bar{1}10]\) superdislocations can also be activated. Thus, the Peierls stress calculated in combination with the P-N model and GSFE curves provides a basis for a theoretical study of the dislocation structure and operative slip modes in \(\text{L}_{10}\text{Ni}_2\text{FeGa}\).

5.5 Experimental Observations and Viewpoints on Martensite Deformation Behavior

5.5.1 In-Situ TEM Observations of Dislocation Slip

Understanding the dislocation slip behavior of shape memory alloys is extremely relevant to understanding the shape memory performance. The higher the resistance to martensite slip, the superior the shape memory performance. During dynamic evolution of phase boundaries, both austenite and martensite may undergo slip due to the high internal stress fields. Because observations of slip are difficult to make during the loading experiments, one way to prepare the samples for such observations is to subject the specimens to phase change, remove the sample, and then conduct heating cooling experiments in an transmission electron microscope (TEM). The first portion of the experiment is sometimes referred to as training to obtain a two way shape memory effect. During this experiment one can transform to the \(\text{L}_{10}\) phase under stress and interrupt the experiment at room temperature, so one can retain the martensite \(\text{L}_{10}\) phase. Then, samples are cut from the \(\text{L}_{10}\) specimens, which are observed in the TEM. Cooling in the TEM further allows observations of the evolution of dislocation slip behaviors. Such experiments were conducted and the results confirm dislocation slip in the martensitic phase. To ensure that the resultant phase is the \(\text{L}_{10}\) phase and not the 10M/14M intermediate martensites, the stress is raised in a stair case fashion to sufficiently high levels, and diffraction peaks were collected to
index the martensite L1\textsubscript{0} phase. When the stress is not sufficiently high (less than 40 MPa), the diffraction peaks corresponded to 14M, an intermediate martensitic structure. When the stress was 80 MPa, the final martensitic phase observed was L1\textsubscript{0}. These results are shown in Figs. 15 and 16 for applied stress levels of 40 MPa and 80 MPa respectively.

At tensile stress of 40 MPa, the transformation steps were L2\textsubscript{1} \rightleftharpoons 10M \rightleftharpoons 14M shown in Figure 5.17. We note that the strain saturates at nearly 6.2\% and the formation of 14M structure is confirmed with diffraction measurements at room temperature. The inset shows a selected area diffraction (SAD) pattern of the 14M structure.

![Graph showing tensile strain-temperature response at 40 MPa](image)

**Figure 5.17** The tensile strain-temperature response at 40 MPa describing the inter-martensitic transformation L2\textsubscript{1} \rightleftharpoons 10M \rightleftharpoons 14M. Red arrows along the curve indicate directions of cooling and heating. A SAD pattern is insetted showing the culmination in formation of the 14M structure.

When the tensile stress was increased to 80 MPa, the transformation steps (cooling) were L2\textsubscript{1} \rightarrow 10M \rightarrow 14M \rightarrow L1\textsubscript{0} shown in Figure 5.18. The strain saturates approximately at 9.5\% and the crystal structure is L1\textsubscript{0} at room temperature. The inset shows a SAD pattern of the L1\textsubscript{0}
structure. Compared to the maximum strain of 6.2% in the transformation \( \text{L}_2 \rightleftharpoons \text{10M} \rightleftharpoons \text{14M} \) in Figure 5.17, we note that once \( \text{14M} \rightarrow \text{L}_1 \) forms, the \( \text{L}_1 \) detwines in tension. Because the test is interrupted near room temperature the specimen has not reverted to the austenitic phase (\( \text{L}_2 \)). In the second phase of the experiments, the sample that is shown in Figure 5.18 was subsequently studied by TEM via in-situ heating and cooling. The existence of dislocations slip of \( \text{L}_1 \) at -6 °C is shown in in Figure 5.19.

![Graph showing the tensile strain-temperature response at 80 MPa indicating the martensitic transformation from the austenite \( \text{L}_2 \) to the non-modulated martensite \( \text{L}_1 \). A SAD pattern in the inset shows resulting \( \text{L}_1 \) structure. The sample is removed from the load frame at ‘T’ and studied with TEM under in-situ temperature cycling.](image_url)

**Figure 5.18** The tensile strain-temperature response at 80 MPa indicating the martensitic transformation from the austenite \( \text{L}_2 \) to the non-modulated martensite \( \text{L}_1 \). A SAD pattern in the inset shows resulting \( \text{L}_1 \) structure. The sample is removed from the load frame at ‘T’ and studied with TEM under in-situ temperature cycling.
Figure 5. Upon cooling to -6°C, the TEM image displays the martensite phase $L_1$ with $<112>|111|$ dislocation slip in a Ni$_{54}$Fe$_{19}$Ga$_{27}$ (at %) single crystal.

5.5.2 Determination of Martensite Slip Stress from Experiments

Our previous compression experiments show that as the temperature increases to 150 °C, the austenite $L_2$ can directly transform to $L_1$ martensite bypassing the intermartensite 10M/14M [8]. A series of experiments were conducted to study the martensite slip behavior ($L_1$) subsequent to austenite to martensite transformation. These experiments involve compression loading of [001] oriented single crystals of Ni$_{54}$Fe$_{19}$Ga$_{27}$ at a constant temperature of 150 °C. A typical compressive stress-strain curve is shown in Figure 5.20. The samples were originally in the $L_2$ state and directly transformed to the $L_1$ regime when the loading reached the martensitic transformation stress of 450 MPa. Upon further loading, the samples were in a fully $L_1$ state and dislocation slip was observed as the stress magnitude exceeded 1500 MPa. After unloading, a finite amount of plastic strain remained due to residual dislocations in the $L_1$. Because the [001] orientation in $L_2$ corresponds to [001] in $L_1$ (Fig. 3), the Schmid factor for the compressive axis [001] and dislocation slip system [11 2](111) in $L_1$ is near 0.5. The shear stress of dislocation slip in $L_1$ at a temperature of 150 °C is then calculated as 750 MPa. We note that the Peierls stress is the shear stress required to move a dislocation at 0 K, where the...
thermal activation is absent and the dislocation moves only due to the influence of stress. On the other hand, at finite temperature, the dislocation movement can be assisted by both thermal activation and stress, and thus the shear stress for dislocation motion is lower than the one required at 0 K \[116, 139\]. Therefore, our Peierls stress of 1.1 GPa can be compared with the experimental value of 750 MPa (Table 5.3); while the theoretical shear strength of 3.65 GPa is much higher than the experimental data. This verification demonstrates that the extended P-N formulation provides a useful and rapid prediction of the dislocation slip stress.

Table 5.3 Comparison of experimental and predicted slip stress levels for L1\textsubscript{0} N\textsubscript{2}FeGa.

<table>
<thead>
<tr>
<th>Slip system</th>
<th>Crystal Structure</th>
<th>Present Theory (GPa)</th>
<th>Experiment (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)(\frac{1}{6}[11\bar{2}])</td>
<td>L\textsubscript{10}</td>
<td>1.1</td>
<td>0.7-1.0</td>
</tr>
</tbody>
</table>

![Figure 5.20 Compressive stress-strain response of Ni\textsubscript{54}Fe\textsubscript{19}Ga\textsubscript{27} at a constant temperature of 150 °C.](image)

**Figure 5.20** Compressive stress-strain response of Ni\textsubscript{54}Fe\textsubscript{19}Ga\textsubscript{27} at a constant temperature of 150 °C.
5.6 Prediction of Dislocation Slip Stress for Shape Memory Alloys

To validate the extended P-N formulation for dislocation slip, we calculated Peierls stresses predicted from the model for several important shape memory alloys in austenite phase and compared to the experimental slip stress data. The martensite slip stress levels are rather high as we show in this study (1.1 GPa versus 0.63 GPa). The austenite slip stress levels, on the other hand, are more readily available in the experiments and are also very important. The austenite of these materials (Ni$_2$FeGa, Co$_2$NiGa, Co$_2$NiAl, NiTi, CuZn and Ni$_2$TiHf) possess the L2$_1$ and B2 cubic structures. We found excellent agreement between the predicted values and experimental data shown in Table 5.4. For each material, the lattice type, the slip system, and the experimental range of critical slip stresses and the theory are shown. If the ideal stress levels are included, these exceed several GPa and are much higher than experiments. Interestingly, the critical stress for CuZn, which has excellent transformation properties, but suffers from plastic deformation, exhibits the lowest levels. For austenitic NiTi the most likely slip system is (011)[100] with a slip stress level of 0.71 GPa consistent with experiments.

The experimental slip stress data are taken from the plot of critical stress vs. temperature. In all the studied materials, a similar stress vs. temperature correlation is observed such that near the $M_d$ temperature the material undergoes slip. The critical stress for martensitic transformation increases with temperature above $A_f$ and the critical stress for dislocation slip of austenite decreases with temperature. When these two values cross at the temperature $M_d$, the stress-induced martensitic transformation is no longer possible, but the dislocation slip of austenite dominates the mechanical response. The critical austenite slip stress at $M_d$ is considered as the experimental data for austenite slip and compared to the (Peierls based) present theory.
Table 5.4 Predicted Peierls stresses for shape memory alloys are compared to known reported experimental values. The slip systems and crystal structures of SMAs are given. (L2₁ and B2 are the crystal structures in austenite phase).

