Elastic Properties and Phase Stability of Shape Memory Alloys from First-Principles Theory

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Abstract

Ni-Mn-Ga and In-Tl are two examples of shape memory alloys. Their shape memory effect is controlled by the martensitic transformation from high temperature face-centered-cubic (fcc) phase to the low temperature face-centered-tetragonal (fct) phase. Experimentally, it was found that the martensitic transformation is related to the elastic properties. In order to better understand the phase transition and facilitate the design of new materials with improved shape memory properties, the atomic scale description of the thermophysical properties of these alloys is needed. In the present thesis, the elastic properties and phase stability of Ni-Mn-Ga and In-Tl shape memory alloys are investigated by the use of first-principles exact muffin-tin orbital method in combination with coherent-potential approximation.

It is shown that the theoretical lattice parameters and elastic constants of stoichiometric Ni$_2$MnGa and pure In agree well with the available theoretical and experimental data, indicating that the employed theoretical approach is suitable to study the elastic properties of both cubic and tetragonal crystals. For most of the off-stoichiometric Ni$_2$MnGa, the excess atoms of the rich component prefer to occupy the sublattice of the deficient one, except for the Ga-rich alloys, where the excess Ga atoms have strong tendency to take the Mn sublattice irrespective of the Mn occupation. With increasing $e/a$ ratio (the number of valence electrons per atom), it is found that the theoretical bulk modulus $B$ and the shear constant $C_{44}$ increase but the tetragonal elastic constant $C'$ decreases. Except for Mn-rich Ga-deficient alloys, $C'$ is generally inversely proportional and the energy difference between parent and martensitic phases is directly proportional to the martensitic transformation temperature $T_M$. For In$_{1-x}$Tl$_x$ alloys, the tetragonal lattice parameter $c/a$ and the shear modulus $C'$ in the fct phase and the total energy difference between the fcc and fct phases decrease with Tl addition, whereas the negative $C'$ of the fcc phase increases with $x$ turning positive around $x=0.35$. All of these composition dependent thermophysical properties can be understood by investigating the electronic structure of In and In-Tl alloys and they are in line with the experimentally observed lowering of $T_M$ with addition of Tl.
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Supplements

The present thesis is based on the following papers:

Paper I  “Site occupancy, magnetic moments, and elastic constants of off-stoichiometric Ni$_2$MnGa from first-principles calculations”  
Qing-Miao Hu, Chun-Mei Li, Rui Yang, Svetlana E. Kulkova, Dmitry I. Bazhanov, Börje Johansson, Levente Vitos  

Paper II “Magnetoelastic effects in Ni$_{2+x}$Mn$_{1-x}$Ga$_{1-x}$ alloys from first-principles calculations”  
Qing-Miao Hu, Chun-Mei Li, Svetlana E. Kulkova, Rui Yang, Börje Johansson, Levente Vitos  

Paper III “First-principles investigation of the composition dependent properties of Ni$_{2+x}$Mn$_{1-x}$Ga shape-memory alloys”  
Chun-Mei Li, Hu-Bin Luo, Qing-Miao Hu, Rui Yang, Börje Johansson, Levente Vitos  

Paper IV “First-principles study of the elastic properties of In-Tl random alloys”  
Chun-Mei Li, Qing-Miao Hu, Rui Yang, Börje Johansson, Levente Vitos  
Contributions to the appended papers

Paper I: Literature survey, part of calculations, part of data analysis and evaluation.

Paper II: Literature survey, part of calculations, part of data analysis and evaluation.

Paper III: Literature survey, calculations, data analysis and evaluation, and major part of writing.

Paper IV: Literature survey, calculations, data analysis and evaluation, and major part of writing.
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1. Introduction

Recently, the shape memory alloys have attracted a lot of attention among researchers. The ternary intermetallic compound Ni$_2$MnGa is one of the most studied systems due to its ferromagnetism and shape memory effect (SME). The two-way SME, induced by magnetic field or thermal change, can enable the quick response and remote control, which is very interesting and important for applications of this type of ferromagnetic shape memory alloys (FSMAs). Thus, Ni$_2$MnGa has been broadly used as an ideal candidate for sensor, actuator, and intelligent device applications.

The SME of shape memory alloys is controlled by the reversible martensitic transformation (MT) between a high-temperature austenitic phase and a low-temperature martensitic phase. Upon alloying, the structural transition temperature $T_M$ can be sensitively tuned. For example, in In-Tl binary shape memory alloy, $T_M$ was experimentally found to decrease from about 400K to 0K with addition of Tl from 20 at.% to 30 at.%.\textsuperscript{1,2} In Ni excess Ni$_{2+y}$Mn$_{1-x}$Ga alloys, both $T_M$ and the magnetic transition temperature $T_C$ are highly composition dependent. Namely, with increasing $x$, $T_M$ goes up and $T_C$ goes down.\textsuperscript{3,4} When $x$ is between 0.18 and 0.20, the two transitions couple to each other and $T_C$ presents an abnormal "jump".\textsuperscript{3} The above interesting trend makes this family of shape memory alloys to possess some special and also attractive properties such as giant magnetocaloric effect, magnetostriction, and magnetoresistance which are important for the application of magnetic refrigeration or magnetostrictive transducers.\textsuperscript{4-6} Different $T_M$ and $T_C$ result in different properties of the alloys with various technological significances. The investigation of the composition dependence of structural and magnetic states are therefore crucial for understanding the properties of shape memory alloys, which in the end will help us to predict and design new alloys with improved shape memory effect.

From the previous experimental and theoretical studies, there are several plausible quantities to connect the composition and $T_M$ of the shape memory alloys, among which the $e/a$ ratio (the number of valence electrons per atom) is very well recognized. It has been shown that by increasing the $e/a$ ratio $T_M$ is enhanced.\textsuperscript{7-9} Second, the total energy difference between the cubic
austenite and the tetragonal martensite phases $\Delta E_{AM}$ is another quantity proposed to correlate $T_M$ with the composition of the alloy: larger $\Delta E_{AM}$ corresponds to higher $T_M$.\textsuperscript{10,11} Third, the MT of the shape memory alloys generally results from soft-phonon modes and their accompanying soft tetragonal shear modulus $C' = \frac{1}{2} (C_{11} - C_{12})$ of the high-temperature cubic phase.\textsuperscript{12-14} For alloys undergoing MT, the composition dependence of $T_M$ is generally related to the composition dependence of $C'$.\textsuperscript{15-17} For example, it has been confirmed in the case of TiNi-based shape memory alloys that the lower the $C'$, the higher the $T_M$ will be,\textsuperscript{18} and in In-Tl random alloy, $T_M$ decreases with the addition of Tl, which is accompanied by a $C'$ which gradually approaches zero.\textsuperscript{1,2} Finally, according to Lanska et al.\textsuperscript{7} and Banik et al.,\textsuperscript{19} the composition dependent tetragonality of the martensite (|$c/a$-1|) (with $a$ and $c$ being the lattice constants of the tetragonal phase), may also serve as a measure of the composition dependence of the $T_M$ (i.e., a larger |$c/a$-1| corresponds to a higher $T_M$). Thus, at least four physical quantities have been reported to be relevant for the composition dependence of the phase transition temperature.

The exact muffin-tin orbitals (EMTO)\textsuperscript{21-25} method in combination with coherent potential approximation (CPA)\textsuperscript{24,26,27} is an important recently developed first-principles tool. The EMTO method is based on density functional theory. It is an improved screened Korringa-Kohn-Rostoker (KKR) method, where the optimized overlapping muffin-tin potential is chosen as the best possible spherical approximation to the exact potential, and for the calculation of the total energy, the full charge density (FCD) technique is adopted.\textsuperscript{28} Thus, the EMTO-CPA method is suitable to describe accurately the total energy of system with chemical and magnetic disorder and by properly accounting for the anisotropic lattice distortions. The EMTO-CPA method has been applied successfully in the ab initio study of the thermophysical properties of random Fe-based alloys,\textsuperscript{29,30} simple and transition metal alloys,\textsuperscript{31-33} and oxide solid solutions.\textsuperscript{34,35} In our present work, we will choose this method to study systematically the physical properties and phase stability of Ni-Mn-Ga and In-Tl shape memory alloys.

In this thesis, first, the first-principles EMTO-CPA method is introduced. Then, using the theoretical lattice parameter and elastic constants of stoichiometric Ni$_2$MnGa alloy, the accuracy and reliability of the calculational tool are demonstrated. Next, the site occupancy, elastic and
magnetic properties, and the phase stability of Ni-Mn-Ga-based alloys are investigated in details. The correlation between the composition dependent $T_M$ and the elastic constants as well as the energy difference between parent and martensitic phases is explored. For future investigations of the elastic properties of the Ni-Mn-Ga ternary alloys in the martensitic phase, the theoretical elastic constants for tetragonal crystals were studied by calculating a relatively simple system: pure In and In-Tl shape memory alloy. The correlation between the composition dependent $T_M$ and the four factors: tetragonality $|c/a-1|$, elastic constants, energy difference between the austenite and martensite, and the electronic structure are also examined in In$_{1-x}$Tl$_x$ alloys.
2. Theoretical Method

2.1 Density Functional Theory (DFT)

Density-functional theory (DFT) is one of the most popular and successful quantum mechanical approaches to study the properties of materials. The main idea behind DFT is to accomplish the electronic structure calculations by using the electronic density as the basic quantity instead of the complex many-body electronic wavefunction. Thus, by reducing the many-body equations into Hartree-type single-particle equations, DFT offers a powerful and elegant way for calculating the ground state properties of interacting electrons.

Developed from the original theory of Hohenberg and Kohn, the most common and widely used DFT scheme is the one proposed by Kohn and Sham. Considering an interacting electron gas moving in an external potential $v_e(r)$ within the Kohn-Sham scheme, the variational principle leads to the effective single-electron Schrödinger equations

$$\{-\nabla^2 + v([n]; r)\} \Psi_j(r) = \epsilon_j \Psi_j(r).$$

The effective potential $v([n]; r)$ is described by the sum of $v_e(r)$, Hartree potential $v_H([n]; r)$, and the exchange-correlation potential $\mu_{xc}(\{n\}; r)$, i.e.

$$v([n]; r) = v_e(r) + v_H([n]; r) + \mu_{xc}(\{n\}; r).$$

The electron density is calculated from the single-electron orbitals according to

$$n(r) = \sum_{\epsilon_j \leq \epsilon_F} |\Psi_j(r)|^2.$$  

From this expression, the number of electrons is obtained by the constraint

$$N_e = \int n(r) \, dr.$$  

Then, from the self-consistent solutions of the Equations (2.1-2.4), the ground state energy of the electronic system is computed by
Here, \( T_s[n] \) and \( E_{xc}[n] \) are the kinetic energy of non-interacting particles and exchange-correlation energy, respectively.

In the case of electrons moving in the external potential created by the fixed nuclei located on lattice sites \( \mathbf{R} \), \( v_e(\mathbf{r}) \) in above equations is formulated by

\[
v_e(\mathbf{r}) = -\sum_{\mathbf{R}} \frac{2Z_R}{|\mathbf{r} - \mathbf{R}|},
\]

where \( Z_R \) are the nuclear charges. Then the total energy of the system formed by electrons and nuclei is obtained by

\[
E_{tot} = E_e[n] + \sum_{\mathbf{R}\mathbf{R}'} Z_R Z_{R'} |\mathbf{R} - \mathbf{R}'|.
\]

The prime indicates that the \( R = R' \) term is excluded from the sum.

