A DFT+U Study of a Ni-Mn-Ga Magnetic Shape Memory Alloy

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Dedication

This work is dedicated to Bhagawan Sri Sathya Sai Baba, the embodiment of knowledge.
Abstract

We have studied the structural, electronic and magnetic properties of the magnetic shape memory alloy Ni$_2$MnGa using Hubbard-rooted DFT+U functional and recent extensions. Both austenite and martensite phases corresponding to high temperature and low temperature phases respectively have been investigated. The obtained results are compared with the results of standard DFT (GGA) calculations and available experiments. DFT+U method is particularly useful in predicting the energy landscape of the tetragonally distorted martensite from which the total energy minimum for $c/a = 1.23$, that has been obtained with GGA functionals, but not observed in experiments, disappears. Our results indicate that, the better description of the energetics of the tetragonal phase can be attributed to a longer extent of localization of electrons due to the Hubbard correction. Phonon dispersion study of austenite show a soft mode along the [110] direction indicating an instability of austenite at low temperatures.
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Chapter 1

Introduction

Magnetic shape memory alloys (MSMAs), also referred to as ferromagnetic shape memory alloys, are a new type of multifunctional materials. In these alloys, magnetic field can induce recoverable strains of up to 10% [1]. This magnitude of strain is an order of magnitude larger than the magnetic field induced strains observed in magnetostrictive materials [1] or electric field induced strains in piezoelectric materials [2]. The huge macroscopic strains observed in MSMAs are caused by the reorientation of martensitic variants upon application of a magnetic field. Martensitic variants have different preferred direction of magnetization (easy axis), and when a magnetic field is applied, a certain variant is selected over others, resulting in a macroscopic shape change. MSMAs have a considerable advantage over conventional shape memory alloys (temperature or stress activated shape memory behavior) in that they can be operated at higher frequency range of up to 1 kHz [3]. These materials are characterized by a significant coupling between magnetic and orbital degrees of freedom that results in a strong magneto-crystalline anisotropy. They undergo structural and magnetic phase transformations which, when coupled, produce interesting effects. For example, a structural transformation induced by stress or temperature variations, could be detected by an electro-magnetic signal generated by the change in the magnetic structure, or a magnetic field could be used to induce a structural transformation. The coupling of structural (mechanical) and magnetic properties makes MSMA’s interesting candidates for smart structures as well as actuators [4], and sensor applications [5]. Thus the coupling of structural and magnetic phase transitions in these materials is of primary
Ni-Mn-Ga alloys are among the most widely investigated magnetic shape memory materials. Other magnetic shape memory alloys that have been studied are Fe-Pd \[6, 7\], Fe-Ni-Co-Ti, Fe-Pt, Co-Ni-Ga, Ni-Mn-Al \[8, 9\] and Co-Ni-Al \[3, 10\]. In the work presented in this thesis, focus is laid on the well-established MSMA Ni$_2$MnGa, and a study of its structural and magnetic properties of different phases involved in magnetic shape memory phenomena is carried out. To this end *ab-initio* calculations based on density functional theory are employed.

Although Ni$_2$MnGa has been investigated extensively for various applications, a proper understanding of the microscopic (electronic) mechanisms involved in the magnetic shape memory phenomena is not achieved. Hence there is a hindrance in the development of systems in which the coupling between structural and magnetic transitions is strong enough to be of practical use. Also there are controversies in the theoretical prediction of the structural properties of martensite. For example, experimentally the low symmetry martensitic structure with a tetragonal distortion (c/a) greater than one is not observed, whereas theoretical calculations predict a structure with a tetragonal distortion greater than one. Thus, the aim of this work is to re-examine the structural, electronic and magnetic properties of both austenite and martensite phases using advanced computational approaches based on Density Functional Theory (DFT).

Most magnetic shape memory alloys contain multiple transition metal (TM) species (Ni and Mn in Ni$_2$MnGa) together with non-TM ions. These non-TM ions contribute s and p orbitals to the valence and conduction manifolds, whereas the TM species contribute d and s orbitals. The valence electrons that are responsible for magnetism are located on very localized, atomic-like d orbitals. Because of their localization, correlation effects can be quite important for these electrons. Thus it is very important to study these materials with corrected functionals that incorporate the effect of localization of electrons due to on-site or inter-site Coulomb interactions.

To deal with strongly correlated systems, many methods were proposed out of which LDA+U is the most popular. This method tends to correct the standard (LDA or GGA) energy functionals with a mean field Hubbard-like term which is meant to improve the description of the electronic correlations. The interaction parameters that describe effective interactions such as Hubbard $U$ (on-site Coulomb repulsion), inter-orbital Coulomb
repulsion $U'$, inter-site Coulomb interaction $V$, and on-site exchange interaction $J$, play an important role in the corrected LDA+U models. In Reference [11, 12], a linear response approach is proposed to compute the interaction parameters without aprioristic assumptions, in close relationship with the behavior of the system under consideration.

Hence DFT+U method as outlined above has been used in this thesis to study the electronic, magnetic and structural properties of magnetic shape memory alloys especially the prototype compound Ni$_2$MnGa. This compound has been extensively studied theoretically by *ab-initio* calculations. But till date no calculations have included the effect of Coulomb interactions of the localized electrons for this system.

The present thesis is organized as follows. A brief introduction to the material of study, the magnetic shape memory alloy Ni$_2$MnGa, is provided in the second chapter. Starting with a description of the shape memory phenomena and magnetic shape memory effect, a literary review of work done on this material is provided. In chapter 3, a brief description of the DFT formulation is outlined along with the description of the linear response method used to calculate the effective interaction parameters. The next chapter presents the results obtained on the different structural phases of Ni$_2$MnGa using GGA functionals. In the fifth chapter, a comparison of results obtained with DFT and DFT+U, on the structural properties of martensite and austenite is provided. Results of linear response calculations to obtain the effective interaction parameters is also provided in this chapter.
Chapter 2

Shape Memory Alloys

2.1 Summary

This chapter begins by briefly explaining shape memory effect and its technological importance. Magnetic shape memory phenomena and the physics behind it are described in the following section. The work done on magnetic shape memory alloys is briefly reviewed in the next section, leading to the motivation of the research work carried out in this thesis.

2.2 Shape Memory Alloys

Shape memory alloys (SMA) are materials of extraordinary scientific and technological appeal due to their ability to undergo a reversible structural transformation at a characteristic temperature and recover the original shape or size. SMA’s have two stable structural phases - the high-temperature, high-symmetric phase, called austenite (named after William Chandler Austen) and the low-temperature, low-symmetric phase, called martensite (named after Adolf Martens). When a SMA is cooled below its transition temperature, it undergoes a transformation from austenite to martensite. This structural transformation, referred to as martensitic transformation, is associated with a non-diffusive inelastic deformation of the crystal lattice that results from a cooperative and collective motion of atoms. The motion of the atoms is caused by a sudden shearing of the lattice, with the atoms moving only a fraction of the normal interatomic
distance. The martensitic phase grows at speeds which can approach that of sound in the material. In the martensitic state, the material can be deformed into other shapes with relatively little force, and the new shape (detwinned martensite in Figure 2.1) is retained provided the material is kept below the martensitic transformation temperature $T_M$. When heated above $T_M$, the material reverts to its parent structure, austenite, causing it to return to its original shape. In martensitic transformations there are a number of equivalent shear directions through which the martensite can form within a region of parent-phase. This results in the formation of martensitic variants within the microstructure of the transformed alloy and the boundary between these variants is called twin boundary. In Figure 2.1 the twinned martensite phase has two crystallographically equivalent martensitic variants created by different atomic shears from the parent phase. Two opposite shears maintain the macroscopic shape of the crystal block, and forms a self-accommodated structure where the shear of one variant is accommodated or cancelled by that of the other.
Figure 2.2 shows the martensitic phase transformation. On cooling, the transformation starts at the $M_s$ temperature and finishes at $M_f$ temperature. On heating, the martensite starts to revert to austenite at $A_s$ and finishes at $A_f$. The overall hysteresis between forward and reverse transformation pathways in shape memory alloys is typically between 10 and 50 °C [13]. These thermoeelastic martensitic transformations form the basis of shape memory alloys behavior. Since martensitic transformation is accompanied by significant strains, it can also be induced by applying stress. If a stress is applied at a constant temperature above $T_M$, the material can transform to its low-temperature structure by undergoing a martensitic shear deformation. This corresponds to shifting the transformation temperature to higher values than $T_M$. When the stress is released, the material again reverts to the high-temperature form. This phenomena is often referred to as super-elasticity [14].

Shape memory alloys have applications in many fields including military, medical, safety and robotics. Nickel-titanium alloys commonly referred to as Nitinol are actively used in medicine, for example, as tweezers to remove foreign objects through small incisions, as anchors to attach tendons to bone, orthodontic wires to reduce the need to re-tighten and adjust the wire etc [15]. They are also being used in fire security and protection systems as automatic actuators able to shut down the flow of highly flammable and toxic fluids once temperature increases above a certain threshold [13].

### 2.3 Magnetic Shape Memory effect

In the past 15 years, a special class of active materials known as Magnetic Shape Memory (MSM) alloys have received considerable attention. These are a subclass of SMA’s which have a ferromagnetic ground state below a material dependent ordering temperature (Curie temperature $T_C$). Magnetic shape memory systems are characterized by
a strong coupling between magnetic and structural degrees of freedom often accompanied by strong magneto-crystalline anisotropy. This strong coupling can possibly be exploited to control the structural transformations and the shape memory property by the application of magnetic field at constant temperature and stress. Magnetic-field control of shape memory offers large actuation strains, improved control and the possibility to operate at frequencies in the range of kHz [1, 16, 17, 18, 19, 20]. Thus, MSM alloys open up several interesting applications such as actuators, sensors [4] and voltage generators [21].

In 1996 Ullakko et al. [1] first realized the ferromagnetic shape-memory effect in the Heusler alloy Ni-Mn-Ga. Heusler alloys (named after Friedrich Heusler) are intermetallic phases with a particular composition. They have a face centered cubic structure (with L2₁ Strukturbericht designation [22]: L stands for alloys and the numbers stand for historical order of the study of the lattice). In stoichiometric Ni₂MnGa, a martensitic transformation from cubic to a tetragonal structure is observed upon cooling below $T_M = 276$ K [23, 24]. This transformation leads to the formation of martensitic variants whose easy axis of magnetization (an energetically favorable direction of the spontaneous magnetization in the absence of external field) can point in different directions.

