Origin of magnetic interactions and their influence on the structural properties of Ni$_2$MnGa and related compounds

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Abstract
In this work, we perform first-principles DFT calculations to investigate the interplay between magnetic and structural properties in Ni$_2$MnGa. We demonstrate that the relative stability of austenite (cubic) and non-modulated martensite (tetragonal) phases depends critically on the magnetic interactions between Mn atoms. While standard approximate DFT functionals stabilize the latter phase, a more accurate treatment of electronic localization and magnetism, obtained with DFT+$U$, suppresses the non-modulated tetragonal structure for the stoichiometric compound, in better agreement with experiments. We show that the Anderson impurity model, with Mn atoms treated as magnetic impurities, can explain this observation and that the fine balance between super-exchange RKKY type interactions mediated by Ni d and Ga p orbitals determines the equilibrium structure of the crystal. The Anderson model is also demonstrated to capture the effect of the number of valence electrons per unit cell on the structural properties, often used as an empirical parameter to tune the behavior of Ni$_2$MnGa based alloys. Finally, we show that off-stoichiometric compositions with excess Mn promote transitions to a non-modulated tetragonal structure, in agreement with experiments.

(Some figures may appear in colour only in the online journal)

1. Introduction

Magnetic shape memory alloys (MSMAs) are being widely explored for many technological applications. Typical representatives of this class of materials are intermetallic Heusler alloys with X$_2$YZ composition (X and Y being transition metals). The high-temperature phase (austenite) of these systems is usually cubic and consists of four interpenetrating fcc lattices. At lower temperatures they often assume a tetragonal structure (martensite). The transition between these phases is of martensitic type and is usually characterized by high reversibility and tunability [1–12]. Being magnetic, these materials can show a strong coupling between structural and magnetic transitions [2–8, 11] which is very appealing for a wealth of different technological applications. In fact, Heusler alloys have been studied quite extensively for their magneto-caloric [13–17] and magneto-mechanical [9–12, 18] properties and more recently for their applications in energy conversion [19].

Ni$_2$MnGa is a prototype representative of MSMAs. The stoichiometric alloy is ferromagnetic below a Curie temperature of $T_C \simeq 365$ K [20]. The martensitic transition to a tetragonal phase, that takes place at $T_M \simeq 200$ K, preserves the ferromagnetic character, albeit with a variation in the magnetic anisotropy. The martensitic phase is observed to have a modulated structure, where the parallel (110) planes are shifted from their equilibrium position along the [110] direction with a period of five unit cells (5 M) and a tetragonal distortion of $c/a \simeq 0.94$ [21–23]. Under applied stress, an orthorhombic structure with a modulation of seven unit cells (7 M) has also been observed [20, 21, 24, 25]. Instead, a non-modulated, tetragonal martensite with $c/a \simeq 1.2$ can be obtained for off-stoichiometric compositions at lower temperatures [21, 26] ($T \lesssim 193$ K). Several groups have also claimed the existence of a pre-martensitic phase...
below a transition temperature of $T_{PM} \simeq 260$ K, where the structure is modulated with a period of three unit cells (3 M) [20]. Co-existence of several modulated and non-modulated phases in a twinned structure has also been observed experimentally [24].

Ni$_2$MnGa and related Heusler alloys have been studied computationally in several works that investigated their electronic and structural properties. These studies, mostly based on the local density approximation (LDA) or the generalized gradient approximation (GGA) for the exchange–correlation functional, have been successful in describing the electronic, structural [27–35], and vibrational properties [36–38], and computing the phase diagram [28, 39] and the Curie temperature [40–42] for these types of compound. A particularly well studied aspect is the relative stability of the cubic austenite phase and a non-modulated martensite phase with $c/a \neq 1$, which has been investigated by first-principles calculations using various functionals [27–33]. With few exceptions, these studies have yielded qualitatively similar results that, while in disagreement on the amount of the tetragonal distortion, generally predict a stable non-modulated martensite phase with $c/a > 1$. Several mechanisms have been proposed as responsible for the structural distortions of this material, such as the Jahn–Teller effect [31, 43, 44] and Fermi surface nesting, which was found to be related to phonon mode softening [37, 45, 46]. It was also found that the number of valence electrons per atom ($e/a$) can control the relative stability of different phases, the martensitic transition temperature and the softening of the phonon modes [23, 47, 48]. However, the microscopic mechanisms responsible for these effects have not yet been completely understood. As a consequence, engineering of these materials for specific applications relies on the empirical optimization of alloy composition and is mostly based on a trial and error approach. Experiments have also found that the samples in which a non-modulated martensitic phase is stable are off-stoichiometric ones, with an excess Mn content in their compositions [12, 23, 26, 49]. In fact, a related compound, Ni$_2$MnSn, has been shown to have a low-temperature tetragonal structure with $c/a > 1$ only with a Mn content larger than the stoichiometric composition, both experimentally and by first-principles calculations [35].

In this work, we perform a detailed study of the relative stability of the cubic and non-modulated martensitic structures and try to clarify some of the conflicting results in the literature. After computing the effective exchange interaction parameters between Mn atoms with constrained density functional theory (DFT), we determine an approximate magnetic energy using the Heisenberg model. We show that the difference in energy between the austenite and martensite phases can be accounted for by the variation of Heisenberg magnetic coupling. By using the DFT + $U$ functional [50–54], we also demonstrate that electronic correlations play an important role in determining the effective exchange interactions. In particular, DFT + $U$ suppresses the stability of the non-modulated martensitic structure for stoichiometric compositions. These results are interpreted using the Anderson impurity model [55], where Mn atoms are treated as a periodic array of magnetic impurities embedded in a conduction electron gas composed of electrons on Ni d and Ga p orbitals, which mediate super-exchange interactions between Mn atoms. Using this idea, we are able to predict the strength of the super-exchange interactions, and to show that the balance between the super-exchange through Ga p and Ni d orbitals determines the stability of the structure. We also study the effect of the number of injected electrons affects the Fermi surface, which in turn modifies the strength of super-exchange interactions and the stability of the martensitic phase. Finally, we show that the martensitic phase can be stabilized when the Mn content in the material exceeds the stoichiometric composition value, which is in agreement with the experimental observations.

This paper is organized as follows. In section 2, we summarize the computational methods we have employed. In section 3, we discuss calculations performed in the austenite and martensite phases, and discuss their relative stability. In section 4, we present the calculation of effective exchange parameters between Mn atoms. In section 5, we discuss the underlying magnetic coupling mechanisms between Mn atoms. In section 6, we discuss the effects of the number of electrons in the unit cell and the extra Mn impurities on the structural properties. Finally, in section 7, we propose some conclusive remarks.