The above formulas represent the non-spin-polarized Kohn-Sham scheme for electrons in a solid matter. The spin-density functional formalism is obtained by introducing two spin-densities, \( n^\uparrow(\mathbf{r}) \) and \( n^\downarrow(\mathbf{r}) \). They are just solutions of the Kohn-Sham equation for the spin-dependent effective potential

\[
\mu_{xc}^\sigma([n^\uparrow, n^\downarrow]; \mathbf{r}) = \frac{\delta E_{xc}[n^\uparrow, n^\downarrow]}{\delta n^\sigma(\mathbf{r})}
\]

(\( \sigma = \uparrow \) or \( \downarrow \)) that depends on both spin densities.\(^{38}\)

Although the Kohn-Sham formalism reduces the many-particle problem of interacting electrons into an effective single-particle Schrödinger equation, the solution of the Equation (2.1) requires certain approximations for the exchange and correlation because they are not known exactly, except for the free (homogeneous) electron gas. The most widely used approximations are the Local Density Approximation (LDA)\(^{39-42}\) and the Generalized Gradient Approximation
Within the LDA, the exchange-correlation energy density per electron is assumed to be the same as that in a homogeneous electron gas,

\[ E^{LDA}_{xc}[n] = \int d^3r n(r) \varepsilon^{hom}_{xc}(n(r)), \tag{2.9} \]

where \( \varepsilon^{hom}_{xc}(n(r)) \) is the sum of the exchange and correlation energies of the homogeneous electron gas of density \( n(r) \). Within GGA, not only the density itself enters in the exchange-correlation energy but also its local gradient \(|\nabla n|\), \( i.e., \)

\[ E^{GGA}_{xc}[n] = \int d^3r n(r) \varepsilon^{GGA}_{xc}(n(r), |\nabla n|). \tag{2.10} \]

For the GGA level the energy density per electron (\( \varepsilon^{GGA}_{xc} \)), several different forms have been suggested. Moreover, in addition to the GGA, other gradient-level approximations for the exchange and correlation have also been developed in the past several years, such as the Local Airy Gas Approximation (LAG)\(^{47,48} \) and AM05\(^{49} \).

### 2.2 Exact Muffin-Tin Orbitals Method

The Exact Muffin-Tin Orbitals (EMTO) theory, developed in the 1990s by Andersen and co-workers\(^{21} \), is an accurate and at the same time efficient tool for solving the Kohn-Sham equations. Recently, it was implemented by many researchers, especially by Vitos’s group\(^{25} \). Within their EMTO method, the single-electron Schrödinger equations are solved separately within the Wigner-Seitz cells or Voronoy polyhedra\(^{38} \) defined around the lattice sites. The Kohn-Sham potential is approximated by the optimized overlapping muffin-tin wells, which are obtained using the Spherical Cell Approximation (SCA)\(^{22} \). Then, by means of the self-consistent calculation, the total charge density is constructed and the total energy is calculated via the so-called Full Charge Density (FCD) technique\(^{28,50-52} \). In addition, in the case of alloys, the problem of chemical and magnetic disorder is easily treated by combining the EMTO method with the Coherent Potential Approximation (CPA)\(^{24,26,27} \). In the present EMTO implementation, the total energy is computed by LDA plus four gradient-level functionals: PBE\(^{45} \), PBEsol\(^{53} \), AM05\(^{49} \), and LAG\(^{47,48} \).
There are two important advantages of EMTO-CPA method, compared with other conventional numerical methods for solving the Kohn-Sham equations. First, by using overlapping spheres, one describes more accurately the crystal potential with the EMTO method than with the conventional non-overlapping muffin-tin approach. Second, the self-consistent EMTO calculation can be combined with the CPA, without losing significantly either the accuracy or the efficiency. This makes the EMTO method to be more convenient in the practical applications on alloys than most the commonly used first-principles full potential (FP) and pseudopotential (PP) methods. In the following subsections, the EMTO formalism will be introduced in detail.

### 2.2.1 Exact Muffin-Tin Potential

Within the overlapping muffin-tin approximation, the effective single-electron potential is approximated by spherical potential wells $v_{R}(r_{R}) - v_{0}$ centered on lattice sites $R$ plus a constant potential $v_{0}$, i.e.,

$$v(r) \approx v_{mt}(r) \equiv v_{0} + \sum_{R} [v_{R}(r_{R}) - v_{0}]. \quad (2.11)$$

By definition, $v_{R}(r_{R})$ becomes equal to $v_{0}$ outside the potential sphere of radius $s_{R}$.

For fixed potential spheres, the spherical and the constant potentials from the right hand side of Equation (2.11) are determined by optimizing the mean of the squared deviation between $v_{mt}(r)$ and $v(r)$, i.e. minimizing the

$$F_{\nu}[[v_{R}], v_{0}] \equiv \int_{R} \left\{v(r) - v_{0} - \sum_{R} [v_{R}(r_{R}) - v_{0}]\right\}^{2} dr \quad (2.12)$$

functional. Here $\Omega$ is the unit cell. Then, the minimum condition can be expressed as

$$\int_{\Omega} \delta v_{R}(r) \frac{\delta F_{\nu}[[v_{R}], v_{0}]}{\delta v_{R}(r)} dr = 0 \quad (2.13)$$

and

$$\frac{\partial F_{\nu}[[v_{R}], v_{0}]}{\partial v_{0}} = 0. \quad (2.14)$$
The solution of these integro-differential equations (2.13) and (2.14) gives the optimal \( v_R(r_R) \) and \( v_0 \), and leads to the so-called optimized overlapping muffin-tin (OOMT) potential.

Within the EMTO formalism, the calculation of the effective single-electron potential involves two steps. First, we calculate the full-potential from the total charge density and second, we construct the optimized overlapping muffin-tin wells. The first step is very demanding and slightly inaccurate in the corners of the unit cell. Moreover, the expression for the effective potential (2.2) involves an integral over the real space due to the Hartree potential. In order to avoid the above two problems, the so-called SCA is adopted.\(^{22}\) There, the main idea is to simplify the solution of the Poisson equation by substituting the Wigner-Seitz cell around each lattice site by a spherical cell during the self-consistent iterations. In this technique, the volume of the spherical cell at \( R, \Omega_{\omega R} \), is chosen to be equal with the volume of the Wigner-Seitz cell \( \Omega_R \), centered on the same lattice site, \( i.e. \)

\[
\Omega_{\omega R} \equiv \frac{4\pi}{3} \omega_R^3 = \Omega_R,  \tag{2.15}
\]

where \( \omega_R \) is the radius of the spherical cell.

Based on the overlapping muffin-tin approximation to the full potential described in the case of spherical cell, the spherical part of the single-electron potential can be expressed by four parts in ordered system. First, the electrostatic potential \( v_e(r) + v_H(r) \), created by the nuclear charges located at the lattice sites \( R \) and all the other electrons, respectively, can be separated into inside and outside of the cell at \( R \). The intra-cell part can be described as

\[
v^I_R(r_R) = -\frac{2Z_R}{r_R} + 2 \int_{\Omega_R} \frac{n_R(r_R')}{|r_R - r_R'|} dr_R'. \tag{2.16}
\]

The effect of charges from the outside of the potential sphere gives the so-called Madelung potential

\[
v^M_R(r_R) = -\sum_{R \neq R'} \frac{2Z_{R'}}{|r_R + R'|} + \sum_{R \neq R'} 2 \int_{\Omega_{R'}} \frac{n_R(r_R')}{|r_R - r_R' + R - R'|} dr_R'. \tag{2.17}
\]

Calculating the spherical part of \( v^I_R(r_R) \) and \( v^M_R(r_R) \), respectively, we have
\[ v^I_R(r_R) \equiv \frac{1}{4\pi} \int v^I_R(r_R) d\hat{r}_R = 8\pi \frac{1}{r_R} \int_{r_R}^{r_R'} r'' n_{RL_0}(r'') d\hat{r}' \]
\[+ 8\pi \int_{r_R}^{s_R} r'' n_{RL_0}(r'') d\hat{r}' - \frac{2Z_R}{r_R}, \]
(2.18)

and

\[ v^M_R \equiv \frac{1}{4\pi} \int v^M_R(r_R) d\hat{r}_R = \frac{1}{\omega} \sum_{R \neq R', L'} M_{RL_0RL} Q^{SCA}_{RL'}, \]
(2.19)

where \( \omega \) is the average atomic radius, \( M_{RL_0RL} \) the elements of the Madelung matrix, and \( Q^{SCA}_{RL} \) the multipole moments.

Second, the number of electrons inside the \( s \)-sphere \( Q(s_R) \) is different from the number of electrons inside the cell, \( Q^{SCA}_{RL_0} + Z_R \). This difference contributes to a constant shift, \( \Delta v^M_R \), to the spherical potential. In the SCA, this extra or missing charge is redistributed equally on the \( N_{NN} \) nearest-neighbor cells, \( i.e. \)

\[ \Delta v^{SCA}_R = \frac{1}{\omega} \sum_{R_{NN}} M_{RL_0R_{NN}L_0} \Delta Q_{R_{NN}}, \]
(2.20)

where \( \Delta Q_{R_{NN}} \equiv \frac{1}{N_{NN}} \left( Q^{SCA}_{RL_0} + Z_R - Q(s_R) \right) \).

In addition, the spherically symmetric part of the exchange-correlation potential can be described by

\[ \mu_{xcR}(r_R) \equiv \frac{1}{4\pi} \int \mu_{xcR}([n_R]; r_R) d\hat{r}_R. \]
(2.21)

Finally, the total potential within the potential sphere is obtained as the sum of contributions from Equations (2.18), (2.19), (2.20) and (2.21), namely

\[ v_R(r_R) = v^I_R(r_R) + v^M_R + \Delta v^{SCA}_R + \mu_{xcR}(r_R). \]
(2.22)

Except for the negligible approximations made in the Madelung terms, \( i.e. \) in Equations (2.19) and (2.20), the above expression gives the exact spherical part of the full potential inside the \( s \)-sphere.
2.2.2 Exact Muffin-Tin Orbitals Wave Function

We solve the single-electron Equation (2.1) for the muffin-tin potential defined in Equation (2.11), by expanding the Kohn-Sham orbital in terms of the exact muffin-tin orbitals $\tilde{\psi}_{RL}(\epsilon_j, r_R)$, i.e.

$$\Psi_j(r) = \sum_{RL} \tilde{\psi}_{RL}^a(\epsilon_j, r_R) u_{RL,j}^a. \quad (2.23)$$

$\tilde{\psi}_{RL}^a(\epsilon_j, r_R)$, forming a complete basis set for the Kohn-Sham problem, are defined for each lattice site $R$ and for each $L \equiv (l, m)$ with the orbital ($l$) and magnetic ($m$) quantum numbers. The expansion coefficients, $u_{RL,j}^a$, are determined from the condition that the above expansion should be solution to the Equation (2.1) in the entire space. In the EMTO formalism, the algebraic formulation of this matching condition is the so-called kink cancellation equation.21-23

The exact muffin-tin orbitals $\tilde{\psi}_{RL}^a(\epsilon_j, r_R)$ are constructed using different basis functions inside the potential spheres and in the interstitial region. In the interstitial region, where the potential is approximated by $v_0$, the basis functions can be described as the solutions of the wave equation,

$$\{\nabla^2 + \kappa^2\} \psi_{RL}^a(\kappa^2, r_R) = 0, \quad (2.24)$$

where $\kappa^2 \equiv \epsilon - v_0$, and $\epsilon$ is the energy. The functions $\psi_{RL}^a(\kappa^2, r_R)$, referred to as the screened spherical waves,21 form a complete basis set in the a-interstitial region and can be expanded in real harmonics $Y_L(\hat{r}_R)$ around any site $R'$ as

$$\psi_{RL}^a(\kappa^2, r_R) = f_{RL}^a(\kappa^2, r_R) Y_L(\hat{r}_R) \delta_{RR'} \delta_{LL'} + \sum_{L'} g_{RL}^a(\kappa^2, r_R) Y_L(\hat{r}_R) S_{RL'}^{a} Y_{L'}(\hat{r}_R). \quad (2.25)$$

The expansion coefficients, $S_{RL'}^{a}(\kappa^2)$, are the elements of the slope matrix, and the $f_{RL}^a$ and $g_{RL}^a$ are the value or head and the slope or tail functions, respectively.

Inside the potential sphere at $R$, the partial waves are chosen for the basis functions. They are defined as the products of the regular solutions of the radial Schrödinger equation41 for the spherical potential $v_R(r_R)$,
\[
\frac{\partial^2 [r_R \phi_{Rl}(\epsilon, r_R)]}{\partial r_R^2} = \left[ \frac{l(l + 1)}{r_R^2} + u_R(r_R) - \epsilon \right] r_R \phi_{Rl}(\epsilon, r_R),
\]  
(2.26)

and the real harmonics,

\[
\phi^a_{RL}(\epsilon, r_R) = N^a_{RL}(\epsilon) \phi_{Rl}(\epsilon, r_R) Y_L(\hat{r}_R),
\]  
(2.27)

where \( N^a_{RL}(\epsilon) \) is the normalization function.