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal Structure</th>
<th>Slip system</th>
<th>Critical Shear Stress-Present Theory (GPa)</th>
<th>Critical Shear Stress-Experiment (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₂FeGa</td>
<td>L₂₁</td>
<td>(1̅1̅0)  1/4[111]</td>
<td>0.63</td>
<td>0.40-0.65 [18]</td>
</tr>
<tr>
<td>Co₂NiGa</td>
<td>B₂</td>
<td>(011)[001]</td>
<td>0.76</td>
<td>0.40-0.70 [16, 140]</td>
</tr>
<tr>
<td>Co₂NiAl</td>
<td>B₂</td>
<td>(011)[001]</td>
<td>0.72</td>
<td>0.60-0.80 [16, 141]</td>
</tr>
<tr>
<td>NiTi</td>
<td>B₂</td>
<td>(011)[001] (011)[01̅1]</td>
<td>0.71 (1.2)</td>
<td>0.40-0.80 [92, 111, 142, 143]</td>
</tr>
<tr>
<td>Ni₂TiHf</td>
<td>B₂</td>
<td>(011)[001]</td>
<td>0.78</td>
<td>0.55-0.75 [17, 144]</td>
</tr>
<tr>
<td>CuZn</td>
<td>B₂</td>
<td>(011)[11̅1]</td>
<td>0.08</td>
<td>0.03-0.07 [145, 146]</td>
</tr>
</tbody>
</table>

5.7 Summary

The present work focuses on the dislocation slip mechanism of L₁₀ Ni₂FeGa, and the rationalization of why 1/6[11̅2] is the favorable dislocation slip system. The simulations underscore a significant quantitative understanding of Ni₂FeGa and extend the P-N formulation for the study of complex faults.

The calculated lattice parameters of L₁₀ are in good agreement with the available experimental results, which form the foundation of the GSFE and Peierls stress calculation. We identified the energies and stresses required for dislocations movement of L₁₀ Ni₂FeGa. To address this issue, we precisely established the GSFE curves and determined energy barriers and
planar faults (SISF, CSF and APB) for possible dislocations, \( \frac{1}{6}[11\overline{2}], \frac{1}{6}[\overline{2}11], \frac{1}{2}[\overline{1}10] \) and \( \frac{1}{2}[\overline{1}01] \). The theoretical shear stresses \( \tau_{\text{shear}} \) were estimated from the maximum slope of the GSFE curves in Table 5.2. The \( \tau_{\text{shear}} \) forms the upper bound of the mechanical strength of the material and it is much higher than experimental results. Once the GSFE curves were established, the Peierls stresses \( \tau_p \) were calculated based on the extended Peierls-Nabarro model. The determination of misfit energy is rather complex and considers the presence of multiple partials.

We illustrated with the energy barrier and Peierls stress \( \tau_p \) that \( \frac{1}{6}[11\overline{2}] \) is preferred over other dislocations of L1\(_0\) Ni\(_2\)FeGa. The slip system \( \frac{1}{6}[11\overline{2}](111) \) possesses the smallest barrier of 168 mJ/m\(^2\) and corresponding Peierls stress of 1.1 GPa. We note that both of the superdislocations \( \frac{1}{2}[\overline{1}10] \) and \( \frac{1}{2}[\overline{1}01] \) can split into \( \frac{1}{6} < 211 > \) partials while planar defects (SISF, CSF and APB) are formed during their dissociation process. However, we emphasize that the glide of \( \frac{1}{2}[\overline{1}01] \) and \( \frac{1}{2}[\overline{1}10] \) can also be activated at higher applied stress. In the present study, we performed a fully atomic relaxation to establish the GSFE, since unrelaxed GSFE does not represent the precise energy barrier in association with the dislocation glide. We compared unrelaxed and relaxed GSFE of slip system \( \frac{1}{6}[11\overline{2}](111) \) in L1\(_0\) Ni\(_2\)FeGa. We note that the barrier for unrelaxed and relaxed GSFE is 180 mJ/m\(^2\) and 168 mJ/m\(^2\), respectively, which represents a 7\% difference between these two values. The results reported in the paper are the relaxed values. The predicted Peierls stress is 1.15 GPa and 1.1 GPa, respectively, a near 5\% difference. We note that the relaxed GSFE predicts a closer result to the experiments. Therefore, by allowing fully atomic relaxation, our GSFE is modified from the rigid shift condition [123, 133, 147-149].

We note that there are alternative approaches to determine the dislocation core by performing direct DFT [147, 150-152] calculations. These approaches confirm the accuracy of
the disregistry function of the arctan form derived from the P-N model [147]. For the case of superdislocation dissociated into four partials in the present study, further developments in the direct DFT approach are needed including modifications of the Lattice Green's functions [150].

To validate our Peierls stress prediction, we conducted a series of experiments to observe the dislocation slip in L1₀ Ni₂FeGa and determined the slip stress of L1₀ approximately as 1.5 GPa (CRRS is 750 MPa) under compression loading of [001] samples. The single crystals underwent slip deformation following austenite to martensite transformation. These results confirmed our Peirerls stress prediction of 1.1 GPa for the \( \frac{1}{6}[11\bar{2}](111) \) slip system. These predicted levels with the P-N model are in far better agreement with experiments in comparison with the theoretical stress level of 3.65 GPa. In addition to the temperature effects discussed earlier, some of the differences may stem from the fact that the actual alloy is off stoichiometry (Ni₅₄Fe₁₉Ga₂₇) compared to the simulations (Ni₅₀Fe₂₅Ga₂₅). The theoretical lattice constants are not exactly the same as the experimental values contributing to some of the differences in stress levels.

We also investigated dislocation slip in several important shape memory alloys and predicted stresses based on the present theory for Ni₂FeGa (austenite), NiTi, Co₂NiGa, Co₂NiAl, CuZn and Ni₂TiHf austenites in excellent agreement with experiments. Overall, we note that the stresses calculated with the extended P-N model and GSFE curves provides an excellent basis for a theoretical study of the dislocation structure and operative slip modes in L1₀ Ni₂FeGa and the some of the most important shape memory alloys. The formulation can be extended to other proposed shape memory alloys with different crystal structures as well.
Chapter 6 Twinning Stress in Shape Memory Alloys-Theory and Experiments

[The material in this chapter is published as J. Wang, H. Sehitoglu, Acta Materialia, Vol 61, 2013].

6.1 Abstract

Utilizing first-principles atomistic simulations, we present a twin nucleation model based on the Peierls-Nabarro (P-N) formulation. We investigate twinning in several important shape memory alloys starting with Ni$_2$FeGa (the 14M-modulated monoclinic and L1$_0$ crystals) to illustrate the methodology, and predict twin stress in Ni$_2$MnGa, NiTi, Co$_2$NiGa, and Co$_2$NiAl martensites in excellent agreement with experiments. Minimization of the total energy led to determination of the twinning stress accounting for twinning energy landscape (GPFE) in the presence of interacting multiple twin dislocations and disregistry profiles at the dislocation core. The validity of the model was confirmed by determining the twinning stress from experiments on Ni$_2$FeGa (14M and L1$_0$ cases), NiTi, and Ni$_2$MnGa and utilizing results from the literature for Co$_2$NiGa, and Co$_2$NiAl martensites. The paper demonstrates that the predicted twinning stress can vary from 3.5 MPa in 10M Ni$_2$MnGa to 129 MPa for the B19' NiTi case consistent with experiments.

6.2 Introduction

To facilitate the design of new transforming alloys, including those proposed for magnetic shape memory, twinning modes associated with these alloys need to be fully understood [1]. The objective of the current paper is to study the most important twin modes in monoclinic and tetragonal (modulated and non-modulated) shape memory martensites and establish their twin fault energy barriers that are in turn utilized to predict the twinning stress. A new model for twin nucleation is proposed which shows excellent overall agreement with experiments.
Martensite twinning and subsequent recovery upon heating is called the 'shape memory effect' [2]. In the 'shape memory' case, when the internally twinned martensite is subsequently deformed, the twin variants that are oriented favorably to the external stress grow in expense of others. The growth of the twin is a process of advancement of twin interfaces and requires overcoming an energy barrier called the 'unstable twin fault energy' [3, 4]. Upon unloading, the twinning-induced deformation remains. If the material is heated above the austenite finish temperature, the material reverts back to austenite. Hence, the heating and cooling changes can make the material behave as an actuator, which is called the 'shape memory effect'. In this paper, we present experimental results of twinning stress for several important shape memory alloys and compare the results to theory.

It is now well known that the phenomenon of twinning during shape memory relies on complex atomic movements in the martensitic crystal. Despite the significant importance of twinning in SMAs, there have been limited attempts to develop models to predict the twinning stress from first-principles. The twinning energy landscapes for ordered binary and ternary alloys are more complex compared to pure fcc metals [5-7]. Thus, a fundamental understanding of twin nucleation is essential to capture the mechanical response of SMAs. This is the subject of this paper.

