Magnetic properties and electronic structure of Mn–Ni–Ga magnetic shape memory alloys

Sunil Wilfred D’Souza¹, Tufan Roy², Sudipta Roy Barman¹ and Aparna Chakrabarti²

¹ UGC-DAE Consortium for Scientific Research, Khandwa Road, Near IT Park, University Campus, Indore, Madhya Pradesh 452001, India
² Raja Ramanna Centre for Advanced Technology, Near Rajendra Nagar, PO CAT, Indore, Madhya Pradesh 452013, India
E-mail: aparna@rrcat.gov.in

Received 12 July 2014, revised 14 October 2014
Accepted for publication 23 October 2014
Published 24 November 2014

Abstract
Influence of disorder, antisite defects, martensite transition and compositional variation on the magnetic properties and electronic structure of Mn₂NiGa and Mn₁₊xNi₂₋ₓGa magnetic shape memory alloys have been studied by using full potential spin-polarized scalar relativistic Korringa–Kohn–Rostocker (FP-SPRKKR) method. Mn₂NiGa is ferrimagnetic and its total spin moment increases when disorder in the occupancy of MnNi (Mn atom in Ni position) is considered. The moment further increases when Mn–Ga antisite defect [1] is included in the calculation. A reasonable estimate of $T_C$ for Mn₂NiGa is obtained from the exchange parameters for the disordered structure. Disorder influences the electronic structure of Mn₂NiGa through overall broadening of the density of states and a decrease in the exchange splitting. Inclusion of antisite defects marginally broaden the minority spin partial DOS (PDOS), while the majority spin PDOS is hardly affected. For Mn₁₊xNi₂₋ₓGa where $1 \geq x \geq 0$, as $x$ decreases, MnMn moment increases while MnNi moment decreases in both austenite and martensite phases. For $x \geq 0.25$, the total moment of the martensite phase is smaller compared to the austenite phase, which indicates possible occurrence of inverse magnetocaloric effect. We find that the redistribution of Ni 3d- MnNi 3d minority spin electron states close to the Fermi level is primarily responsible for the stability of the martensite phase in Mn–Ni–Ga.

Keywords: electronic structure of bulk materials, ferromagnetic shape memory alloy, martensite transition

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

1. Introduction

Mn₂NiGa is a magnetic shape memory alloy (MSMA) that has become focus of intensive research due to its important properties of technological relevance such as sizable magnetic field induced strain of about 4%, high Curie temperature (588 K) [2], and recently discovered spin-valve like magnetoresistance behavior [1]. However, there are only a few theoretical studies in the literature that provide a basic understanding of the electronic structure and magnetic properties in this system. *Ab initio* density functional theory based calculation using full potential linearized augmented plane wave (FPLAPW) method has shown that Mn₂NiGa can undergo a volume conserving structural transition from austenite to martensite phase, with $c/a = 1.25$ implying that this material can exhibit shape memory effect [3]. It was demonstrated by considering different starting magnetic configurations that the ground state of this material is
ferromagnetic with antiparallel coupling between the two nearest neighbor Mn atoms in both the austenite and martensite phases [4]. The ferromagnetic state originates from the difference in hybridization of the majority and minority spin states: the hybridization between the majority spin Ni and MnMn 3d states is stronger than the hybridization between Ni and MnNi 3d minority spin states (the notations such as MnMn and MnNi are defined in the caption of table 1) [3]. It was pointed out that the self consistent calculations could converge to a local minimum that is not the actual ground state [4], as was the case in [5] where, in the martensite phase, Mn2NiGa was claimed to be ferromagnetic (FM) with almost zero moment on Mn(B) atoms. Subsequently, different theoretical studies on related MSMA systems such as Mn2NiIn [6], Mn2NiAl [7], and Mn2NiSn [8] have reported antiparallel coupling of the MnMn and MnNi moments. Using total energy minimization and considering different starting magnetic states, Mn2NIn was predicted to be a MSMA with ferrimagnetic ground state and stable tetragonal structure with \(c/a = 0.967\) [6]. A martensite transformation has indeed been observed experimentally in Mn2Ni1.6In0.4 ribbons [9]. It has been shown that existence of disorder between Mn and Ni atoms in Mn2NiSn increases the magnetic moment compared to the ordered structure [8].