In order to make \( \psi^a_{RL}(\kappa^2, r_R) \) and \( \phi^a_{RL}(\epsilon, r_R) \) matched up at the a-sphere, an additional free-electron solution with pure \((lm)\) character is introduced, which can be written in the form

\[
\phi^a_{RL}(\epsilon, r_R) = f^a_{RL}(\kappa^2, r_R) + g^a_{RL}(\kappa^2, r_R) D^a_{RL}(\epsilon),
\]  
(2.28)

where \( D^a_{RL}(\epsilon) = D[\phi^a_{RL}(\epsilon, a_R)] \) is the logarithmic derivative of \( \phi^a_{RL}(\epsilon, a_R) \) calculated for \( r_a = a_R \).

Finally, the exact muffin-tin orbitals are constructed as the superposition of the screened spherical waves (2.25), the partial waves (2.27) and the free-electron solution (2.28), i.e.

\[
\tilde{\psi}^a_{RL}(\epsilon, r_R) = \psi^a_{RL}(\kappa^2, r_R) + N^a_{RL}(\epsilon) \phi_{Rl}(\epsilon, r_R) Y_L(\hat{r}_R) - \phi^a_{RL}(\epsilon, r_R) Y_L(\hat{r}_R),
\]  
(2.29)

With the exact muffin-tin orbitals defined in Equation (2.29), the trial wave function (2.23) around site \( R \) can be expressed as

\[
\Psi(r_R) = \sum L N^a_{RL}(\epsilon) \phi_{Rl}(\epsilon, r_R) Y_L(\hat{r}_R) u^a_{RL} + \sum g^a_{RL}(\kappa^2, r_R) Y_L(\hat{r}_R)
\times \sum_{RL'} [S^a_{RLR'L'}(\kappa^2) - \delta_{R'RL} \delta_{LL'} D^a_{RL}(\epsilon)] u^a_{RL'}.  
\]  
(2.30)

The trial function will be a solution of the Equation (2.1) for the muffin-tin potential (2.11), if inside the s-spheres the \( l \leq l_{max} \) part of the second term from the right hand side of (2.30) vanishes for any \( r_R \). That is, if the \( l \leq l_{max} \) components of the screened spherical waves, multiplied by the expression coefficients, are cancelled exactly by \( \phi^a_{RL}(\epsilon, r_R) Y_L(\hat{r}_R) u^a_{RL,j} \). This is realized if the kink cancelation equation,

\[
\sum_{RL} a_R [S^a_{RLR'L'}(\kappa^2) - \delta_{RL} \delta_{L'L} D^a_{RL}(\epsilon)] u^a_{RL,j} = 0
\]  
(2.31)
is satisfied for all $R^\prime$ and $l^\prime \leq l_{max}$. Here and in the following $\kappa_j^2 \equiv \epsilon_j - \nu_0$, and $\epsilon_j$ is a Kohn-Sham single-electron energy for which Equation (2.30) has a non-trivial solution. The difference between the slope matrix and the logarithmic derivative matrix is called the kink matrix,

$$K^a_{R^\prime L^\prime R L}(\epsilon_j) \equiv a^a_{R^\prime L^\prime R L}((\kappa_j^2)) - \delta_{R^\prime R} \delta_{L^\prime L} a^a_{R R^\prime L L^\prime}((\epsilon_j)). \quad (2.32)$$

Thus, using the kink-cancellation equation, the wave function inside the potential sphere at $R$ reduces to

$$\Psi_j(r_R) = \sum_{L} N^a_{R L}(\epsilon_j) \phi_{R^\prime L^\prime}(\epsilon_j, r_R) Y_L(\hat{r}_R) u_{R L^\prime j}^a + \sum_{L} g^a_{R L^\prime}(\kappa_j^2, r_R) Y_L(\hat{r}_R) \sum_{R^\prime L} S^a_{R R^\prime L^\prime L}(\kappa_j^2) u_{R^\prime L^\prime j}^a. \quad (2.33)$$

2.2.3 Electron Density

Based on the one-center expression of the Kohn-Sham orbital $\Psi_j(r_R)$ in the Equation (2.33), the one-center form of the total charge density $n(r)$ is set up. It is divided into components $n_R(r_R)$ defined inside the Wigner-Seitz cells,$^{42}$ i.e.

$$n(r) = \sum_R n_R(r_R). \quad (2.34)$$

Around each lattice site, the density components in terms of the real harmonics are expanded as

$$n_R(r_R) = \sum_L n^{}_{R L}(r_R) Y_L(\hat{r}_R). \quad (2.35)$$

The partial components $n^{}_{R L}(r_R)$ are radial functions, which are obtained using the Equation (2.33).

During the self-consistent iterations of the Kohn-Sham equations (2.1), the Fermi energy $\epsilon_F$ is established using the condition that the total number of states $N(\epsilon_F)$ below the Fermi level should be equal with the number of electrons $N_e$ from the system, i.e.

$$N(\epsilon_F) = N_e. \quad (2.36)$$
2.2.4 The Full Charge Density (FCD) Total Energy

Within the EMTO method, the total energy is calculated from the total charge density by using the FCD technique.\textsuperscript{28,50-52} This technique is designed to maintain high efficiency but at the same time to give total energies with an accuracy similar to that of the full-potential methods. Within the FCD approach, the shape function technique\textsuperscript{28} is adopted as the space integrals method; the interaction energy between remote Wigner-Seitz cells is taken into account through the Madelung term; a particularly delicate contribution to this energy arises from Wigner-Seitz cells with overlapping bounding spheres, which is calculated by the so-called displaced cell technique.\textsuperscript{54,55}

The EMTO-FCD total energy is separated into the kinetic energy, the exchange-correlation energy and the electrostatic energy. Furthermore, the latter is divided into the intra-cell and inter-cell contributions. Then, the total energy becomes

\[
E_{\text{tot}} = T_s[n] + \sum_R (F_{\text{intra}R}[n_R] + E_{\text{xc}R}[n_R]) + F_{\text{inter}}[n], \tag{2.37}
\]

where the intra-cell \(F_{\text{intra}R}[n_R]\) and exchange-correlation energies \(E_{\text{xc}R}[n_R]\) depend only on the charge density within the actual cell, whereas \(F_{\text{inter}}\) depends on the charge distributions around different cells and \(T_s\) is a nonlocal functional of the density. All of them are accurately calculated within the FCD scheme.

2.2.5 Coherent Potential Approximation (CPA)

The Coherent Potential Approximation (CPA) is the most powerful technique in the case of multicomponent random alloys. Within the EMTO, the CPA is implemented using two main approximations. First, it is assumed that the local potentials around a certain type of atom from the alloy are the same, \textit{i.e.}, the effect of local environments is neglected. Second, the system is replaced by a monoatomic set-up described by the site-independent coherent potential \(\bar{P}\). In terms of the Green function, the real Green function is approximated by a coherent Green function \(\bar{g}\) \((\bar{g} = [S - \bar{P}]^{-1}, S \text{ denotes the structure constant matrix})\). For each alloy component,
a single-site Green function \( g_i \) is introduced, which is expressed mathematically via the real-space Dyson equation

\[
g_i = \tilde{g} + \tilde{g}(p_i - \tilde{p})g_i, i = A, B, C \ldots
\]  

(2.38)

The average of the individual Green functions should reproduce the single-site part of the coherent Green function, i.e.

\[
\tilde{g} = ag_A + bg_B + cg_C + \ldots
\]  

(2.39)

After iterative solution, the output of \( \tilde{g} \) and \( g_i \)’s equations are used to determine the electronic structure, charge density and total energy of the random alloy.

By combining with the CPA method, the formalism of the EMTO is renewed accordingly. The complete non-spherically symmetric charge density of the alloy component \( i \) in one-center form is represented by

\[
n_R^i(r_R) = \sum_L n_{RL}^i(r_R)Y_L(\hat{r}_R).
\]  

(2.40)

Since the impurity problem is treated within the single-site approximation, the Coulomb system of a particular alloy component may contain a non-zero net charge. The effect of the charge misfit on the spherical potential is taken into account using the screened impurity model (SIM) by Korzhavyi et al.\(^{56, 57}\) Thus, an additional shift of \( \Delta u_R^{SIM} \) is added to the spherical part of the full-potential around site \( R \) described by the Equation (2.22). The total potential within the potential sphere of the \( i \)-th alloy component is obtained as

\[
v_R^i(r_R) = v_R^{i,i}(r_R) + v_R^M + \Delta u_R^{SCA} + \Delta u_R^{SIM,i} + \mu_{xcR}(r_R).
\]  

(2.41)

The EMTO-CPA total energy of the random alloy is calculated according to

\[
E_{tot} = T_s[n] + \sum_R \sum_L c_l(F_{intrk}^l[n_R^i] + E_{xcR}^l[n_R^i]) + F_{inter}[Q] + \Delta E^{SIM}.
\]  

(2.42)
2.3 Calculational Methodology

2.3.1 Equation of State

For a system with specific space group, chemical composition and magnetic structure, the equation of state is obtained from the volume dependence of the total energy. In the present work, we adopt a Morse-type equation of state.\textsuperscript{58} Within this scheme, the total energy is fitted by an exponential function

$$E(w) = a + be^{-\lambda w} + ce^{-2\lambda w}, \quad (2.43)$$

which is written in terms of the average Wigner-Seitz radius $w$. The four independent Morse parameters $\lambda$, $a$, $b$, and $c$ are determined by fitting the total energy to nine different volumes in the present implementation.

The expression for the pressure becomes

$$P(w) = \frac{x\lambda^3}{4\pi(\ln x)^2} (b + 2cx), \quad (2.44)$$

where $x \equiv e^{-\lambda w}$. The equilibrium Wigner-Seitz radius, defined by $V_0 = 4\pi w_0^3/3$, is obtained from the condition $P(w_0) = 0$ as $w_0 = -\frac{\ln x_0}{\lambda}$ with $x_0 = -\frac{b}{2c}$.

The bulk modulus as a function of the Wigner-Seitz radius is expressed by

$$B(w) = -\frac{x\lambda^3}{12\pi \ln x} \left[ (b + 4cx) - \frac{2}{\ln x} (b + 2cx) \right], \quad (2.45)$$

which at $w_0$ reduces to

$$B_0 = -\frac{cx_0^2\lambda^3}{6\pi \ln x_0}. \quad (2.46)$$

2.3.2 Single-Crystal Elastic Constants

At a fixed volume $V$, the elastic constants of a single crystal can be evaluated by straining the lattice and calculating the variation of the total energy induced by the strain. For a cubic crystal, $C_{11} = C_{22} = C_{33}$, $C_{12} = C_{13} = C_{23}$, and $C_{44} = C_{55} = C_{66}$. Therefore, by means of the
relationship \( B = 1/3 (C_{11} + 2C_{12}) \), two different deformations are needed to calculate the three independent elastic constants. We choose the volume-conserving orthorhombic and monoclinic deformations, namely

\[
\begin{pmatrix}
1 + \delta & 0 & 0 \\
0 & 1 - \delta & 0 \\
0 & 0 & \frac{1}{1-\delta^2}
\end{pmatrix}
\quad \text{and} \quad
\begin{pmatrix}
1 & \delta & 0 \\
\delta & 1 & 0 \\
0 & 0 & \frac{1}{1-\delta^2}
\end{pmatrix},
\]

which yields the energy change of \( \Delta E(\delta) = V(C_{11} - C_{12})\delta^2 + O(\delta^4) \) and \( \Delta E(\delta) = 2VC_{44}\delta^2 + O(\delta^4) \), respectively.