Several methodologies exist for evaluation of the twin nucleation and migration stresses of materials [4, 8-12]. However, the early models either require one or more fitting parameters or depend only on the intrinsic stacking fault energy, and they predict unrealistically high twinning stress. The Peierls–Nabarro (P-N) formalism can be utilized for rapid assessment of deformation behavior of binary and ternary shape memory materials and to evaluate different crystal structures of martensites. In the P-N model, the stress required to overcome a Peierls valley is determined for dislocation motion. The calculations for Peierls stress represent the breakaway of an atom within the core region of the dislocation. The Peierls stress is the minimum applied shear stress to move a dislocation. In recent years, the model benefited significantly from atomistic simulations which precisely calculate the energy landscape associated with atomic movements in different planes and directions. A brief description of P-N model used to predict the Peierls stress is given in Appendix. The formalism for dislocation slip stress determination utilizing the P-N concepts is well established, while the twinning stress determination is not as
well developed. If a P-N based twinning model is developed, then it can lead to a quantitative prediction of twinning stress in SMAs, and a better understanding of the factors that govern the shape memory effect. The current study addresses this important issue.

In recent years, several noteworthy approaches for twinning have been developed based on the P-N methodology. Yip and colleagues [4] determined the twin migration stress where a dislocation advance at the twin boundary represented twin growth. Their formula for twinning stress provides a simple and powerful relation linking the Peierls stress for twinning to the twin migration energy, the difference between unstable twin energy and twin stacking fault energy. Paidar and colleagues [13], accounting for anisotropy effects, undertook a similar treatment. Since the twinning motion involves a collective treatment of multiple dislocations, and their mutual interaction should affect their glide [14-16], we propose a modified treatment of the calculation of twin nucleation stress.

Martensite can undergo twinning deformation associated with shape memory effect as explained earlier. The stress levels for martensite twinning can be determined from experiments at temperatures below the martensite finish temperature. Figure 1 shows a schematic of the stress-strain curve of Ni$_2$FeGa at the temperature below the martensite finish temperature. During loading, twin interfaces advance in 14M (modulated monoclinic structure) followed by twinning of the L1$_0$ structure at higher strains. As we show later these two crystal structures of Ni$_2$FeGa have distinctly different twin stresses. Upon unloading the detwinned martensitic structure remains, which is recovered upon heating above the austenite finish temperature.
Figure 6.1 Schematic of stress-strain curve showing the detwinning of internally twinned martensite (multiple variant) to detwinned martensite (single crystal) of Ni$_2$FeGa at low temperature. Upon unloading, plastic strain is observed in the material, which can be fully recovered upon heating.

From our previous tests, we note that compressive loading experiments are better suited to avoid premature fracture in tension [17]. When the specimen is deformed, the martensite twinning process initiates at a finite stress level. There are very limited experiments in the literature on the martensite twinning stress of ferromagnetic shape memory alloys such as Ni$_2$FeGa, Co$_2$NiAl and Co$_2$NiGa. There have been more experiments on NiTi and Ni$_2$MnGa. The research teams of Sehitoglu and Chumlyakov have conducted experiments below the martensite finish temperature on a number of advanced shape memory alloys [18, 19]. Since the twin thicknesses are of nano-dimensions, it is difficult to observe in-situ the onset of twinning experimentally. Additionally, several twin systems can co-exist, hence making it rather complicated to discern experimentally the twin stress when multiple systems interact such as in NiTi and Ni$_2$FeGa. Therefore, the theoretical calculations provide considerable insight.

At the mesoscale, our current treatment deals with the dislocation movements leading to the twin formation. Several modifications to the original Peierls-Nabarro treatment were
implemented in the course of the study. At the atomic scale, during the calculations of the generalized planar fault energy (GPFE) curve, full internal atom relaxation was allowed. This allows a three dimensional description of the energy landscape with displacements in two other directions in addition to the imposed shear. The misfit energy expression accounts for the discreteness in the lattice across atomic pairs and not treated as a continuous integral. This energy description is dependent on the spacing between two adjacent twinning partials and results in a more realistic twin stress evaluation. Both of these modifications enrich the original approach forwarded by Peierls-Nabarro. A further advancement forwarded in this study is to incorporate the elastic strain fields in the overall energy expression accounting for the mutual interaction of dislocation fields. Upon minimization of the total energy, we seek for the critical twin nucleation stress. We show results for Ni$_2$FeGa in comparison to our experiments, but the methodology developed is appealing and was applied to other materials. The outcome of these calculations is that one can evaluate magnitudes of critical twin nucleation stress in better agreement with experiments.

In the first calculation, we note that the ideal shear stress value obtained from the fault energy curves without accounting for the discreteness of the crystal structure is rather high (GPa levels). In the second calculation, the calculated Peierls stress from the original P-N model gives a reasonable value (MPa range), but it is still higher than experimental data. Consequently, the third calculation, i.e. the proposed twin nucleation model, which is based on the extended Peierls-Nabarro treatment and considers the elastic strain fields in the twin nucleation, points to a significant advantage and certainty. This model can be used for rapid and accurate prediction of twin stresses of potential shape memory alloys before undertaking costly experimental programs.

6.3 Methodologies for twin nucleation

We model the deformation process of twin nucleation at the atomic level and integrate with the mesoscale description of overall energy. At the atomic level, the twinning energy landscape (GPFE) is established representing the lattice shearing process due to the passage of twinning partials [12]. At the mesoscale level, an extended P-N formulation is proposed to determine the twin configuration and address the total energy associated with the twin nucleation.
Figure 2 shows a schematic of methodology adopted in this study and different length scales associated with twinning in Ni$_2$FeGa (14M and L1$_0$) alloys. Here we proposed a twin nucleation model based on Peierls-Nabarro formulation describing the mesoscale twinning partial dislocation interactions using dislocation mechanics [20] incorporating the ab initio DFT simulations. We minimized the total energy associated to the twin nucleation and calculated the critical twin nucleation stress of 14M and L1$_0$ Ni$_2$FeGa (shown in detail as examples in this paper) and other important shape memory alloys. We note that for NiTi there are several twin systems activated and we calculate twin stress for the most important ones consistent with experiments.

![Diagram showing schematics of methodology and stress-strain response](image.png)

**Figure 6.2** Schematic description of the multi-scale methodology for modeling of deformation twinning in Ni$_2$FeGa alloys.

### 6.3.1 DFT calculation setup

The generalized planar fault energy (GPFE) provides a comprehensive description of twins, which is the energy per unit area required to form $n$-layer twins by shearing $n$ consecutive layers along twinning direction [76]. The first-principles total-energy calculations were carried out using the Vienna ab initio Simulations Package (VASP) with the projector augmented wave (PAW) method and the generalized gradient approximation (GGA) [25, 26]. Monkhorst Pack 9×9×9 k-point meshes were used for the Brillouin-zone integration to ensure the convergence of results. The energy cut-off of 500 eV was used for the plane-wave basis set. The total energy was
converged to less than $10^{-5}$ eV per atom. Periodic boundary conditions across the supercell were used to represent bulk material. We have used $L$-layer based cell to calculate fault energies to generate GPFE curve in the certain system. We assessed the convergence of the GPFE energies with respect to increasing $L$, which indicates that the fault energy interaction in adjacent cells due to periodic boundary conditions will be negligible. The convergence is ensured once the energy calculations for $L$ and $L+1$ layers yield the same GPFE. For each shear displacement $u$, a fully internal atom relaxation, including perpendicular and parallel directions to the fault plane, was allowed for minimizing the short-range interaction between misfitting layers near to the fault plane. During the shear deformation process, the volume of the supercell was maintained constant ensuring the correct twin structure $[153, 154]$. This relaxation process caused a small additional atomic displacement $r (r = \sqrt{r_x^2 + r_y^2 + r_z^2})$ in magnitude within 1% of the Burgers vector $b$. Thus, the total fault displacement is not exactly equal to $u$ but involves additional $r$. The total energy of the deformed (faulted) crystal was minimized during this relaxation process through which atoms can avoid coming too close to each other during shear $[85, 122, 123]$. From the calculation results of deformation twinning, we note that the energy barrier after full relaxation was near 10% lower than the barrier where the relaxation of only perpendicular to the fault plane was allowed.

6.3.2 Twinning energy landscapes (GPFE)- the L1$_0$ Ni$_2$FeGa example

The deformation twinning system $<1\bar{1}2>\{111\}$ has been observed experimentally for L1$_0$ structure in past work $[11, 155-159]$, which is the same with fcc metals. In this study, we conducted simulations to determine the GPFE of L1$_0$ Ni$_2$FeGa by successive shearing every (111) plane over $\frac{1}{6}[\bar{1}1\bar{2}]$ dislocation. We note that the formation of twin system $\frac{1}{6}[\bar{1}1\bar{2}]$ of L1$_0$ Ni$_2$FeGa requires no additional atomic shuffle, which is also observed in other L1$_0$ structures $[155, 160-162]$ and fcc materials $[76, 130, 163-165]$. Figure 6.3 shows the L1$_0$ fct (face centered tetragonal) structure with corresponding lattice parameters of $a=b=3.68$ Å, and $c=3.49$ Å. We note that the tetragonal axis is $2c$, so the L1$_0$ unit cell contains two fct unit cells. These lattice parameters are in a good agreement with experimental measurements $[9]$. These precisely
determined lattice parameters form the foundation of atomistic simulations to establish GPFE. The twinning plane (111) is shaded violet and the [11\( \bar{2} \)] direction is denoted with the red arrow in L1\(_0\) Ni\(_2\)FeGa and shown in Figure 6.3. We note that if the tetragonal axis is denoted as \( c \), not 2\( c \), the corresponding twinning plane will be (112).