Powder diffraction studies reported that Mn2NiGa has a disordered cubic (L2_1) structure in the austenite phase with \(Fm\overline{3}m\) space group [10, 11], in disagreement with an earlier x-ray diffraction (XRD) study that showed that Mn2NiGa has ordered Hg2CuTi type inverse Heusler structure with \(F\overline{4}3m\) space group [5]. XRD studies showed that the structure of Mn2NiGa is highly dependent on residual stress [11]. The total moment in the martensite phase was found to be lower than the austenite phase by theory [3], which was later confirmed by magnetization and Compton scattering studies [12].

Recently, an unusual asymmetric magnetoresistance variation indicating a spin-valve like behavior in Mn2NiGa was attributed to the formation of ferromagnetic clusters in the ferrimagnetic lattice [1]. This was concluded on the basis of neutron diffraction studies that established existence of about 13% Mn–Ga antisite defects in Mn2NiGa lattice that is ferrimagnetic. It was established by our spin polarized relativistic Korringa–Kohn–Rostoker (SPRKKR) calculations [1] that ferromagnetic clusters occur because of the Mn–Ga antisite defects. Thus, disorder and defects play important role in Mn2NiGa, and it is crucial to understand their influence on its electronic structure and magnetic properties. So, in this paper, using the SPRKKR method, we investigate these issues in Mn–Ni–Ga \((\text{Mn}_{1-x}\text{Ni}_{x}\text{Ga})\) where \(1 \geq x \geq 0\) with major emphasis on Mn2NiGa. The paper is organized as follows: The Computational Details section discusses the method of calculation and provides the details of the structures used. The Results and Discussions section is divided into six sub-sections: In the first two sections 3.1 and 3.2, the behavior of the magnetic moments of Mn–Ni–Ga are discussed. Subsequently, the exchange interaction parameters and the Curie temperature of Mn2NiGa are discussed (section 3.3). The next two sub-sections deal with the effect of disorder and martensite transition on the electronic structure of Mn2NiGa. Section 3.6 discusses the influence of compositional variation on the electronic structure.

2. Computational details

The electronic structure calculations have been carried out by full potential spin polarized scalar relativistic Korringa–Kohn–Rostocker (FP-SPRKKR) Green’s function technique [13]. Substitutional disorder has been accounted for by the coherent potential approximation (CPA). The exchange-correlation effects are taken into consideration by using the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof parametrization scheme [14]. An angular momentum expansion up to \(l_{\text{max}} = 3\) on a \(22 \times 22 \times 22\) \(k\)-point mesh in the irreducible wedge of the Brillouin zone was used.
to obtain an accurate ground state potential through the self-consistent cycles. Both the energy convergence criterion and the CPA tolerance were set to $10^{-5}$ Ry.

Table 1 depicts the different crystal structures that have been used in this work. In the austenite phase, disorder has been considered by using the $Fm\bar{3}m$ space group and this structure is henceforth referred to in the text as $D_A$ (Disordered Austenite).

For the purpose of comparison, the calculations have also been performed using the ordered inverse Heusler structure referred to as $O_A$ (Ordered Austenite). Disorder in the martensite phase has been considered through the $Fmmm$ (S.G. 69) space group and is referred to as $D_M$ (Disordered Martensite). We have also carried out the SPRKKR calculation for Mn$_2$NiGa using the recent structure provided by neutron diffraction [1] that reports presence of Mn–Ga antisite defects $D_{W\bar{A}}$ i.e. Disordered with Antisite defect) and Martensite ($D_{W\bar{A}M}$) phases to examine the effect of the antisite defects on the magnetic properties and the electronic structure (table 1). In the above notations, if the subscript (A and M indicating austenite and martensite phase, respectively) is not used, both the phases are indicated. The lattice constants used in the present calculations (table 2) for all the compositions in the austenite and martensite phase were obtained by carrying out total energy minimization using FPLAPW method as implemented in the WIEN97 code for the corresponding ordered structures [15]. The parameters used for the calculations are provided elsewhere [3].

### 3. Results and discussion

#### 3.1. Magnetic moments of Mn$_2$NiGa

The magnetic moments of Mn$_2$NiGa-$O_A$ in table 3 portrays a ferrimagnetic ground state where Mn$_{Mn}$ and Mn$_{Ni}$ spin moments are antiparallel. Calculations with Mn$_{Ni}$ parallel to Mn$_{Mn}$, resulted in $638\text{ meV}$ larger total energy. The results of atomic sphere approximation (ASA) and FP-SPRKKR calculations are similar, although Mn$_{Ni}$ moment is somewhat overestimated in ASA, resulting in marginally smaller total spin moment (table 3). The individual orbital moments calculated by fully relativistic (FR) ASA SPRKKR method by us and by FR-KKR-ASA method by Galanakis [16] show that these values are negligible compared to the spin moments, and hence can be neglected. Table 3 also shows that the moments obtained from FP-SPRKKR for both Mn$_2$NiGa-$O_A$ and Ni$_2$MnGa are in excellent agreement with the moments calculated by the FPLAPW method [3, 6, 17–19].