When an external magnetic field $H$ is applied, it favors the alignment of the magnetization $M$ of these variants with the field $H$. The resulting alignment of magnetization can take place either by switching the variants or by a rotation of the magnetization. When the required energy for the twin boundary (boundary between two martensitic variants) motion is lower than the required energy for rotation of the magnetization vector, twin boundaries move to accomplish realignment of variants (Figure 2.3), producing large strains [25] of up to 6.5% [1, 18].

Figure 2.3: Schematic visualization of the magnetic shape memory effect (magnetic field induced reorientation). Applying a magnetic field favors the martensitic twins with their easy axis parallel to the direction, causing a large magnetic field induced strain (MFIS).
This strain is an order of magnitude larger than the strain observed in giant magneto-restrictive materials such as Terfenol-D and piezoelectric materials such as PZT \cite{26, 27}. Thus, for colossal deformation to be induced by a magnetic field, the martensitic phase has to possess sufficiently large magneto-crystalline anisotropy energy for the twin boundary motion.

A different type of magnetic actuation, presently being explored in MSM alloys, is based on a radical change in the magnetic properties during the martensitic transformation. These MSM alloys can develop a ferromagnetic martensitic phase from a non-magnetic austenite one or vice versa \cite{28}, and undergo a sharp demagnetization upon cooling below \( T_M \). In this case, the application of a magnetic field could significantly shift the martensitic transition temperature and induce the instantaneous, reversible structural transformation of the material at a constant temperature and stress \cite{20}. The transformation temperature change (\( \Delta T \)) induced by the magnetic field change (\( \Delta B \)) is approximately given by the Clausius-Clapeyron relation

\[
\frac{dB}{dT} = \frac{\Delta S}{\Delta M} ; \quad \Delta T = \frac{\Delta M}{\Delta S} \cdot \Delta B, \tag{2.1}
\]

in the magnetic phase diagram \cite{29}. \( T \) is the absolute temperature, \( B \) is the applied magnetic field, and \( \Delta M \) and \( \Delta S \) are the differences in magnetization and entropy between parent and martensite phases, respectively. Thus for material with a large change in \( \Delta M \) between the two phases, there can be a larger shift in the transformation temperature even at moderate applied fields. This mechanism is attractive as it can produce larger output stress than that resulting from the variant rearrangement in the martensite phase, which is limited by anisotropy energy. Also, the hysteresis accompanied with the phase transformation in this mechanism can be extremely reduced compared to regular shape memory alloys. One of the possible applications of this phenomena is in magneto-caloric cooling technology \cite{30, 31}. The coincidence of \( T_M \) and \( T_C \) which results in a magneto-structural phase transition, reduces the magnetic randomness, i.e., the magnetic component of the total entropy. The reduction of magnetic entropy is compensated by an increase in the other components of total entropy. In magneto-caloric materials, this compensation results in the heating of the material.
2.4 Literature Review

Intense study has been conducted to understand magnetic shape memory phenomena and, in particular, to discover improved alloys showing large strains, appreciable thrust and rapid response times. Ni$_2$MnGa in its stoichiometric composition has a non-magnetic L$_2$$_1$ Heusler structure at high temperature with a lattice constant $a = 5.825$ Å \cite{32, 33} and undergoes magnetic phase transformation from paramagnetic to ferromagnetic state at temperature $T_C \approx 380$ K \cite{23, 24}. A martensitic phase transformation occurs at temperature $T_M = 276$ K into a distorted tetragonal lattice with $a = 5.92$ Å and $c = 5.54$ Å ($c/a = 0.94$) in the $Fmmm$ space group \cite{34, 33}. Martensitic variants with distortion and a periodic shear of the (110) planes along [1 ¯10] direction have also been reported \cite{23}. High resolution neutron powder diffraction patterns revealed that martensitic phase has a 7-layered orthorhombic structure with $Pnnm$ space group and lattice constants of $a = 4.21$Å, $b = 29.3$Å, and $c = 5.55$Å \cite{35}. These lattice constants are related to the $Fmmm$ space group unit cell giving $c_{Fmmm}/a_{Fmmm}$ of 0.932. Thus it is fairly well established from the XRD and neutron diffraction studies that the martensite structure is modulated, with the $Fmmm$ unit cell having the $c/a$ ratio of 0.94. However, the theoretical prediction of martensitic structure is not complete. Total energy calculations revealed that in the martensitic phase, Ni$_2$MnGa shows three different structures: a tetragonal distortion with $c/a < 1$ \cite{36}, a modulated orthorhombic \cite{23} structure leading to a L$_2$$_1$ $c/a$ of 0.94, and another tetragonal structure with $c/a > 1$ \cite{37, 38}. A modulated structure with 5-fold modulation was observed to have a minimum $E_{tot}$ at $c/a = 0.955$ \cite{39}. However, the structure with $c/a > 1$ is a non-modulated tetragonal structure and is reported to be four times more stable than the modulated structure \cite{39}. More recently Barman et al. \cite{40} reported a non-modulated tetragonal stable martensite structure with $c/a = 0.97$. There is a little consensus between the different theoretically observed martensitic structures. Also these calculations \cite{36, 38} have predicted a martensitic structure with $c/a > 1$ that is not experimentally observed.

The magnetic moment in Ni-Mn-Ga is mainly localized on Mn and the Mn-Mn ferromagnetic interaction is believed to be an indirect exchange interaction mediated by the Ni conduction electrons \cite{41}. Magnetization and neutron diffraction studies reported the total magnetic moment of Ni$_2$MnGa to be $\approx 4.17 \mu_B$ with $\approx 3.84 \mu_B$ localized on
Mn and $\approx 0.33 \, \mu_B$ on Ni \cite{34}. On the other hand, Brown \textit{et al.} \cite{42} reported a 2.74 $\mu_B$ magnetic moment for Mn and 0.24 $\mu_B$ for Ni from polarized neutron measurements.

The transition from austenite to martensite was studied both experimentally and with calculations. Both concluded that a band Jahn-Teller like mechanism is responsible for the phase transformation \cite{37, 36, 38}. In a band Jahn-Teller mechanism, the degenerate bands around the Fermi level split with a slight distortion of the lattice, lowering the symmetry of the crystal. This splitting is favored when a gain in energy due to the occupation of the lower split bands overcompensates the elastic energy cost of distortion. Recent ultraviolet photo-electron spectroscopy measurements \cite{43} confirmed the depletion of states (pseudo-gap) (in comparison with austenite) below the Fermi level which forms the electronic basis for the stabilization of martensite at lower temperatures. The martensitic transitions can be signaled by the softening of particular phonons and elastic constants. A significant softening in the transverse acoustic (TA$_2$) phonon branch along the [110] direction, at a wave vector $\mathbf{q}=(2\pi/a) (0.33,0.33,0)$ \cite{44} is observed in inelastic neutron-scattering experiments, for the austenite phase of Ni$_2$MnGa. This phonon softening is attributed to the presence of a premartensite phase in between austenite and martensite \cite{24}. This phase has a cubic structure with a superimposed [110]-transverse shuffling modulation, analogous to the modulation of the martensitic phase but with a different periodicity \cite{44} and is stable between the martensitic and premartensitic transition temperature $T_{PM}=247$ K \cite{43}. Shear elastic constant calculations of parent cubic phase indicate a marginal elastic instability towards a uniform tetragonal distortion \cite{45}. First principle calculations by Enkovaara \textit{et al.} \cite{46} of thermodynamic free energies, revealed that the transition from cubic to tetragonal structure with $c/a = 1.27$ is driven by vibrational free energy and occurs at a temperature of 200 K. Recently Uijttewaal \textit{et al.} \cite{47} considered the intermediate modulated premartensite phases and studied the influence of the temperature dependent magnetization on structural stability and quantitatively reproduced the complete phase sequence (martensite $\leftrightarrow$ premartensite $\leftrightarrow$ austenite) of stoichiometric Ni$_2$MnGa as a function of temperature.

Off-stoichiometric compositions of Ni$_2$MnGa have been experimentally studied particularly to couple structural and magnetic transitions. It is reported that replacing Mn by Ni in Ni$_{2+x}$Mn$_{1-x}$Ga for $x = 0$ to 0.2 causes the Curie temperature ($T_C$) to decrease from 376 K to 325 K and the martensitic transition temperature ($T_M$) to increase.
from 210 K to 325 K [28, 48]. Enkovaara et al. showed that in Mn-rich Ni$_2$MnGa, the doped Mn atoms are antiferromagnetically aligned with the other Mn atoms [49, 50]. A co-occurrence of magnetic and structural transitions is also observed in compositions where Ga atoms are replaced with Ni [51]. In a more recently discovered material Ni$_{45}$Co$_5$Mn$_{40}$Sn$_{10}$ [52], a reversible martensitic phase transformation from a nonmagnetic martensite to a strongly ferromagnetic austenite is observed.

No theoretical calculations have reported the effect of strong correlations in Ni$_2$MnGa due to its metallic nature and the effects of the localization of the $d$ electrons is unquestioned. However, some calculations on other half metallic Heusler compounds have been reported namely Co based compounds. For example, calculations on Co$_2$FeAl were successful in opening up the gap leading to an increase in the localized magnetic moment on Fe [53]. Other calculations on Co$_2$Mn$_{1-x}$Fe$_x$Si by Kandpal et al. [54] used a constant value for the Coulomb interaction parameter on Co, Fe, and Mn irrespective of Fe concentration and reported better magnetic structure than that of the GGA calculations. Although these calculations considered the effect of on-site interaction, the value of the parameters are determined semi-empirically.

