Electronic and magnetic properties of Ni$_2$MnGa: Monte-Carlo and ab-initio calculations

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Abstract. This paper describes computational calculations based on the density functional theory (DFT), in order to investigate the electronic and magnetic properties of Ni$_2$MnGa alloys. The local density approximation (LDA) and generalized gradient approximation (GGA) methods were used, which are implemented in the MACHIKANEYAMA package designed and made by Akai [1]. As result, we found that the alloys possess a ferromagnetic behaviour with magnetic moment of 4.07μB/cell. The analysis of the density of states (DOS) shows that the alloys have a half-metallic behaviour due to the Mn-d and Ni-d states crossing the Fermi level. Moreover, the Monte-Carlo simulation method in the framework of the Ising model gives the magnetization and the susceptibility values, respectively.

1. Introduction
In recent years, there has been a growing interest in the family of Heusler (full- and half-Heusler) compounds, discovered by Heusler in the 1903, with general formula X$_2$YZ and XYZ. Current research on the Heusler alloys is focused on the phenomena of coupled magnetic and structural phase transitions, which are very rare in condensed matter physics. Such systems can display various interesting properties including giant magnetocaloric, magneto-resistance and magnetostriction, which consequently have great technological potential [2]. The initial Heusler alloys studied were crystalized in the L2$_1$ structure (space group Fm$ar{3}$m), which contain 4 fcc sublattices (see Figure.1). Next, it was discovered that it is possibly to obtain an alloy with one of the four sublattices empty (C1b structure). This second type of alloys is frequently called half- or semi-Heusler compounds, while the first one is known as full-Heusler compounds. Among these compounds, the Heusler intermetallic alloys and their magnetic properties have been in sharp focus [3-7]. Their excellent properties are based on the relationship between the structural and the magnetic order. Currently, magnetic shape memory alloys are potential materials both for sensors and actuators. One well-known prototype magnetic shape memory alloy is the Heusler intermetallic Ni$_3$MnGa compound [8-14]. An interesting feature of these Heusler alloys is a large magnetocaloric effect (change of magnetic entropy) around the structural transition and the ferromagnetic-paramagnetic transition. This characteristic makes these alloys to be good candidates for magnetic refrigeration. Among the most important studies in this topic for the Ni2MnGa system is the magnetocaloric effect of Ni$_{2+x}$Mn$_{1-x}$Ga, which was studied using the Monte Carlo method [21]. Moreover, the field-induced entropy change
and the magnetocaloric effect (MCE) of ferromagnetic Ni$_2$Mn$_{1-x}$Cu$_x$Ga shape memory alloys have been calculated theoretically on the basis of phenomenological free energy [22].

The objective of this paper is to investigate the electronic and magnetic properties of Ni$_2$MnGa alloy using two simulations approach: ab-initio calculations (DFT) by KKR-CPA package and Monte Carlo simulation based on Metropolis algorithm. These two methods are interrelated, such as some results obtained by the ab-initio method are inputted in our Monte Carlo program (as the exchange interaction, magnetic moment). The validation of this work has done by the experimental results comparison. In addition, more details and explication of the computational method (ab-initio calculation) as well as discussion of the results obtained by the KKR-CPA package and the Monte Carlo simulation model are presented.

2. Ab-initio Calculation:

2.1. Computational method:

In order to investigation the electronics and magnetsics properties of Ni$_2$MnGa system, our method was valued by comparison with experimental results. We have calculated the electronics and magnetsics properties of Ni$_2$MnGa system, using ab-initio calculations, with the code KKR-CPA (Korringa-Kohn-Rostoker and the coherent potential approximation), which developed by Akai [1]. This code was performed by two approximations: LDA (Local-density approximations) and GGA (Generalized Gradient Approximation). For LDA we have used two forms; the first reported in ref [15] and the second based on the parameterization given by Moruzzi, Janak and Williams (MJW) [16]. For GGA, reported by the Perdew Burke Ernzerhof (PBE) and based on gradient-corrected functional [17]. We have used the highest K-points up to 600 for Energy and moment magnetic calculations, and up to 250 for the density of state (DOS). The relativistic effect has been considered using the scalar relativistic approximation. Our system Ni$_2$MnGa is among the family of Heusler compounds, which crystallized in the L2$_1$ structure with the space group of Fm$ar{3}$m (225), its lattice parameter are a=b=c=5.82Å [18], represented as four interpenetrating face-centred cubic sublattices. The Ga and Mn atoms occupy the positions (0;0;0) (1/2;1/2;1/2), although the Ni atoms get the sites (1/4;1/4;1/4) and (3/4;3/4;3/4). This is mentioned in Figure 1. The potential form is approximately, given by the muffin tin model. The corresponding wave functions in the muffin-tin spheres have been expanded with the real harmonics up to l =2, where l is the angular momentum defined at different sites.
2.2. Results and discussion:
It has been found that the total energy of Ni$_2$MnGa system obtained by GGA approximation was small than LDA approximation. This result means that GGA is optimal for our compound (table 1), because LDA is the simplest physical path to treat the exchange-correlation energy. However, various research group have reported that GGA includes more physical information than the LDA.