For a tetragonal crystal, \( C_{11} = C_{22}, C_{13} = C_{23}, C_{44} = C_{55} \). The six independent elastic constants \( C_{11}, C_{33}, C_{12}, C_{13}, C_{44}, \) and \( C_{66} \) are calculated as follows. First, the volume dependence of the tetragonal axial ratio \( (c/a)_0 \) can be formulated by

\[
R = -\frac{d \ln (c/a)_0(V)}{d \ln V},
\]

where \( R \) is a dimensionless quantity, which in terms of the tetragonal elastic constants becomes

\[
R = \frac{C_{33} - C_{11} - C_{12} + C_{13}}{C_s},
\]

where \( C_s = C_{11} + C_{12} + 2C_{33} - 4C_{13} \).

Second, at the optimized \( c/a \) ratio, the bulk modulus \( B \) for a tetragonal crystal can be expressed as

\[
B = \frac{C^2}{C_s},
\]

where \( C^2 = C_{33}(C_{11} + C_{12}) - 2C_{13}^2 \). When \( R \) is close to zero (that is, when the volume dependence of the \( (c/a)_0 \) is very small), \( B = \frac{2}{9}(C_{11} + C_{12} + 2C_{13} + C_{33}/2) \).

Then, we need to make another set of four independent volume deformations. Here, we choose the two deformations employed for the cubic crystal, i.e., the Equation (2.47), corresponding to the energy change of \( \Delta E(\delta) = V(C_{11} - C_{12})\delta^2 + O(\delta^4) \) and \( \Delta E(\delta) = 2VC_{66}\delta^2 + O(\delta^4) \). For
other two deformations, we choose the volume-conserving orthorhombic and monoclinic deformations, namely

\[
\begin{pmatrix}
1 & 0 & \delta \\
0 & \frac{1}{1-\delta^2} & 0 \\
\delta & 0 & 1
\end{pmatrix}
\quad \text{and} \quad
\begin{pmatrix}
1 + \delta & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & \frac{1}{1+\delta}
\end{pmatrix},
\]

(2.51)

which leads to the energy change of \( \Delta E(\delta) = 2V C_{44} \delta^2 + O(\delta^4) \) and \( \Delta E(\delta) = \frac{1}{2} V (C_{11} - 2C_{13} + C_{33}) \delta^2 + O(\delta^4) \), respectively.

### 2.3.3 Debye Temperature

On a large scale, a polycrystalline material can be considered as quasi-isotropic or isotropic, and it is completely described by the bulk modulus \( B \) and the shear modulus \( G \). Depending on the symmetry of the structure, \( B \) and \( G \) have the different expressions for different crystals. For a cubic lattice the polycrystalline bulk modulus is identical with the single-crystal bulk modulus. For the shear modulus we adopt the arithmetic Hill average \( G = (G_R + G_V)/2 \),\(^{25}\) where the Reuss and Voigt bounds are given in terms of the single-crystal elastic constants, \( i.e. \),

\[
G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad \text{and} \quad G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}. \tag{2.52}
\]

For a tetragonal lattice, which is similar to the case of hexagonal one, the polycrystalline bulk modulus is also described by the arithmetic Hill average \( B = (B_R + B_V)/2 \).\(^{25}\) For \( B_R \) and \( B_V \), we have

\[
B_R = \frac{C_2}{C_5} \quad \text{and} \quad B_V = \frac{2(C_{11} + C_{12}) + 4C_{13} + C_{33}}{9}. \tag{2.53}
\]

and \( G_R \) and \( G_V \)

\[
G_R = \frac{5C_{44}C_{66}C_5}{2(C_{44} + C_{66})C_5^2 + 3B_V C_{44}C_{66}} \quad \text{and} \quad G_V = \frac{12C_{44} + 12C_{66} + C_5}{30}. \tag{2.54}
\]

The longitudinal sound velocity is given by \( \rho u_L^2 = B + (4G)/3 \), and the transversal velocity \( \rho u_T^2 = G \). In these expressions \( \rho \) is the average density. Using the average sound velocity given by \( 3u_m^{-3} = u_L^{-3} + 2u_T^{-3} \), we obtain the elastic Debye temperature for a polycrystalline material as

\[
\Theta = \left( \frac{\hbar}{k_B} \right) \left( \frac{6\pi^2}{V} \right)^{1/3} u_m, \tag{2.55}
\]
where $V$ is the average atomic volume, and $h$ and $k_B$ are Planck’s and Boltzmann’s constants, respectively.

### 2.3.4 Heisenberg Model

In Heusler alloys with localized magnetic moments, the Curie temperature ($T_C$) may be estimated using the well-established Heisenberg model in combination with the Mean Field Approximation (MFA). Within the Heisenberg model, the interatomic exchange interactions are described in terms of the classical Heisenberg Hamiltonian

$$H_{\text{eff}} = -\sum_{\mu,\nu} \sum_{\mathbf{R},\mathbf{R}'} J^\mu_\mathbf{R}\mathbf{R}^\nu_\mathbf{R}\mathbf{R}' s^\mu_\mathbf{R} s^\nu_\mathbf{R}' \quad \mu\mathbf{R} \neq \nu\mathbf{R}', \quad (2.56)$$

where $J^\mu_\mathbf{R}\mathbf{R}^\nu$ are the intrasite exchange integrals, the indices $\mu$ and $\nu$ represent different sublattices, $\mathbf{R}$ and $\mathbf{R}'$ are the lattice vectors specifying the atoms within sublattices, and $s^\mu_\mathbf{R}$ and $s^\nu_\mathbf{R}'$ are the unit vector pointing in the direction of the magnetic moment at site $(\mu, \mathbf{R})$ and $(\nu, \mathbf{R}')$, respectively. In Equation (2.56) the size of the magnetic moments is included in the exchange interaction parameters.

Within the mean-field solution of the Heisenberg model, $T_C$ is obtained by solving the system of coupled equations\textsuperscript{20, 59}

$$\langle s^\mu \rangle = \frac{2}{3k_B T} \sum_\nu J^\mu_0 \langle s^\nu \rangle, \quad (2.57)$$

where $J^\mu_0 \equiv \sum_\mathbf{R} J^\mu_0\mathbf{R}$ is the effective exchange parameter, and $\langle s^\mu \rangle$ and $\langle s^\nu \rangle$ are the average $z$ component of $s^\mu_\mathbf{R}$ and $s^\nu_\mathbf{R}'$, respectively. Equation (2.57) has non-trivial solutions if the corresponding determinant is zero, i.e.

$$\text{Det} \{J - TI\} = 0, \quad (2.58)$$

where the matrix elements are $J^\mu_\nu = (2/3k_B) J^\mu_0 \nu$ and $I^\mu_\nu = \delta^\mu_\nu$ (Kronecker delta). The largest eigenvalue of the Equation (2.58) gives the magnetic transition temperature.\textsuperscript{20, 59} In the present application, the exchange interactions for cubic and tetragonal alloys were calculated using the magnetic force theorem\textsuperscript{60} implemented in the EMTO method.\textsuperscript{25}
3. Results and Discussion

In the present work, we have performed a series of calculations and analysis on both Ni-Mn-Ga and In-Tl shape memory alloys by using the EMTO-CPA method. For Ni-Mn-Ga alloys, first the equilibrium properties of the stoichiometric Ni$_2$MnGa alloy in the cubic phase are examined, then the site occupancy, elastic properties and phase stability of off-stoichiometric cubic Ni-Mn-Ga alloys are investigated in details. In addition, the magnetic properties of Mn excess Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ and Ni excess Ni$_{2+y}$Mn$_{1-x}$Ga families are studied. For In-Tl binary alloy, we calculated the composition dependence of the lattice parameter, elastic constants, the total energy in both parent and martensitic phases, and the electronic structure. Then, based on the obtained results, the correlation between their composition dependence and the phase stability is explored. The results of the above works have been published in the attached four papers. In this section, I will briefly present and discuss the main results.

3.1 Elastic and Magnetic Properties of Ni-Mn-Ga Alloys

3.1.1 Properties of Ni$_2$MnGa

![Geometric structure of $L2_1$-Ni$_2$MnGa.](image)

Figure 3.1 Geometric structure of $L2_1$-Ni$_2$MnGa.

The standard stoichiometric Ni$_2$MnGa in parent phase possesses cubic $L2_1$ structure, where Ni atoms locate at the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ sublattices, Mn atoms occupy the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ sublattice, and Ga atoms occupy the $(0, 0, 0)$ sublattice as shown in Figure 3.1.
In order to test the accuracy and reliability of our calculations, we first compare the equilibrium lattice parameter and elastic constants of the stoichiometric Ni$_2$MnGa with other available theoretical and experimental values.\textsuperscript{12, 61-66}

Table 3.1 Equilibrium lattice parameter ($a$) (in Å), bulk modulus ($B$) (in GPa), shear moduli ($C'$ and $C_{44}$) (in GPa), and the total magnetic moment ($\mu_0$) (in $\mu_B$) per unit cell of cubic Ni$_2$MnGa, in comparison with other theoretical and experimental data.

<table>
<thead>
<tr>
<th>Method</th>
<th>$a$</th>
<th>$B$</th>
<th>$C'$</th>
<th>$C_{44}$</th>
<th>$\mu_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMTO ($spd$, GGA-PBE)</td>
<td>5.8922</td>
<td>151.9</td>
<td>15.9</td>
<td>99.4</td>
<td>4.05</td>
</tr>
<tr>
<td>EMTO ($spdf$, GGA-PBE)</td>
<td>5.8208</td>
<td>157.5</td>
<td>7.9</td>
<td>107.0</td>
<td>3.96</td>
</tr>
<tr>
<td>EMTO ($spdf$, LSDA)</td>
<td>5.6563</td>
<td>202.2</td>
<td>11.7</td>
<td>134.7</td>
<td>-</td>
</tr>
<tr>
<td>PP\textsuperscript{12, 61}</td>
<td>5.8368</td>
<td>151.6</td>
<td>6.3</td>
<td>102.0</td>
<td>4.27</td>
</tr>
<tr>
<td>FLAPW\textsuperscript{62}</td>
<td>5.8104</td>
<td>156.0</td>
<td>-</td>
<td>-</td>
<td>4.09</td>
</tr>
<tr>
<td>Exp.</td>
<td>5.8250\textsuperscript{63}</td>
<td>146\textsuperscript{64}, 106\textsuperscript{65}</td>
<td>4.5\textsuperscript{64}, 22\textsuperscript{65}, 6.5\textsuperscript{66}</td>
<td>103\textsuperscript{64}, 102\textsuperscript{65}, 98\textsuperscript{66}</td>
<td>4.17\textsuperscript{64}</td>
</tr>
</tbody>
</table>

Table 3.1 lists the equilibrium lattice parameter ($a$), the bulk modulus ($B$), the shear moduli ($C'$ and $C_{44}$), and the total magnetic moment ($\mu_0$) per unit cell of cubic Ni$_2$MnGa. Within the GGA-PBE, the theoretical lattice constant (5.8922Å), calculated with the frozen-core approximation and $spd$ basis-set, is larger than those from experiment (about 1%)\textsuperscript{63} as well as from the first-principles plane-wave pseudopotential (PP)\textsuperscript{12} and full-potential linearized augmented plane-wave (FLAPW) calculations.\textsuperscript{62} If the soft-core approximation and $spdf$ basis-set are used, the obtained lattice parameter (5.8208Å) is in a better agreement with the experimental value (5.8250Å)\textsuperscript{63} and theoretical values from other studies. In addition, with the soft-core approximation and $spdf$ basis-set, a more accurate value for the shear modulus $C'$ (7.9GPa) is obtained as well, which is very close to that of the PP calculations as well as most of the experimental values (4.5GPa\textsuperscript{64} and 6.5GPa\textsuperscript{66}). As expected, LSDA yields smaller lattice parameter (5.6563Å) and larger bulk modulus than the GGA-PBE since LSDA generally overestimates the binding between the atoms.

In the present work, all of the calculations concerning of the Ni-Mn-Ga-based alloys were carried out by using the GGA-PBE exchange-correlation functional. Except for the calculations of Ni$_{2+y}$Mn$_{1-x}$Ga, where the relatively large $spdf$ basis set and soft-core approximation were
chosen for a higher accuracy, for all of other off-stoichiometric Ni$_2$MnGa alloys studied in our work, the $spd$ basis set and the frozen-core approximation were used in order to reduce the computational load.