### 2.5 Motivation and Objectives

Magnetic shape memory alloys have been extensively investigated for various applications in the past decade, however a proper understanding of the electronic mechanisms which enable efficient coupling of the magnetic and structural transitions is not achieved, thereby hindering the development of systems for which the interplay between these degrees of freedom is strong enough to be of practical use. Moreover there are discrepancies in the theoretical prediction of the martensitic structure and the agreement with experiments is not always excellent. Thus there is a need to study these materials with more rigorous theoretical models. For example, in calculations based on standard LDA or GGA functionals the effect of electronic correlation, which plays an important role in deciding the properties of transition metal compounds, is not explicitly treated. And no calculations have considered the strong localization effects in inter-metallic compounds like MSM alloys. Thus it is necessary to understand the relative importance of itinerant versus localized properties of $d$ electrons in the alloys of interest in this thesis.
To this end, DFT+U approach that includes the effect of localization of electrons is used to study the structural and magnetic properties of Ni$_2$MnGa. This might make a difference for the $d$ electrons on Mn which are believed to be responsible for magnetization. The effective interaction parameters that appear in the correction functionals are strongly dependent on the crystal environment. For this reason it is necessary to evaluate the parameters for the crystal of interest, rather than using semi-empirical values. Thus the aim of this thesis is to evaluate the interaction parameters for different transition metal atoms in the compound of interest and study the effect of electron correlations in this compound. In this regard, a comparison of results using standard DFT and DFT+U approach is provided in this thesis.
Chapter 3

Computational Methodology

3.1 Summary

This chapter provides a brief description of the computational methodology that is employed in the calculations. Starting with density functional theory and the approximations involved in it, a description of the corrected functional, the DFT+U method, is provided. In section 3.3 density functional perturbation method to calculate phonons is illustrated. In the last section a linear response method to calculate the effective parameters in outlined.

3.2 Density Functional Theory

To study the structural, magnetic and electronic properties of different structural phases, \textit{ab initio} Density Functional Theory (DFT) calculations are employed. Within the Born-Oppenheimer approximation \cite{55} the ionic and electronic degrees of freedom are decoupled due to the large mass difference between them. Under this approximation, for each considered ionic configuration, the ground state properties of a system are obtained by minimizing the electronic energy \( E\{\mathbf{R}\} \). Density functional theory \cite{56,57} describes the ground state properties of an interacting multi-electron system through its ground state electronic charge density \( n(\mathbf{r}) \). This is a convenient quantity to compute as it depends only on three spatial coordinates, compared to the multi-electron wave function that depends on \( 3N \) space coordinates (\( N \) being the total number of electrons). The
Hohenberg and Kohn [56] theorem demonstrates a one-to-one correspondence between the external potential $V_{\text{ext}}(\mathbf{r})$ (i.e., the Coulomb interaction with the ions of the lattice) and $n(\mathbf{r})$, in other words, for an interacting electron gas, the external potential acting on the particles determines the ground state charge density, making all physical quantities of the ground state as functional of the external potential. This theorem also guarantees the existence of a unique functional $F[n(\mathbf{r})]$ that contains kinetic energy and electron-electron interactions, such that, the ground state energy and charge density can be obtained by minimizing the energy functional

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

(3.1)

where $V_{\text{ext}}(\mathbf{r})$ represents the external potential acting on the particles. This universal functional $F[n(\mathbf{r})]$ is unknown in practice.

This minimization problem was converted into a practical computational tool by Kohn and Sham [57], who showed that the ground state problem of multi-electron interacting system can be solved by mapping it onto a fictitious, non-interacting one that is constrained to have the same ground state charge density. For the interacting system, $F[n(\mathbf{r})]$ can be rewritten as the sum of kinetic energy of the non interacting electron gas (with the same density as the real one) and additional terms that describe the inter-particle interaction:

$$F[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[n(\mathbf{r})].$$

(3.2)

The total energy functional of the interacting system can be expressed as:

$$E[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[n(\mathbf{r})],$$

(3.3)

where $T_0$ is the kinetic energy functional of a non-interacting system of density $n(\mathbf{r})$, Hartree energy is the classical Coulomb interaction between the electronic densities and $E_{\text{xc}}$ is the exchange-correlation energy ($xc$) that contains all the terms of the electronic interactions not contained in $E_H$ and the difference between the exact kinetic energy and $T_0$. Minimization of this energy functional with the constraint that the total number
of particles $N$, is preserved:
\[ \int n(r) \, dr = N, \]  
(3.4)
corresponds to solving a set of single-particle Schrödinger-like equations (called Kohn-Sham (KS) equations) for the non interacting system:
\[ \hat{H}_{KS} \psi_i^\sigma(r) = \left[ -\frac{\hbar^2 \nabla^2}{2m} + V^\sigma_{KS}(r) \right] \psi_i^\sigma(r) = \epsilon_i^\sigma \psi_i^\sigma(r), \]  
(3.5)
where $V^\sigma_{KS}(r)$ is constructed so as to obtain the same ground state charge density as that of the interacting system:
\[ V^\sigma_{KS}(r) = V_{\text{ext}}(r) + e^2 \int \frac{n(r')}{|r-r'|} \, dr' + \frac{\delta E_{xc}[n^\sigma(r)]}{\delta n^\sigma(r)}. \]  
(3.6)
The charge density is conveniently written as:
\[ n(r) = \sum_{i,\sigma} f_i^\sigma \lvert \psi_i^\sigma(r) \rvert^2, \]  
(3.7)
$\sigma$ is spin state and $f_i^\sigma$ is the occupation of Kohn-Sham states according to the Fermi distribution of their eigen values $\epsilon_i^\sigma$. This set of Kohn-Sham equations are strongly non-linear as the potential $V_{KS}$ depends on $n(r)$ and hence need to be solved self-consistently. Thus an iterative method is used to solve these equations.

Although DFT is exact in principle, the precise formulation of $E_{xc}$ is not known and approximations are made to use it as a practical computational tool. The most popular ones are Local Density Approximation \[57\] (LDA) and Generalized Gradient Approximation \[58, 59, 60, 61\] (GGA). LDA assumes that the $xc$ energy is locally the same as of a homogeneous electron gas having the same density. The $xc$ energy thus depends only on the local density of the system and can be written as:
\[ E_{xc}^{\text{LDA}}[n] = \int \epsilon_{xc}^{\text{hom}}[n(r)] n(r) \, dr \]  
(3.8)
where $\epsilon_{xc}^{\text{hom}}[n(r)]$ is the $xc$ energy density of the homogeneous system. Within GGA, the $xc$ energy is a functional of density and it’s local spatial variations and can be written as:
\[ E_{xc}^{\text{GGA}}[n] = \int \epsilon_{xc}^{\text{GGA}}(n(r), |\nabla n(r)|) n(r) \, dr. \]  
(3.9)
3.3 Plane wave pseudopotential method

In order to solve the KS equations (Eq. 3.5), the integro-differential equations are transformed into a set of algebraic equations. This is achieved by expanding the KS wave functions on a basis set. In the plane-wave pseudopotential method, a plane-wave basis set is used to expand the electronic wave functions, and the KS equations are solved in reciprocal space. The Bloch theorem is used to expand the wave functions as:

$$\psi_{kv}(r) = \frac{1}{(N\Omega)^{1/2}} \sum_G e^{i(k+G).r} c_v(k + G)$$

(3.10)

where $\Omega$ is the volume of the unit cell, and $G$ are the reciprocal vectors. $c_v(k + G)$ are the Fourier coefficients. The normalization of the wave functions can be written as:

$$\sum_G |c_v(k + G)|^2 = 1$$

(3.11)

Thus the KS equations can be written in the reciprocal space as

$$\sum_{G'} \left( \frac{\hbar^2}{2m} |k + G|^2 + v_h(G - G') + v_{xc}(G - G') + v_{ext}(G, G') \right) c_v(k + G') = \epsilon_{kv} c_v(k + G).$$

(3.12)

For each $k$-point only a finite number of the lowest-energy electronic states are computed to obtain the charge density. In each step of the self-consistent cycle, the charge density evaluated as in Eq. 3.7 is used to construct a new guess of the potential to be reintroduced in the Kohn-Sham equations for the successive step of the iterative procedure. The process is stopped when self-consistency is achieved. The plane-wave expansion is exact in the limit of infinite number of reciprocal lattice vectors $G$. In practice only a limited number of $G$ vectors can be used whose maximum kinetic energy

$$E_{cut} \geq \frac{\hbar^2}{2m} |k + G|^2,$$

(3.13)

is increased until convergence of total energies and their derivatives is achieved.

To describe the internal electrons localized on atomic cores, a large number of $G$ vectors would be needed. The pseudopotential (PP) technique [62, 63, 64, 65, 66] assumes that the most relevant physical properties of a system, as bonding and chemical reactivity, are brought about by its valence electrons only, and considers ionic cores as
frozen in their atomic configurations. The valence electrons thus move in the effective external field produced by these inert ionic cores whose scattering properties are reproduced by the pseudopotential. However, the \( xc \) potential that is calculated using the valence charge density \( n_v(r) \), is linear in charge density only if the core electrons and the valence state do not overlap. As a result, for systems having valence electrons strongly penetrating into the core regions, PP techniques lead to a reduced transferability and introduces systematic errors. Thus, to include the core states with strong overlap with the valence ones in the valence manifold and not increase the computational cost, the non-linear core correction (NLCC) approximation is used. In this approximation the non-linear parts of the \( xc \) energy are treated explicitly not from \( n_v(r) \) alone, but from a modified density:

\[
n(R) = n(R) + n_{\text{core}}(R),
\]

(3.14)

where \( n_{\text{core}}(R) \) is the density that is equal to core density of the atomic reference state \( R \) in the region of overlap with the valence density.

The equilibrium geometry of the system is obtained by the condition that the forces acting on individual nuclei and the stress on the crystal both vanish. Using the Hellmann-Feynman theorem, which states that the first derivative of total energy of a system with respect to a generic parameter \( \lambda \) is given by the expectation value of the derivative of the Hamiltonian, the forces on the atoms are can be computed as,

\[
F_I = -\frac{\partial E(R)}{\partial R_I} = -\left\langle \Psi(R) \left| \frac{\partial H_{BO}(R)}{\partial R_I} \right| \Psi(R) \right\rangle = 0,
\]

(3.15)

In a similar way the stresses are obtained from the first derivative of the total energy with respect to strain.

