Influence of Co and Mn on Electronic and Magnetic properties of Ni$_2$MnGa Heusler alloy

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June 27, 2022

Abstract

The ferromagnetic Heusler alloy Ni$_2$MnGa had been of major interest in past few years because of its magnetic properties which can be easily tuned. Ni$_2$MnGa Heusler alloys are intermetallic alloy with L2$_1$ structure. Here we report a detailed investigation of effect of doping of Co and Mn in Ni$_2$MnGa. Magnetic properties and electronic structure of Ni$_2$$_{x}$Co$_x$MnGa$_1$$_{x}$Mn$_z$ Heusler alloys have been studied by using Green’s function based KKR-CPA method based DFT calculations. We will show the magnetization can be tuned depending on the site Mn occupies. We will also discuss the magnetic interactions and magnetic stability of the systems.

1 Introduction

Heusler alloys (HAs) has gained a lot of attention from the community due to their possible usage in magnetocaloric(MC) [1], magnetic shape memory [2], spintronics [3] and GMR devices [4, 5, 6]. These ternary alloys, with generic symbol X$_2$YZ, where X and Y are d-block and Z is main group elements, shows various structures [7]. The completely ordered phase demonstrates L2$_1$ structure, Y-Z disordered phase demonstrates B$_2$ phase and the complete X - Y - Z disorder demonstrates A$_2$ structure. Wyckoff positions 4a(0, 0, 0), 4b(1/2, 1/2, 1/2) and 8c(1/4, 1/4, 1/4) are occupied by Z, Y and X respectively [8, 9, 10]. As we are having more lab-scale results, both theoretical and experimental, the commercial implementation is getting nearer. The downsized of the material with various applications like topological insulators, magnetic cooling and spintronics becomes imperative [11, 12].

Among the HAs, Ni-Mn-Ga system has got much attention due to their demonstration of both magnetic and structural phase transition [13, 14]. Ni-Mn-Ga systems also show properties like shape memory effect (SME) and magnetic field induced strain (MFIS) favourable to be used as actuators and sensors [15, 16]. They have also shown very favourable MC properties, suitable to replace the century old Joule-Thomson cooling [17, 18]. Ni-Mn-Ga system has a magneto structural phase transition with huge change in isothermal magnetic entropy ($\Delta S_m$), but relatively narrow range of working temperature ($T_{fwhm}$), typical to the materials with first order phase transition(FOPT) [19]. However, the thermal hysteresis of FOPT and the Curie temperature is detrimental for magnetic refrigeration.

One of the best characteristics of HAs are the extreme tunability of their various properties due to doping. After Groot’s [20] theoretical observation of half-metallicity in half-heusler NiMnSb alloy, the same
was demonstrated soon in full-heusler $L2_1$ structure [21, 22, 23] as well. Electronic structure and magnetic properties has also been proposed in Ni doped Co$_2$Ga$_{1-x}$Ni$_x$MnAl [21] and Co doped Ni$_2$MnAl [23] systems in the $X$ position only. Off-stoichiometric Ni$_{2-x}$Q$_x$MnGa and Ni$_{2-x}$Q$_x$MnGa$_{1-z}$R$_z$, where Q and R is any suitable elements has used to improve the various properties of Ni$_2$MnGa. Ni$_{2-x}$Q$_x$MnGa/Al is under study for long time for their martensite phase transition ($M_s$) and magnetic critical temperature ($T_C$). It is observed that MC effect is the highest around 0.18 $\leq x \leq$ 0.27 as magnetic and structural phase change occurs in this range [6, 26]. Partially substituting Ni with Co is known to enhance the ferromagnetic coupling and hence the $T_C$, and decreases the martensitic temperature, $T_M$. This increases the possibility of that the quaternary system undergoes a martensitic transition together with a meta magnetic phase transition [27].

In General, both structural and magnetic properties are highly depends on off-stoichiometric combination of $Z$. There are also a few studies to observe the effect of $Y$ replacing $Z$, mostly Ni$_2$MnZ$_{1-y}$Mn, $Z =$ Ga, In etc. [28, 27, 5, 29]. Substituting the Mn element in $Z$ position, can stabilize the ferromagnetic cubic state [14] and these Mn$_Z$ atom interact antiferromagnetically between the surrounding Mn$_Y$ and normal Mn$_Y$ because the distance between the Mn$_Y$-Mn$_Z$ is less compared to the Mn$_Y$-Mn$_Y$ and Mn$_Z$-Mn$_Z$ [30]. Here, Mn$_Z$ is denoting the Mn atom in Ga site ($Z$), and Mn$_Y$ is the Mn’s normal position ($Y$). We expected to enhance the magnetic moments of the material for doping of Mn in Ga site.