### 3.1.2 Site Occupancy of Off-stoichiometric Ni$_2$MnGa

For the off-stoichiometric Ni$_2$MnGa, we first determine the stable site occupancy of Ni, Mn, and Ga atoms. Then, for the different atoms occupying on the same sublattice, we assume that they distribute randomly on the sublattice, and the random distribution of the atoms is taken into account by using the CPA.$^{24,26,27}$

The stable site occupancy is determined by comparing the free energies per atom of the alloy with different site occupations. In our calculations, the free energy takes into account the chemical mixing entropy but neglects the lattice vibrations and electronic temperature effects since their contribution is typically two orders of magnitude smaller than that from the electronic energy. Thus, the free energy is expressed as

$$F = E + \frac{1}{4}k_B T \sum_{i=1}^{4} \left[ x_i \ln x_i + (1 - x_i) \ln(1 - x_i) \right],$$

where $E$ is the electronic energy per atom, $x_i$ is the concentration of the sublattice $i$, $k_B$ is the Boltzmann constant, and $T$ is the temperature.

In the present work, we consider nine types of off-stoichiometric Ni$_2$MnGa alloys with 12 different compositions as shown in the Table 3.2. In this table, the electronic energy ($E$) and free energy ($F$) of these alloys with different site occupations relative to that with the normal site occupation (the excess atoms of the rich component simply occupy the sublattice of the deficient one) are listed. It is clear that the relative stability of the site occupations determined in this work is reasonable since the stability sequences for Ni$_{2+2x}$Mn$_{1-x}$Ga$_{1-x}$ (type 1), Ni$_{2-2x}$Mn$_{1+3x}$Ga$_{1-x}$ (type 2), and Ni$_{2-2x}$Mn$_{1-x}$Ga$_{1+3x}$ (type 3) alloys are shown not to change by varying the composition ($x=0.05, 0.10$). Moreover, the difference between relative electronic energy ($\Delta E$) and free energy ($\Delta F$) for an alloy with the same site-occupation configuration is very small at 300K. Therefore,
in the temperature range of interest, the mixing entropy cannot change the relative stability of the site occupations, which means that the electronic energy comparison is actually sufficient to determine the stable site occupancy.

As shown in Table 3.2, the normal site occupation for most of the off-stoichiometric alloys is more stable than the abnormal one (the excess atoms of the rich component occupy the sublattice of the component at standard composition instead of the sublattice of the component in deficiency) except for the case of Ni$_{2-2x}$Mn$_{1-x}$Ga$_{1+3x}$ (type 3) and Ni$_{2-3x}$MnGa$_{1+x}$ ($x=0.10$, type 6). In the Ni$_{2-2x}$Mn$_{1-x}$Ga$_{1+3x}$ alloy, the excess Ga atoms do not occupy evenly the two Ni sublattice and the Mn sublattice but occupy solely the Mn sublattice whereas some of the Mn atoms move to the Ni sublattices. Similarly, in the Ni$_{2-3x}$MnGa$_{1+x}$ ($x=0.10$) alloy, the excess Ga atoms again prefer the Mn sublattice although it is Ni instead of Mn that is in deficiency, which is line with the most recently determined site occupancy of Ni$_{2-3x}$MnGa$_{1+x}$ by Sanchez-Alarcos et al. $^6$7

In this work, it is confirmed that the site occupancy of the off-stoichiometric Ni$_2$MnGa is strongly controlled by the complex interaction between the chemical and magnetic effects because the atoms (mainly Mn) exhibit different magnetic moments when occupying different sublattices: on the Mn, Ni, and Ga sublattices, the magnetic moments of a Mn atom are roughly $3.5 \mu_B$, $-2.5 \mu_B$ and $\pm 3.2 \mu_B$ (+ and – means the atom can be ferromagnetic or antiferromagnetic coupling with that of the Mn atoms on the Mn sublattice), respectively, and consequently, the magnetic property of the alloy also changes with different site-occupancy. Comparing the relative electronic energies $\Delta E$ and $\Delta E'$ calculated, respectively, with and without spin polarization, it is seen that, for the same alloy, if there exist Mn atoms occupying different sublattices in different site-occupation configurations, $\Delta E$ differs dramatically from $\Delta E'$, indicating that the magnetic effect on the site occupancy is very strong. For some of the alloys, the magnetic effect even alters the stability sequence of the site occupations. For example, the abnormal site occupation of the Ni$_{2+x}$MnGa$_{1-x}$ ($x=0.10$, type 4) and Ni$_{2}$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.10$, type 8) is more stable than the normal one from nonspin-polarized calculations but the latter becomes more stable from spin-polarized calculations. However, for the alloy in which there is no Mn atom changing its sublattice in different site-occupation configurations (e.g., Ni$_2$Mn$_{1-x}$Ga$_{1+x}$,
Table 3.2: Relative electronic energy $\Delta E$ and $\Delta E'$ (in mRy), and free energy $\Delta F$ (in mRy) of the off-stoichiometric cubic Ni$_2$MnGa to that of the alloy with normal site occupancy configuration, at temperature of 300K. $\Delta E'$ is the relative electronic energy from nonspin-polarized calculations but using the spin-polarized equilibrium lattice constants.

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition</th>
<th>Site occupancy</th>
<th>$\Delta E$</th>
<th>$\Delta F$</th>
<th>$\Delta E'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni$<em>{2.12}$Mn$</em>{1.52}$Ga$_{0.4}$ (x=0.05)</td>
<td>Ni$<em>2$(Mn$</em>{0.99}$Ni$<em>{0.01}$)(Ga$</em>{0.90}$Ni$_{0.10}$)</td>
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<td>Ni$<em>2$(Mn$</em>{0.88}$Ga$<em>{0.12}$)(Ga$</em>{0.88}$Ni$_{0.12}$)</td>
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<td>0.06</td>
<td>0.01</td>
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<tr>
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<td>0.32</td>
<td>0.26</td>
<td>-0.26</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{2.12}$Mn$</em>{1.52}$Ga$_{0.4}$ (x=0.10)</td>
<td>Ni$<em>2$(Mn$</em>{0.90}$Ni$<em>{0.10}$)(Ga$</em>{0.88}$Ni$_{0.12}$)</td>
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<tr>
<td></td>
<td></td>
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<td>0.59</td>
<td>-0.50</td>
</tr>
<tr>
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<td>Ni$<em>{2.2}$Mn$</em>{1.8}$Ga$_{0.3}$ (x=0.05)</td>
<td>(Ni$<em>{1.90}$Mn$</em>{0.10}$)Mn(Ga$<em>{0.88}$Mn$</em>{0.12}$)</td>
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<td>0</td>
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<tr>
<td></td>
<td></td>
<td>(Ni$<em>{1.45}$Mn$</em>{0.55}$)Mn(Ga$<em>{0.88}$Ni$</em>{0.12}$)</td>
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<td>0.22</td>
<td>-0.59</td>
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<td>Ni$<em>{2.2}$Mn$</em>{1.8}$Ga$_{0.3}$ (x=0.10)</td>
<td>(Ni$<em>{1.90}$Ga$</em>{0.10}$)Mn(Ga$<em>{0.88}$Mn$</em>{0.15}$)</td>
<td>1.67</td>
<td>1.56</td>
<td>2.71</td>
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<td>Ni$<em>{2.3}$Mn$</em>{1.7}$Ga$_{0.1}$ (x=0.05)</td>
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<td>-0.78</td>
<td>-3.25</td>
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<tr>
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<td>0.87</td>
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<td>(Ni$<em>{1.70}$Ga$</em>{0.30}$)(Mn$<em>{0.88}$Ga$</em>{0.15}$)Ga</td>
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<tr>
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<td>-1.66</td>
<td>-6.53</td>
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<td>1.69</td>
<td>1.60</td>
<td>1.08</td>
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<td>4</td>
<td>Ni$<em>{2.1}$MnGa$</em>{0.9}$ (x=0.10)</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
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<td></td>
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<td>0.49</td>
<td>-0.52</td>
</tr>
<tr>
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<td>Ni$<em>{2.1}$Mn$</em>{0.9}$Ga (x=0.10)</td>
<td>Ni$<em>2$(Mn$</em>{0.90}$Ni$_{0.10}$)Ga</td>
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<td>0</td>
<td>0</td>
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<td></td>
<td></td>
<td>Ni$<em>3$(Mn$</em>{0.80}$Ga$<em>{0.20}$)(Ga$</em>{0.88}$Ni$_{0.12}$)</td>
<td>0.59</td>
<td>0.44</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>Ni$<em>{2.1}$MnGa$</em>{0.9}$ (x=0.10)</td>
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<td>0</td>
<td>0</td>
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<tr>
<td></td>
<td></td>
<td>(Ni$<em>{1.90}$Mn$</em>{0.10}$)Mn(Ga$<em>{0.88}$Ga$</em>{0.12}$)Ga</td>
<td>-0.62</td>
<td>-0.77</td>
<td>-3.02</td>
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<td>7</td>
<td>Ni$<em>{2.1}$Mn$</em>{0.9}$Ga (x=0.10)</td>
<td>(Ni$<em>{1.90}$Mn$</em>{0.10}$)MnGa</td>
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<td>0</td>
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<tr>
<td></td>
<td></td>
<td>(Ni$<em>{1.90}$Ga$</em>{0.10}$)(Ga$<em>{0.88}$Mn$</em>{0.12}$)</td>
<td>1.86</td>
<td>1.71</td>
<td>2.70</td>
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<tr>
<td>8</td>
<td>Ni$<em>{2.1}$Mn$</em>{0.9}$Ga (x=0.10)</td>
<td>Ni$<em>2$Mn(Ga$</em>{0.90}$Mn$_{0.10}$)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ni$<em>{1.90}$Mn$</em>{0.10}$)Mn(Ga$<em>{0.88}$Ni$</em>{0.12}$)</td>
<td>0.59</td>
<td>0.40</td>
<td>-1.28</td>
</tr>
<tr>
<td>9</td>
<td>Ni$<em>{2.1}$Mn$</em>{0.9}$Ga (x=0.10)</td>
<td>Ni$<em>2$(Mn$</em>{0.90}$Ga$_{0.10}$)Ga</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ni$<em>{1.90}$Ga$</em>{0.10}$)(Mn$<em>{0.88}$Ni$</em>{0.12}$)Ga</td>
<td>1.96</td>
<td>1.78</td>
<td>1.44</td>
</tr>
</tbody>
</table>
$x=0.10$, and Ni$_{2+x}$Mn$_{1-x}$Ga, $x=0.10$), the difference between $\Delta E$ and $\Delta E'$ is much smaller than that in the case discussed above. The magnetic effect is complicated and composition-dependent. For most of these alloys involved in this study, $\Delta E$ is larger than $\Delta E'$, which means that the magnetic effect tends to stabilize the normal site-occupation configuration.

### 3.1.3 Elastic Properties of Off-stoichiometric Ni$_2$MnGa

With the established site occupancy, we calculated the elastic moduli of these off-stoichiometric Ni$_2$MnGa alloys. It was found that both the bulk modulus $B$ and the shear elastic constants $C'$ and $C_{44}$ are highly dependent on the electron-to-atom ratio ($e/a$). This may be due to the fact that both elastic constants and $e/a$ are believed to be related to the MT behavior of the Ni$_2$MnGa shape memory alloy, and consequently there should also be certain intrinsic connection between them. Figure 3.2 shows the relationship between the bulk as well as the shear moduli with the $e/a$ ratio of these off-stoichiometric Ni$_2$MnGa alloys. We see that the general trend is that the bulk modulus increases with the $e/a$. The $C'$ and $C_{44}$ change oppositely with increasing $e/a$: $C'$ decreases but $C_{44}$ increases. The bulk modulus is changed more significantly at the low $e/a$ side than at the high $e/a$ side, which is an opposite behavior to the one shown by the $C'$ and $C_{44}$.