| Composition | Austenite a | Martensite a | Martensite c |
|-------------|-------------|-------------|-------------|
| Mn$_2$NiGa (x = 1) | 5.850 | 5.409 | 6.762 |
| Mn$_{75}$Ni$_{12.5}$Ga (x = 0.75) | 5.846 | 5.388 | 6.882 |
| Mn$_{12.5}$Ni$_{15}$Ga (x = 0.5) | 5.834 | 5.377 | 6.869 |
| Mn$_{12.5}$Ni$_{15}$Ga (x = 0.25) | 5.822 | 5.364 | 6.856 |
| Ni$_2$MnGa (x = 0) | 5.820 | 5.378 | 6.776 |

### Table 2. Optimized lattice constants (in Å) for Mn$_{1+x}$Ni$_{2-x}$Ga in the austenite and martensite phase.

### Table 3. Spin magnetic moments ($\mu_B$/f.u.) of Mn$_2$NiGa-$O_A$ and Ni$_2$MnGa in the austenite phase.

| Composition | Mn$_{Mn}$ | Ni | Mn$_{Ni}$ | Total spin |
|-------------|-----------|---|-----------|------------|
| Mn$_2$NiGa-$O_A$ | 3.42 | 0.24 | -2.76 | 0.9 |
| Ni$_2$MnGa | 3.54 | 0.32 | — | 4.09 |

#### Table 4. Spin magnetic moments ($\mu_B$/f.u.) of the disordered and ordered structures of Mn$_2$NiGa in austenite and martensite phases using FP-SPRKKR method.

| Mn$_2$NiGa structures | Mn$_{Mn}$ | Ni | Mn$_{Ni}$ | Total spin |
|-----------------------|-----------|---|-----------|------------|
| $O_A$ | 3.31 | 0.34 | -2.52 | 1.13 |
| $D_A$ | 3.29 | 0.43 | -1.5 | 2.22 |
| $D_{W\bar{A}}$ | 3.28 | 0.46 | -1.47 | 3.38 |

In Mn$_2$NiGa-$O_A$, which is the ordered inverse Heusler structure, Mn$_{Ni}$ occupies one of the two allowed Ni positions: (0.25, 0.25, 0.25) or (0.75, 0.75, 0.75). On the other hand in Mn$_2$NiGa-$D_A$, Mn gets randomly distributed in both the Ni sites. Interesting influence of disorder on the magnetic moments is evident from table 4. The total spin moment in the austenite phase increases from 1.13 to 2.22 $\mu_B$/f.u. between $O_A$ and $D_A$. This increase is due to the decrease in the magnitude of the antiparallel Mn$_{Ni}$ moment from 2.52 to 1.5 $\mu_B$/f.u. in presence of disorder, while the Mn$_{Mn}$ and Ni parallel moments remain largely unchanged. The origin of this effect can be traced to substantial changes in the density of states (discussed latter in section 3).

In Mn$_2$NiGa-$D_{W\bar{A}}$, where there are multiple magnetic interactions, the self-consistency calculations might converge to a local minimum depending on the starting magnetic moment configuration [3, 4, 6]. So, to obtain the lowest energy magnetic state, different starting configurations of Mn$_{Ni}$, Mn$_{Mn}$ and Mn$_{Ga}$ moments have been considered (table 5) [1]. We find that for the ferromagnetic state, where all the three types of Mn atoms are parallel, the total energy ($E_{tot}$) is largest (381 meV, third row in table 5). The ground state is obtained when Mn$_{Ga}$ is parallel to Mn$_{Mn}$, but anti-parallel to Mn$_{Ni}$ spin moments. Thus, SPRKKR theory supports the results obtained from neutron diffraction [1]. While the Mn$_{Ni}$ and
Table 5. The starting and converged MnMn, MnGa, and MnNi spin magnetic moments (\(\mu_B/\text{f.u.}\)) of Mn2NiGa-DwA\(_m\) along with the corresponding converged total energies (\(E_{\text{tot}}\)). The lowest \(E_{\text{tot}}\) is taken to be zero meV.