### 3.4 Phonon Calculations

Density functional perturbation theory \(^{[67]}\) as implemented by Baroni \textit{et al.} \(^{[68]}\), is employed in the study of lattice dynamics of the compounds of interest. As mentioned in the starting of this chapter, Born-Oppenheimer approximation is used to de-couple the vibrational and electronic degrees of freedom. Under this approximation, the lattice dynamical properties are studied by solving for the eigenvalues and eigenfunctions of
the Schrodinger equation:

$$\left( -\sum_{I} \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial R_I^2} + E(R) \right) \Phi(R) = \epsilon \Phi(R)$$  \tag{3.16}$$

where $R_I$ is the coordinate of the $I$th nucleus with mass $M_I$. $R \equiv \{R_I\}$ is the set of all nuclear coordinates. $E(R)$, called as Born Oppenheimer (BO) energy, is the energy of the system of interacting electrons moving in the field of fixed nuclei as described in section 3.2.

The vibrational frequencies $\omega$ are determined by the eigenvalues of the Hessian of the BO energy, scaled by the nuclear masses defined as:

$$\det \left| \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E(R)}{\partial R_I \partial R_J} - \omega^2 \right| = 0,$$  \tag{3.17}$$

The second derivatives of the BO energy surface are obtained by using the Hellmann-Feynman theorem. The Hellmann forces acting on the $I$th nucleus in the electronic ground state is written as:

$$F_I = -\frac{\partial E(R)}{\partial R_I} = -\left\langle \Psi(R) \left| \frac{\partial H_{BO}}{\partial R_I} \right| \Psi(R) \right\rangle$$  \tag{3.18}$$

and the Hessian of Born-Oppenheimer energy surface in Eq. 3.17 is obtained by differentiating the Hellmann forces with respect to nuclear coordinates,

$$\frac{\partial^2 E(R)}{\partial R_I \partial R_J} \equiv -\frac{\partial F_I}{\partial R_J} = \int \frac{\partial n_R(r)}{\partial R_I} \frac{\partial V_R(r)}{\partial R_I} dr + \int n_R(r) \frac{\partial^2 V_R(r)}{\partial R_I \partial R_J} dr + \frac{\partial^2 E_N(R)}{\partial R_I \partial R_J}.  \tag{3.19}$$

This requires calculation of the ground-state electron charge density $n_R(r)$ as well as its linear response to a distortion of the nuclear geometry, $\frac{\partial n_R(r)}{\partial R_I}$. The linear response is obtained from the density functional perturbation theory.

### 3.5 DFT+U

The standard DFT functionals namely LDA and GGA fail to describe the electronic structure of strongly correlated systems. For example, they fail to predict the insulating behavior of many simple transition metal oxides by producing a qualitatively wrong metallic ground state. Corrections to these functionals that could describe accurately these systems by first principle calculations are proposed in the recent times. LDA+U
or DFT+U approach first introduced by Anisimov and co-workers \cite{71, 72, 73, 74, 75, 76, 77, 78, 79}, has proved to be very effective in describing a large variety of different systems while retaining the relatively low computational cost of standard DFT approximations. In this method, the corrective functional is shaped as an additive Hubbard Hamiltonian \cite{80, 81, 82, 83, 84, 85} with effective “on-site” interactions. The DFT+U energy functional is written as follows:

\[ E_{\text{DFT+U}} = E_{\text{DFT}} + E_U = E_{\text{DFT}} + E_{\text{Hub}} - E_{\text{dc}}. \] (3.20)

\( E_{\text{Hub}} \) contains the corrective Hubbard functional while \( E_{\text{dc}} \) is a mean-field approximation to \( E_{\text{Hub}} \) that is subtracted from the total energy to avoid double-counting of the same electronic interactions. In a commonly used simplified expression \cite{78} of the rotationally invariant formulation \cite{75} the total corrective functional is given by

\[ E_U = E_{\text{Hub}} - E_{\text{dc}} = \sum_{I,\sigma} \frac{U^I}{2} \text{Tr}[n^I\sigma(1-n^I\sigma)]. \] (3.21)

where \( n^I\sigma \) is the occupation matrix defined as the projection of Kohn-Sham orbitals on the atomic states (typically of \( d \) or \( f \) character) of site \( I \):

\[ n^I_{m,m'} = \sum_{k,v} f_{k\sigma}^I \langle \phi_{m\sigma}^I | \psi_{kv}^\sigma \rangle \langle \psi_{kv}^\sigma | \phi_{m'\sigma}^I \rangle. \] (3.22)

The strength of the “+U” correction contained in \( E_U \) is controlled by the effective on-site electronic interaction, the Hubbard \( U \). This parameter can be calculated from linear-response theory \cite{86} which is described in the next section. Within this method, \( U \) corresponds to the effective electronic coupling when electrons are described through the occupations of atomic orbitals. This DFT+U corrective functional contains only on-site electron-electron interactions and forces the occupations of atomic states to be either 1 or 0, suppressing the hybridization between orbitals that belong to different atomic sites. This formulation represent a drastic approximation for the materials that are considered in this project, where the ground state is characterized by the formation of covalent bonds or, in general, by more itinerant electronic states. The excessive suppression of interatomic hybridization can lead to particularly serious consequences in magnetic systems if coupling between magnetic moments is mediated by bonds with non-magnetic ions.
In a recent formulation that handles higher degrees of hybridization and delocalization, developed by Campo et al.\cite{87}, the corrective Hamiltonian is constructed from the extended Hubbard model with on-site and inter-site electronic interactions\cite{83,84}. The total energy functional in this scheme is given by,

\[
E_{DFT+U+V} = E_{DFT} + \sum_I \frac{U_I}{2} Tr [n_I (1 - n_I')] - \sum_{IJ} \frac{V^{IJ}}{2} Tr (n^{IJ} n^{JI})
\]

where \(n^{IJ}_{m,m'} = \sum_{k,v} f_k \langle \phi^I_m | \psi^\sigma_{kv} \rangle \langle \psi^\sigma_{kv} | \phi^J_{m'} \rangle\) and \(I\) and \(J\) denote distinct atomic sites. The inter-site electronic interaction \(V^{IJ}\) favors the occupation of states with finite components on neighbor atoms (hybridized). This tendency competes with the occupation of atomic orbitals stabilized by the on-site coupling \(U^I\) and allows one to treat more general localization regimes. This scheme has been proved to provide significant improvements in quite diverse systems like NiO (strongly-correlated, charge-transfer insulator), Si and GaAs (hybridized, band semiconductors)\cite{87}.

In the above formulated energy functional, the effect of exchange interaction is implicitly included as:

\[
U_{eff} = U - J
\]

In an ongoing work on the inclusion of the effect of exchange interaction \((J)\) explicitly, Himmetoglu et al.\cite{88} have developed an energy functional that explicitly treats magnetic interactions. The corrective Hubbard functional can be written as:

\[
E_{Hub} = \frac{1}{2} \sum_{I,\sigma} \left\{ U^I [ (n^I\sigma)^2 + n^I\sigma n^{I-\sigma} - Tr[n^I\sigma n^{I\sigma}] + J^I [ Tr[n^I\sigma n^{I\sigma} + n^{I\sigma} n^{I-\sigma}] - (n^I\sigma)^2 ] \right\}
\]

and the double counting (dc) term is written as:

\[
E_{dc} = \sum_I \frac{U^I}{2} n^I (n^I - 1) - \sum_{I,\sigma} \frac{J^I}{2} n^I\sigma (n^{I\sigma} - 1) + \sum_{I,\sigma} \frac{J^I}{2} n^{I\sigma} n^{I-\sigma}.
\]

So the corrective functional results:

\[
E_U = E_{Hub} - E_{dc} = \sum_{I,\sigma} \left\{ \frac{(U^I - J^I)}{2} Tr[n^I\sigma (1 - n^{I\sigma})] + \sum_{I,\sigma} \frac{J^I}{2} (Tr[n^I\sigma n^{I-\sigma}] - n^{I\sigma} n^{I-\sigma}) \right\}
\]

This functional is in the development stage and it is used in some of the calculations in this thesis.
3.6 Linear response calculation of interaction parameters

Effective interaction parameters used in DFT+U calculations are often evaluated semi-empherically. However, these parameters strongly depend on crystal environment. Thus, it is needed to evaluate effective interaction parameters of a particular system self-consistently without any aprioristic assumptions. Hence, a linear response approach as proposed and described in Ref. [86] is employed to evaluate the effective interaction parameters.

The linear response method is based on the fact that standard LDA and GGA functionals produce total energies with unphysical curvatures for non-integer occupations, leading to a spurious minima that corresponds to fractional occupation of the orbitals. This non-linear behavior is generated by a spurious self-interaction of electrons that survives in the approximate \( xc \) functionals. DFT+U method tries to recover the actual physical situation by adding a correction to the LDA/GGA total energy which vanishes for integer number of electrons and eliminates the curvature of the LDA/GGA energy profile for fractional occupations. According to this reasoning, the interaction parameter \( U \) is the unphysical curvature of the LDA/GGA energy as a function of occupation which is associated with the spurious self-interaction of the electrons.

Thus \( U \) is computed from the dependence of total energy as a function of the localized occupations of the atomic sites. Numerically it is obtained as the curvature of the total energy with respect to the variation around the unconstrained values of occupation of the isolated atom. According to this procedure \( U \) is written as:

\[
U = \frac{\partial^2 E[n_I]}{\partial n_I^2} - \frac{\partial^2 E^{KS}[n_I]}{\partial n_I^2} \tag{3.28}
\]

where the second term is the Kohn-Sham response that includes contributions from the re-hybridization of orbitals. This is subtracted from the first term to get the term of the second derivative that only depends on electron-electron interactions. The second derivatives are computed by a Legendre transform of the energy functional,

\[
E[\alpha_I] = \min_{n(r)} \{ E[n(r)] + \sum_I \alpha_I n_I \} \tag{3.29}
\]

where \( \alpha \) is the strength of the perturbation. This expression leads to

\[
\frac{\partial^2 E}{\partial n^I \partial n^J} = -\frac{d\alpha^I}{dn^J}, \tag{3.30}
\]
The Legendre transformed energy functional $E[\alpha_I]$ is calculated for each small perturbation $\alpha_I$ on the specific site of interest, the the second derivative of energy is constructed through the response matrices:

$$\chi_{IJ} = \frac{dn^I}{d\alpha^J}. \tag{3.31}$$

Thus the $U$ is obtained as:

$$U = \frac{\partial \alpha_{I}^{KS}}{\partial n^I} - \frac{\partial \alpha_{I}}{\partial n^I} = (\chi_{0}^{-1} - \chi^{-1})_{II}. \tag{3.32}$$

and the inter-site interaction $V_{IJ}$ are the off-diagonal elements of the response matrices given as:

$$V_{IJ} = \frac{\partial \alpha_{I}^{KS}}{\partial n^J} - \frac{\partial \alpha_{I}}{\partial n^J} = (\chi_{0,I}^{-1} - \chi_{I}^{-1}) \tag{3.33}$$

Quantum espresso [69, 70], an open source suite of computer codes for electronic-structure calculations is used in all the calculations involved in this thesis. Starting from the total energy calculations, DFT+U and the phonon calculations are done using this package. It also includes the post processing tools like the plotting of density of states and band structure. It is a highly parallelized package that takes the advantage of massive supercomputers.
Chapter 4

Study of Austenite and Martensite Structures using GGA

4.1 Summary

This chapter presents the results of spin-polarized ab initio calculations on the Heusler alloy Ni$_2$MnGa using standard approximated energy functionals. In the following section, computational details of the calculations are outlined. In section 4.3, the structural and magnetic properties are presented in comparison with the previous experimental and theoretical calculations from literature. Discussion of the results follow in the last section.