Table 1. Energy total of Ni$_2$MnGa by the used approximations

| Approximation used | Total Energy (Ry) |
|--------------------|-------------------|
| LDA (mjw)          | -12268.594299232  |
| LDA (vwn)          | -12269.073027098  |
| GGA (pbe)          | -12288.554729713  |

From that result, the calculation will be treated by GGA approximation. We have introduced a new approach to determine the exchange interaction by the calculation of total energy difference $\Delta E$ between the disordered local moment (DLM) and the ferromagnetic state, based on the mean field (MF) approximation, we obtained the three equations (1) (Table2).

$$\Delta E_{N\tilde{i}2Mn(1)Ga}^{Ni2Mn(1)Ga} = E_{DLM}^{Ni2Mn(1)Ga} - E_{FM} = J_{Mn-Mn} \frac{Z_1}{2} (S)^2$$

$$\Delta E_{N\tilde{i}2(1)MnGa}^{Ni2(1)MnGa} = E_{DLM}^{Ni2(1)MnGa} - E_{FM} = J_{Ni-Ni} \frac{Z_2}{2} (\sigma)^2$$

$$\Delta E_{N\tilde{i}2(1)Mn(1)Ga}^{Ni(1)Mn(1)Ga} = E_{DLM}^{Ni(1)Mn(1)Ga} - E_{FM} = J_{Ni-Mn} \frac{Z_3}{2} (\sigma S)$$

Where:
$Z_1 = 12$, is the number of first close neighbours of the Mn atom of the same type.
$Z_2 = 6$, is the number of first close neighbours of the Ni atom of the same type.
$Z_3 = 4$, is the number of first close neighbours of the Ni atom of the type Mn.
Table 2. The calculation of Total Energy difference $\Delta E = E_{\text{DLM}} - E_{\text{FM}}$

|              | E$_{\text{DLM}}$(Ry) | $\Delta E$(Ry) |
|--------------|----------------------|----------------|
| Mn (↑↓)      | -12288.54890374      | 0.005739339    |
| Ni (↑↓)      | -12288.554729541     | 0.000000172    |
| Mn (↑↓)-Ni (↑↓) | -12288.548990019    | 0.005739694    |

We can also estimate the Curie temperature $T_c$ from the total energy difference between the DLM and the ferromagnetic State by the equation (2), it has been found that $T_c=603K$.

$$T_c = \frac{3}{2K_B} E_{\text{DLM}} - E_{\text{FM}}$$

Where $K_B=8.617330 \cdot 10^{-5}$ eV K$^{-1}$ is the Boltzmann’s constant.

The total magnetic moment obtained by our approach is $\mu_{\text{tot}}=4.07\mu_B$, the local magnetic moment of the alloy is: $3.51\mu_B$ for Mn and $0.32\mu_B$ for Ni (Table 3). It is noted that total and local magnetics moments of Ni$_2$MnGa is estimated better with GGA approximation compared to the experimental data [19].

Table 3. Calculated total and local magnetic moments in units of $\mu_B$.

|              | Ni($\mu_B$) | Mn($\mu_B$) | Ga($\mu_B$) | $\mu_{\text{tot}}$($\mu_B$) |
|--------------|-------------|-------------|-------------|-----------------------------|
| L2$_4$ Cubic |             |             |             |                             |
| Th. LDA (vwn)| 0.31477     | 3.36051     | -0.06110    | 3.9129                      |
| Th. GGA (pbe)| 0.31786     | 3.50934     | -0.06911    | 4.0749                      |
| Experimental| 0.24        | 2.74        | -0.013      | 4.17                        |

As may be seen in Figure 2, the Density of State (DOS) gives important information about the system magnetic order. There is an overlap at the Fermi level, which means that our system has a metallic behaviour, it is concluded that the orbitals (3d of nickel (Ni), 3d of manganese (Mn) and 4p of gallium (Ga)) contribute the most in total density of state of Ni$_2$MnGa, because these orbitals are not occupied. The contribution of the orbital 4p-Ga is negligible (Figure 2).

Figure 2. Density of state from GGA-KKR-CPA calculations of Ni$_2$MnGa alloy.
The band structure in Figure 3, confirmed that our compound Ni2MnGa has a metallic behaviour, illustrated by the overlap of bands at the level Γ. The high dispersed bands (Conduction Band) are due to the strong hybridization of Mn-d and Ni-d electrons, including a contribution from Ga-p states in the occupied valence states. At Γ there is a sequence of twofold degenerate states (e\textsubscript{g}) derived completely from Mn-d and Ni-d states and threefold degenerate states (t\textsubscript{2g}) that permit hybridization of Mn-d and Ni-d states with the Ga-p states. We attain good agreement with the results of Picozzi et al [23].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure3.png}
\caption{The band structure of the system Ni\textsubscript{2}MnGa obtained by LDA}
\end{figure}