| Starting moments | Converged moments | \(E_{\text{tot}}\) (meV) |
|------------------|------------------|-----------------------|
| \(M_{\text{Mn}}\) | \(M_{\text{Ga}}\) | \(M_{\text{Ni}}\) | \(M_{\text{Mn}}\) | \(M_{\text{Ga}}\) | \(M_{\text{Ni}}\) |
| 3.00 | 3.00 | -3.00 | 3.29 | 3.39 | -2.32 | 0 |
| 3.00 | -3.00 | -3.00 | 3.27 | -3.29 | -2.38 | 48 |
| 3.00 | 3.00 | 3.00 | 2.98 | 3.14 | 2.25 | 381 |

\(M_{\text{Mn}}\) are antiparallel because of direct interaction at relatively short nearest neighbor distances \([4, 6, 20]\), \(M_{\text{Ga}}\) being the next nearest neighbor of \(M_{\text{Mn}}\) at a larger separation, their interaction is ferromagnetic.

Having established the magnetic ground state of Mn2NiGa-DwA\(_m\), we focus on the influence of the Mn–Ga antisite defects on the magnetic properties. From table 4, comparison of \(D_A\) and \(DwA_A\) moments show that the local moments are mostly unchanged while between \(D_M\) and \(DwA_M\) the local moments increase slightly in the latter. However, the main reason for the increase in the total moment is the ferromagnetic contribution from \(M_{\text{Ga}}\), although only about 13% \([1]\), is sizable because of its large moment (3.38 \(\mu_B\)). This causes the total moment to increase substantially, e.g. from 2.22 to 2.85 \(\mu_B/\text{f.u.}\) in the austenite phase and from 1.25 to 2.07 \(\mu_B/\text{f.u.}\) in the martensite phase. Experimentally however, a saturation moment of 1.5 \(\mu_B/\text{f.u.}\) is obtained at 5 K indicating that for such a complicated disordered system with two types of magnetic interactions, SPRKKR might be overestimating the moment or it is also possible that the structure might not be fully disordered. Moreover, possibility of rotated or tilted Mn magnetic moments at the interface of the ferromagnetic cluster formed by Mn–Ga antisite defect has been proposed \([1]\), which has not been considered in the present calculation.

### 3.2. The magnetic moments in Mn\(_{1+x}\)Ni\(_{2−x}\)Ga as a function of composition (x)

The total magnetic moment clearly increases with decreasing Mn content from 2.22 \(\mu_B/\text{f.u.}\) in Mn2NiGa (\(x = 1\)) to 4.13 \(\mu_B/\text{f.u.}\) for Ni2MnGa (\(x = 0\)) in the austenite phase, and similar variation is observed also in the martensite phase (table 6) (see figure 1(a)). As \(x\) decreases, although the magnetic moment of Ni remains almost unchanged and \(M_{\text{Mn}}\) moment increases while \(M_{\text{Ni}}\) moment decreases (figure 1(b)), the large increase in the total moment is caused by the increase in the number of \(M_{\text{Ni}}\) atoms that reduces the contribution of MnMn–MnNi antiferromagnetic (AFM) interaction to the total moment. This can be correlated with the decrease in the \(M_{\text{Ni}}\) 3d partial DOS with decreasing \(x\), as shown later in figure 5(b). As the composition approaches Ni2MnGa, the MnMn–MnMn ferromagnetic interaction mediated by Ni dominates and a nearly linear variation of the total moment with \(x\) is observed (figure 1(a)).