2. Computational method

The calculations in this paper were performed using the plane-wave pseudopotential implementation of DFT contained in the ‘pwscf’ code of the Quantum ESPRESSO package [56]. The generalized gradient approximation (GGA) functional with the Perdew–Burke–Ernzerhof (PBE) parametrization [57] was employed for the exchange–correlation energy. The Ni, Mn and Ga atoms were all represented by ultrasoft pseudopotentials [58]. The electronic wavefunctions and charge density were expanded up to kinetic energy cut-offs of 45 Ryd and 480 Ryd respectively. The Brillouin zone integrations were performed using a $12 \times 12 \times 12$ Monkhorst and Pack special point grid [59] and a Methfessel and Paxton smearing of the Fermi–Dirac distribution function [60], with a smearing width of 0.01 Ryd.

In order to improve the description of electronic correlation and localization, the Hubbard-model-based DFT + $U$ corrective functional was employed. The on-site Coulomb repulsion parameters were computed using the linear response method introduced in [50]. The s states of Ni, Mn, and Ga were treated as a charge ‘reservoir’ as described in [61]. The linear response calculation of $U$ provides the intersite interaction parameters ($V$) [62] as well; however, we found that they are significantly smaller than the on-site interaction parameters ($U$), therefore we neglected them in the calculations presented in this paper. The crystal structures presented in this paper were generated using the XCrysDen software [63].
tetragonal deformation of the unit cell, the ratio $c$ being the $d_{xy}$ orbitals. The peaks corresponding to majority and minority spin states nearly separate, with minority spin states nearly at the Fermi level. On the contrary, the metallic character is mainly due to Ni $d$ ($e$) and Ga $p$ states that dominate the density of states at the Fermi level. The $U$ on Ni $d$ and Ga $p$ states, as well as the interaction terms between electrons in different manifolds (e.g., $d$ and $s$ states of Mn) or on different sites (intersite interactions $V$ [62]) are neglected in this work as they are found to be largely irrelevant for the conclusions of this work. Also, the calculation of the electronic parameters was not performed self-consistently as in [65], nor they were recomputed for different distortions of the unit cell [66], as their variation with $c/a$ is generally used as measured from the cubic cell ($c/a = 1$). The equilibrium lattice parameter and magnetization determined with GGA calculations reported in table 1 are in good agreement with experiments [64]. Our calculations show that the Mn $d$ states split into two groups of three and two degenerate states, which according to tetrahedral group notation are indicated by $t_2$ and $e$ respectively, whose density of states, obtained with the GGA functional, are shown in figure 2. This shows that the Mn $d$ states are subject to a cubic crystal field. More precisely, with respect to the Cartesian coordinates on the tetragonal unit cell (when $c/a = 1$) in figure 1, the $d_{xy}$ and $d_{z^2}$ orbitals of Mn are the $e$ states and the $d_{xz}$, $d_{yz}$, and $d_{x^2−y^2}$ orbitals are the $t_2$ states. Similarly, the Ni $d$ orbitals are also split into $e$ and $t_2$ states, with the $d_{xy}$ and $d_{z^2}$ orbitals being the $e$ and the $d_{xz}$, $d_{yz}$, and $d_{x^2−y^2}$ orbitals being the $t_2$ states.

Another feature clearly visible in the density of states is that the magnetization density is mainly localized on the Mn $d$ orbitals. The peaks corresponding to majority and minority states are clearly separated, with minority spin states nearly empty. The localized nature of the magnetization on the Mn $d$ orbitals suggests that on-site Coulomb repulsion could play a dominant role. It can also be expected that GGA functionals would not be able to account for this interaction accurately, since they tend to delocalize the electronic density. To improve the description of the localized electrons responsible for the magnetism, we adopted the DFT + $U$ approach [50–54].
The projected density of states calculated using the GGA + U functional. The Fermi level is set to the zero of the energy. The inset shows the density of states in the close proximity of the Fermi level.

recently on Ni2MnGa(Sn) [35, 45, 67] and the data presented were able to provide information mainly on states close to the Fermi level. These states are mainly of Ni e type, and, as [35, 45] also suggest, they are responsible for the nesting of the Fermi surface. Our GGA + U calculations modify almost entirely Mn d states, pushing them to lower energies, where experiments are not conclusive. Instead, the U correction has little effect on the states at the Fermi level, and therefore our results are still consistent with existing data.

The more complete filling of electrons on the majority spin states of Mn leads to a larger magnetization, 4.80 \( \mu_B \) per unit cell. The magnetization of each atom, computed with the GGA + U functional, is shown in table 1. In our calculations we fixed the cubic lattice parameter to the value obtained from the GGA functional for simplicity. As can be seen from table 1, while the magnetization of Ga remains at the same value, the magnetization of Mn increases and the magnetization of Ni decreases compared to the GGA. The GGA + U results are in overall agreement with the neutron scattering data [43], even if the Mn magnetization is slightly overestimated. In this regard, it should be noted that the extraction of the magnetic moment of each atom from the data requires a priori assumptions, which affect the overall outcome of the analysis, and lead to large uncertainties. We can obtain a better understanding of the effects of the Hubbard correction by considering the trace of the occupation matrices \( n_{\sigma m}^{i} \) defined in [50], which is a measure of how many electrons localize on a site \( I \) with spin \( \sigma \) (while \( n_{\sigma}^{i} = \sum_{m,\sigma} n_{\sigma m}^{i} \) is the total number of electrons on site \( I \)). In the GGA ground state, we found that \( n_{\text{Ni} d} \approx 8.83, n_{\text{Mn} d} \approx 5.47 \) and \( n_{\text{Ga} p} \approx 2.43 \) while in GGA + U, \( n_{\text{Ni} d} \approx 8.90, n_{\text{Mn} d} \approx 5.21 \) and \( n_{\text{Ga} p} \approx 2.46 \). In the GGA ground state, there are \( n_{\text{Mn} d}^{\uparrow} \approx 0.9 \) minority spin electrons shared between the \( t_2 \) states of Mn, compared to \( n_{\text{Mn} d}^{\uparrow} \approx 4.57 \) of majority spin. In GGA + U, which favors integer occupation of orbitals, the minority spin d states are almost empty with \( n_{\text{Mn} d}^{\downarrow} \approx 0.34 \), while \( n_{\text{Mn} d}^{\uparrow} \approx 4.86 \) for majority spin, closer to being fully occupied. While some of the minority spin electrons in Mn \( t_2 \) states are transferred to the majority spin states in GGA + U, the rest mostly contribute to the conduction electrons of Ni d type (since the increase in Ga p occupation in GGA + U is small). This electronic re-organization in the GGA + U ground state has important consequences in the structural properties of the material, as shown in section 3.2.