4.2 Computational details

A GGA ultra-soft pseudopotential [89] constructed with the Perdew-Burke-Ernzerhof (PBE) [90] prescription is used in the calculations. For Ni with atomic configuration [Ne]3s$^2$3p$^6$3d$^9$4s$^1$, 3s and 3p electrons are frozen in the core while 3d and 4s are included in the valence. For Mn [Ne]3s$^2$3p$^6$3d$^5$4s$^2$, all the 15 outer shell electrons are considered as valence electrons. For Ga [Ar]3d$^{10}$4s$^2$4p$^1$, 13 electrons are considered to be in valence states. In all the atoms, the nonlinear core correction is used to account for the overlap between the core and valence charges [91]. An energy cutoff of 45 Ry for the plane-wave
expansion is used. The augmentation charges, required by the use of ultrasoft pseudopotentials, are expanded with an energy cutoff of 480 Ry. As Ni$\textsubscript{2}$MnGa shows a metallic nature, the Brillouin-zone integration is performed using the Marzari-Vanderbilt smearing technique \cite{92} of the Fermi distribution, which is suitable for metallic systems. A smearing width of $\sigma = 0.01$ Ry with $10 \times 10 \times 10$ Monkhorst-Pack grid \cite{93}, yielding 94 $k$ points in the irreducible wedge of the Brillouin zone (IBZ) produced converged results for the structural properties of the cubic phase. The calculations were performed with the convergence criterion for $E_{\text{tot}}$ to be 0.1 mRy/f.u., i.e., the accuracy of $E_{\text{tot}}$ is $\pm 0.025$ mRy/atom ($\pm 0.34$ meV/atom). This number is at least 5 times smaller than the $E_{\text{tot}}$ variation observed in Figure 4.6 for example, the stabilization of $c/a = 1.23$ is about 1.5 meV/atom. The $E_{\text{tot}}$ value for each self consistent calculation is fully converged starting from the crystalline charge density for each of the $c/a$ values.

4.3 Austenite

The high temperature phase of Ni$\textsubscript{2}$MnGa is a cubic Heusler alloy with L$\textsubscript{2}$\textsubscript{1} symmetry, a crystal that can be described in terms of four interpenetrating face-centered-cubic (f.c.c) lattices each offset by 1/4,1/4,1/4, with Mn occupying the (0,0,0), Ga (1/2,1/2,1/2) and Ni occupying (1/4,1/4,1/4) and (3/4,3/4,3/4) sites as shown in Figure 4.1. Magnetic and non-magnetic configurations are studied by considering different starting spin configurations. The Ferromagnetic configuration shown in Figure 4.2(a), where all the atoms have their spin in the same direction, is found to be 27 mRy/atom more stable than the non-magnetic configuration. An anti-ferromagnetic configuration where adjacent Mn planes have opposite spins is considered as shown in Figure 4.2(b). The ferromagnetic configuration is found to be 1.48 mRy/atom more stable than the anti-ferromagnetic configuration. Another anti-ferromagnetic configuration where Ni
Figure 4.2: Schematic representation of Ferromagnetic and Anti-ferromagnetic configurations

has positive and Mn has negative spins is also found to be less stable than the ferromagnetic case. The stability of the ferromagnetic state obtained in these calculations is in agreement with other reported results [37]. The equilibrium lattice parameter and bulk modulus for stable magnetic configuration are obtained by fitting the total energies to the Murnaghan equation of state [94]. The calculated total energies as a

Figure 4.3: The total energy as a function of lattice constants $a$. function of the lattice constant are plotted in Fig. [18].
Table 4.1: The calculated lattice constant \(a\), bulk modulus \(B\), total moment \(\mu^{\text{tot}}\) and local magnetic moments on each site. FM-Ferromagnetic, AFM-Anti-ferromagnetic, NM-Non-Magnetic

<table>
<thead>
<tr>
<th>Austenite</th>
<th>(a) (au)</th>
<th>(B) (Mbar)</th>
<th>(\mu^{\text{tot}})</th>
<th>(\mu^{\text{Ni}})</th>
<th>(\mu^{\text{Mn}})</th>
<th>(\mu^{\text{Ga}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>FM</td>
<td>11.004</td>
<td>1.46</td>
<td>3.84</td>
<td>0.28</td>
<td>3.72</td>
<td>-0.14</td>
</tr>
<tr>
<td>AFM</td>
<td>11.003</td>
<td>1.506</td>
<td>0.0</td>
<td>0.00</td>
<td>3.83</td>
<td>0.074</td>
</tr>
<tr>
<td>NM</td>
<td>10.803</td>
<td>1.84</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reported results

| Theory | 10.98 | 1.56 | 4.09 | 0.36 | 3.43 | -0.04 |
| Exp.   | 11.01 | 1.46 | 4.17 | 0.24 | 2.74 | -0.013 |

Table 4.1 lists the lattice constants and bulk modulus obtained in these calculations. These lattice constants are in better agreement with the experimental values (within 0.05\%) than the previous calculations. The total magnetization per formula unit is found to be 3.84 \(\mu_B\). The local magnetic moment of Mn is 3.72 \(\mu_B\). The local magnetic moment on Ga is anti-ferromagnetic with respect to Mn, with a small value of -0.14 \(\mu_B\). The moment on Ni is ferromagnetic but not as large as on Mn and has a value of 0.28 \(\mu_B\).

Figure 4.4: Density of states for cubic Ni\(_2\)MnGa.
The electronic density of states (DOS) is given in Figure 4.4(a) and 4.4(b). It is clear that Ni$_2$MnGa is metallic with the Fermi level ($E_F$) occupied predominantly by minority states (states with a magnetic moment anti-parallel to the magnetization). Looking at the site projected density of states, Ga $d$ states are present several eV ($\sim 15$eV) below the Fermi level, however Ga $p$ states have little contribution around $E_F$. Mn $d$ states of majority spin are mostly below the $E_F$, while those of minority spin are mostly above the $E_F$. This distribution makes Mn mostly responsible for the magnetization. Their contribution to the DOS at the $E_F$ is relatively small. Ni $d$ electrons have similar distribution in the majority and minority spin, resulting in a rather small magnetization. Although they are almost completely filled (8 electrons), they provide the dominant contribution to DOS at $E_F$. This contribution is particularly high for minority spin states. This distribution of Ni states at the Fermi level corroborates the idea that Ni might be responsible for the structural instability of the austenite phase at low temperatures (through Jahn-Teller distortion) [42].

4.4 Martensite

The structure of Ni$_2$MnGa in the martensitic phase can be described as a tetragonal structure as shown in Figure 4.5. The unit cell of martensite is obtained by taking the lattice vectors along the [1 1 0], [1 1 0] and [0 0 1] directions of the austenite crystal. Hence, the structure is regarded as a body-centered-tetragonal structure which transforms through a continuous change of $c/a$, from the ideal L2$_1$ lattice ($c/a = 1$). The total energy calculations for uniform tetragonal distortions of the cubic structure are performed. The region of $c/a$ from 0.91 to 1.27 is examined in considerable detail with 25 separate calculations. The volume of the unit cell is maintained at constant value equal to that of the experimentally observed L2$_1$ phase (1334.63 (a.u.$^3$)). In fact a little variation
(1%) of volume is expected during the martensitic transformation.

Experimentally three distinct ferromagnetic martensitic phases have been reported \[23\]. Two of them are tetragonal (\(\beta'\) and \(\beta''\)), and one orthorhombic (\(\beta''\)). The \(\beta'\) phase has a \(c/a\) of 0.94, with a shuffling of the (1 1 0) planes along [1 1 0]. This shuffling has a periodicity of five interplanar distances \[44\]. Under uniaxial compression the \(\beta'\) phase transforms into the orthorhombic \(\beta''\) phase which is also modulated with [1 1 0] displacements of the (1 1 0) planes with a periodicity of seven interplanar distances. On further application of stress to the \(\beta''\) phase along the [1 1 0] direction, \(\beta'''\) is obtained. This phase has a \(c/a\) = 1.18 and is metastable with respect to the removal of the applied stress \[96\]. The total energy calculations shown in Figure 4.6 has a local minimum at \(c/a = 1\) that corresponds to the cubic L2\(_1\) structure, and a global minimum at \(c/a = 1.23\) with total energy \(\sim 2\) meV lower than the L2\(_1\) structure. FPLAPW calculations of Ayuela et al. \[36\] observed a local minimum at \(c/a = 1\) and a global minimum at \(c/a = 1.25\) with energy slightly lower than the L2\(_1\) structure. These findings are in agreement with our results. Moreover these theoretical calculations produce a minimum for \(c/a > 1\) that is not observed experimentally. However, there is no minimum or any anomaly observed at \(c/a = 0.94\) in our results. We believe that the experimentally observed shuffling in the atomic planes (110) play a crucial role.

\[\text{Figure 4.6: The total energy difference relative to the L2}_1\text{ phase as a function of } c/a \text{ in the tetragonal distortion.}\]
in stabilizing the structure at $c/a = 0.94$, and hence no minimum. The presence of the minimum at $c/a = 1.23$ is still an unsolved problem.