![Diagram](image)

**Figure 6.3** L1\(_0\) structure and twinning system of Ni\(_2\)FeGa. The L1\(_0\) fct structure with lattice parameters \( a, a \) and 2\( c \) contains two fct unit cells. The twinning plane (111) is shown in shaded violet and direction [11\( \bar{2} \)] in red arrow. The blue, red and green atoms correspond to Ni, Fe and Ga atoms, respectively.

Figure 6.4 shows a top view from the direction perpendicular to the (111) twinning plane with three-layers of atoms stacking in L1\(_0\) Ni\(_2\)FeGa. Different sizes of atoms represent three successive (111) layers. The twinning partial dislocation is \( \frac{1}{6}[11\bar{2}] \) (Burgers vector \( b=1.45 \) Å) and is shown with a red arrow.
Figure 6.4 Schematic of top view from the direction perpendicular to the (111) twinning plane in L1$_0$ Ni$_2$FeGa. Different sizes of atoms represent three successive (111) layers. Twinning partial $\frac{1}{6}[1\bar{1}2]$ is shown in red arrow.

We conducted simulations to determine the GPFE of L1$_0$ Ni$_2$FeGa by successive shear of every (111) plane over $\frac{1}{6}[1\bar{1}2]$ partial dislocation. Figure 6.5a shows the perfect L1$_0$ lattice of Ni$_2$FeGa, while Figure 6.5b is the lattice with a three-layer twin after shearing displacement, u (shown with red arrow), in successive (111) planes (twinning plane is marked with a brown dashed line). The atomic arrangement is viewed in [11\bar{0}] direction. We note that the stacking sequence ABCABCA….. in the perfect lattice changed to ABCACBA….. in the three-layer twin (i.e. moving plane B into the position of plane C after one-layer twin generated, and moving plane C into the position of plane B when two-layer twin is created.)
Figure 6.5 Deformation twinning in (111) plane with partial dislocation $\frac{1}{6}[1\bar{1}2]$ (Burgers vector $b=1.45$ Å) of L1$_0$ Ni$_2$FeGa. (a) The perfect L1$_0$ lattice viewed from the [1\bar{1}0] direction. Twining plane (111) is marked with a brown dashed line. (b) The lattice with a three-layer twin after shearing along $\frac{1}{6}[1\bar{1}2]$ dislocation, u, shown in red arrow.

In Figure 6.6, the shear displacement in each successive plane (111), u, is normalized by the respective required Burgers vector $b=1.45$ Å along [1\bar{1}2] direction. We define $\gamma_{us}$ as the stacking fault nucleation barrier, which is the barrier preventing a one-layer partial fault from becoming a one-layer full fault, $\gamma_{isf}$ as the first layer intrinsic stacking fault energy (SFE), $\gamma_{ut}$ as the twin nucleation barrier, which is the barrier against a one-layer partial fault becoming a two-layer partial fault, and $2\gamma_{isf}$ as twice the twin SFE [76, 130]. Note that $\gamma_{us}$ and $\gamma_{ut}$ cannot be experimentally measured and must be computed [76]. The twin migration energy is denoted by $\gamma_{TM} = \gamma_{ut} - 2\gamma_{isf}$ (shown in vertical green arrow in Figure 6.5), which is most relevant in the presence of existing twins and determines the twin migration stress [20]. Table 6.1 summarizes
the calculated fault energies for twin system $\frac{1}{6}[1\bar{1}2](111)$ of L1$_0$ Ni$_2$FeGa and for twin system $\frac{1}{7}[100](010)$ of 14M Ni$_2$FeGa (twinning in 14M will be discussed in next section). We will see in the next section that the critical twin nucleation stress, $\tau_{\text{crit}}$, for L1$_0$ Ni$_2$FeGa strongly depends on these fault energies and barriers. Thus, utilizing ab initio DFT to precisely establish the GPFE landscape is essential in computing $\tau_{\text{crit}}$.

Figure 6.6 GPFE in (111) plane with $\frac{1}{6}[1\bar{1}2]$ twinning dislocation of L1$_0$ Ni$_2$FeGa. The calculated fault energies are shown in Table 6.1.


Table 6.1 Calculated fault energies (in mJ/m²) for twin system $\frac{1}{6}[1\bar{1}2](111)$ of L1₀ Ni₂FeGa and $\frac{1}{7}[100](010)$ 14M Ni₂FeGa.

<table>
<thead>
<tr>
<th>Material</th>
<th>Twin system</th>
<th>$\gamma_{us}$</th>
<th>$\gamma_{tsf}$</th>
<th>$\gamma_{ut}$</th>
<th>$2\gamma_{tsf}$</th>
<th>$\gamma_{TM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1₀ Ni₂FeGa</td>
<td>$\frac{1}{6}<a href="111">1\bar{1}2</a>$</td>
<td>168</td>
<td>85</td>
<td>142</td>
<td>86</td>
<td>56</td>
</tr>
<tr>
<td>14M Ni₂FeGa</td>
<td>$\frac{1}{7}<a href="010">100</a>$</td>
<td>87</td>
<td>49</td>
<td>83</td>
<td>49</td>
<td>34</td>
</tr>
</tbody>
</table>

6.3.3 Twinning energy landscapes (GPFE)- the 14M Ni₂FeGa example

Experiments have shown that Ni₂FeGa alloys exhibit phase transformations from the austenite L2₁ (cubic) to intermartensite 10M/14M (modulated monoclinic), and martensite L1₀ (tetragonal) phases [9, 12, 13]. The modulated monoclinic 14M is a internally twinned long-period stacking-order structure, and it can be constructed from L2₁ cubic structure by combination of shear (distortion) and atomic shuffle [166] (Figure 6.7a and 6.7b). Twinning system (110)[110] in the austenite L2₁ coordinates has been observed for the 14M structure [167-169] (Figure 6.7c), which corresponds to (010)[100] in the 14M coordinates. Figure 6c shows the internally twinned 14M structure, and Fig. 7d is the detwinned structure after shearing in certain (110)₁L₂₁ planes. To establish the GPFE curve for twinning in 14M, we calculated the lattice parameters and monoclinic angle of 14M first. We constructed a supercell containing 56 atoms to incorporate the full period of modulation in the 14M supercell [170, 171]. The initial calculation parameters and the monoclinic angle are estimated by assuming the lattice correspondence with the 10M structure [9, 15, 166, 172, 173]. The calculated lattice parameters $a_{14M} = 4.24$ Å, $b_{14M} = 5.38$ Å and $c_{14M} = 4.181$ Å and monoclinic angle $\beta = 93.18^\circ$ are in an
excellent agreement with experimental data [9]. Figure 6.8 shows the calculated GPFE curve of 14M, and the calculated fault energies for twin system $\frac{1}{7}[100](010)$ are summarized in Table 6.1.

**Figure 6.7** Crystal structures of modulated monoclinic 14M(internally twinned) and detwinned 14M of Ni$_2$FeGa. Like modulated monoclinic 10M structure, the 14M can be constructed from L2$_1$ cubic structure by combination of shear (distortion) and atomic shuffle [15]. (a) Schematic
of the L2₁ cubic structure of Ni₂FeGa, (b) the sublattice of L2₁ (face centered tetragonal structure) displaying the modulated plane (110)₁₂₁ (violet color) and basal plane (001)₁₂₁ (brown color), (c) the modulated monoclinic 14M(externally twinned) structure with twin plane (110)₁₂₁ and twin direction [110]₃₃. Note the twin system (110)[110] in the austenite L2₁ coordinates corresponds to (010)[100] in the intermartensite 14M coordinates, (d) the detwinned 14M structure.

![Generalized Planar Fault Energy](image)

**Figure 6.8** GPFE in (010) plane with \( \frac{1}{7}[100] \) twinning dislocation of 14M Ni₂FeGa. The calculated fault energies are shown in Table 6.1.

### 6.3.4 Peierls-Nabarro Model Fundamentals

The Peierls-Nabarro model considers two semi-infinite continuous half crystals joined at the slip plane with a dislocation inserted [133]. The behavior of the half crystals is confined to
linear elasticity and all nonlinear behavior is confined to a single plane as shown in Figure 6.9 [174].

\[ E_{\text{tot}} = E_{\text{elast}} + E_{\text{mis}} = \]
\[ -\frac{K}{4\pi} \int \int_{-\infty}^{\infty} \frac{df(x)}{dx} \frac{df(x')}{dx'} \ln|x-x'| \, dx \, dx' + \lim_{R \to \infty} \frac{Kb^2}{4\pi} \ln R + \int_{-\infty}^{\infty} \gamma[f(x)] \, dx \quad (1) \]

where \( E_{\text{elast}} \) accounts for the elastic strain energy stored in the two half crystals; while \( E_{\text{mis}} \) is the misfit energy representing the non-linear interatomic interactions in the dislocation core and depends on the position of the dislocation line within a lattice cell and hence is periodic [120, 133].