In the present article, we have reported our systematic study of Ni$_{2-x}$Co$_x$MnGa$_{1-z}$Mn$_z$ (which will be referred as NiMnGa($x,z$), where, $x, z$ is the concentration of Co and Mn in Ga site, respectively, for brevity. For example, Ni$_{1.88}$Co$_{0.12}$MnGa$_{0.74}$Mn$_{0.26}$ will be denoted as NiMnGa(0.12, 0.26). We have studied the variation of electronic structure, magnetic exchange and magnetic critical temperature of NiMnGa($x,z$) with $z$ ranging from 0 to 0.24 (up to 24%) and $z$ ranging from 0 to 0.5 (up to 50%) for cubic phase only.

This is technologically relevant as the $T_C$ is one of the detrimental factor of working temperature range.

2 Methods

The off-stoichiometric composition are best handled like Ni$_{2-x}$Q$_x$MnGa$_{1-z}$R$_z$ are using greens function based formalism [31]. We have performed ab-initio calculations using multiple scattering greens function formalism as implemented in SPRKKR code [32, 33, 34]. We have used the Perdew-Burke-Ernzerhof(PBE) [35] method is used as GGA functional. First Brillouin zone integrations were performed on the 2500 grid of k-points and energy convergence criteria was set at the calculation in the range $10^{-5}$Ry. We have implemented full potential spin polarized scalar relativistic implementation of SPRKKR with angular momentum cut-off $\ell_{max} = 2$ as suitable for our system.

The Lattice parameter with minimum energy of Ni$_2$MnGa(NiMnGa(0, 0)) is calculated using the following procedure: (i) Obtained the lattice parameter from materials project database [36]; (ii) Calculate the SCF of the system, with varying lattice parameter ranging from 94% to 106%, with identical calculation for each lattice parameters. (iii) Fit the lattice parameter vs energy plot obtained in last step using a 4th order polynomial. The minima of the curve is the optimized lattice parameter. For NiMnGa($x,z$), we have taken the optimized lattice parameter of previous calculations that has a minimum $x, z$ change as the starting point and followed the steps above. We have shown the optimization curve of Ni$_2$MnGa in Figure 1(a). Other minimization energy curves are not shown here due to brevity.

The magnetic exchange energy ($J_{ij}^{\nu\mu}$) was calculated to understand the properties of magnetic interactions. The Heisenberg model, defined as

$$H = \sum_{\nu,\mu} \sum_{i,j} J_{ij}^{\nu\mu} \mathbf{e}_i^{\nu} \cdot \mathbf{e}_j^{\mu}$$

(1)
where $\nu, \mu$ represent atoms in different sublattices, $i, j$ is different lattice point, $\mathbf{e}_i^\nu$ is the magnetic orientation of $i$th atom at $\nu$ sublattices. The $J_{ij}^{\nu\mu}$ is calculated via the energy difference due to infinitesimal change of magnetic direction, as formulated by Lichtenstein [37].

Finally, the $T_C$ is estimated using mean field theory, yielding

$$k_B T_C = \frac{3}{2} J_l$$

where $J_l$ is the largest eigenvalue of the determinant, as described in [30]. It must be remembered that mean field calculations generally overestimate the $T_C$, which is true for our calculations, as well.

3 Results

The Ni$_2$MnGa ground state structure in $FM\bar{3}M$ (space group 225). The Ni atom occupies 4c (.25, .25, .25) and 4d (.75, .75, .75) Wyckoff positions, Mn occupies 4b (.5, .5, .5) and Ga occupies 4a (0, 0, 0) Wyckoff positions. We have calculated the electronic and magnetic properties of NiMnGa($x$, $z$) for ($x$ = 0.0, 0.12 and 0.24) and ($z$ = 0.0, 0.15, 0.26, 0.35 and 0.5). The optimized lattice parameter of each sample calculated using the method described in the sec. (2) are tabulated in Table (1, 2, 3). The Figure (1b) shows the variation of lattice parameters with $x$ and $z$, which is mostly linear.