![Figure 3.2 Bulk (left panel) and shear (right panel) moduli of off-stoichiometric Ni$_2$MnGa alloys with respect to $e/a$ ratio. The vertical and horizontal lines within the figures refer to the elastic moduli and $e/a$ ratio of the standard stoichiometric Ni$_2$MnGa. The fitting curves are to guide the view.](image-url)
It is noted that there are three data points (the green open symbols in figure) heavily deviating from the general trend of the elastic moduli with respect to the $e/a$ ratio. This is true especially for $B$. These three data points correspond to $\text{Ni}_{2-2x}\text{Mn}_{1+3x}\text{Ga}_{1-x}$ ($x=0.05$, 0.10, type 2) and $\text{Ni}_{2}\text{Mn}_{1+x}\text{Ga}_{1-x}$ ($x=0.10$, type 8). We suggest that the deviation might be due to the magnetic interaction between the Mn atoms on the Ga sublattice and those on the Mn sublattice since all the three alloys have their excess Mn atoms located on the Ga sublattice. A direct confirmation of this point is a difficult task. However, we note that the deviation disappears if the nonspin-polarized calculations are performed. The bulk modulus increases monotonously if spin-polarization is neglected, with increasing $e/a$ ratio, showing values of 184.5GPa ($\text{Ni}_{2-2x}\text{Mn}_{1+3x}\text{Ga}_{1-x}$ ($x=0.10$)), 186.3GPa ($\text{Ni}_{2}\text{Mn}_{1+x}\text{Ga}_{1-x}$), and 190.0GPa ($\text{Ni}_{2}\text{Mn}_{1+x}\text{Ga}_{1-x}$ ($x=0.10$)). This result demonstrates that magnetic interactions indeed play an important role in the relationship between the elastic modulus and $e/a$. In the next section 3.2, we will study in detail the effect of the magnetic coupling on the elastic properties of Mn-rich and Ga-deficient alloys.

3.1.4 Phase Stability

In the present work, the phase stability of the Ni-Mn-Ga-based alloy is mainly investigated through the correlation between the composition dependence of $C'$ and $T_M$. We collect the experimental $T_M$ values of some off-stoichiometric Ni$_2$MnGa alloys. These alloys match roughly the studied nine types of off-stoichiometric Ni$_2$MnGa although their compositions may slightly deviate from those studied in our work. In Figure 3.3, the experimental $T_M$ data are shown along with the $C'$ and $e/a$ ratio of these alloys. The $C'$ of the alloys not included in the present calculations are obtained through linear interpolation or extrapolation from the calculated ones. In the right panel of the Figure, $T_M$ goes up with increasing $e/a$ ratio as it has been noted previously in literature. From the left panel of the Figure, it is seen that the alloy of larger $C'$ generally possesses lower $T_M$ with the only exception for Ni$_2$Mn$_{1+2}\text{Ga}_{1-x}$ ($x=0.20$, the red triangle in the Figure). Therefore, in addition to the $e/a$ ratio, the $C'$ generally can also be taken as a measure for the composition-dependent $T_M$, the larger $C'$ is, the lower $T_M$ generally is. Especially for the alloys with the same composition but with different long-range atomic order (site
occupancy) corresponding to different heat treatment history, the $C'$ is a better measure since in this case, the $e/a$ ratio is exactly the same but the $C'$ changes.

**Figure 3.3** Experimental martensitic transformation temperature ($T_M$) with respect to the shear modulus $C'$ (left panel) and $e/a$ ratio (right panel) of the off-stoichiometric Ni$_2$MnGa alloys. The vertical lines within the figures refer to the $C'$ and $e/a$ ratio, and the horizontal lines refer to the $T_M$ of the standard stoichiometric Ni$_2$MnGa.

**Figure 3.4** Theoretical formation energy difference between the $L2_1$ and $\beta'''$ phases and experimental martensitic transition temperature $T_M$ (Ref. 3) of Ni$_{2+x}$Mn$_{1-x}$Ga ($0 \leq x \leq 0.2$) alloys with respect to the concentration $x$ (and $e/a$ ratio, upper abscissa).
In our work, we also try to determine the phase stability from the formation energy difference between the austenite and martensite ($\Delta E_{AM}$) and the electronic structure with respect to the composition. For example, in $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ ($0 \leq x \leq 0.2$) alloys, both the $\Delta E_{AM}$ and $T_M$ increase almost linearly with increasing $x$ as shown in Figure 3.4, which implies increasing stability of the $\beta'''$ phase relative to the $L2_1$ phase with increasing $x$. Furthermore, by analyzing the Density of States (DOS) of both the two phases, the more stability of $\beta'''$ phase than the $L2_1$ phase is ascribed to the stronger covalent bond in the former phase than the latter phase, and with increasing $x$ the covalent bond between minority spin states of Ni and Ga becomes gradually weakened, which accounts for the decreasing stability of the $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ alloy in both the two phases with the Ni excess.

3.2 Magnetic Properties of Ni-Mn-Ga Alloys

3.2.1 Magnetic Properties of Mn excess $\text{Ni}_2\text{Mn}_{1+x}\text{Ga}_{1-x}$

In the section 3.1, it has been demonstrated that for the Mn-rich and Ga-deficient Ni-Mn-Ga-based alloys, the excess Mn atoms prefer to occupy the Ga sublattice, and depending on the compositions of the alloys, the magnetic moment of an Mn antisite on Ga sublattice (denoted as $\text{Mn}_{\text{Ga}}$) can be parallel (for $\text{Ni}_2\text{Mn}_{1+x}\text{Ga}_{1-x}$, $x=0.10$) or antiparallel (for $\text{Ni}_{2-2x}\text{Mn}_{1+3x}\text{Ga}_{1-x}$, $x=0.10$) to those of the Mn atoms on Mn sublattice (denoted as $\text{Mn}_{\text{Mn}}$). Based on the determined site occupancy and magnetic ordering, the calculation of the elastic modulus shows that the bulk moduli $B$ of these types of alloys do not fit to the picture described by the general $e/a$-$B$ relationship for the off-stoichiometric $\text{Ni}_2\text{MnGa}$ alloys (as shown in the left panel of Figure 3.2), whereas $B$ from paramagnetic calculations follows the general $e/a$-$B$ relationship. In addition, the shear modulus $C^\prime$ of $\text{Ni}_2\text{Mn}_{1+x}\text{Ga}_{1-x}$ ($x=0.10$) with parallel $\text{Mn}_{\text{Ga}}$-$\text{Mn}_{\text{Mn}}$ magnetic coupling is also found to be an exception of the general $C^\prime$-$T_M$ relationship (as shown in the right panel of Figure 3.2). These results inspired us to carry out a more detailed investigation on the magnetic coupling between $\text{Mn}_{\text{Ga}}$ and $\text{Mn}_{\text{Mn}}$ and its effect on the elastic moduli of the Mn-rich but Ga-deficient alloys. Thus, in our work, the Mn excess $\text{Ni}_2\text{Mn}_{1+x}\text{Ga}_{1-x}$ type of alloy was selected to study the magnetism of the Ni-Mn-Ga shape memory alloys.
We first calculated the equation of states of Ni$_{2}$Mn$_{1+x}$Ga$_{1-x}$ using full-potential linearized augmented plane-wave (FPLAPW) and EMTO with both the supercell (SC) and CPA two methods. The FPLAPW calculations were carried out by using the WIEN2K package, where the muffin-tin radii for Ni, Mn, and Ga were set to 2.2, 2.2, and 2.1 a.u., respectively, the plane-wave cutoff was 16Ry, the Brillouin zone was sampled by a $6 \times 6 \times 6$ $k$-point mesh, and the exchange-correlation was described by the GGA-PBE.

Figure 3.5 (a) and 3.5 (b) show the curves of the total energy $E$ versus volume $V$ of Ni$_{2}$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.25$) from both EMTO (SC) and FPLAPW calculations. It is seen that both methods yield similar equation of states. At or below equilibrium volume the antiparallel (AP) state is slightly more stable than the parallel (P) state. The latter becomes more stable only if the volume is expanded. The enthalpy with respect to pressure was also calculated. Comparing the enthalpies of the P and AP states, we obtain that the AP to P transition occurs at the pressure of about -10GPa (FPLAPW calculations) and the EMTO calculations predict a slightly smaller transition pressure.

![Equation of states for Ni$_{2}$Mn$_{1+x}$Ga$_{1-x}$](image)

Figure 3.5 Equation of states of Ni$_{2}$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.25$). (a) and (b) for the energy versus volume from EMTO and FPLAPW calculations, respectively.

Figure 3.6 shows the curves of total energy versus volume of Ni$_{2}$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.10$) with both P and AP states from EMTO-CPA calculations. Similar to the high-concentration ($x=0.25$) case, the AP state is slightly more stable than the P state when the system is compressed whereas the latter is more stable when the system is expanded. However, the energy difference between the
two states is much smaller compared to that of the high-concentration off-stoichiometric alloys. At the equilibrium state, the P and AP states are almost degenerated with an energy difference close to the accuracy of the employed first-principles method.

![Figure 3.6](image_url)

**Figure 3.6** Total energy versus volume of the Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.10$) alloy with parallel and antiparallel Mn$_{Ga}$-Mn$_{Mn}$ magnetic couplings.

The equilibrium properties of Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ ($x=0, 0.10, 0.25$) are summarized in Table 3.3. The lattice constants of FPLAPW calculations are smaller than those of the EMTO and vice versa for the bulk modulus, which is due to the relatively small basis set and frozen-core approximation adopted in the EMTO calculations as discussed in our previous work. For both first-principles methods, the bulk modulus as well as the lattice constant of the alloys with AP state is slightly smaller than that of the P state. This, to some extent, might be related to the change in the magnetic moment from the P to AP state. As shown in the Table 3.3, the magnetic moment of Ni atom decreases from the P to AP state, whereas those of Mn and Ga atoms do not change significantly excluding the magnetic moment of the Mn$_{Ga}$ atom, which alters its orientation. Thus, the total magnetic moment for the AP state is much smaller than that for P state. When $x=0.25$, the AP state is slightly (with a fraction of millirydberg per atom) more stable than the P state. Since with $x$ increasing, Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ alloy becomes gradually preferring the AP state with respect to the P state, i.e., the ferromagnetic coupling between Mn$_{Ga}$ and Mn$_{Mn}$ gradually transforms to the antiferromagnetic coupling with increasing concentration of excess Mn, the
The saturation magnetization of the alloy decreases accordingly, which is in agreement with the experiments of Enkovaara et al.\textsuperscript{75} and Albertini et al.\textsuperscript{73}

Table 3.3 Properties of Ni\textsubscript{2}Mn\textsubscript{1-x}Ga\textsubscript{x} (\textit{x}=0.00, 0.10, and 0.25) alloys with parallel (P) and antiparallel (AP) magnetic couplings between Mn atoms on the Ga sublattice (Mn\textsubscript{Ga}) and on the Mn sublattice (Mn\textsubscript{Mn}). The \textit{a}\textsubscript{0} (in Å) is the equilibrium lattice constant, \(\Delta E = E_{\text{AP}} - E_{\text{P}}\), where \(E_{\text{AP}}\) and \(E_{\text{P}}\) are the energies (in mRy/atom) of the alloys with antiparallel and parallel Mn\textsubscript{Ga} and Mn\textsubscript{Mn} magnetic couplings, respectively. The \(\mu_{\text{0}}, \mu_{\text{X}}\) (X=Ni, Mn, and Ga), and \(\mu'_{\text{Mn}}\) (for Mn\textsubscript{Ga}) are the total and local magnetic moments (in \(\mu_{\text{B}}\)). The \(B_0, C^\prime,\) and \(C_{44}\) are the bulk and shear moduli (in GPa). The \(e/a\) is the number of valence electrons per atom.