The magnetic moment as a function of $c/a$ is shown in Figure 4.7. It shows a sharp minimum at $c/a = 1$. The decomposed atomic magnetic moments are also shown. The magnetic moment of Ga remains almost the same for the total $c/a$ range with less than 0.05 $\mu_B$ change. Mn magnetic moment is flat in the $c/a$ range of 0.92 to 1.1 and then decreases steeply. However the interesting aspect to note is that the variation of total magnetic moment follows the variation of Ni magnetization. These features of the magnetic moment variations are in good agreement with the calculations of Godlevsky et al. \[38\].

In order to understand the electronic origin of the distortions and the variation of magnetization observed, the density of states is calculated for different values of $c/a$. 

![Figure 4.7: Total magnetic moment and contributions associated with individual elements as a function of $c/a$. The quantities are in Bohr magnetons per formula unit.](image-url)
Figure 4.8: Spin projected $d$-electron state densities for Ni (red lines) and Mn (blue dots) for (a) $c/a = 0.94$, (b) $c/a = 1$, and (c) $c/a = 0.23$. Decomposed Ni spin-projected $d$-electron state densities (red - $d_{xz}$, green - $d_{yz}$, pink - $d_{xy}$, black - $d_{x^2-y^2}$, blue - $d_{z^2}$): d, e, and f corresponds to $c/a = 0.94, 1, 1.23$ respectively.

Figure 4.8 a, b and c shows the spin-projected $d$-electron density of states for Ni and Mn at different tetragonal distortions ($c/a$). As the $c/a$ value increases, a variation in the Ni local density of states can be seen. For the cubic $L2_1$ structure ($c/a = 1$), a peak in Ni minority states can be observed at 0.18 eV below the Fermi energy. As $c/a$ value is decreased to 0.94, the peak is split into two, with the Fermi level lying in between. For $c/a = 1.23$, the Ni minority peak moves to an energy greater than Fermi energy. This provides justification for the variation of the magnetic moment on the Ni site and also for the peak at $c/a = 0.92$. The Mn density of states remains approximately unchanged for all values of $c/a$ with minority and majority states preserving their distribution.
above and below the Fermi level respectively, which is consistent with the behavior of
the magnetic moment as shown in Figure 4.7. Figure 4.8 d, e and f show partial spin
projected density of states for Ni. For the cubic L2₁ structure, it is evident that the
peak in the Ni minority density of states at -0.18 eV is primarily due to the eg states.
The dₓ² and dₓ²−y² contribute equally to this peak (Fig. 4.8(e)). For c/a = 0.94, the
peak is split into two (Fig. 4.8(d)). The peak at -0.33 eV is dominated by the
dₓ²−y² states and the peak at 0.10 eV is related to the dₓ² states. This splitting of a peak at
the Fermi level into two peaks below and above E_F corroborates the idea that the band
Jahn-Teller effect stabilizes the martensitic phase [97].

4.5 Phonon dispersion study of austenite phase

The displacive, diffusionless structural transformations that occur in MSMAs are often
associated with phonon anomalies in the parent austenite phase [98, 99, 100]. Experimental studies have observed several phonon anomalies in Ni₂MnGa with decreasing
temperature. At T ≈ 270 K, a nearly complete softening of the [1/3,1/3,0](2π/a)
transverse-acoustic (TA₂) mode with polarization along [1 1 0] is observed [35]. In an
try to understand the microscopic origin of the instabilities in the high temperature
austenite phase of Ni₂MnGa and the occurrence of modulated structures, the phonon
dispersion of L2₁ structure is studied.

The calculations for lattice dynamics are performed within the density-functional-
perturbation theory as described in section 3.4. The dynamical matrices are computed
on a (4,4,4) q point grid in the fcc Brillouin zone (BZ) and interatomic force constants
are obtained by Fourier transformation of the dynamical matrices. The phonon disper-
sions are obtained by interpolating the dynamical matrices on a finer mesh of q points
in between the high symmetry directions. Since this material is metallic, the electronic
temperature is expected to play an important role in lattice dynamical properties. To
account for finite electronic temperature, we had to use a Fermi-Dirac smearing of the
distribution function. Dispersion at higher effective electronic temperatures are ob-
tained by using smearing widths of 0.005, 0.01, and 0.02 Ry corresponding to 788, 1577
and 3155 K respectively. Although these are quite high temperatures, lower values
would require to use a finer k-point mesh and will be accomplished in future work. It is
Figure 4.9: Phonon dispersion of austenite structure along high-symmetry lines of the fcc BZ. Dispersion at three different effective electronic temperatures 0.02, 0.01 and 0.005 Ry are shown. Experimental measurements at 400 K is shown in red marks [24].

Important to notice that in our finite temperature calculations, the effects of vibrational entropy are not taken into account.

The phonon dispersions of the austenite structure with $a = 11.004$ a.u. is shown in Figure 4.9. The most interesting feature to note in the dispersion is the anomalous dip in the lowest branch of transverse-acoustic modes ($TA_2$) along [110] direction. The minimum is at the incommensurate wave vector $q = (2\pi/a)(\xi, \xi, 0)$, with $\xi = 0.3$. The wave vector of the experimentally observed anomaly is at $\xi = 0.33$ [24]. Qualitatively our results are in agreement with experiments. The discrepancy in the wave vector at which the anomaly is observed could be due to the higher electronic temperature (788 K) in our calculations compared to 400 K at which experiments are done. Using an effective electronic temperature of 0.001 Ry could give an exact value for the wave vector of the
anomaly. Previous theoretical studies have also observed this anomaly but at $\xi = 0.33$ with an imaginary frequency \[45\]. However, in this work authors used cold smearing \[101\] technique that represents calculations at 0 K. This anomaly in the phonon dispersion suggest that the crystal is dynamically unstable to a lattice distortion corresponding to the eigenvector of this mode. It can be seen that this unusual anomaly is highly temperature dependent. For effective electronic temperatures higher than 0.01 Ry, the softening in the mode disappears. Thus it can be seen that the austenite structure is unstable to a lattice distortion at low temperatures.

### 4.6 Conclusion and Discussion

The structure of austenite is predicted accurately with a lattice parameter within 0.05% of the experimental value. The magnetic moments obtained by the GGA calculations are in good agreement with experimental observations. The phonon dispersion calculations have shown that the austenite structure is dynamically unstable to a lattice distortion with a soft mode at a wave vector $(1/3,1/3,0)2\pi/a$, is in good agreement with experimental observations.

Although the austenite structure is well described by our calculations, there are still controversies between the experimental and theoretical findings on the structure of martensite that need to be solved. For example, the minimum at $c/a < 1$ is believed to be due to shuffling in the atomic planes, however, some theoretical calculations predicted a minimum for $c/a < 1$ with out any modulation. Ayuela et al. \[36\] observed a shallow local minimum at 0.94 and Barman et al \[40\] predicted a global minimum at $c/a = 0.97$ which are in controversy with each other and we don’t find in our results. More over all theoretical calculations \[37, 36, 38\] except Ref. \[40\] predicted a stable structure with a $c/a > 1$. However this structure with $c/a > 1$ is experimentally observed to be metastable only under pressure. Thus the prediction of martensitic structure is still an unsolved problem.

Till date all theoretical calculations are done either using LDA or GGA functionals. It is well known that these functionals fail to describe strongly correlated systems. Ni$_2$MnGa contains transition metals whose localized $d$ electrons participate in bonding
and play a crucial role in determining structural and magnetic properties. The localization of Mn $d$ orbitals is mostly responsible for the observed magnetization in the material. Also it has been found that the Ni $d$ states around the Fermi level could be responsible for the instability of the austenite structure at low temperatures. Thus our next aim is to study the effect of localization of electrons (on Mn and Ni $d$ states) on the structural and magnetic properties.
Chapter 5

DFT+U study of Ni$_2$MnGa

5.1 Summary

It was seen in the previous chapter that the martensitic structure predicted by the standard GGA functionals was controversial. There was no consensus between the observed minimum energy structure and some of the previous theoretical and experimental findings. Correlation effects could be quite important in Ni$_2$MnGa as it contains transition metals Ni and Mn whose atomic like $d$ orbitals are localized. These correlation effects could play a role in deciding the structural and magnetic properties of martensite. Thus, in this chapter our aim is to study the effect of localization of $d$ orbital electrons of Mn and Ni on the properties of martensitic phase. This is achieved by evaluating the effective interaction parameters, namely the on-site ($U$), on-site inter-orbital ($U'$) and inter-site ($V$) interaction parameters, and using them in the DFT+U calculations. In section 5.2 presents the calculated interaction parameters. The results of DFT+U (GGA+U) calculations using the obtained interaction parameters on the martensite phase are presented in the next section. Conclusions are drawn in the last section.

5.2 On-site and Inter-site Interactions

The on-site, and inter-site interaction parameters are computed by using linear response method as described in section 3.6. Since the martensitic unit cell is constructed from the high symmetry austenite unit cell, first the interaction parameters for the austenite
are calculated and then for the martensite structure.

5.2.1 Austenite

A supercell containing 16 atoms (8 atoms of Ni and 4 each of Mn and Ga) is used in computing the response matrices. First, a well converged GGA ground state calculation for an unconstrained system is performed. Starting from this self-consistent potential, a perturbation $\alpha_I = \pm 0.15$ is applied to the potential on each of the nonequivalent Ni, Ga and Mn atoms at site $I$. Then the variation of the occupations $n^I_J$ with the perturbation for all sites in the supercell is used to calculate the response matrices $\chi_{IJ}$ and $\chi_{IJ}^0$. $\chi_{IJ}$ is obtained from the derivatives of occupations after allowing the perturbed system to readjust self-consistently. $\chi_{IJ}^0$ is obtained from the derivatives of unscreened occupations that are obtained after the first iteration in the self-consistent cycle. The response of $s$ and $p$ manifolds of Ga, $d$ and $s$ manifolds of Mn and Ni are taken into consideration when the response matrices are constructed. In Table 5.1

Table 5.1: Interaction parameters $U$ and $V$ (eV) for Ni$_2$MnGa. Inter-site terms are for first-neighbors and listed values are for the experimental lattice parameter. Indexes $s$ stand for ‘standard’ and $b$ stand for ‘background’ orbitals.