3.1 Pure Ni$_2$MnGa system

Figure (2) shows the density of states (DOS) (Figure (2a)) and magnetic exchange interactions ($J_{ij}$) (Figure (2b)) with Mn atom at the center for Ni$_2$MnGa. The $J_{ij}$ is highest for Mn-Ni interactions, with the value $\approx 5$meV. All the interactions are predominantly ferromagnetic in this case. The complete table of optimized lattice parameter, total and individual magnetic moment per atom and Curie temperature of pure system is tabulated in Table (1).
3.2 NiMnGa(\(x, 0\)) systems

The NiMnGa(\(x, 0\)) system, i.e., doping in Ni site only, though heavily studied within the austenite phase, we have included them for completeness. Doping of Co in \(X\) position will decrease the lattice parameter of the material shown in Figure 1b and Table 1. The electronic and magnetic structures of NiMnGa(\(x, 0\)) is shown in Figure 3 as representative of the series. The Co atom has much higher magnetic moment (\(\approx 1\mu B\)) compared to Ni (\(\approx 0.3\mu B\)), and the \(J_{ij}\) is much higher compared to Ni\(_2\)MnGa. Due to very fragile magnetic moment of Ni, it is seen that moment of Ni increases rapidly with increase of doping concentrations of Co, as shown in Table 1. Of course, in current case, Mn\(_Z\) =0.

3.3 NiMnGa(0, \(z\)) systems

The opposite systems of the one shown in the previous section (3.2) is NiMnGa(0, \(z\)) system, where \(X\) site is fully ordered, but Ga is replaced by Mn, yielding Ni\(_2\)MnGa\(_{1-x}\)Mn\(_x\) system. Doping of Mn in \(Z\) position will increase the lattice parameter of the material shown in Figure 1b and Table 2. The electronic structure
Table 1: Optimized lattice parameter and magnetic moments on individual atoms for NiMnGa(0, 0) and NiMnGa(x, 0) system.

| Concentrations | Lattice Parameter (au) | Magnetic Moment(µB) | $T_C$ (K) |
|----------------|------------------------|---------------------|----------|
|                | x z                    | Total Ni Co MnZ Ga Mny |          |
| 0 0            | 11.061                 | 4.08 0.29 0 - -0.08 | 3.56 392.975 |
| 0.12 0         | 11.047                 | 4.21 0.31 1.07 - -0.08 | 3.50 1138.093 |
| 0.24 0         | 11.032                 | 4.34 0.33 0.95 - -0.09 | 3.45 1147.953 |

doesn’t change much due to doping (Figure 4a.1), but the absence of Co in Ni site decreases the magnetic interactions of Mn-Ni by half w.r.t. the case of NiMnGa(x, 0) (Figure 4b.2).

The most dominant interaction is Mn$_Y$-Mn$_Z$ interaction, which are antiferromagnetically coupled as shown in Figure (4b.1-4b.4) for each concentration.

Figure 4: The (a) DOS and (b) exchange interaction of NiMnGa(0, z) (z = 0.15, 0.26, 0.35 and 0.50).

Table 2: Optimized lattice parameter and magnetic moments on individual atoms for NiMnGa(0, z) system.

| Concentrations | Lattice Parameter (au) | Magnetic Moment(µB) | $T_C$ (K) |
|----------------|------------------------|---------------------|----------|
|                | x z                    | Total Ni Co MnZ Ga Mny |          |
| 0.15           | 11.074                 | 4.76 0.35 - 3.65 -0.08 | 3.57 741.170 |
| 0.26           | 11.084                 | 5.27 0.40 - 3.65 -0.08 | 3.58 690.785 |
| 0.35           | 11.091                 | 5.69 0.44 - 3.65 -0.09 | 3.59 664.351 |
| 0.50           | 11.101                 | 6.39 0.51 - 3.65 -0.10 | 3.60 622.667 |
3.4 Complete disorder: NiMnGa($x$, $z$) systems

Finally, we study the systems with disorder both at $X$ and $Z$ site, i.e., $\text{Ni}_{2-x}\text{Co}_x\text{MnGa}_{1-z}\text{Mn}_z$. Figure 5 and Figure 6 represents the electronic and magnetic structures of NiMnGa($x$, $z$) for ($x = 0.0$, $0.12$ and $0.24$) and ($z = 0.0$, $0.15$, $0.26$, $0.35$ and $0.5$).