<table>
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<th>Method</th>
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<th>(\Delta E)</th>
<th>(\mu_0)</th>
<th>(\mu_{\text{Ni}})</th>
<th>(\mu_{\text{Mn}})</th>
<th>(\mu_{\text{Ga}})</th>
<th>(\mu'_{\text{Mn}})</th>
<th>(B_0)</th>
<th>(C^\prime)</th>
<th>(C_{44})</th>
<th>(e/a)</th>
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<td>0.50</td>
<td>3.38/3.42</td>
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<td>3.52</td>
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<td>(x=0.25)(AP)</td>
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<td>0.23</td>
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<td>16.0</td>
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<td>13.5</td>
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</tbody>
</table>

From P to AP state for Mn\textsubscript{Ga}, the change in the magnetic moment of Ni atoms can be explained by the density of states (DOS) of Ni atoms as shown in Figure 3.7. It is seen that, in the minority DOS for the P state, there exists a pseudogap at the energy around -1.5eV, which is mainly resulted from the hybridization \(\text{n}\) between the electronic states of Ni and Ga atoms. For the AP state, an additional state occurs at about -0.7eV in the pseudogap of the minority DOS, which is responsible for the decrease in the magnetic moment of Ni atoms from the P to AP state. This additional state represents the weakening of the hybridization between the states of Ni and Ga from P to AP state, and therefore, might result in the decreasing of both lattice constant and bulk modulus.
Figure 3.7 Density of states (DOS) of Ni atom in Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.25$) for both (a) parallel and (b) antiparallel Mn$_{Ga}$-Mn$_{Mn}$ magnetic couplings from FPLAPW calculations.

Based on the investigation on the magnetic coupling between Mn$_{Ga}$-Mn$_{Mn}$ of Ni$_2$Mn$_{1+x}$Ga$_{1-x}$, we examined the effect of the magnetic coupling on the elastic properties. The shear moduli $C'$ and $C_{44}$ as well as the bulk modulus $B$ of Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.10$) were calculated within the antiparallel Mn$_{Ga}$-Mn$_{Mn}$ magnetic coupling. The obtained $C'$ is 13.5GPa, $C_{44}$ is 100.6GPa, and $B$ is 147.9GPa for the AP state, in comparison with 16.0, 99.6, and 148.6GPa for the P state as listed in Table 3.3. Although the bulk modulus of Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.10$) with the AP state is still smaller than that of the ideal Ni$_2$MnGa, deviating significantly from the general $e/a$-$B$ relationship, the data points of the shear moduli, $C_{44}$ and $C'$, versus $e/a$ for Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.10$) with the AP state are closer to the fitting curves of those nine types of off-stoichiometric Ni$_2$MnGa-based alloys in Figure 3.2, and match better to the general $C_{44}$-$e/a$ and $C'$-$e/a$ relationships than those of the P state. On the other hand, within the AP state, the calculated $C'$ of Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.10$) is smaller than that of the perfect Ni$_2$MnGa, corresponding to a higher $T_M$ of Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ compared to that of the Ni$_2$MnGa, in line with the general $C'$- $T_M$ trend. Moreover, by a linear extrapolation of the $C'$-$x$ relationship determined by the $C'$ of Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.10$) and that of the ideal Ni$_2$MnGa, the $C'$ of Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.20$) of the AP state is evaluated to be 11.2GPa, and the $T_M$ versus $C'$ of Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ ($x=0.20$) with the AP state also fits the general $C'$- $T_M$ trend very well. This indicates that with the antiparallel Mn$_{Ga}$-Mn$_{Mn}$ magnetic coupling, the relationship $C'$- $T_M$ of Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ alloy is in line with the
general one for Ni$_2$MnGa-based alloys, in contrast to the case with the parallel Mn$_{Ga}$-Mn$_{Mn}$ magnetic coupling.

3.2.2 Magnetic Properties of Ni excess Ni$_{2+x}$Mn$_{1-x}$Ga

Recent experimental studies on off-stoichiometric Ni$_{2+x}$Mn$_{1-x}$Ga have shown that both transition temperatures, $T_M$ and $T_C$, are very sensitive to changes in the chemical composition as shown by the increase in $T_M$ and decrease in $T_C$ with Ni excess. Moreover, in the range of compositions $0.18 \leq x \leq 0.27$, the structural and magnetic transitions couple to each other. This makes this type of Ni-Mn-Ga alloys to possess some attractive properties such as giant magnetocaloric effect, magnetostriction, and magnetoresistance, which are important for the application of magnetic refrigeration or magnetostrictive transducers. Thus, in our work, the effect of Ni excess on the magnetic property, especially for the magnetic transition temperature of Ni$_{2+x}$Mn$_{1-x}$Ga type of alloy was also studied.

First, based on the EMTO-CPA total energy calculations, we analyze the composition dependence of the magnetic moments of Ni$_{2+x}$Mn$_{1-x}$Ga. It is found that the magnetic moment of the excess Ni atoms on the Mn sublattice (Ni$_{Mn}$) is ferromagnetically coupled to those of the Ni atoms on the Ni sublattice (Ni$_{Ni}$) and the Mn atom on the Mn sublattice. The magnetic splitting of Ni$_{Mn}$ is suppressed in a way that its magnetic moment is about half that of Ni$_{Ni}$. With increasing $x$, the magnetic moments of the Ni atoms decrease slightly whereas those of Mn and Ga remain almost unchanged. Thus, the total magnetic moment of the Ni$_{2+x}$Mn$_{1-x}$Ga decreases slowly with increasing concentration of the excess Ni.

Second, we investigate in detail the effect of Ni excess on the $T_C$ using the Heisenberg model in combination with the mean-field approximation. Figure 3.8 shows the composition dependence of our theoretical $T_C$ for the $L2_1$ and $\beta''$ phases of Ni$_{2+x}$Mn$_{1-x}$Ga ($0 \leq x \leq 0.36$), in comparison with the experimental results. It is shown that for both phases, $T_C$ decrease with increasing $x$. $T_C$ of the $\beta''$ phase is higher than that of the $L2_1$ phase. For the experimental data shown in the Figure, when $x<0.18$, the experimental transition temperature decreases almost linearly with increasing $x$. However, for $x>0.18$, the experimental $T_C$ value increases suddenly with increasing $x$. After
reaching a maximum at about $x=0.25$, it decreases again with $x$. This interesting experimental trend of $T_C$ can be understood qualitatively from the present results. For $x<0.18$, the $T_M$ is well below the $T_C$ so that the magnetic transition occurs in the $L2_1$ phase. Therefore, the $T_C$ of system corresponds to that of the $L2_1$ phase and decreases with increasing $x$, in line with the present finding. Since $T_M$ increases whereas $T_C$ decreases with increasing $x$, they become close to each other for $x\approx 0.18$. Around this composition, the austenite and martensite phases may coexist and thus the measured $T_C$ corresponds to a mixed rather than to a single phase. Since according to the present study the $T_C$ of the martensite phase is higher than that of the austenite $L2_1$ phase, it is understandable that the measured $T_C$ goes up with increasing $x$, i.e., with increasing content of the $\beta'''$ phase in the system. When $x$ exceeds 0.25, $T_M$ becomes higher than the $T_C$ and the magnetic transition occurs within the $\beta'''$ phase. Therefore, the measured $T_C$ corresponds solely to that of the martensite and decreases again with increasing $x$, in line with the present theory. In our work, we would like to point out the excellent agreement between the theoretical and experimental “jump” in the $T_C$ around $x\approx 0.18$.

![Figure 3.8](image)

**Figure 3.8** Theoretical $T_C$ values as a function of the Ni concentration in Ni$_{2+x}$Mn$_{1-x}$Ga ($0\leq x\leq 0.36$) alloys. Results are shown for both $L2_1$ (squares) and $\beta'''$ (spheres) structures. The experimental $T_C$ values are from Ref. 3.
3.3 Elastic Properties of In-Tl Alloys

3.3.1 Elastic Properties of Pure In

In order to establish the accuracy and reliability of our calculational method for the elastic constants of tetragonal crystal, the elastic constants of pure In and In-Tl binary shape memory alloy were also calculated in our work.

Table 3.4 Theoretical (present results obtained using the LDA, PBE and AM05 approximations) equilibrium lattice parameters (in Å), bulk modulus $B$ (in GPa) of pure fct and fcc In and hcp Tl. For comparison, the available theoretical results and experimental data are also included. PAW stands for projector augmented wave and PW91 is the exchange-correlation approximation by Perdew and Wang.\textsuperscript{43}

<table>
<thead>
<tr>
<th>Phase</th>
<th>Method</th>
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<th>$c$</th>
<th>$c/a$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
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<tr>
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<td></td>
<td>Exp.\textsuperscript{76}</td>
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<td>4.947</td>
<td>1.076</td>
<td>41.1</td>
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<td></td>
<td>PAW-LDA\textsuperscript{77}</td>
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<td>4.923</td>
<td>1.101</td>
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<td></td>
<td>PAW-PW91\textsuperscript{77}</td>
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<td>5.030</td>
<td>1.076</td>
<td>35.8</td>
</tr>
<tr>
<td></td>
<td>TB\textsuperscript{78}</td>
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<td>4.815</td>
<td>1.146</td>
<td>52.0</td>
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<td>-</td>
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</tr>
<tr>
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<td>PBE</td>
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<td>35.7</td>
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<tr>
<td></td>
<td>TB\textsuperscript{78}</td>
<td>4.651</td>
<td>-</td>
<td>-</td>
<td>52.0</td>
</tr>
<tr>
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<td>5.210</td>
<td>1.601</td>
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<td>5.416</td>
<td>1.583</td>
<td>31.0</td>
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<td>Exp.\textsuperscript{79}</td>
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<td>5.539</td>
<td>1.599</td>
<td>34.0</td>
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</table>

We first compare the equilibrium lattice parameter and elastic constants of pure In with other available theoretical and experimental values. Table 3.4 lists the equilibrium lattice parameters and bulk modulus of fcc and fct In and hcp Tl, in comparison with the other theoretical and
As expected, the LDA underestimates the lattice parameters and overestimates the bulk modulus for both fct and fcc In and hcp Tl. For fct In, PBE generates \( c/a \) (1.132) in better agreement with the experimental value (1.076) than AM05 (1.151). The AM05 \( c/a \) ratio, on the other hand, is in agreement with that of a tight-binding (TB) calculation (1.146) and only slightly larger than those from the experiments and the first-principles projector augmented wave (PAW) calculations. For hcp Tl, the PBE generates lattice parameters \( a \) and \( c \) in better agreement with experimental values than the LDA and AM05. However, the theoretical \( c/a \) values from all three functionals are close to each other, and in good agreement with the experimental measurement.

Table 3.5: Theoretical elastic constants (in GPa) and Debye temperature (\( \Theta \), in K) for pure fct and fcc In, respectively, in comparison with the available theoretical results and experimental data.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Method</th>
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<th>( C_{12} )</th>
<th>( C_{13} )</th>
<th>( C_{33} )</th>
<th>( C_{44} )</th>
<th>( C_{66} )</th>
<th>( C' )</th>
<th>( \Theta )</th>
</tr>
</thead>
<tbody>
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<td>42.9</td>
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<td>11.2</td>
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<td>6.8</td>
<td>136.5</td>
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<td>PBE</td>
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<td>28.3</td>
<td>30.7</td>
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<td>7.2</td>
<td>14.9</td>
<td>4.9</td>
<td>111.1</td>
</tr>
<tr>
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<td>AM05</td>
<td>49.1</td>
<td>37.3</td>
<td>38.8</td>
<td>46.6</td>
<td>6.6</td>
<td>15.7</td>
<td>5.9</td>
<td>113.1</td>
</tr>
<tr>
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<td>Exp. (298K) (^{80})</td>
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<td>39.4</td>
<td>40.4</td>
<td>44.3</td>
<td>6.5</td>
<td>12.2</td>
<td>2.5</td>
<td></td>
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<tr>
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<td>Exp. (300K) (^{81})</td>
<td>45.4</td>
<td>40.1</td>
<td>41.5</td>
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<td>12.1</td>
<td>2.7</td>
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<td>44.6</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>111.3</td>
</tr>
<tr>
<td></td>
<td>PAW-LDA (^{77})</td>
<td>69.6</td>
<td>36.2</td>
<td>46.2</td>
<td>57.5</td>
<td>13.7</td>
<td>17.6</td>
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<td>PAW-PW91 (^{77})</td>
<td>44.6</td>
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<td>TB (^{78})</td>
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<td>fcc-In</td>
<td>LDA</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>AM05</td>
<td>35.9</td>
<td>43.1</td>
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<td>13.0</td>
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<td>PAW-LDA (^{77})</td>
<td>42.4</td>
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<td>PAW-PW91 (^{77})</td>
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<td>5.5</td>
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</tr>
</tbody>
</table>
Table 3.5 presents the calculated elastic constants and Debye temperature ($\Theta$) of the fct and fcc In in comparison with those values from other theoretical calculations and experimental measurements.\textsuperscript{77,78,80,81} For both fct and fcc phases, the elastic constants from the AM05 are in between those obtained by the LDA and PBE. The PBE underestimates most of the elastic constants, except the $C_{44}$ and $C_{66}$, whereas the LDA overestimates seriously the $C_{66}$. In general, the AM05 elastic constants are in better agreement with those from experimental measurements at low temperature (77K).\textsuperscript{81} The largest error is only about 14\% for the $C_{13}$. In addition, the AM05 elastic Debye temperature for a polycrystalline In is about 113.1K, which is very close to the experimental value of 111.3K.\textsuperscript{81} Therefore, for the alloys we will present results obtained using the AM05 approximation only.