3.2. Tetragonal distortions

We first discuss the electronic structure of the low-temperature phase of Ni2MnGa, with an experimental tetragonal distortion of \( c/a \approx 1.2 \) [21, 26]. This phase has often been studied in the literature for the stoichiometric compound, as many calculations obtain it as a ground state. In order to investigate the electronic re-organizations when the unit cell is tetragonally distorted at constant volume, we have computed the density of states using both the GGA (shown in figure 4) and the GGA + U (shown in figure 5) at \( c/a = 1.2 \). The
value of $U$ was set to the calculated value from the cubic phase. We have verified the validity of this approximation by recomputing $U$ for various tetragonal distortions (at constant volume), and we found that $U$ is almost constant.

In the tetragonal cell, the Mn and Ni $t_2$ and $e$ orbitals split (the $t_2$ orbitals split into a doublet $d_{xy}$, $d_{yz}$ and a singlet $d_{z^2}$, while the $e$ splits into two singlets), as can be seen from figures 4 and 5. Some previous works in the literature relate the existence of the tetragonal phase at $c/a \simeq 1.2$ to a Jahn–Teller type distortion [31, 43, 44]. From the inset in figure 4, we observe that the Ni minority spin $e$ peak, which represents the dominant contribution at the Fermi level, splits, forming a shoulder towards the lower energy direction. This shoulder is due to the lower energy $d_{z^2}$ orbitals, while the $d_{xy}$ orbitals are pushed to higher energy. However, peaks corresponding to both types of orbital move above the Fermi level while maintaining a tail below it. This feature is much stronger in GGA + $U$, where both minority spin Ni $e$ orbitals move entirely above the Fermi level, as shown in the inset of figure 5. Jahn–Teller type distortions would tend to place the Fermi level between the split orbitals, resulting in a fully occupied lower energy and an empty higher energy orbital. Instead, we observe that the split orbitals both move above the Fermi level. Therefore, we argue that another mechanism is responsible for determining the energy landscape of the material and, in particular, the stability of the tetragonal phase. In order to investigate this point further, we have performed total energy calculations in GGA and GGA + $U$ as a function of the tetragonal distortion ($c/a$) at constant volume, which are shown in figure 6. As can be seen, the GGA functional yields a local minimum at $c/a = 1$ and a global minimum at $c/a \simeq 1.23$. The energy difference between the two minima is very small and is around 4 meV. Numerous studies in the literature have previously found similar results to our GGA calculation [27–30, 32]. However, these studies have identified energy minima at slightly different values of $c/a$, and proposed different explanations for the relative stabilities of different phases. For example, [29] has identified a local energy minimum for a non-modulated orthorhombic structure at $c/a \simeq 1.11$ and $b/a \simeq 1.04$, besides the local minimum at $c/a = 1$ and a global minimum at $c/a \simeq 1.2$. Reference [27] has found a local energy minimum at $c/a \simeq 0.94$ and a global energy minimum at $c/a \simeq 1.3$ for the non-modulated structure, while [33] has found a local energy minimum at $c/a \simeq 0.94$ for the off-stoichiometric non-modulated compound Ni$_2$Mn$_{1.25}$Ga$_{0.75}$. Instead, [28, 30, 32] have found that an energy minimum for $c/a < 1$ is only possible for modulated structures. Experimentally, a distortion with $c/a < 1$ seems to correlate with the modulation of the structure [20, 22, 24, 25]. A tetragonal non-modulated phase seems to be stable only for significant deviations from the stoichiometric compositions [12, 23, 26, 49]. Therefore, experiments seem to not support the existence of a non-modulated tetragonal phase at the stoichiometric composition, which is in contrast with the result of the GGA calculation.

In GGA + $U$, the global energy minimum at $c/a \simeq 1.23$ is suppressed, as shown in figure 6. This finding indicates that it is important to obtain a more accurate description of the electronic localization on $d$ states to predict the relative stabilities of different phases. The suppression of the stable tetragonal phase shows that GGA + $U$ is in better agreement with experiments, compared to GGA. In order to understand the relative energies of different phases, and their relation to the magnetism in the GGA and GGA + $U$, we have computed the magnetizations of each atom as a function of $c/a$, and the results are reported in figures 7–9. An interesting feature that is apparent from figure 7 is that the energy minima in the GGA functional correspond approximately to extrema of magnetization of the Ni atom (i.e. the minimum magnetization of Ni is obtained at $c/a = 1$, while the maximum magnetization is obtained at $c/a \simeq 1.2$). On the other hand, the magnitude of the magnetization of the Ga atoms has the lowest value of around 1.1 $\lesssim c/a \lesssim 1.2$ but increases monotonically for $c/a > 1.2$. The Mn atoms have the highest magnetization at $c/a = 1$, and it decreases monotonically for $c/a > 1.2$, with a rather featureless profile. Therefore, the magnetizations of the Ni

Figure 6. Energy of the ground state per unit cell as a function of $c/a$ at constant volume in GGA and GGA + $U$. The zero of energy is set to be at $c/a = 1$ in each case.

Figure 7. Magnetization of the Ni atoms as a function of $c/a$ computed using GGA and GGA + $U$. 
and Ga atoms seem to correlate with opposite minima in the total energy as a function of $c/a$. The oscillatory variation of the magnetization of the Ni atoms suggests a correlation with electronic screening, since the dominant contribution to the Fermi surface comes from the minority spin electrons of the Ni atoms. It is well known that, when an impurity is embedded in a gas of conduction electrons, its potential is screened and leads to an oscillatory variation of the charge density of free electrons, whose period depends on the Fermi momentum (Friedel oscillations). If the Mn atoms are treated as a periodic array of ‘impurities’ and the Ni d states as the conduction electron sea, a similar oscillatory behavior can be expected. Since the minority spin $e$ electrons of Ni provide the dominant contribution to the density of states at the Fermi level, they contribute to the screening of the impurity potential most significantly. According to this picture, the oscillations in the magnetization of the Ni d states can be thought of as due to spin-polarized Friedel oscillations. Notice that the oscillations are with respect to $c/a$ and not the distance between the Ni atoms. As $c/a$ increases, the distance between Ni atoms decreases in the basal plane, while the vertical distance between them increases, which introduce a more complicated dependence of the oscillations on $c/a$ than in the free electron case (through the anisotropies of the Fermi surface). We therefore treat these oscillations at a qualitative level.