3. Model and Monte Carlo simulations:

3.1. The Model:
The Hamiltonian H of the Heusler Ni\textsubscript{2}MnGa alloy including the exchange interactions is:

\[ H = -J_{\text{Ni--Ni}} \sum_{<i,j>} \sigma_i \sigma_j - J_{\text{Ni--Mn}} \sum_{<i,k>} \sigma_i S_k - J_{\text{Mn--Mn}} \sum_{<k,m>} S_k S_m \]  

(3)

Where \(<i, j>, <i, k>\) and \(<k, m>\) denotes the nearest neighbour spins at i, j, k and m sites. \(J_{\text{Ni--Ni}}, J_{\text{Ni--Mn}}\) and \(J_{\text{Mn--Mn}}\) are the exchange interaction between Ni\textsuperscript{2+} -Ni\textsuperscript{2+}, Ni\textsuperscript{2+} -Mn\textsuperscript{2+}, and Mn\textsuperscript{2+} -Mn\textsuperscript{2+}, respectively. The spin moment of Mn\textsuperscript{2+} and Ni\textsuperscript{2+} are S=5/2 and \(\sigma=1\). In this study, we have used the values of the exchanges interaction \(J_{\text{Ni--Mn}} = 3.90 \text{ meV}, J_{\text{Ni--Ni}} = 7.8 \times 10^{-4} \text{ meV}, J_{\text{Mn--Mn}} = 2.08 \text{ meV}\), this is obtained from the DFT calculations, they are employed as the input for the Monte Carlo program.

3.2. Monte Carlo simulations:
The Monte Carlo (MC) simulation is a powerful tool for the investigation of the magnetization and the magnetic susceptibility (\(\chi_T\)). We use the Metropolis algorithm [20], our system composed by two elements magnetics Ni and Mn, with the spin moment of Mn\textsuperscript{2+} and Ni\textsuperscript{2+} are S=5/2 and \(\sigma=1\), therefore, we take into account the possible projections: (-5/2, -3/2, -1/2, 1/2, 3/2 and 5/2) and (-1,0,+1). The structure of Ni\textsubscript{2}MnGa is composed of three elements Ni (3d\textsuperscript{8} 4s\textsuperscript{2}), Mn (3d\textsuperscript{5} 4s\textsuperscript{2}), Ga (4s\textsuperscript{2} 3d\textsuperscript{10} 4p\textsuperscript{1}). We used the linear size L=13 and the cyclic boundary conditions on the lattice are treated. With the Monte Carlo simulation, we calculate the following elements: the energy of the system (E) (4), the total magnetization (M) (5), and the magnetic susceptibilities (\(\chi_T\)) (6):
\[ E = \frac{1}{N} < H > \] (4)

The total magnetization is given by:

\[
M_\sigma = \left( \frac{1}{N_\sigma} \sum_i \sigma_i \right) \\
M_S = \left( \frac{1}{N_S} \sum_i S_i \right) \\
M = \frac{N_\sigma M_\sigma + N_S M_S}{N_\sigma + N_S}
\] (5)

\[ \chi_T = \beta N (< M^2 > - < M >^2) \] (6)

Where N is the total number of spins, with \( N = N_\sigma + N_S \)

### 3.3. Result and Discussion:

The total magnetization of Ni\(_2\)MnGa Heusler alloy is shown in Figure 4 as a function of temperature. We note that the magnetization decreases with increasing the temperature (figure.4). The transition from Ferromagnetic phase (FM) to the paramagnetic phase (PM) is indicated at the Curie temperature \( T_c = 550 \) K, as determined by the Figure 4 and 5.

**Figure 4.** The total magnetization \( M \) of Ni\(_2\)MnGa system as a function of the temperature \( T(K) \).

The magnetic susceptibility \( (\chi_T) \) of Ni\(_2\)MnGa system is shown in figure 5 as a function of temperature. It is detected that the peak of the magnetic susceptibility corresponds to the critical temperature \( T_c \). Nicholson et al have found that \( T_c \) is near to 393K [24]. From Monte Carlo, we have found that the total moment magnetic is around 3\( \mu_B \), however in the ab-initio calculation \( \mu_{\text{tot}}=4.07 \mu_B \) \( \mu_{\text{tot}}=4.17 \mu_B \)
from experimental result). These results are in good agreement with our results found above by the mean field approximation.

![The Magnetic Susceptibility (XT)](image)

**Figure 5.** The magnetic susceptibility ($\chi_T$) of Ni$_2$MnGa system as a function of the temperature T(K).

4. Conclusions:
In summary, it can be concluded that our method used to investigate the electronic and magnetic properties of Ni$_2$MnGa alloy has been very successful. The KKR-CPA and Monte-Carlo were employed to attend our goal. The total and local moments magnetic calculated are in good agreement with values reported experimentally. The density of states (DOS) revealed that our system has a half metallic behaviour, this result confirmed by the band structure. We can also establish that the order magnetic of our system is a Ferromagnetic (FM). The total magnetization and the magnetic susceptibility indicated that the ferromagnetic-paramagnetic phase transition is second-order type and the Curie temperature is determined. These properties show that the alloys are considered to be most promising candidates for various applications including shape memory, spin injectors, magnetocaloric and other spintronics applications.

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