### 3.3.2 Elastic Properties of In-Tl Alloys

In order to investigate the composition dependence of elastic properties of In$_{1-x}$Tl$_x$ random alloys, first we calculate the equilibrium lattice parameters for both fct and fcc phases as a function of the composition. From the obtained results, it is found that for both fct and fcc In$_{1-x}$Tl$_x$, with increasing $x$, the $a$ increases almost linearly, whereas the $c/a$ ratio in fct In$_{1-x}$Tl$_x$ decreases. These trends of both the $a$ and $c/a$ ratio are just in accordance with the available experimental measurements.\textsuperscript{82,83}

Using the determined equilibrium lattice structures, we calculated the elastic constants of In$_{1-x}$Tl$_x$ ($0< x \leq 0.4$) alloys. Figures 3.9 and 3.10 show the elastic constants relative to those of the pure In for both fct and fcc phases, as a function of $x$. As shown in Figure 3.9, for the tetragonal phase, it is clear that these obtained relative changes of the six independent elastic constants are in accordance with the experimental results.\textsuperscript{84} The $C_{11}$, $C_{33}$, and $C_{66}$ decrease significantly with increasing $x$: for $x=0.4$, the $C_{11}$ is 20\% smaller than that of pure In whereas the $C_{33}$ and $C_{66}$ reduce about 15\%. The $C_{13}$ also decreases linearly with increasing $x$ but the decreasing is moderate compared to those shown by the $C_{11}$, $C_{33}$, and $C_{66}$: with $x$ up to 0.4, $C_{13}$ decreases only about 5\%. The variation of $C_{12}$ and $C_{44}$ with $x$ is quite small and non-linear: the $C_{12}$ decreases...
**Figure 3.9** The relative change of elastic constants of fct In$_{1-x}$Tl$_x$ (0$\leq$x$\leq$0.4) alloys as a function of $x$. The experimental results are from Ref. 84.

**Figure 3.10** The relative change of elastic constants of fcc In$_{1-x}$Tl$_x$ (0$\leq$x$\leq$0.4) alloys with the composition $x$. 
slightly with increasing \( x \) and remains almost constant with \( x \approx -0.25 \), whereas the \( C_{44} \) increases first slightly and then decreases with increasing \( x \) when \( x \approx -0.25 \).

Figure 3.10 shows the variation of the elastic constants of fcc \( \text{In}_{1-x}\text{Tl}_x \) against \( x \). It is seen that the \( C_{11} \) increases whereas the \( C_{12} \) decreases with increasing \( x \). The \( C_{44} \) increases first with \( x \) and then remains almost unchanged for \( x \approx -0.25 \).

### 3.3.3 Phase Stability

The relative stability between the fcc and fct In-Tl random alloys is investigated using four factors in our work. The first one is the composition dependence of the equilibrium lattice structure. The lattice parameter \( c/a \) ratio of the tetragonal phase has been related to the martensitic transition temperature \( T_M \) in some shape memory alloys such as Ni-Mn-Ga, where a larger \( |c/a-1| \) corresponds to a higher \( T_M \). The decrease of theoretical \( |c/a-1| \) value of \( \text{In}_{1-x}\text{Tl}_x \) with increasing \( x \) obtained in our work indicates that \( T_M \) should decrease accordingly. This is in line with the experiments showing that the \( T_M \) of \( \text{In}_{1-x}\text{Tl}_x \) decreases from about 400K to 0K with \( x \) increasing from about 0.2 to 0.3.

Second, the present calculations reproduce well the experimental trends of the \( C' \) against the compositions for both phases as shown in Figure 3.11: the \( C' \) of the fct phase decreases whereas the \( C' \) of the fcc phase increases with increasing \( x \), and at 0K, the fcc phase becomes mechanically stable for \( x \approx -0.30 \) since \( C' \) turns out to be positive. These trends indicate that with the addition of Tl, the low temperature fct phase becomes mechanically soft (less stable) whereas the high temperature fcc phase becomes more stable, corresponding to the lowering the MT temperature.

Third, the relative phase stability can be measured by the free energy difference \( \Delta F_{tot}^{\text{fcc}-\text{fct}} = \Delta E_{tot}^{\text{fcc}-\text{fct}} + \Delta F_{vib}^{\text{fcc}-\text{fct}} \) with \( \Delta E_{tot}^{\text{fcc}-\text{fct}} \) being the total electronic energy difference and \( \Delta F_{vib}^{\text{fcc}-\text{fct}} \) being the vibrational energy difference between fcc and fct phases. At 0K, \( \Delta F_{vib}^{\text{fcc}-\text{fct}} \approx \frac{9}{8} k_B \Delta \Theta \) with \( \Delta \Theta \) being the difference of Debye temperatures between the fcc and fct phases and \( k_B \) the Boltzmann constant. For example, when \( x = 0.35 \), \( \Delta E_{tot}^{\text{fcc}-\text{fct}} = 0.20 \) mRy/atom and \( \Delta F_{vib}^{\text{fcc}-\text{fct}} = -0.31 \) mRy/atom, the overall free energy difference thus
reduces from +0.20mRy/atom (corresponding to static conditions) to -0.11mRy/atom. Therefore, the fcc In$_{1-x}$Tl$_x$ with $x=0.35$ turns out to be thermodynamically stable at 0K, in perfect agreement with the experimental findings.\textsuperscript{1,2}

**Figure 3.11** The composition dependence of shear modulus $C'$ of In$_{1-x}$Tl$_x$ ($0 \leq x \leq 0.4$) alloys with fct (upper panel) and fcc (lower panel) structures. The experimental data are from the Refs. 84, 85, 86.

Finally, the phase stability can be explained by the electronic structure. We calculated the density of states (DOS) for pure In and In$_{1-x}$Tl$_x$ ($x=0.15$ and $x=0.30$) alloys. The components of $s$, $p$, and $d$ states of the total DOS are shown in Figure 3.12. The DOS around the Fermi level is mainly governed by the $p$ states of In/Tl with a small contribution from the $s$ state. For the fcc phase of pure In ($x=0$), there exists a strong peak above the Fermi level, which is ascribed to the degenerated non-bonding $p$-states of the In atoms. In the fct phase, the degenerated states split. Therefore, the Fermi level of fct In locates in a wide pseudogap from -0.05 to 0.05Ry, indicating further hybridization between the $p$ states of fct In atoms and stronger bonding between the In
atoms than in the fcc phase. This is why the fct phase is more stable than the fcc phase of pure In at 0K.

Figure 3.12 The density of states (DOS) of In$_{1-x}$Tl$_x$ (x=0, 0.15, and 0.30) alloys for fcc (a) and fct (b) crystallographic phases. $s$, $p$, and $d$ denote the three decomposed states of the total DOS. The vertical line indicates the Fermi level.

With $x$ increasing, the number of $p$ states at the Fermi level of the fcc phase remains almost unchanged. For the fct phase, however, the pseudogap becomes narrower, indicating weaker hybridization between the electronic orbitals. On the other hand, the Fermi level shifts away from the bottom of the pseudogap and the DOS at the Fermi level increases. Therefore, the fct phase becomes less stable. We conclude that the trend of DOS against the composition of the In$_{1-x}$Tl$_x$ alloy explains satisfactorily the decreasing stability of fct phase relative to that of the fcc one.
3.4 Conclusion

The elastic properties and phase stability of two selected shape memory alloys: Ni-Mn-Ga in fcc phase and In-Tl in both fcc and fct phases, were investigated by using the first-principles EMTO-CPA method. The main results may be summarized as follows:

(1) For most of the off-stoichiometric Ni$_2$MnGa, the normal site occupation is favorable, i.e., the excess atoms of the rich component occupy the sublattice of the deficient component. However, for the Ga-rich alloys, the excess Ga atoms always prefer to take the Mn sublattice irrespective of the Mn deficiency/excess.

(2) Generally, for most of the off-stoichiometric Ni$_2$MnGa, the bulk modulus $B$ increases with the increasing $e/a$ ratio. The cubic shear moduli $C'$ and $C_{44}$ change oppositely with the $e/a$ ratio: $C'$ decreases but $C_{44}$ increases with increasing $e/a$. However, the Mn-rich Ga-deficient alloys deviate significantly from this general trend.

(3) The composition dependent martensitic transformation temperature $T_M$ of off-stoichiometric Ni$_2$MnGa is confirmed relative with the shear elastic constant $C'$ as well as the energy difference between parent and martensitic phases $\Delta E_{AM}$. Except for the Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ family, a larger $C'$ generally means a lower $T_M$, whereas a bigger $\Delta E_{AM}$, indicating a larger driving force for the $L2_1$-$\beta''$ martensitic phase transition, in accordance with the higher $T_M$.

(4) In Mn excess Ni$_{2+x}$Mn$_{1-x}$Ga$_{1-x}$, the ferromagnetic MnGa-MnMn coupling will gradually be transformed into the antiferromagnetic one with increasing the concentration of excess Mn, so that the saturation magnetization of the alloys decreases accordingly, which is in line with the experimental results. In Ni excess Ni$_{2-x}$Mn$_{1-x}$Ga, with increasing $x$, the magnetic transition temperatures decrease for both the $L2_1$ and $\beta''$ phases, and the obtained theoretical $T_C$ values explain well the abnormal change found experimentally around $x \approx 0.18$.

(5) For fct In$_{1-x}$Tl$_x$ alloys, with increasing $x$, the $C_{11}$, $C_{13}$, $C_{33}$, and $C_{66}$ decrease, whereas the variations of $C_{12}$ and $C_{44}$ are quite small and non-linear. For fcc In$_{1-x}$Tl$_x$ alloys, first $C_{11}$ increases, $C_{12}$ decreases, and $C_{44}$ increases with increasing $x$ and then remain almost unchanged for $x > \sim 0.25$. Thus, they reproduce well the experimental trends of $C'$ against the
composition for both phases: the $C'$ of the fct decreases and the $C'$ of the fcc phase (which is negative at low $x$) increases with increasing $x$.

(6) In In$_{1-x}$Tl$_x$ alloys, the tetragonality $|c/a-1|$ and $C'$ in the fct phase and the total energy difference between the fcc and fct phases decrease with Tl addition, at the same time $C'$ for the fcc phase and the DOS at the Fermi level for the fct phase increase but that for the fcc phase remains almost unchanged. All of these theoretical trends confirm the lowering of the critical temperature of the martensitic transformation from the fct to fcc In-Tl.
4. Future Work

With the ultimate aim to predict and design new Ni-Mn-Ga-based Heusler alloys with improved magnetic shape memory effect, in the future we will put our emphasis on carrying out research along the following three lines:

(1) The alloying effect on the properties of Ni-Mn-Ga alloys, such as adding Fe, Co, or Cu to Ni-Mn-Ga system, will be investigated using the EMTO-CPA method.

(2) Based on the established methodology to calculate the elastic constants for tetragonal crystals, the elastic constants of Ni-Mn-Ga alloys in the martensite phase will be calculated with the EMTO-CPA method. Furthermore, by using the Debye model, attempts will be made to compute the free energy change with respect to the temperature for both parent and martensitic phases in order to quantitatively predict the phase transition temperature.

(3) The magnetic transition temperature of Ni-Mn-Ga-based shape memory alloys needs to be studied furthermore by employing with spin dynamics (SD) and Monte Carlo (MC) methods.
5. References