**Figure 6.9** Configuration of Peierls-Nabarro model for dislocation slip. (a) \( b \) is the lattice spacing along the slip plane and \( d \) is the lattice spacing between adjacent planes. (b) The enlarged configuration of the green box in (a). The grey and blue spheres represent the atom positions before and after the extra half-plane is created. \( u_A(x) \) and \( u_B(x) \) are the atom displacements above slip plane (on plane A) and below slip plane (on plane B), and their difference \( u_A(x) - u_B(x) \) describes the disregistry distribution \( f(x) \) as a function of \( x \).
The parameter $K$ is a material property measuring the elastic response of the lattice to displacement along the Burgers vector direction [129], and $\gamma$ is the generalized stacking fault energy representing the fault energy associated with dislocation motion [15, 72].

By considering the lattice discreteness, the misfit energy $E_{\text{mis}}$ can be defined as the sum of all the misfit energies between pairs of atoms rows as a function of $u$ [85, 133],

$$E_{\text{mis}}(u) = \sum_{m=-\infty}^{+\infty} \gamma[f(ma' - u)]a'$$

(2)

where, $a'$ is the periodicity of $E_{\text{mis}}(u)$ and defined as the shortest distance between two equivalent atomic rows in the direction of the dislocation’s displacement [113, 114, 131]. The solution of the disregistry function $f(x)$ in the dislocation core is [114, 133, 173, 175]:

$$f(x) = b + \frac{b}{\pi} \arctan \left( \frac{x}{\xi} \right)$$

(3)

where $\xi = \frac{d}{2(1-\nu)}$ is the half-width of the dislocation for an isotropic solid [129], $d$ is the interplanar distance between the twinning planes and $\nu$ is the Poisson’s ratio. By using the Frenkel expression [133], the $\gamma[f(x)]$ can be written as:

$$\gamma[f(x)] = \frac{\gamma_{\text{max}}}{2} \left[ 1 - \cos \frac{2\pi f(x)}{b} \right]$$

(4)

where, $\gamma_{\text{max}}$ is maximum fault energy. After substituting Eq. (3) and Eq. (4) into Eq. (2), we have the following summation form with $m$ as integer:

$$E_{\text{mis}}'(u) = \sum_{m=-\infty}^{+\infty} \gamma[f(ma' - u)]a' = \sum_{m=-\infty}^{+\infty} \frac{\gamma_{\text{max}}}{2} \left[ 1 + \cos \left( \frac{2\pi f}{b} \left( \frac{ma' - u}{\xi} \right) \right) \right]a'$$

(5)
Because the elastic strain energy $E_{\text{elast}}$ is independent on the location of dislocation line $u$, the Peierls stress $\tau_p$ is then given by the maximum stress required to overcome the periodic barrier in $E_{\text{mis}}(u)$ only,

$$\tau_p = \max \left\{ \frac{1}{b} \frac{dE_{\text{tot}}}{du} \right\} = \max \left\{ \frac{1}{b} \frac{dE_{\text{mis}}(u)}{du} \right\}$$

(6)

### 6.4 Twin nucleation model based on P-N formulation - the L1$_0$Ni$_2$FeGa example

It is experimentally observed that the morphology of twinning dislocations array near the twin tip is thin and semi-lenticularly shaped [176-179]. The critical stage of twin nucleation is the activation of the first twinning partial dislocation on twin plane involving an intrinsic stacking fault [176, 179-181]. This can occur in a region of high stress concentration such as the inclusions, grain boundaries and notches [180]. Figure 6.10 shows the schematic illustration of the twin morphology with twinning plane (111) and twinning partial $\frac{1}{6}[11\overline{2}]$ in L1$_0$ Ni$_2$FeGa. The $h$ is the twin thickness and $N$ is the number of twin-layers, and $d$ is the spacing between two adjacent twinning dislocations and varies depending on their locations relative to the twin tip. It is experimentally observed that twinning partials near the twin tip are more closely spaced ($d$ is smaller) compared to the dislocations far away from the twin tip ($d$ is larger) [176]. The $\tau$ is the applied shear stress and the minimum $\tau$ to form a twin is called critical twin nucleation stress, $\tau_{\text{crit}}$. Once the first twinning partial (leading twinning dislocation) has nucleated, subsequent partials readily form on successive twin planes [181]. We note that a three-layer fault forms the twin nucleus in L1$_0$ Ni$_2$FeGa, which reproduces the L1$_0$ structure. Thus, the number of twin-layers, $N$, equals to 3 and we seek for the minimization of the total energy as described below.
Figure 6.10 Schematic illustration showing the semi-lenticular twin morphology of L1₀ Ni₂FeGa, which is viewed in the [1 1 0] direction. The twinning plane is (111) and twinning direction is [11 2]. h is the twin thickness and N is the number of twin-layers (N=3 for twin nucleation). d is the spacing between two adjacent twinning dislocations and considered as a constant for three-layer twin.

The total energy associated with the twin nucleation shown in Figure 6.10 can be expressed as:

$$E_{total} = E_{int} + E_{GPFE} + E_{line} - W$$  

where $E_{int}$ is the twin dislocations interaction energy, $E_{GPFE}$ is the twin boundary energy (GPFE), $E_{line}$ is the twin dislocations line energy and $W$ is the applied work. These energy terms can be described as follows:

(1) Twinning dislocations interaction energy, $E_{int}$

The energy for the ith twinning dislocation interacting with the (i+n)th or (i-n)th dislocation is [182, 183]
\[ E_{i,i+n/i-n} = \frac{\mu b^2}{4\pi (1 - \nu)} \left( 1 - \nu \cos^2 \theta \right) \ln \frac{L}{nd} \]  

(8)

where \( \mu \) is the shear modulus of the twinning system, \( b \) is the Burgers vector of the twinning dislocations, \( \nu \) is the Poisson’s ratio, and \( \theta \) is the angle between the Burgers vector and the dislocation line, and \( L \) is the dimensions of the crystal containing the twin. After summing for all twinning dislocations, we have the energy for the \( i \)th dislocation as [182, 183]

\[ E_i = \frac{\mu b^2}{4\pi (1 - \nu)} \left( 1 - \nu \cos^2 \theta \right) \left[ \sum_{n=1}^{N-i} \ln \frac{L}{nd} + \sum_{m=1}^{n+1} \ln \frac{L}{md} \right] \]  

(9)

where, \( N \) is the number of layers in the twin nucleus.

The total interactions energy of all twinning dislocations is:

\[ E_{\text{int}} = \frac{\mu b^2}{4\pi (1 - \nu)} \left( 1 - \nu \cos^2 \theta \right) \left[ N^2 \ln \frac{L}{d} - \ln (N - 2)! + \sum_{i=2}^{n=N-1} \ln (N - i)! + \ln (i - 1)! \right] \]  

(10)

(2) Twin boundary energy (GPFE), \( E_{\text{GPFE}} \)

Considering the interaction of multiple twinning dislocations, the disregistry function \( f(x) \) can be described in Eq. (11) and Figure 6.11 shows a schematic of normalized \( f(x)/b \) variation with \( x/\zeta \). \( \zeta \) is defined as the half-width of the dislocation for an isotropic solid [129].

\[ f(x) = \frac{b}{2} + \frac{b}{N\pi} \left\{ \tan^{-1} \left( \frac{x}{\zeta} \right) + \tan^{-1} \left( \frac{x-d}{\zeta} \right) + \tan^{-1} \left( \frac{x-2d}{\zeta} \right) + \ldots + \tan^{-1} \left( \frac{x-(N-1)d}{\zeta} \right) \right\} \]  

(11)
In the GPFE curve, the energy required to create an intrinsic stacking fault can be expressed as:

$$\gamma_{SF}(f(x)) = \gamma_{isf} + \left(\frac{\gamma_{us} - \gamma_{isf}}{2}\right)\left\{1 - \cos\left[2\pi \frac{f(x)}{b}\right]\right\} \quad \text{for} \quad 0 \leq f(x) \leq b \quad (12)$$

The energy required to nucleate a twin can be expressed as:

$$\gamma_{twin}(f(x)) = \left(\frac{2\gamma_{us} + \gamma_{isf}}{2}\right) + \frac{1}{2}\left[\gamma_{us} - \left(\frac{2\gamma_{us} + \gamma_{isf}}{2}\right)\right]\left\{1 - \cos\left[2\pi \frac{f(x)}{b}\right]\right\}$$

$$\quad \text{for} \quad b < f(x) \leq Nb \quad (13)$$

Thus, the twin boundary energy $E_{GPFE}$ can be expressed as:

$$E_{GPFE}(d) = \sum_{m=-\infty}^{\infty} \gamma_{isf}[f(m\cdot b - d)]b + \sum_{m=-\infty}^{\infty} \gamma_{SF}[f(m\cdot b - d)]b + (N - 1) \sum_{m=-\infty}^{\infty} \gamma_{twin}[f(m\cdot b - d)]b \quad (14)$$
(3) **Dislocation line energy, \( E_{\text{line}} \)**

\[
E_{\text{line}} = N \left[ \frac{\mu b^2}{2(1-v)} \left( 1 - v \cos^2 \theta \right) \right] = \frac{N \mu b^2}{2(1-v)} \left( 1 - v \cos^2 \theta \right)
\]

(15)

As we will see in the total energy expression that the dislocation line energy, \( E_{\text{line}} \), does not depend on the spacing \( d \), so it will not contribute to the critical twin nucleation stress.