4. Exchange interaction between Mn atoms

The ferromagnetic ordering is a consequence of the magnetic interactions in the system, mainly between Mn atoms. Therefore, we can approximate the magnetic interaction energy through the Heisenberg Hamiltonian, that depends only on the magnetization of Mn atoms:

$$\mathcal{H}_{\text{mag}} = \sum_{\langle i,j \rangle} J_{i,j} S_i \cdot S_j.$$  \hspace{1cm} (1)

In equation (1) $J_{i,j}$ are the exchange parameters, the $S_i$s are magnetizations of Mn atoms and $\langle i,j \rangle$ denotes that the sum runs over nearest neighbor Mn atoms. This approximation is justified by our expectation that the strength of the exchange parameter decays rapidly with distance. In order to compute the exchange parameters $J_{i,j}$, we use constrained DFT calculations in a 16 atom supercell that contains four Mn atoms. In this calculation, the magnetic moment of one of the Mn atoms is flipped to an opposite direction with respect to the rest of the Mn atoms (while its magnitude turns out to remain unchanged). The energy difference from the original ferromagnetic configuration is then mapped on the Heisenberg model of equation (1) to obtain $J_{i,j}$. This calculation is performed for a range of $c/a$ values. For the tetragonal cells, there are two relevant exchange parameters: one in the $x$–$y$ plane ($J_b$) between the Mn atoms connected in the [110] direction and one in the $y$–$z$ plane ($J_v$) between the Mn atoms connected in the [011] direction, as shown in figure 10. Naturally, the two exchange parameters $J_v$ and $J_b$ are equal in the cubic limit ($J_v = J_b = J_{\text{cubic}}$ at $c/a = 1$). The
magnetic energy per supercell is given by
\[ \mathcal{H}_{\text{mag}} = (4J_b + 8J_v) (S_+^2 + S_- S_-) \] (2)
where \( S_+ \) is the magnetization of the spin up Mn atoms and \( S_- \) is the magnetization of the flipped spin Mn atom. The calculation is performed by first fixing the basal plane dimension \( a \) (thus, \( J_b = J_{\text{cubic}} \)) and varying \( c \) to determine \( J_v \) as a function of \( c \) using equation (2). Then, \( c \) is fixed (thus, \( J_v = J_{\text{cubic}} \)) and \( a \) is varied to determine \( J_b \) as a function of \( a \). The values of \( c \) and \( a \) for each constrained DFT calculation are chosen such that \( a^2 c = \text{constant} \) and therefore both \( J_v \) and \( J_b \) can be expressed as a function of \( c/a \) (corresponding to constant volume deformations) only. The resulting values of \( J_v \) and \( J_b \) as a function of \( c/a \) are shown in figure 11 for both the GGA and GGA + \( U \) functionals. As can be seen from figure 11, the magnitude of the exchange parameter \( J_b \) increases with \( c/a \), while that of \( J_v \) decreases until \( c/a \sim 1.1 \) after which it plateaus. This is expected, since for larger \( c/a \) the distance between Mn atoms in the \( x-y \) plane decreases, resulting in a stronger magnetic interaction in the plane (\( J_b \)), while the distance between Mn atoms in the \( y-z \) and \( x-z \) planes increases, resulting in a weaker interaction (\( J_v \)). The plateau in \( J_v \) is probably related to the vertical alignment of Mn atoms that partially compensates for the increased distance between (001) planes. The dependence shown in figure 11 also justifies the energy minimum at \( c/a > 1 \) for GGA. The stronger increase in magnitude of \( J_b \) compared to \( J_v \) indicates that the magnitude of the magnetic energy in equation (2) increases with \( c/a \) (since the increase in absolute magnetic energy due to \( J_b \) dominates the decrease due to \( J_v \)). Instead, for \( c/a < 1 \), the increase in \( J_b \) is almost symmetrically canceled by a decrease in \( J_v \), so no energy minimum is observed.

Another important result we obtain is that the magnitudes of both interaction parameters are significantly smaller in GGA + \( U \) than in GGA. In the simple Hubbard model, the exchange interaction between electrons localized on neighboring atomic sites can be determined from second order perturbation theory as \( J \sim t^2/U \), where \( t \) is the hopping amplitude between sites [68, 69]. In light of this fact, smaller exchange parameters between Mn atoms in GGA + \( U \) are expected, since the effective on-site Coulomb repulsion is larger. Notice that the \( J \) in the simple Hubbard model is positive, indicating an anti-ferromagnetic interaction, while in our constrained DFT calculations we find negative \( J_s \), resulting in a ferromagnetic ground state. This discrepancy is due to a different type of mechanism that leads to magnetism in our system compared to the simple Hubbard model. We will discuss this point in detail in section 5. Notice also that both exchange parameters \( J_x \) and \( J_y \) have an oscillatory modulation, as was the case for the magnetization of Ni d states shown in figure 7. This modulation seems to suggest that Ni d states contribute to the mediation of magnetic interactions between Mn atoms. Indeed, the oscillation of the exchange parameters between localized magnetic impurities in a free electron gas is a well known effect [70]. We postpone the study of possible mechanisms until the next section, where we will provide a detailed discussion on the nature of the magnetic interaction between the Mn atoms. In the rest of this section, we study the effect of the magnetic energy on the structural properties of the material. Since we have computed the parameters \( J_x \) and \( J_y \), the magnetic Heisenberg energy in equation (2) can be determined as a function of \( c/a \) (in the fully ferromagnetic case with \( S_+ = S_- \)). Doing so, we have a rough estimate of the magnetic energy in the system. To understand its contribution to the total energy, we subtract \( \mathcal{H}_{\text{mag}} \) from the total energy at each \( c/a \) value. The results are shown in figures 12 and 13 for the GGA and GGA + \( U \) respectively. As can be seen from figure 12, when the magnetic energy is subtracted from the total energy, the minimum at \( c/a \approx 1.2 \) disappears in the GGA. In the GGA + \( U \), the subtracted magnetic energy does not change the overall profile of the dependence on \( c/a \). Notice that the magnetic energy is larger in magnitude in the GGA than in the GGA + \( U \). Although the magnetization of Mn atoms is higher in the GGA + \( U \), the effective exchange parameters are significantly smaller in magnitude (as seen in figure 11), leading to a smaller absolute magnetic energy. There is always an upper bound in Mn magnetization, which
cannot be exceeded no matter how large the Hubbard $U$ is. However, larger Hubbard $U$ will always lower $|J|$ (in consistency with the perturbation expansion $J \sim r^2/U$), thus leading to a lower absolute magnetic energy. Therefore, we argue that the appearance of the stable structure at $c/a \simeq 1.2$ is determined by the magnetic energy. Then, the magnitudes of the exchange interactions $J_v$ and $J_b$ need to be determined accurately for a correct description of the structural properties. In fact, the overestimation of the exchange parameters leads to the (spurious) structural minimum at $c/a \simeq 1.2$ for the stoichiometric compound with the GGA, which is eliminated with the Hubbard correction.