![DOS plots](image1)

Figure 5: The DOS for completely disordered NiMnGa($x$, $z$). Figure 5(a) shows the DOS of $x = 0.12$ Figure 5(c-d) shows the DOS of $x = 0.24$ respectively with ($z = 0.15$, and $0.35$). $z=0.26$ and $0.5$ has not been plotted for brevity.

![Exchange interaction plots](image2)

Figure 6: The Exchange interaction for completely disordered NiMnGa($x$, $z$) system. Figure 6(a-c) shows the $J_{ij}$ of $x = 0.12$ Figure 6(c-d) shows the $J_{ij}$ of $x = 0.24$ respectively with ($z = 0.15$, and $0.35$). $z=0.26$ and $0.5$ has not been plotted for brevity.

The variation of magnetic moments of NiMnGa($x$, $z$) are tabulated in Table 3. This shows the presence of Co at Ni induces magnetism in a negative way to all other atoms except the Ni, and their total magnetic moment is changed accordingly.

Replacing Ga with Mn$Z$ on the other hand has a positive effect on magnetic moment. Specially, Mn$Z = 50\%$ gives a comparatively large magnetic moment compare to others.

The variation of magnetic moment of NiMnGa($x$, $z$) as a function of doping concentration is shown in Figure 7(a). The change in magnetic moment in the system changes very linearly within the doping range. This well-behaved nature is good for tuning and applicability of this system.

Finally, we have done mean field based calculations to find the $T_C$ of the systems. Our result shows that doping both $X$ and $Z$ sites increases the $T_C$. But, for NiMnGa(0, $z$), $T_C$ is the highest around $z = 0.12$, then it starts decreasing. On the other hand, doping a little in $X$ site, increases the $T_C$ and increases steadily. Our $T_C$ for NiMnGa(0,0) commensurate with $59$. Unfortunately we are unable to find any literature on variation of $T_C$ with doping. The variation of $T_C$ is shown in Figure 7(b) and tabulated in Table 1 for NiMnGa(0 and $x$, 0), NiMnGa(0, $z$) and NiMnGa($x$, $z$) respectively.
Table 3: Optimized lattice parameter and magnetic moments on individual atoms for NiMnGa(0, z) system.

| Concentrations | Lattice Parameter (au) | Magnetic Moment(µB) | $T_C$ (K) |
|----------------|------------------------|---------------------|----------|
| $x$ , $z$     | Total Ni Co Mn$_Z$ Ga Mn$_Y$ |                     |          |
| 0.12           | 0.15 11.062 4.90 0.37 1.08 3.60 -0.09 3.51 | 1374.932          |          |
|                | 0.26 11.066 5.41 0.42 1.14 3.60 -0.09 3.52 | 1464.969          |          |
|                | 0.35 11.073 5.82 0.46 1.18 3.59 -0.09 3.52 | 1538.180          |          |
|                | 0.50 11.082 6.52 0.52 1.26 3.59 -0.10 3.54 | 1653.155          |          |
| 0.24           | 0.15 11.042 5.03 0.39 1.08 3.54 -0.09 3.46 | 1388.860          |          |
|                | 0.26 11.048 5.54 0.44 1.13 3.54 -0.09 3.47 | 1476.459          |          |
|                | 0.35 11.054 5.95 0.48 1.18 3.54 -0.10 3.47 | 1548.840          |          |
|                | 0.50 11.063 6.63 0.54 1.25 3.54 -0.10 3.48 | 1661.804          |          |

(a) Variation of magnetic moment with doping concentration.

(b) Variation of $T_C$ with doping concentration.

Figure 7: Variation of magnetic moment and $T_C$ of NiMnGa($x$, $z$).

4 Discussions

In the pristine Ni$_2$MnGa, there is a pseudogap in minority channel $\approx$ 1ev below the Fermi-level. This pseudogap is originated due to the hybridization between $d$ orbitals of Ni and 3$p$ states of Ga. The gap is terminated by a peak just below the Fermi-level originated from the hybridization of same orbitals and drives the system to Jahn-Teller instability. In NiMnGa($x$, 0) and NiMnGa($x$, $z$) sytems, with the doping at Ni site stabilize the Jahn-Teller instability as the peak smears out and the pseudogap becomes narrower with higher $x$ value, as shown in Figure 4 for NiMnGa($x$, 0) and Figure 5 for NiMnGa($x$, $z$). In NiMnGa(0, $z$) systems the pseudogap almost remains same throughout the doping range as shown in Figure 6.