<table>
<thead>
<tr>
<th></th>
<th>$U_{ss}$</th>
<th>$U_{sb}$</th>
<th>$U_{bs}$</th>
<th>$U_{bb}$</th>
<th>$V_{ss}$</th>
<th>$V_{sb}$</th>
<th>$V_{bs}$</th>
<th>$V_{bb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga-Ga</td>
<td>2.43</td>
<td>2.27</td>
<td>2.27</td>
<td>2.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>6.35</td>
<td>2.89</td>
<td>2.89</td>
<td>1.77</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Ni</td>
<td>8.11</td>
<td>3.63</td>
<td>3.63</td>
<td>2.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga-Mn</td>
<td></td>
<td>0.226</td>
<td>0.289</td>
<td>0.112</td>
<td>0.170</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-Ni</td>
<td></td>
<td>0.341</td>
<td>0.142</td>
<td>0.336</td>
<td>0.281</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga-Ni</td>
<td></td>
<td>0.477</td>
<td>0.493</td>
<td>0.351</td>
<td>0.348</td>
<td></td>
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</tr>
</tbody>
</table>

the on-site ‘$U$’ and inter-site ‘$V$’ interaction parameters computed at the experimental lattice parameter are presented. We call the higher $l$ states of Ga ($p$) and that of Ni and Mn ($d$) standard states, and the other $l$ manifold, the $s$ orbital of Ga, Mn and Ni, background states. It can be observed that the Us of Ga are very similar irrespective of the orbital manifold (s or p states) the parameters acts on. This can be understood from the fact that the Ga standard and background states are hybridized. The value of $U = 6.35$ eV on Mn standard $d$ orbitals suggests that the Coulomb interaction between these orbitals is quite strong. Similarly a $U$ of 8.11 eV is obtained on Ni standard states.
However, the inter-orbital $U$s of Mn and Ni are considerably smaller than that of the $U$ on $d$ states.

Looking at the values of inter-site Coulomb interaction parameters $V$, it can understand that there is little interaction (and thus hybridization) between the inter-site orbital manifolds. The highest of the inter-site interaction is between the Ga $p$ and Ni $s$ and $d$ orbitals and is about 0.5 eV. This suggests that there is little hybridization between these states compared to the others.

A more accurate values for the interaction parameters are obtained by carrying out a self-consistent calculation. In this iterative procedure, first the interaction parameter, say $U_0$, is computed from a GGA ground state. Then this $U_0$ is used to obtain a GGA+$U$ ground state. From this GGA+$U$ ground state, $U_1$ is computed with the same linear response procedure keeping the Hubbard potential fixed during the perturbative process. This ensures that the calculated response of perturbation is only due to the spurious curvature that is produced by GGA for non-integer occupations. The $U_1$ obtained is again used to get $U_2$ in a similar fashion as explained above. This cyclic procedure is continued until convergence of the interaction parameters is achieved.

![Figure 5.1: On-site Coulomb interaction $U$ values of Ga, Mn and Ni at different volumes around the volume of equilibrium structure.](image)

In the self-consistent calculation of $U$, only the on-site Coulomb interaction between the Mn-$d$ orbitals is used. The other interaction parameters are not used for the reasons explained later in the next section. First the variation of the $U$ with respect to the lattice
parameter of the unit cell is studied. In Figure 5.2.1, the variation of $U$, around the equilibrium lattice value (11.01 a.u.), for the standard states of Ga, Mn and Ni are shown. With increasing ‘a’, the $U$ on Ga $p$ orbitals increases with total variation of around 0.14 eV and similarly the $U$ on Mn-$d$ orbitals increases with a variation of about 0.3 eV. In contrast the $U$ on Ni-$d$ orbitals decrease monotonously with increasing ‘a’. This is expected as with the increase in ‘a’ the distance between adjacent atoms increase resulting in decreased hybridization of the orbitals. The increase in the $U$ of Mn can be explained by the following argument: because the ratio of the Mn-Ni and Mn-Mn or Ni-Ni distance is $<1$, with the increase in the value of lattice parameter the interaction between Mn and Ni becomes more prominent than the interaction between Mn-Mn or Ni-Ni. As a result, there is an increase in the Coulomb repulsion between the Mn $d$ electrons leading to an increase in $U$. Similar argument could explain the increase in $U$ on Ga $p$ states.

5.2.2 Martensite

A supercell with 8 atoms in the unit cell is considered for the computation of interaction parameters. As for the austenite, the response of $s$ and $p$ of Ga, and $d$ and $s$ of Mn and Ni are considered during the response matrix calculations. Since a unit cell with a fewer number of atoms is used than that used in the austenite case (16 atoms), a comparison of the $U$ values obtained for the cubic austenite and the tetragonal martensite with $c/a = 1$ (equivalent to the cubic austenite) revealed that the values were within a difference of 0.05 eV. The interaction parameters are computed for several values of $c/a$ in the range where the martensitic structure is observed (0.92 to 1.24) with fixed volume equal to that of the L2$_1$ structure.

In Figure 5.2.2 the on-site Coulomb interaction $U$ is plotted for the standard states of Ga ($p$), Mn ($d$) and Ni ($d$). It is interesting to note that the $U$ values remain constant for the whole range of $c/a$. From this observation it can be concluded that the interaction parameters are independent of the tetragonal distortion with a constant volume. Thus in all further calculations, the $Us$ obtained for the austenite structure are also used for the martensite structure.
Figure 5.2: On-site Coulomb interaction on standard states of Ga, Mn and Ni for different values of \( c/a \)

### 5.3 Energy vs \( c/a \) profile of Martensite structure

The energy vs \( c/a \) profile is studied with ‘+\( U \)’ corrected functionals using the interaction parameters calculated for the austenite structure at equilibrium lattice value (11.01 a.u.). Figure 5.3 shows the E vs \( c/a \) profile obtained with different corrected functionals.

As seen earlier, GGA produces a local minimum at \( c/a = 1 \) and a global minimum at \( c/a = 1.23 \). It is interesting to note that using corrected functionals, only one global minimum at \( c/a = 1 \) is obtained in the E vs \( c/a \) profile. The minimum at \( c/a = 1.23 \) observed with the standard GGA is disappeared. This is in agreement with the experimental observations as discussed earlier. The profile is similar to the one calculated by Barman et al. [40] except that a minimum at \( c/a = 0.97 \) is reported. From careful observation of these profiles, it can be concluded that the on-site, iter-orbital interaction and inter-site interaction corrected functionals do not have a significant effect on the minimum energy structure. However, the ‘+\( V \)’ corrected energy profile increases
Figure 5.3: Energy vs $c/a$ profile obtained with different corrected functionals. Red- GGA, green - GGA+U on standard states of Ga, Mn, and Ni, blue - U on standard and background states of all atoms, pink- U and V on all states, light blue - U only Mn-$d$ states

steeply with increasing $c/a$. Moreover a correction of ‘+U’ on the Ga $p$ and Ni $d$ states decreases the slope of the energy profile. Thus with on-site Coulomb correction for the Mn-$d$ orbitals, the min at $c/a = 1.23$ can be eliminated. This explains why only $U$ on Mn $d$ states is used in the self-consistent computation of the interaction parameters.

To understand this kind of behavior in the energy profile, especially the absence of minimum at $c/a = 1.23$, the density of states is studied. Figure 5.4(a) shows the total density of states of the martensite structure with $c/a = 1.23$. We compare the DOS obtained with GGA and GGA+$U_{Mn}$ ($U$ on Mn $d$ states). It can be seen that with ‘+U’ correction, there is a shift in the peak at 3.45 eV below the Fermi level in the majority states towards lower energies (-6.35 eV). However the minority peak at 1.5 eV shifts towards a higher energy of 3.77 eV, increasing the magnetization of the system from 4.28 $\mu_B$ to 4.87 $\mu_B$. From the projected DOS shown in Figure 5.4(b), it
Figure 5.4: Density of states (DOS) calculated with GGA, and GGA+U\(_{Mn}\) for \(c/a = 1.23\). 'a' shows the total density of states, 'b' shows the states projected on to the Mn \(d\) orbitals. The Fermi level is set to zero. Inset is magnification of DOS at the Fermi level.

Can be seen that the increase in the magnetization is due to the separation between the majority and minority peaks of the Mn \(d\) states. Another interesting aspect to note is that the two peaks of Mn in the majority states obtained with GGA combine to form a single peak, when a ‘+U’ correction is used. At the Fermi level \((E_F)\), with GGA, Mn \(d\) and Ni \(d\) states contribute almost equally to the DOS. However with the correction for on-site interaction, the DOS at \(E_F\) is considerably decreased. Specifically Mn majority contribution goes to zero, while there is a little contribution by the Mn minority spins (inset in Fig. 5.4(b)). Instead, the contribution of Ni \(d\) states to the \(E_F\) is opposite. The DOS due to minority spins decreases a little and due to majority states increases by almost the same amount.

The reason why +\(U\) correction do not predict a minimum at \(c/a = 1.23\) can be understood with the following argument: with a \(c/a\) of 1.23, the Mn-Mn distance along the [1 0 0] direction is smaller than for \(c/a = 1\). This decreases the distance between the adjacent Mn atoms while increasing the distance between Mn-Ga and Ni-Ni atoms along [0 0 1]. GGA, with an incorrect description of the localization of Mn-\(d\) orbitals, de-localizes the Mn-\(d\) electrons and predicts a more metallic state with total energy lower than that for \(c/a = 1\). However with the ‘+U’ correction, the localization of the \(d\) orbitals is treated appropriately and a “less metallic” state is predicted with a higher
total energy. This is evident in the DOS at $E_F$ as described above.

5.4 Structure of Austenite

The structure of austenite is re-examined by using the ‘+U’ correction that predicted an energy vs $c/a$ profile with only minimum at $c/a = 1$. We have studied the structure with different GGA+$U$ functionals. The total energies are calculated at different lattice constants around the experimental lattice value and are fit to Murnaghan equation of state. Figure 5.5 shows a set of Murnaghan plots for different cases.

![Murnaghan plots](image)

Figure 5.5: Murnaghan plots obtained with different corrected functionals.