5. Magnetic coupling mechanisms

Due to the large separation between Mn atoms in the crystal, it is very unlikely that a direct exchange interaction between Mn atoms could be responsible for the magnetic interactions. Instead, Ni and Ga atoms between Mn atoms are more likely to mediate super-exchange [71] type interactions. Indeed, hints of this possibility were highlighted in section 4. For instance, we found that the oscillations in the effective exchange parameters between Mn atoms show strong similarity to the oscillations observed in the Ni d state magnetization. Magnetic interactions mediated by conduction electrons (like Ni d and Ga p states) have long been known, characterized by an effective exchange parameter having an oscillatory behavior, known as the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction [70]. The RKKY interaction arises from the polarization of free electrons in response to the presence of a magnetic impurity which, reaching other impurities, results in a magnetic interaction between them. The oscillatory behavior in the magnetic interaction strength can be interpreted as a result of electronic screening. The free electron response to a perturbation is measured by the Lindhard function, which has an oscillatory behavior in real space and decays as the third power of distance (i.e. $\sim \cos(k_F R)/(k_F R)^3$, where $k_F$ is the Fermi momentum) between the impurities. If localized Mn d electrons are treated as a periodic array of ‘magnetic impurities’, and the Ni d and Ga p electrons are treated as conduction electrons, then a magnetic interaction of RKKY type can be expected. Indeed, this possibility has been considered in the literature before [40, 41, 72–74].

Before discussing the relevance of RKKY interactions for our system, we first provide a brief summary of the results from a model Hamiltonian approach, which brings some insight into the problem. The RKKY interaction can be derived starting from the Anderson impurity model [55, 75], which can be expressed as

$$\mathcal{H} = \sum_{k,\sigma} \epsilon_k \hat{c}_{k\sigma} + \sum_d E(\hat{n}_{d\uparrow} + \hat{n}_{d\downarrow}) + \sum_d U\hat{n}_{d\uparrow}\hat{n}_{d\downarrow} + \sum_{k,d,\sigma} (V_{dk} \hat{c}_{k\sigma} \hat{c}_{d\sigma} + \text{h.c.})$$

(3)

where $\epsilon_k$ denote the energy levels and $\hat{n}_{k\sigma} = \hat{c}_{k\sigma} \hat{c}^{\dagger}_{k\sigma}$ is the number operator for free electrons respectively (or Bloch electrons in the context of a periodic system). $E$ denotes the energy of electrons localized on the impurity, $U$ is the Coulomb repulsion between two electrons localized on the same impurity and $\hat{n}_{d\uparrow(\downarrow)}$ are the number operators. $V_{dk}$ is the hopping amplitude of electrons from the impurity site to the free electron states, and so it accounts for interactions. In writing the Hamiltonian (3), we have ignored the direct coupling between impurity sites: $\sum_{d,d'} (V_{dd'} \hat{c}_{d\sigma} \hat{c}_{d'\sigma} + \text{h.c.})$. In fact, we assume that such interactions are negligible, due to spatial separation between Mn sites. Moreover, it was also shown in [75] that such interactions are generally anti-ferromagnetic for two impurities, when the Fermi level well separates the impurity energies $E$ and $E + U$. This is the case for our system, as can be seen from figures 2 and 3. For both the GGA and the GGA + U, the filled and empty d-bands of Mn are well separated. The simplest realization of equation (3) is when there is only a single impurity ($d = 1$). In this case, one can derive an effective exchange interaction parameter between the impurity states and conduction electrons in second order perturbation theory as [76]

$$J_{dk} \simeq \frac{2|V_{dk}|^2 U}{|E(U - |E|)\rangle}$$

(4)

where it is assumed that the impurities are maximally polarized, $\langle n_{d\uparrow}\rangle \sim 1$, $\langle n_{d\downarrow}\rangle \sim 0$, $E < 0$, $E + U > 0$, and the Fermi energy is set to zero. Similarly, the magnetization of free electrons, as a response to the magnetization of the impurity, can be derived as [55]

$$\mu_k \simeq \frac{1}{2} |V_{dk}|^2 \frac{d\rho}{de} \ln \left[ \frac{E^2 + \Delta^2}{(E + U)^2 + \Delta^2} \right]$$

(5)

where it is assumed that the density of free electron states, $\rho(\epsilon)$, is a slowly varying function of $\epsilon$. In the above equation, $\Delta = \pi \langle |V_{dk}|^2 \rho(\epsilon)\rangle$ is a measure of the mixing between free electron and impurity states (more precisely, $\Delta$ corresponds to the line width of impurity states, due to interactions with the free electrons). Comparing equations (4) and (5) we see that
the exchange interaction between the impurity and conduction electrons is proportional to the same factor $|V_{dk}|^2$, so the larger the $|V_{dk}|^2$, the larger the magnetization of free electrons would be. Moreover, the interaction between the conduction electrons and the impurity states is anti-ferromagnetic ($J_{dk} < 0$). The RKKY interaction can be obtained from a fourth order perturbation theory starting from a two impurity Hamiltonian analogous to equation (3). The resulting impurity–impurity interaction energy is given by [70]

$$\mathcal{H}_{dd} = -J_{dd} f(k_R) S_1 \cdot S_2$$

where

$$J_{dd} \sim mk^2 |J_{dk}|^2, \quad f(x) = \frac{2\cos(2x) - \sin(2x)}{x^4} \tag{7}$$

where $m$ is the electron mass (replaced with effective mass $m^*$ in a crystal), $R$ is the distance between impurities and $S_{1,2}$ are their spins. For $k_R R \ll 1$, the interaction between the impurities is ferromagnetic, and its strength decays with the third power of their distance. In Ni$_2$MnGa, we treat the Ni d and Ga p states as the conduction electrons. Notice that Ga p states are polarized anti-ferromagnetically with respect to Mn d states, which is in agreement with the picture the Anderson model provides. On the other hand, Ni d states are ferromagnetically ordered. This is probably related to the fact that the above picture does not take into account the topology of the Fermi surface, which is more important for Ni d states. Indeed, we observe from equation (5) that the sign of the free electron polarization can change depending on the derivative of the density of states.