(4) **Applied work, \( W \)**

Assuming the applied stress \( \tau \) is uniform within the twin, the work done by the applied shear stress on the crystal is

\[
W = N \tau d s h
\]

(16)

where \( s \) is the twinning shear.

When all the terms in the total energy expression are determined, the total energy for the twin nucleation can be expressed as follows:

\[
E_{\text{total}} = E_{\text{int}} + E_{\text{GPFE}} + E_{\text{line}} - W =
\frac{\mu b^2}{4\pi(1-v)} \left( 1 - v \cos^2 \theta \right) \left\{ N^2 \frac{L}{d} \left[ \ln (N - 2)! + \sum_{i=2}^{N-1} \ln (N - i)! + \ln (i-1)! \right] \right\} +
\sum_{m=-\infty}^{\infty} \gamma_{\text{SF}} [f(mb-d)]b + (N-1) \sum_{m=-\infty}^{\infty} \gamma_{\text{twin}} [f(mb-d)]b + \frac{N \mu b^2}{2(1-v)} \left( 1 - v \cos^2 \theta \right) - N \tau d s h
\]

(17)

For a constant value of \( N \) in specific twin systems, the total energy is a function of the spacing between adjacent twinning partials, \( d \). The equilibrium \( d \) corresponds to the minimum total energy. To determine the critical twin nucleation stress, \( \tau_{\text{crit}} \), we minimized the total energy for the twin nucleation, \( E_{\text{total}} \), with respect to \( d \):

\[
\frac{\partial E_{\text{total}}}{\partial d} = 0
\]

(18)
The derived explicit and closed-form expression for $\tau_{\text{crit}}$ is given by

$$\tau_{\text{crit}} = \frac{\mu b^2 \left(1 - \nu \cos^2 \theta\right) N}{4\pi (1 - \nu) \text{sh} d} + \frac{b}{N^2 \text{sh} d} \left\{ \gamma_{\text{us}} - \gamma_{\text{isf}} + (N - 1) \left[ \gamma_{\text{ut}} - \left( \frac{2\gamma_{\text{isf}} + \gamma_{\text{isf}}}{2} \right) \right] \right\}$$

$$\times \sum_{m=-\infty}^{\infty} \sin \left( \frac{2}{N} \left[ \tan^{-1} \left( \frac{mb - d}{\zeta} \right) + \ldots + \tan^{-1} \left( \frac{mb - Nd}{\zeta} \right) \right] \right)$$

$$\times \left[ \frac{-\zeta}{\zeta^2 + (mb - 2d)^2} + \ldots + \frac{-(N-1)\zeta}{\zeta^2 + (mb - Nd)^2} \right]$$

(19)

We compared the critical twin nucleation stress, $\tau_{\text{crit}}$, for L1$_0$ and 14M Ni$_2$FeGa predicted from our P-N formulation based twin nucleation model with the experimental twinning stress data, and found excellent agreement without any fitting parameters (Table 6.2). The 'ideal twinning stress' is calculated by the maximum slope of GPFE curve with respect to the shear displacement and in the form of $\tau_{\text{Tm,ideal}} = \pi \left( \frac{\gamma_{\text{Tm}}}{b} \right)$ [130]. Based on the P-N model shown earlier [130], the 'Peierls stress $\tau_p$' needed to move a twin partial dislocation is also determined. Note in the Eq. (4), the $\gamma_{\text{max}}$ is replaced by $\gamma_{\text{Tm}}$. We note that the ideal twinning stress of 1420 MPa for L1$_0$ is an order of magnitude larger than the twin nucleation stress observed experimentally; even though the Peierls stress of 230 MPa is smaller than ideal twinning value, it is still much larger than experimental data of 35-50 MPa. Similarly for 14M case, the ideal twinning stress and Peierls stress are much larger than experimental data. Our model shows favorable agreement between experiment and theory for 14M (27.5 MPa experiment (our experiment) vs 30 MPa theory Eq. (19)). This observation demonstrates that the P-N formulation based twin nucleation model provides an accurate prediction of the twin nucleation stress.
Table 6.2 The predicted critical twin nucleation stress, $\tau_{\text{crit}}$, is compared with ideal twinning stress, $\tau_{\text{TMideal}}$, Peierls stress, $\tau_p$, and available experimental data in L1$_0$ Ni$_2$FeGa.

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Ideal Twin Stress (MPa)</th>
<th>Twin Stress based on Peierls (MPa)</th>
<th>Twin Stress-this study (MPa) $\tau_{\text{crit}}$</th>
<th>Experimental Twin Stress (MPa)[9]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$FeGa</td>
<td>$\tau_{\text{TMideal}} = \pi \left{ \frac{\gamma_{1\text{M}}}{b} \right}$</td>
<td>$\tau_p = \max \left{ \frac{1}{b} \frac{E^{\text{T}M}_\gamma (u)}{du} \right}$</td>
<td>$\tau_{\text{crit}}$ Eq.(13)</td>
<td></td>
</tr>
<tr>
<td>L1$_0$</td>
<td>1420</td>
<td>230</td>
<td>52</td>
<td>35-50</td>
</tr>
<tr>
<td>14M</td>
<td>1779</td>
<td>120</td>
<td>30</td>
<td>25-35</td>
</tr>
</tbody>
</table>

We note that in the energy expressions, the spacing between the first (leading) and the second dislocation, $d$, i.e. the tip behavior or the first two layers, governs the results. Therefore, the role of varying spacing $d$ along the length of the twin was considered, but this modification did not change the stress values obtained in this work (the stress values calculated by varying equilibrium spacing and by assuming constant equilibrium spacing are within 5%). For example, for the case of Ni$_2$MnGa 10M 3.8 MPa, for Ni$_2$FeGa L1$_0$ 49 MPa and for NiTi$^3$ B19' 126 MPa were obtained for variable $d$ values in comparison with 3.5 MPa, 51 MPa and 129 MPa respectively for constant $d$ values.

### 6.5 Prediction of Twinning Stress in Shape Memory Alloys

To validate the P-N formulation based twin nucleation model, we calculated the critical twinning stress $\tau_{\text{crit}}$ predicted from the model for several important shape memory alloys and compared the results to experimental twinning stress data. The martensitic crystal structures of these materials present 10M (five-layered modulated tetragonal structure for Ni$_2$MnGa and five-layered modulated monoclinic structure for Ni$_2$FeGa), 14M(seven-layered modulated monoclinic
structure), $L_1$ (non-modulated tetragonal structure) and B19' (monoclinic structure). We found excellent agreement between the predicted values and experimental data without any fitting parameters in theory as shown in Table 3. The equilibrium $d$ corresponding to the minimum total energy for different materials is also shown in Table 6.3. We considered both the important crystal structures 10M and 14M in $Ni_2MnGa$, and the monoclinic B19’ structure of NiTi. In all cases, we determined the lattice constants prior to our simulations. The twin system and unstable twin nucleation energy $\gamma_{ut}$ corresponding to SMAs are also given.
Table 6.3 Predicted critical twin nucleation stresses $\tau_{\text{crit}}^{\text{theory}}$ for Shape Memory Alloys are compared to known reported experimental values $\tau_{\text{crit}}^{\text{expt}}$. The twin systems, equilibrium spacing $d$ and unstable twin nucleation energy $\gamma_{ut}$ corresponding to SMAs are given. (10M, 14M, $L_{10}$ and $B_{19}'$ are the martensitic crystal structures explained in the text).

<table>
<thead>
<tr>
<th>Material</th>
<th>Twin system</th>
<th>$\gamma_{ut}$ (mJ/m²) (predicted)</th>
<th>$d$ (Å) (predicted)</th>
<th>$\tau_{\text{crit}}^{\text{theory}}$ (MPa) (predicted)</th>
<th>$\tau_{\text{crit}}^{\text{expt}}$ (MPa) (experiment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$MnGa 10M</td>
<td><a href="010">100</a></td>
<td>11</td>
<td>38</td>
<td>3.5</td>
<td>0.5-4 Ref. [184-190]</td>
</tr>
<tr>
<td>Ni$_2$MnGa 14M</td>
<td><a href="010">100</a></td>
<td>20</td>
<td>21</td>
<td>9</td>
<td>2-10 Ref. [168, 188]</td>
</tr>
<tr>
<td>NiTi$^1$</td>
<td>$B_{19}'$</td>
<td>(001)[100]</td>
<td>25</td>
<td>20</td>
<td>20-28 Ref. [20, 191]</td>
</tr>
<tr>
<td>Co$_2$NiGa</td>
<td>$L_{10}$</td>
<td>(111)[112]</td>
<td>41</td>
<td>26</td>
<td>22-38 Ref. [16, 159]</td>
</tr>
<tr>
<td>Ni$_2$FeGa</td>
<td>14M</td>
<td><a href="010">100</a></td>
<td>87</td>
<td>30</td>
<td>25-40 Ref.[9, 18]</td>
</tr>
<tr>
<td>NiTi$^2$</td>
<td>$B_{19}'$</td>
<td>(100)[001]</td>
<td>102</td>
<td>43</td>
<td>26-47 Ref.[20, 191]</td>
</tr>
<tr>
<td>Co$_2$NiAl</td>
<td>$L_{10}$</td>
<td>(111)[112]</td>
<td>124</td>
<td>48</td>
<td>32-51 Ref [16, 141]</td>
</tr>
<tr>
<td>Ni$_2$FeGa</td>
<td>$L_{10}$</td>
<td>(111)[112]</td>
<td>142</td>
<td>51</td>
<td>35-50 Ref [9, 18]</td>
</tr>
<tr>
<td>NiTi$^3$</td>
<td>$B_{19}'$</td>
<td>(20$\bar{1}$)[10$\bar{2}$]</td>
<td>180</td>
<td>129</td>
<td>112-130 Ref [20, 153]</td>
</tr>
</tbody>
</table>
We plot the predicted and experimental twinning stress of SMAs considered here against $\gamma_{ut}$ in Figure 12. We note that the monotonic increase in twinning stress with $\gamma_{ut}$, which, for the first time, establishes an extremely important correlation between $\tau_{crit}$ and $\gamma_{ut}$ in SMAs. The similar correlation between $\tau_{crit}$ and $\gamma_{ut}$ has also been observed for fcc metals [76]. The physics of twinning indicates that in order to form a twin boundary and for layer by layer growth to the next twinning plane, the twinning partials must overcome the twin nucleation barrier $\gamma_{ut}$. However, the relationship is affected by other parameters in the model so both the model and experiment point to a rather complex relationship.