The magnetic moments are of NiMnGa($x$, 0), NiMnGa(0, $z$) and NiMnGa($x$, $z$) are shown in Table 1, Table 2 and in Table 3, respectively. From the tables and Figure 7a, which shows the variation of total magnetic moment as a function of $x$ and $z$ concentrations, we see the general features: (i) Magnetic moment is increasing linearly with doping. (ii) Magnetic moments increase faster in doping in $Z$ site than doping in $X$ site. This is due to the overall magnetic moments of $X$ site occupants, i.e., Ni and Co has less magnetic moment that of Mn$_Z$. (iii) Mn$_Z$ has higher magnetic moment that Mn$_Y$ site. The variation in $x$ and $z$ affects the atomic moments in various sites and in turn, affects the total magnetic moments. General observations are (i) Atomistic moments of $X$ site is most susceptible to $x$ and $z$ concentrations, while $Y$ and $Z$ sites moment remains almost unchanged. (ii) Both Ni and Co moment increases with $x$, $z$ concentration
but more with $z$ concentrations.

The Curie temperature $T_C$ has been calculated using mean field approximations (MFA). As expected, MFA overestimates the $T_C$. For pure Ni$_2$MnGa, our calculated $T_C \approx 392K$ is in good agreement with experimental finding 365K [39]. For NiMnGa($x$, $z$), the qualitative variation of $T_C$ increases monotonously, with the quantitative value matching the previous findings [24]. $T_C$ for NiMnGa($0$, $z$) first increase from 392K to 741K for $z = 0.15$. Higher doping of Mn$_Z$ decrease the $T_C$ monotonously. For Co-doped systems, both NiMnGa($x$, $0$) and NiMnGa($x$, $z$) increases monotonously and gives approximately same $T_C$ irrespective of Mn$_Z$ concentrations. To get an understanding of the variation of $T_C$, we have calculated the magnetic pair interaction $J_{ij}$ as shown in Figure (2b), (3b.1b.2), (4b.1b.4) and (6a-3b) for Ni$_2$MnGa, NiMnGa($x$, $0$), NiMnGa($0$, $z$) and NiMnGa($x$, $z$) respectively with Mn$_Y$ at the center. When Co atom is present, i.e., $x \neq 0$ (as in NiMnGa($x$, $0$) and NiMnGa($x$, $z$) case), Mn$_Y$-Co is the dominant interaction. The difference is for NiMnGa($x$, $0$) the maximum interaction is almost constant (3b.1b.2) but for NiMnGa($x$, $z$) the interaction keeps increasing. The same variation is evident from Figure (7b) for $x = 0.15, 0.24$. For NiMnGa($0$, $z$), the there is a ferro-antiferro competition between Mn$_Y$-Ni and Mn$_Y$-Mn$_Z$. This brings the $T_C$ down after initial increase from pure Ni$_2$MnGa.

5 Conclusion

We have investigated the electronic and magnetic properties of Ni$_{2-x}$Co$_x$MnGa$_{1-z}$Mn$_z$, with $0 \leq x \leq 0.24$, $0 \leq z \leq 0.5$. The study of replacing both $X$ and $Z$ is significantly sparse compared to any one of them. We have used DFT and Mean Field approximations to study the compound effect of dual-doping. Electronic structures, DOS and magnetic properties including magnetic exchange and moments are calculated using DFT as implemented in SPRKKR package. The critical temperature, $T_C$ is calculated using MFA. Our calculation shows the existence of strong Mn-Mn antiferromagnetic interaction between Mn at Ga and Mn at its own sub-lattice. It is also noticed that changing concentration at Mn$_Z$ does not change the magnetic exchange significantly. This is an interesting result, as opposed to the findings in the case of Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ [30].

The $T_C$’s are obtained using MFA simulations using the magnetic exchange values obtained from ab-initio calculations. The numerical results for pure system are very close to that reported by experiments.

We would like to point out the calculations are done in cubic($c/a = 1$) phases only. Nevertheless, the dual-doping case, we have shown the variation of magnetic exchange parameters and magnetic critical temperatures. We believe, these findings will be helpful for designing the functional properties like MCE and shape memory alloys by alloying Ni$_2$MnGa suitably.

6 Acknowledgement

We acknowledge the High Performance Computing Center (HPCC), SRM IST for providing the computational facility to carry out this research work effectively.

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