In an alloy, the situation is more complicated than a model with impurities embedded in free electrons for mainly two reasons: first, the ‘impurities’, i.e. localized Mn d states, form a lattice and, second, the conduction electrons that mediate the magnetic interactions are not free and therefore the strength of the interaction depends on the nontrivial topology of the Fermi surface. However, several studies in the literature have found (using a frozen magnon approach) the oscillatory behavior of the Mn–Mn exchange parameter indicated in equations (7) [40, 41, 73, 74]. Indeed, the possibility that the magnetic interactions are mediated by ‘X’ and ‘Z’ atoms of generic X$_2$YZ Heusler alloys was considered long before in the literature [77], by studying the features in the density of states. In a similar way, we will use some basic arguments to understand the nature of the magnetic interactions in our system, in light of the Anderson impurity model and of the RKKY interaction. A more rigorous study would require calculation of the Lindhard susceptibility using a linear response approach [78–80]. Comparing equations (4), (5) and (7), we observe that the strength of the interaction between the impurities is proportional to the square of the magnetization of the conduction electrons. Using this result, we model the exchange parameters $J_e$ and $J_b$ in order to investigate the relative strengths of the RKKY interactions mediated by Ni d and Ga p states separately as

$$J_{b,\text{model}} = (j_{b1} \mu^2_{N_{\text{Ni}}} + j_{b2} \mu^2_{G_{\text{Ga}}}) r_b^{-3}$$

$$J_{v,\text{model}} = (j_{v1} \mu^2_{N_{\text{Ni}}} + j_{v2} \mu^2_{G_{\text{Ga}}}) r_v^{-3} \tag{8}$$

where $r_b$ and $r_v$ are the relevant distances between Mn atoms (more precisely, their ratios to the cubic lattice parameter) and the coefficients $j_{1,2b}$ and $j_{1,2v}$ are constants to be determined by fitting to the data obtained from GGA and GGA + $U$ calculations in the magnetic energy given in equation (2). The functional form of equations (8) does not take into account effects coming from the Fermi surface topology that determines the ($c/a$-dependent) screening by conduction electrons (especially from Ni d states). Instead, they provide an average dependence on the magnetic moments. In order to fit the parameters $j_{1,2b}$ and $j_{1,2v}$, we fit the expressions in equations (8) using (2) ($E_{\text{model}}$) to the Heisenberg energy obtained from constrained DFT calculations for every $c/a$. The fit is obtained by the least squares method and the values obtained for $j_{1,2b}$ and $j_{1,2v}$ are reported in table 2. The comparison of the fitted and the computed magnetic energies is shown in figures 14 and 15. The quality of the fits can be tested quantitatively by evaluating the ratio $\tilde{\chi}^2 = \sum_i (E_{\text{mag}}(i) - E_{\text{model}}(i))^2 / \sum_i E_{\text{mag}}^2(i)$, where $i$ runs over the $c/a$ values considered. For an accurate fit, $\tilde{\chi}^2 \ll 1$. We find that $\tilde{\chi}^2 \approx 1.1 \times 10^{-3}$ for the GGA and $\tilde{\chi}^2 \approx 2.5 \times 10^{-4}$ for the GGA + $U$. As can be seen from table 2, the GGA + $U$ predicts larger exchange parameters (in magnitude) for the Mn–Ni interaction ($j_{1,v,b}$) than the GGA, and smaller ones for the Mn–Ga interaction ($j_{2,v,b}$). The larger Mn–Ga interaction in GGA can actually be understood using equation (4) and the density of states. From figure 2, we observe that the lowest energy filled Mn d states are peaked around 3.6 eV below $E_F$, while the unoccupied Mn d states are peaked around

| $GGA$ (Ryd/$\mu_B^2$) | $GGA + U$ (Ryd/$\mu_B^2$) |
|---------------------|---------------------|
| $j_{1b}$ | $-1.94 \times 10^{-4}$ | $-2.73 \times 10^{-4}$ |
| $j_{2b}$ | $5.63 \times 10^{-4}$ | $-1.61 \times 10^{-4}$ |
| $j_{1v}$ | $4.99 \times 10^{-5}$ | $1.68 \times 19^{-4}$ |
| $j_{2v}$ | $-1.19 \times 10^{-3}$ | $-3.17 \times 10^{-4}$ |

Table 2. Fitted parameters in the model for $J_e$ and $J_b$ found in the GGA and GGA + $U$.
energies shown in figures 14 and 15 are less accurate for magnetic interactions also explains why the fitted magnetic inaccuracy in modeling the Fermi surface topology in the describing the magnetic interaction in an average way. The $U$ is $|c|Ga$ magnetization for $j$ use it to estimate the relative strength of the Mn–Ni exchange interaction. However, equation (4) is not sufficient to account the Fermi surface) is more important for the Mn–Ni exchange interactions, which determines the magnetic energy as a function of $c/a$ as $\frac{1}{2}$. The model in equations (8) provides a simple average measure of the dependence of magnetic interactions on the magnetization of Ga and Ni atoms, which can be used to explain different mechanisms that determine the relative stabilities of cubic and tetragonal phases. Specifically, equations (8) provide an accurate estimate of the dependence of the magnetic energy on $c/a$ and show that Mn–Ni super-exchange is prevalent for $c/a \leq 1$, while Mn–Ga super-exchange is prevalent for $c/a \geq 1$. In table 2, we report the effective interaction strengths related to these mechanisms. While the Mn–Ga exchange interaction is easily realized through the Anderson impurity model, the Mn–Ni interaction requires a careful study of the Lindhard electronic response function, that is closely related to the Fermi surface topology. Indeed, the softening of phonon modes, the dependence of the stability of the structure on the number of valence electrons per unit cell, and the appearance of modulated structures have been argued to be connected to the Fermi surface topology [37, 45, 46]. Our study is a further confirmation of these hypothesis.

Figure 15. Comparison of the computed and fitted magnetic Heisenberg energies in the GGA + $U$.

Figure 16. Energy of the unit cell as a function of $c/a$ for different values of added charge, using the GGA.

6. Electron injection and off-stoichiometric alloys

6.1. Extra electrons in the unit cell

The correlation between the total number of valence electrons per atom ($c/a$) in the unit cell and the structural properties of Heusler alloys, such as the martensitic transition temperature, the stability of the cubic structure and the vibrational spectra, has been studied extensively in the literature [23, 36, 47–49]. In order to investigate the effects of $c/a$, we have introduced fractional electrons in the unit cell in the range $0.1 \leq e \leq 0.7$, compensating the extra charge with a uniform positively charged jellium. In each case, we have relaxed the unit cell and optimized the cubic cell parameter, which is $a_0 \approx 5.91 \text{ Å}$ for $e = 0.1$ (slightly larger than the original cell) and increases monotonically up to $a_0 \approx 6.48 \text{ Å}$ for $e = 0.7$. In figure 16 we show the ground state energy (the zero of the energy corresponds to the cubic phase in each case) as a function of $c/a$ for a selection of extra fractional charges using the GGA functional. Although the GGA is not sufficient to predict the
relative stabilities of different structural phases, it will be the functional of choice in this part to discriminate the effects of varying \(\epsilon/a\) on the exchange couplings from those due to the electronic localization. The Hubbard (+U) correction will be taken into account when computing the value of the exchange parameters in the presence of a fixed amount of extra electrons. At the level of the Anderson model, the GGA exchange parameters in the presence of a fixed amount of extra electrons will be taken into account when computing the value of the electronic localization. The Hubbard (+U) functional of choice in this part to discriminate the effects relative stabilities of different structural phases, it will be the corresponding, in our case, to model parameters for larger \(\epsilon/a\) and found no significant difference from the original system, except a shift of the Fermi energy to higher values for larger \(\epsilon/a\).