![Image](image_url)

**Figure 6. 12** The predicted and experimental twinning stress for SMAs versus unstable twin nucleation energy $\gamma_{ut}$, from Table 6.3. The predicted twinning stress (red square) is in excellent agreement with the experimental data (blue circle). The P-N formulation based twin nucleation model reveals an overall monotonic trend between $\tau_{crit}$ and $\gamma_{ut}$. Note that NiTi$^1$, NiTi$^2$ and NiTi$^3$ indicate three different twinning systems in NiTi as shown in Table 6.3.
6.6 Determination of twinning stress from experiments

We determined the critical martensite twinning stress for shape memory alloys Ni$_2$MnGa, Ni$_2$FeGa and NiTi experimentally in our early work (the Ni$_2$MnGa data was unpublished) which is reported here. Figure 6.13 shows the critical martensite twinning stress vs. temperature for the fully martensitic phase of Ni$_2$MnGa 10M, Ni$_2$FeGa 14M and Ni$_2$FeGa L1$_0$, and NiTi B19'. We note that the twinning stress levels are nearly temperature independent in the martensite regime as shown. We note that the experimental stress levels are shown in the martensitic regime only, and different alloys have different martensite finish temperatures. To ensure fully martensitic microstructure, our experiments were conducted near -200°C in some cases.

![Graph showing critical martensite twinning stress vs. temperature for Ni$_2$MnGa 10M, Ni$_2$FeGa 14M and L1$_0$, and NiTi B19'.](image)

**Figure 6.13** The critical martensite twinning stress from deformation experiments conducted in Sehitoglu’s group. The materials are in the fully martensitic phase of Ni$_2$MnGa 10M, Ni$_2$FeGa 14M and L1$_0$, and NiTi B19'. NiTi$^1$, NiTi$^2$ and NiTi$^3$ indicate three different twinning systems in NiTi as shown in Table 6.3. Note that the critical stress is nearly temperature independent.

A set of stress-strain experiments was conducted on Ni$_2$FeGa in this study. The typical compressive stress-strain curve of Ni$_2$FeGa 14M at -190 °C, which is below the martensite finish
The experiments were conducted in compression loading of [001] oriented single crystals of Ni$_{54}$Fe$_{19}$Ga$_{27}$. For T<M$_t$, the crystal is in the 14M state [18] subsequent to detwinning and reorientation when the loading reached the critical twinning stress of 55 MPa. Because the Schmid factor for the compressive axis [001] and twin system $\{110\}<1\bar{1}0>$ in Ni$_2$FeGa 14M is 0.5, the critical twinning stress at a temperature of -190 °C is then calculated as 27.5 MPa. This experimentally measured twinning stress is in excellent agreement with the predicted value from P-N formulation based twin nucleation model (30 MPa based on Equation 13). Upon unloading the twinning-induced deformation remains as plastic strain. However, If the material is heated above the austenite finish temperature (A$_f$), the martensite to austenite transformation occurs and the plastic strain can be fully recovered (shown in blue arrow).

Figure 6.14 Compressive stress-strain response of Ni$_{54}$Fe$_{19}$Ga$_{27}$ at a constant temperature of -190 °C.

6.7 Discussion of Results

We presented a general framework for describing twinning in shape memory materials with attention to the processes at the atomistic scale. Inevitably, there is complexity in twinning of monoclinic, tetragonal, modulated monoclinic and orthorhombic martensitic structures. The
paper tries to demonstrate this complexity and revises the original P-N model. Without such understanding, the characterization and design of new shape memory systems do not have a strong scientific basis. We suggest that the results can serve as the foundation to develop a shape memory materials modeling and discovery methodology, where the deformation behavior of the material at the atomic level directly using quantum mechanics informs the higher length scale calculations. This methodology incorporates the mesoscale P-N calculation. Previously, we showed how energy barriers (calculated using first-principles DFT) are utilized in fcc metals to capture the twinning stress. We noted the added complexities in the ordered shape memory alloys, and the need to understand the mechanisms for the complex twinning where shear and relaxation of atoms lead to accurate GPFE descriptions. We note that the magnitude of Peierls stress calculated from the ‘classical’ Peierls-Nabarro model depends exponentially on the dislocation core, which predicts significant core size dependence of critical stress nearly an order of magnitude [130, 156, 166]. However, the derived formula of the critical twin nucleation stress in the present study does not hold this exponential form and it is dependent on the elastic strain energy due to the interaction of twinning partials in addition to the misfit energy. Therefore, the core size of dislocation affects the twinning stress very slightly. For example, for the L10 Ni2FeGa varying ζ in the range of 1 Å to 1.5 Å (θ for 0º to 90º) resulted in τcrit in the range of 49 to 51 MPa. We also performed calculations using the local density approximation (LDA) to determine the planar fault energies and performed simulations with the modified fault energies. LDA and GGA are two widely used methods to describe the electronic exchange-correlation interaction. Generally, LDA underestimates slightly the crystal lattice parameter; while, GGA calculates the lattice parameter in a better agreement with experiments [192, 193] and provides a substantially improved description of the ground state properties [194]. We calculated the lattice parameter of cubic L21 Ni2FeGa, and found that the lattice parameter of 5.755 Å using GGA is closer to experiments than that of 5.6 Å using LDA [15]. Since LDA underestimates the lattice parameter and overestimate the cohesive energy, it will lead to shorter Burgers vector, smaller interplanar distance and larger stacking fault energy [86, 192, 195]. These changes will cause different (less accurate) twinning stress from the proposed twin nucleation model compared to our present study using GGA. Here we compare calculated results of L10 Ni2FeGa by using LDA and GGA as an example. We note that the twinning stress predicted from the present twin nucleation model by using LDA is 59 MPa, which is 15% greater than the one of 51 MPa by
using GGA and much larger than the experimental results. However, the use of LDA does not change the model itself and the critical twinning stress formula, so we believe that the conclusions regarding to the twinning stress as a function of Burgers vector, interplanar distance and twinning fault energies and the monotonic relation between $\tau_{\text{crit}}$ and $\gamma_{\text{ut}}$ will still hold.

Table 6.4 Results comparison of LDA and GGA in L1$_0$ Ni$_2$FeGa.

<table>
<thead>
<tr>
<th>Calculations</th>
<th>LDA</th>
<th>GGA</th>
<th>Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter, $a$ (Å)</td>
<td>3.58</td>
<td>3.68</td>
<td>3.81[9]</td>
</tr>
<tr>
<td>Lattice parameter, $c$ (Å)</td>
<td>3.4</td>
<td>3.49</td>
<td>3.27[9]</td>
</tr>
<tr>
<td>Burgers vector (Å)</td>
<td>1.41</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>Interplanar distance (Å)</td>
<td>2.03</td>
<td>2.09</td>
<td></td>
</tr>
<tr>
<td>$\gamma_{\text{us}}$ (mJ/m$^2$)</td>
<td>181</td>
<td>168</td>
<td></td>
</tr>
<tr>
<td>$\gamma_{\text{isf}}$ (mJ/m$^2$)</td>
<td>89</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>$\gamma_{\text{ut}}$ (mJ/m$^2$)</td>
<td>153</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>$2\gamma_{\text{tsf}}$ (mJ/m$^2$)</td>
<td>91</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>Twinning stress (MPa)</td>
<td>59</td>
<td>51</td>
<td>35-50 Ref [9, 18]</td>
</tr>
</tbody>
</table>

We note that the results are in agreement within 15% in most cases (for example, $\gamma_{\text{isf}}$ values were 89 (mJ/m$^2$) and 85 (mJ/m$^2$) and $\gamma_{\text{ut}}$ levels were 153 (mJ/m$^2$) and 142 (mJ/m$^2$) for LDA and GGA, respectively). The GGA based results compare more favorably with the experimental twin stress levels.