Several combinations of $U$ and $V$ are studied and compared with the GGA structural properties. It is evident that the lattice parameter increases with ‘+U’ correction. Table 5.2 lists the lattice parameter and bulk moduli obtained from GGA+$U$+$V$ calculations with different corrected functionals. When an on-site Coulomb correction is used for the standard states of Ga, Mn, and Ni, the lattice parameter obtained is the highest at 11.982 a.u. with a bulk modulus of 0.632 Mbar. When an inter-site interaction
Table 5.2: The calculated equilibrium lattice constant ($a$) and bulk modulus with different correlation correction.

<table>
<thead>
<tr>
<th>Correction</th>
<th>$a$(a.u.)</th>
<th>$B$(Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>11.004</td>
<td>1.46</td>
</tr>
<tr>
<td>GGA+U</td>
<td>11.982</td>
<td>0.653</td>
</tr>
<tr>
<td>GGA+U+V</td>
<td>11.978</td>
<td>0.632</td>
</tr>
<tr>
<td>$U_{Mn}$</td>
<td>11.433</td>
<td>1.116</td>
</tr>
<tr>
<td>$U_{Mn}$+V$<em>{Mn-Ni}$+V$</em>{Mn-Ga}$</td>
<td>11.424</td>
<td>1.113</td>
</tr>
<tr>
<td>Exp</td>
<td>11.01[22]</td>
<td>1.46[95]</td>
</tr>
</tbody>
</table>

is also included, the lattice parameter is decreased by 0.004 a.u. This suggests that the inter-site interactions have very little or no effect on the structural properties of austenite. Since the martensitic structure was well described with $U$ only on Mn $d$ states, the equation of state with $U_{Mn}$ is calculated. The lattice value obtained is closer to the that of the experimental value. However, inclusion of $V$ between Mn-Ni and Mn-Ga along with $U_{Mn}$ increased the value of lattice parameter. The lattice constant predicted with ‘+$U_{Mn}$’ correction is around 5% higher than the value predicted by GGA. The increase in lattice constant value with ‘GGA+U’ is expected for the reason that,

Figure 5.6: Murnaghan plots obtained with GGA, GGA+U and GGA+U+J functionals.
the Coulomb interaction correction localizes the electrons on their respective manifolds decreasing the hybridization of orbitals between neighboring atoms. This leads to a decrease in the binding force, giving rise to an increase in the lattice constant.

To obtain a better lattice parameter for the austenite structure with the ‘+U’ correction, another corrective functional where the magnetic interactions are treated explicitly with exchange interaction parameter ‘\( J \)’ is used. This corrected energy functional is given in Eq. 3.27. We have used a test value of 0.5 for ‘\( J \)’ on Mn-\( d \) states. This ‘\( J \)’ is expected to give a better description of magnetism in the system. Total energy calculations were performed for different lattice parameters around the experimental value and are fitted to Murnaghan equation of state. Figure 5.6 shows the Murnaghan fits of total energies obtained with GGA, GGA+U and GGA+U+J functionals. It is interesting to find that with an inclusion of exchange correction explicitly on Mn-\( d \) orbitals along with on-site correction, the lattice parameter increases by only 0.3%.

![Figure 5.6: Murnaghan fits of total energies obtained with GGA, GGA+U and GGA+U+J functionals.](image)

**Figure 5.6:** Murnaghan fits of total energies obtained with GGA, GGA+U and GGA+U+J functionals. It is interesting to find that with an inclusion of exchange correction explicitly on Mn-\( d \) orbitals along with on-site correction, the lattice parameter increases by only 0.3%.

![Figure 5.7: Density of states (DOS) with different corrections at GGA equilibrium structure.](image)

**Figure 5.7:** Density of states (DOS) with different corrections at GGA equilibrium structure. ‘a’ shows the total density of states, ‘b’ shows the states projected on to the Mn-\( d \) orbitals. The Fermi level is set to zero. Inset is magnification of DOS at the Fermi level.

To understand the effect of the treatment of magnetic interactions explicitly, the density of states (DOS) is studied. In Figure 5.7 DOS obtained with GGA, GGA+U and GGA+U+J functionals is plotted. Figure 5.7-a shows the total DOS. There is a slight decrease in the states around the Fermi level when a correction is applied. Figure 5.7-b shows the DOS projected on to Mn atomic \( d \) orbitals. Here it is evident that the increase in the separation between the Mn minority and majority peaks is decreased.
Table 5.3: The calculated lattice constant ($a$), bulk modulus and magnetic moments ($\mu_B$) obtained with different corrected functionals.

<table>
<thead>
<tr>
<th>Correction</th>
<th>$a$ (a.u.)</th>
<th>$B$ (Mbar)</th>
<th>$\mu^{tot}$</th>
<th>$\mu^{Ni}$</th>
<th>$\mu^{Mn}$</th>
<th>$\mu^{Ga}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>11.004</td>
<td>1.46</td>
<td>3.84</td>
<td>0.28</td>
<td>3.72</td>
<td>-0.14</td>
</tr>
<tr>
<td>GGA+$U_{Mn}$</td>
<td>11.433</td>
<td>1.116</td>
<td>4.94</td>
<td>0.14</td>
<td>4.76</td>
<td>-0.13</td>
</tr>
<tr>
<td>GGA+$U_{Mn}$+$J_{Mn}$</td>
<td>11.04</td>
<td>1.288</td>
<td>4.66</td>
<td>0.29</td>
<td>4.19</td>
<td>-0.16</td>
</tr>
<tr>
<td>Exp.</td>
<td>11.01$^{[32]}$</td>
<td>1.46$^{[95]}$</td>
<td>4.17$^{[32]}$</td>
<td>0.24$^{[42]}$</td>
<td>2.74$^{[42]}$</td>
<td>-0.013$^{[42]}$</td>
</tr>
</tbody>
</table>

when ‘+$J$’ correction is explicitly included. In the inset it can be seen that the ‘+$U$+$J$’ correction increases the DOS due to the Mn-$d$ minority spins, predicting a more metallic state than the ‘+$U$’ corrected functional.

Table 5.3 summarizes the lattice constants, bulk modulus, total magnetization and individual atomic magnetic moments of the structures obtained with different corrected functionals. We can see that the Coulomb interaction correction for the Mn-$d$ orbitals increases the lattice constant by 4%. However the explicit inclusion of exchange interaction gives a better lattice constant with only 0.3% larger than the experimental value. The ‘+$U$+$J$’ functional also produces better bulk modulus for the system. The local magnetic moment on Ni and Ga predicted by ‘+$U$+$J$’ corrected functional is similar

![Energy vs c/a profile](image)

Figure 5.8: Energy vs $c/a$ profile obtained with GGA, GGA+$U$ and GGA+$U$+$J$ functionals
to the GGA predicted magnetic moments. But the local magnetic moment on Mn has increased by almost 0.5 $\mu_B$.

To make sure that ‘+$J$’ correction preserves the martensitic E vs $c/a$ profile obtained earlier with no minimum at $c/a = 1.23$, the energy profile of martensite with ‘$GGA + U_{Mn} + J_{Mn}$’ functional is calculated. Figure 5.8 shows the energy vs $c/a$ profile. We can see that the functional where exchange interaction is treated explicitly also eliminated the minimum at $c/a = 1.23$. However, the energy landscape is flat compared to the one obtained with a functional where the exchange interaction is included in the $U$.

## 5.5 Conclusions

In conclusion, we have found that the Coulomb interaction between the Mn-$d$ electrons play an important role in describing the energy landscape of martensitic structure. The minimum at $c/a = 1.23$ produced by GGA is due to the delocalization and over hybridization of Mn-$d$ electrons. GGA+U by treating these localized electrons appropriately, eliminates the minimum by predicting a “less metallic” structure at $c/a = 1.23$. This is evident in the depletion of Mn contribution to the density of states at the Fermi level. However, the structure of austenite is well described only with a functional where the exchange interaction is explicitly included. This functional treats the magnetic interactions more accurately which are dominant in this system.
Chapter 6

Summary and Conclusions

In the present thesis the structural, electronic and magnetic properties of the magnetic shape memory alloy Ni$_2$MnGa are studied. These properties have been analyzed using a computational approach based on density functional theory. The Extended DFT+U functional that includes the effects of Coulomb interaction between the localized electrons has been used. The results of the structural, electronic and magnetic properties obtained with the DFT+U calculations have been compared with those obtained using the standard DFT (GGA) functional and available experimental measurements.

GGA calculations have accurately predicted the structural and magnetic properties of the high temperature austenite structure. The ferromagnetic structure of Ni$_2$MnGa is more stable at low temperatures and is metallic in nature mostly because of the Ni contribution to the density of states at the Fermi level. The magnetization in the material is mainly due to the magnetic moment on Mn. An instability in the austenite structure at low temperatures is observed in the phonon dispersion that show a soft mode along the [110] direction.

The structure of martensite is well predicted by the DFT+U functionals. Specifically the spurious minimum at $c/a > 1$ obtained using standard DFT functional has been eliminated by correcting the localization of electrons on Mn $d$ states with DFT+U. DFT (GGA), due to over-delocalization of the Mn-$d$ orbitals, predicts a more metallic structure for a tetragonal distortion of $c/a = 1.23$ than that predicted by the DFT+U
functional. However, the standard DFT+U corrective functional predicts a lattice parameter for the austenite structure which is in worse agreement with experimental results. Using an explicit exchange interaction, DFT+U+J functional, a better structural parameter was obtained for austenite structure. This is mainly due to a more accurate description of the magnetism by this functional.

In conclusion, our analysis shows that the DFT+U method provides a description of the martensitic structure in better agreement with experiments. Although the structural parameter of austenite is over estimated by this functional, an explicit inclusion of exchange interaction predicts a value closer to the experimental one. The tetragonal martensitic structure with $c/a < 1$ is not observed. We expect that the minimum in total energy at $c/a < 1$ could be due to the shuffling of (110) planes along the $[110]$ direction. This expectation already discussed by other authors, seems corroborated also by the soft mode in the phonon dispersion of austenite along $[110]$ direction, suggest that the modulation in the martensitic structure at $c/a < 1$ could be along the same $[110]$ direction as reported in Ref. [45]. The effect of electron localization on lattice dynamic properties is under consideration and will be compared with the results obtained with GGA.
References