The effect of adding charge is most dominant in Ni e states whose density of states is shown in figure 17. As can be seen, for larger \(\epsilon/a\) the peaks just below the Fermi level become stronger since more electrons need to be accommodated below the Fermi energy. Therefore, the addition of extra charge in the system modifies the \(k_F^a/|k_F|\) term in the RKKY interaction of equations (7) for the free electron case, and an analogous averaged quantity depending on the Fermi surface corresponding, in our case, to model parameters \(J_{1,v,b}\) in equations (8). Indeed, as we show in figure 18, as the extra charge injected into the system increases, the Friedel-like oscillations (which also depend on the same factor \(k_F^a/|k_F|\)) for free electrons) have larger wavelength. Since the period of charge oscillations is inversely proportional to \(k_F\), figure 18 suggests that the larger the charge \(\epsilon\), the smaller \(k_F\). Therefore, from equations (7), we expect a smaller exchange coupling, that leads to a smaller Heisenberg magnetic energy. This is indeed visible in the total energy calculations in figure 16 as the stable structure at \(c/a \approx 1.2\) disappears when \(\epsilon > 0.1\). In order to verify this claim, we have computed the exchange couplings and the magnetic energy, as we did in the previous section, for \(\epsilon = 0.5\). In figure 19, we show the Mn–Mn exchange parameters \(J_v\) and \(J_b\) computed with constrained DFT calculations using GGA and GGA + U functionals (\(U\) has the same value as in the original structure). Notice that, as was the case for the original neutral cell, the exchange parameters in the GGA + U are smaller than in the GGA as expected. Comparing with the values obtained from the original structure with no extra electrons, shown in figure 11, we observe that the exchange parameters are smaller for \(\epsilon = 0.5\). This can also be seen from figures 20 and 21 in comparison with figures 12 and 13, where we show the difference between the magnetic Heisenberg energy and the total ground state energy. Moreover, the oscillatory behavior in the original \(\epsilon = 0\) system is also suppressed. Both these observations are in agreement with the previous discussion based on Friedel type oscillations having a higher period for \(\epsilon = 0.5\), thus leading to smaller exchange parameters \(J_{1,v,b}\) with suppressed oscillatory behaviors. Therefore, we expect the model given in equations (8) for the exchange parameters to be more precise in the case of \(\epsilon = 0.5\), since the effects of the Fermi surface are less pronounced. Indeed, this is what we observe in figures 22 and 23. In section 5, we have argued that the inaccuracies between the computed and fitted exchange parameters arise due to the model in equations (8) being unable to capture effects of the Fermi surface topology. In the current case, these effects are suppressed, thus the model adheres more closely to the direct calculation. We find that \(\chi^2 \approx 1.92 \times 10^{-6}\) in the GGA and \(\chi^2 \approx 1.2 \times 10^{-5}\) in the GGA + U, almost an order of magnitude smaller than the case for the neutral cell. In table 3 we report the values of the fitted parameters for \(J_v\) and \(J_b\), which are on average smaller than the fitted values of table 2 for the neutral cell as expected. As was the case for the neutral cell, the Mn–Ga interaction is suppressed in the GGA + U compared to the GGA. For Mn–Ni interactions, we again observe the fitting parameters to be an average of the oscillatory behavior, with random signs. Notice that the stable structure is again determined from a competition between Mn–Ni and Mn–Ga super-exchange interactions, as described on average by equations (8).

We would like to remark that the suppression of the tetragonal structure in the GGA + U, as demonstrated in section 3, does not preclude the stabilization of the martensitic
Figure 19. Exchange parameters $J_v$ and $J_b$ computed using GGA and GGA + $U$ functionals with additional $e = 0.5$ electrons.

Figure 20. Comparison of the total ground state energy and the magnetic energy per unit cell in the GGA with extra charge $e = 0.5$.

Figure 21. Comparison of the total ground state energy and the magnetic energy per unit cell in the GGA + $U$ with extra charge $e = 0.5$.

Figure 22. Comparison of the computed and fitted magnetic Heisenberg energies per unit cell in the GGA with $e = 0.5$.

Table 3. Fitted parameters in the model for $J_v$ and $J_b$ found in the GGA and GGA + $U$ with extra charge $e = 0.5$.

|        | GGA (Ryd/$\mu_B^2$) | GGA + $U$ (Ryd/$\mu_B^2$) |
|--------|----------------------|-----------------------------|
| $J_{vb}$ | $5.94 \times 10^{-5}$ | $-1.64 \times 10^{-4}$       |
| $J_{vb}$ | $-9.47 \times 10^{-4}$ | $9.67 \times 10^{-5}$       |
| $J_{vb}$ | $-6.66 \times 10^{-5}$ | $5.97 \times 10^{-5}$       |
| $J_{vb}$ | $-2.67 \times 10^{-4}$ | $-2.30 \times 10^{-4}$       |

phase for the stoichiometric compound. As we have shown, the relative stabilities of the cubic and non-modulated tetragonal phases for the stoichiometric compound are determined by the magnetic energy. Instead, the appearance of modulated structures, as well as phonon mode softening, are expected to be related to Fermi surface nesting [37, 45, 46]. The magnetic interactions also depend on the Fermi surface properties, as discussed in this section. However, the dominant contributions come from electronic localization on Mn d states, as demonstrated in section 5. Since the Hubbard $U$ correction does not modify the states responsible for the Fermi surface nesting (Ni $e$ states), the GGA + $U$ is not expected to suppress modulated structures. Indeed, preliminary GGA + $U$ calculations (not reported here) on the 5 M modulated structure revealed the existence of a stable martensitic phase with $c/a \simeq 0.92$, in agreement with experiments [21–23]. Moreover, larger $e/a$ values suppress the tetragonal phase, as can be seen in figure 16, in analogy with the effect of $U$. At the same time it has been shown in the literature that larger values of $e/a$ lead to stronger softening of phonon modes and some of the elastic constants [47, 48]. These results, which are both based on the GGA, are indications of the fact that the two phenomena (pure tetragonal distortions and modulations/phonon mode softening) are largely independent.