The modeling results were checked with selected experiments to test the capability of the methodology proposed. The simulations have been undertaken on new shape memory alloys such as Ni$_2$FeGa, Co$_2$NiAl and Ni$_2$MnGa exhibiting low twinning stress (<50 MPa). This is in addition to the more established but equally complex NiTi which has multiple twin modes with
higher twin stresses (reaching >150 MPa). We further verified the predictions with experiments measuring the twinning stress in 14M (modulated monoclinic) Ni$_2$FeGa with excellent agreement.

There are several observations that are unique to the findings in this study. We note that twinning in these alloys cannot be classified with a simple mirror reflection; the shuffles due to relaxation at the interfaces need to be considered. This modification provides more accurate energy barriers. In addition to establishing the twinning stress our study provides a wealth of information, such as the lattice constants (hence the volume change that plays an important role in shape memory alloys), the shear moduli which can be all measured experimentally. It is the determination of the twinning stress that is far more difficult experimentally because the experiments need to be performed well below room temperature in several cases and very precise stress-strain curves measurements on samples with uniform gage sections need to be established.

Large amount of efforts have been devoted to lowering the magnitude of twinning stress in magnetic shape memory (MSM) alloys. The main alloy system of study has been Ni$_2$MnGa because it undergoes twinning at stress levels less than 10 MPa. The other candidate alloys of interest include Ni$_2$FeGa, Co$_2$NiAl and Co$_2$NiGa. Their twinning stress levels are also rather low (less than 30 MPa). We predict the twinning stress in these materials with considerable accuracy and without adjustable constants. The NiTi presents a complex system because the twin modes change with deformation, from the {001} system to the {012} and higher order ones. This results in an overall higher twin stress in the case of NiTi.

Finally, we note that in the 'pseudoelasticity' case, when the shape memory alloy undergoes isothermally stress-induced transformation from austenite to martensite, the martensite undergoes detwinning and this contributes to the overall recoverable strain. Upon unloading, the martensite reverts back to austenite, and this called 'pseudoelasticity'. The magnitude of the correspondence variant pair formation strain is of the order of 5% in NiTi while the shear associated with detwinning is also nearly 5% making the total near 10%. In the case on Ni$_2$FeGa, the magnitude of the strains are higher (near 14%), and the process of twinning plays a considerable role [8]. It is difficult to determine the twinning stress during pseudoelasticity
experiments; therefore theoretical calculations such as presented in this paper provide significant understanding.

6.8 Conclusions

The work supports the following conclusions:

(1) The proposed twin nucleation model shows that Ni$_2$MnGa 10M undergoes twinning at stress level as low as 3.5 MPa in agreement with experiments (<4 MPa). The Ni$_2$FeGa 14M undergoes twinning at 30 MPa also in very close agreement with experiments conducted in this study (27.5 MPa). The predicted twinning stresses for NiTi are higher (43 MPa for the (100) case and 129 MPa for the (201) case) which are also in close agreement with experiments.

(2) The twinning stress for the newly proposed ferromagnetic shape memory alloys Co$_2$NiGa, Co$_2$NiAl are 26 MPa and 48 MPa respectively, also in close agreement with experiments (22-38 MPa for Co$_2$NiGa and 32-51 MPa for Co$_2$NiAl).

(3) Depending on the martensitic structure and twin systems, the twinning processes may involve combined shear and atomic shuffles such as for the case of B19' NiTi (100), which makes the determination of GPFE landscape challenging. Nevertheless, the recognition of the out of plane displacements at twin interfaces during simulations provides increasingly accurate results for the energy barriers.

(4) The proposed twin nucleation model reveals that $\tau_{\text{crit}}$ has an overall monotonic dependence on the unstable twin nucleation energy $\gamma_{\text{ut}}$. The $\tau_{\text{crit}}$ vs $\gamma_{\text{ut}}$ plot was chosen to demonstrate theory and experiment comparison. We note that $\tau_{\text{crit}}$ prediction depends on the entire GPFE landscape, the elastic constants, and the Burgers vectors, so a simple relationship can not be written in an algebraic form. To achieve smaller twinning stress in shape memory alloys, shorter Burgers vectors, lower unstable twin energies and larger interplanar distances are desirable.
Chapter 7  Summary and Future work

7.1 Summary

In this thesis, we first present an energetic approach to comprehend a better understanding of phase stability, martensitic phase transformation and dislocation slip in SMAs utilizing first principles simulations. By precisely determining energy barriers associated with the phase transformation and dislocation slip, we provide an important insight of understanding the role of energy barriers in SMAs. In the second part of the thesis, we extended the Peierls-Nabarro (P-N) formulation with atomistic simulations to determine the Peierls stress in SMAs, and developed a twin nucleation model based on P-N formulation to predict twin nucleation stress in SMAs. These new models provide a precise, rapid and inexpensive approach to predict the slip and twin stress in SMAs, and a better understanding to design new SMAs.

In Chapter 2, by utilizing atomistic simulations and considering small shear steps in phase transformation, we discovered energy barriers in transformation path of NiTi and provide a more authoritative explanation regarding the discrepancy between the experimental observations and theoretical studies. The results resolved a longstanding problem plaguing the NiTi for decades. We calculate the energy barriers in the phase transformation of $B2 \rightarrow B19' \rightarrow B33$ and determine the crystal structure of transition states. In addition, we also investigated the effect of hydrostatic pressure on the phase stability of $B19'$ and $B33$, and found that the $B19'$ can be energetically more stable than $B33$ at high tension pressure.

In Chapter 3, we calculated the energy barriers associated with the martensitic transformation from austenite $L2_1$ to modulated martensite 10M of Ni$_2$FeGa incorporating shear and shuffle and slip resistance in [111] direction as well as in [001] direction. The results show that the unstable stacking fault energy barriers for slip by far exceeded the transformation transition state barrier permitting transformation to occur with little irreversibility. This explains the experimentally observed low martensitic transformation stress and high reversible strain in Ni$_2$FeGa. Our methodology is a foundational advance as it overcomes the limitations of the modern understanding of SMAs that rely on the phenomenological theory, which does not deal with the presence of dislocation slips.
In Chapter 4, we make quantitative advances towards understanding of plastic deformation in B2 NiTi. We established the energetic pathway and calculated the theoretical shear strength of several slip systems in B2 NiTi. The results show the smallest and second smallest energy barriers and theoretical shear strength for the (011)[100] and the (011)[1\bar{1}1] cases, respectively, which are consistent with the experimental observations of dislocation slip reported in this study. This work presents a quantitative understanding of plastic deformation mechanism in B2 NiTi, and the methodology can be applied for consideration of a better understanding of SMAs.

In Chapter 5, we extended the Peierls-Nabarro (P-N) model to precisely predict the dislocation slip stress in SMAs utilizing atomistic simulations and mesomechanics tools combined with experiments. We considered the sinusoidal series representation of GSFE in SMAs and incorporated the energies into the P-N formulation. We validated our model by performing experiments and the results show that this model provides precise and rapid results compared to traditional experiments. This extended P-N model with GSFE curves provides an excellent basis for a theoretical study of the dislocation structure and operative slip modes, and an understanding to discovery of new compositions avoiding the trial-by-trial approach in SMAs.

In Chapter 6, we developed a twin nucleation model based on the classical Peierls-Nabarro formulation to precisely predict twin nucleation stress in SMAs. This research is aimed at developing a hierarchical methodology for advanced materials design utilizing the advanced first principles/mesomechanics tools combined with experiments. We classified different twin modes that are operative in different crystal structures and developed a methodology by establishing the fault energy barriers that are in turn utilized to predict the twinning stress. This new model provides a science-based understanding of the twin stress for developing alloys with new methodologies.
7.2 Future work

Following the studies described in this thesis, a number of research projects could be taken up based on the energetic approach and the proposed models for dislocation slip and twin nucleation in SMAs.

- In this thesis, we investigated the crystal structure, slip/twinning plane and direction of alloys having the atomic percentage in the same magnitude order. For example, the binary alloy NiTi has the atomic ratio of 1:1, and the ternary alloy Ni$_2$FeGa has the atomic ratio of 2:1:1. However, some intermetallic/alloys have the different atomic percentage in a magnitude order. For example, the intermetallic Ni$_{12}$Al$_3$Ta has the atomic ratio of 12:3:1. To generate the ordered crystal structure for this type of materials, a large supercell is needed. Therefore, the GSFE for slip and GPFE for twin require further attention and methods to capture the complex crystallography.

- In the proposed models for dislocation slip and twin nucleation, the extended core structure of dislocations derived from the Peierls-Nabarro (P-N) model has an arctan form and predicts the slip/twin stresses in good agreement with experiments. We can also perform atomic simulations using direct DFT to examine the dislocation core, and compare the results (disregistry function of dislocation core) with the P-N approach. Furthermore, the disregistry function of dislocation core determined using direct DFT can be incorporated into the proposed dislocation slip and twin nucleation models to predict the corresponding stresses, which can be compared to the results reported in this thesis.
References


Heo YU, Lee HC. The twin and twin system in FCT L10 0-MnNi phase in an equiatomic Mn-Ni alloy. MATERIALS TRANSACTIONS 2007;48:2546.


Publications