6.2. Off-stoichiometric compounds

The effects of extra Mn in Ga sites have been discussed in detail in the literature before [27, 34, 48, 49, 81], and
Mn in place of Sn for the related Heusler alloy Ni$_2$MnSn in [35]. It has been shown that the Mn in Ga sites prefers an anti-ferromagnetic ordering with respect to normal Mn sites [27, 35]. Moreover, the samples that undergo a martensitic transition to a tetragonal structure with Mn sites [27, 35]. This is expected, since the extra Mn impurities are energetically favored in agreement with previous studies [27, 35].

The total energy versus c/a profiles for Ni$_2$MnGa, Ni$_2$Mn$_{1.25}$Ga$_{0.75}$ and Ni$_2$Mn$_{1.5}$Ga$_{0.5}$ using the GGA and GGA + $U$ are shown in figures 24 and 25. For the off-stoichiometric compounds we have used a 16 atom supercell and replaced one Ga with a Mn in the case of Ni$_2$Mn$_{1.25}$Ga$_{0.75}$, and two Ga with Mn atoms in the case of Ni$_2$Mn$_{1.5}$Ga$_{0.5}$. In the latter case, the second Mn impurity is placed in the same x–y plane as the first Mn impurity. We have also studied the system where the second Mn impurity is placed in a different x–y plane with respect to the first Mn impurity and found that both systems have similar electronic and structural properties. For both off-stoichiometric compounds, we have relaxed the unit cell, optimized the cubic lattice parameter (using the GGA) and studied constant volume tetragonal distortions. We have used the same $U$ on Mn atoms calculated for the stoichiometric cell. Although a more precise approach should involve a re-calculation of the Hubbard $U$ in this case, as a first approximation the same $U$ value is sufficient to study the general trends.

We have found that an anti-ferromagnetic ordering of extra Mn atoms with respect to the original Mn atoms is energetically favored in agreement with previous studies [27, 35]. This is expected, since the extra Mn impurities are nearest neighbors to the original Mn atoms (instead of being separated by Ni and Ga atoms), and therefore the exchange interaction is mainly mediated by a direct hopping of electrons between them (i.e. through the term $\sum_{d,\sigma}(V_{dc}\hat{c}^\dagger_d\hat{c}_{c,\sigma} + \text{h.c.})$ we have neglected previously). This type of direct hopping results in an anti-ferromagnetic coupling with an exchange parameter $J \sim |V_{dc}|^2/U$. Addition of extra Mn notably increases the magnitude of the magnetic Heisenberg energy, leading to a stronger decrease of total energy in both the GGA and the GGA + $U$. However, since the GGA overestimates the magnetic couplings, it yields a local energy minimum at c/a < 1 and a global energy minimum at c/a > 1.2 for Ni$_2$Mn$_{1.25}$Ga$_{0.75}$. This result is in contradiction with experimental data (an energy minimum for c/a < 1 was observed only for modulated structures). In the case of Ni$_2$Mn$_{1.5}$Ga$_{0.5}$, there is no local minimum for c/a < 1.2 and the global minimum is placed at c/a $\simeq$ 1.3, overestimating the experimental value. In contrast, the GGA + $U$ functional yields only a global minimum for c/a $\simeq$ 1.15 for Ni$_2$Mn$_{1.5}$Ga$_{0.5}$. This finding is also in agreement with the

**Figure 23.** Comparison of the computed and fitted magnetic Heisenberg energies per unit cell in the GGA + $U$ with $e = 0.5$.

**Figure 24.** Energy of the ground state as a function of c/a at constant volume per unit cell in the GGA. The zero of energy is set to be at c/a = 1 in each case.

**Figure 25.** Energy of the ground state as a function of c/a at constant volume per unit cell in the GGA + $U$. The zero of energy is set to be at c/a = 1 in each case.
case of Ni$_2$Mn$_{1+x}$Sn$_{1-x}$, where the martensitic transition (to a non-modulated structure) is observed only when $x \gtrsim 0.5$ [35].

7. Conclusions

In this work we have studied the electronic and structural properties of Ni$_2$MnGa and investigated the relative stabilities of the cubic austenite and non-modulated tetragonal martensite phases. We have shown that the relative stabilities of these phases critically depend on the magnetic energy due to exchange interactions between Mn atoms. This result was demonstrated by modeling the magnetic energy with the Heisenberg Hamiltonian and computing the effective exchange couplings with constrained DFT calculations for every structure. Comparing the results obtained from GGA and GGA + $U$ functionals, we showed that electronic localization has an important effect on the magnetic energy and on the relative stabilities of the two structures. In particular, the GGA + $U$ removes the spurious energy minimum at $c/a \simeq 1.2$ for the stoichiometric compound. An explanation of these results was obtained by using the Anderson impurity model. Within this model, we have treated the Mn d orbitals as ‘magnetic impurities’ embedded in conduction electrons on Ni d and Ga p orbitals, which mediate RKKY type interactions between Mn atoms. Using this theoretical framework, we were able to provide an explanation for the relative stabilities of cubic and non-modulated tetragonal structures in various circumstances. We have also formulated a simplified model for the Mn–Mn exchange interaction based on a linear combination of two contributions, (1) super-exchange mediated by Ga p states and (2) super-exchange mediated by Ni d states, and were able to uncover the competition between these mechanisms in determining the stable structure. This model was also used to study the effect of $e/a$, and it showed that the stability of the non-modulated martensitic phase is suppressed by increasing the number of electrons. We also studied off-stoichiometric compounds with excess Mn (substituting Ga atoms). We have shown that, in agreement with experiments, the non-modulated martensitic structure with $c/a > 1$ can only be stabilized by excess Mn content, which increases the exchange couplings $J$ between Mn atoms. This result was obtained using the GGA + $U$ functional. The GGA functional predicts, instead, the non-modulated tetragonal phase to be stable at any composition, in contradiction with observations.

The study offered in this work shows that a precise account of magnetism and magnetic interactions is essential to predict the relative stabilities of different phases and to rationalize the experimental observations. The simple RKKY interaction is able to explain most of the physics of the systems studied in this paper and to capture the effects of doping. In spite of the metallic character of these systems, DFT + $U$ proved to be crucial for an accurate description of the localization of electrons and of magnetic properties that play a key role in the relative stabilities of different structural phases. To the best of our knowledge, DFT + $U$ has not been used previously to study the electronic structure of Ni$_2$MnGa. However, a different Heusler alloy, Co$_2$Mn$_{1-x}$Fe$_x$Si, was studied with DFT + $U$ [82] and the importance of electronic correlations was stressed. In light of these results, we argue that the study of phonons, Fermi surface nesting and off-stoichiometric alloys should be revisited using the DFT + $U$ functional. A recently developed extension of DFPT [83] to the DFT + $U$ scheme [84] will greatly facilitate the development of these studies. Our future calculations will use the theoretical framework developed in this work to explore the effects of various substitutional impurities and to characterize modulated martensitic structures.

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