Having discussed the behavior of the magnetic moments with composition, we turn our attention to what happens across the martensite transition. For Ni2MnGa (\(x = 0\)), the difference in the total moment between the austenite phase and the martensite phase i.e. \(\Delta M\) is negative (figure 1, table 6). On the contrary, for \(x \geq 0.25\), the total moment in the martensite phase is smaller than the austenite phase (\(\Delta M > 0\)). This behavior for Mn excess compositions originates mainly due to the decrease in \(M_{\text{Ni}}\) moments in the martensite phase (figure 1(b)). The origin of this effect is related to the martensite phase transformation resulting in the modification of the magnetic exchange interactions due to change in the crystal structure. From table 4, it is evident that the total spin moment is smaller in the martensite phase for both Mn2NiGa-D and -DwA, the corresponding \(\Delta M\) being 44% and 27%, respectively. Experimentally, about 10% decrease in magnetization is observed in Mn2NiGa in both cooling and heating cycles across the martensite transition at 5 Tesla \([22]\). An interesting property of metamagnetic shape memory alloys is inverse magnetocaloric effect in which a magnetic material cools down under the application of external magnetic field adiabatically, due to an increase in the isothermal magnetic entropy \((\Delta S > 0)\) of the spin structure \([23, 24]\). This effect has been related to the decrease of magnetization in the martensite phase across the martensite transition temperature and has been observed in metamagnetic shape memory alloys such as Ni–Mn–Sn and Ni–Mn–In \([25, 26]\). Recent \textit{ab initio} calculations show that magnetic ordering governed by the \(d\) electrons result in the magnetostructural instability that is accompanied by a drop in magnetization \([27]\). In contrast, for conventional magnetocaloric effect, magnetization increases in the martensite phase. The sign of \(\Delta M\) calculated by us could be used to predict inverse or conventional magnetocaloric behavior, since the change in magnetization across the martensite transition temperature is related to the structural change between the two phases. It is interesting to note that our calculations for Mn–Ni–Ga systems show that \(\Delta M\) is positive in almost the whole range \((x \geq 0.25)\) of Mn excess compositions predicting that inverse magnetocaloric behavior would be observed. Very recently, this has been corroborated by experiment: both Mn2NiGa and Mn1.75Ni1.25Ga exhibit inverse magnetocaloric effect, while the conventional magnetocaloric cooling is observed for Ni3MnGa \([22, 28, 29]\).

### 3.3. Exchange interaction parameter and Curie temperature of Mn2NiGa

Large Curie temperature of 588 K is one of the major advantages of Mn2NiGa over Ni2MnGa from technological perspective. In this section, we have calculated the exchange interaction parameters of Mn2NiGa based on the real space approach as proposed by Lichtenstein \textit{et al} \([30]\). The \(J_{ij}\)'s for inter sublattice (\(M_{\text{Mn}}\)–Ni, \(M_{\text{Ni}}\)–Ni, \(M_{\text{Mn}}\)–MnMn) and the intra sublattice (\(M_{\text{Mn}}\)–MnMn, \(M_{\text{Ni}}\)–MnMn, Ni–Ni) interactions for Mn2NiGa–O\(_A\) are shown in figure 2(a). \(M_{\text{Mn}}\)–Ni is clearly the dominant ferromagnetic interaction in the first nearest neighbor (nn) (5.4 meV). The \(M_{\text{Mn}}\)–MnMn ferromagnetic interaction, although weaker in the first nn (0.8 meV), extends up to the 4th coordinate shell. The Ni–Ni interaction is also ferromagnetic in the first nn (0.01 meV). The most dominant antiferromagnetic interaction (−34 meV) in the
Table 6. Spin magnetic moments ($\mu_B$/f.u.) of Mn$_{1+x}$Ni$_{2-x}$Ga in the austenite ($D_A$ structure) and martensite phase ($D_M$ structure).

| Composition       | Austenite | Martensite |
|-------------------|-----------|------------|
|                   | Mn$_{Mn}$ | Ni | Mn$_{Ni}$ | Total | Mn$_{Mn}$ | Ni | Mn$_{Ni}$ | Total |
| Mn$_2$NiGa ($x = 1$) | 3.29      | 0.43 | −1.49 | 2.22 | 3.12 | 0.34 | −2.21 | 1.25 |
| Mn$_{0.75}$Ni$_{1.25}$Ga ($x = 0.75$) | 3.34      | 0.40 | −1.56 | 2.64 | 3.21 | 0.34 | −2.33 | 1.85 |
| Mn$_{1.5}$Ni$_{1.5}$Ga ($x = 0.5$) | 3.39      | 0.37 | −1.78 | 3.03 | 3.28 | 0.37 | −2.34 | 2.63 |
| Mn$_{2.25}$Ni$_{1.75}$Ga ($x = 0.25$) | 3.45      | 0.36 | −2.08 | 3.54 | 3.35 | 0.39 | −2.36 | 3.41 |
| Ni$_2$MnGa ($x = 0$) | 3.52      | 0.34 | — | 4.13 | 3.42 | 0.41 | — | 4.16 |

Figure 1. (a) The variation of the total magnetic moment of Mn$_{1+x}$Ni$_{2-x}$Ga as a function of $x$ (1 $\geq x \geq 0$) i.e. decreasing Mn concentration from Mn$_2$NiGa to Ni$_2$MnGa. The experimental magnetization data [1, 5, 21] are also indicated by symbols. (b) The variation of the Mn$_{Mn}$ and Mn$_{Ni}$ spin magnetic moments of Mn$_{1+x}$Ni$_{2-x}$Ga as a function of $x$. In reality the structure exhibits disorder. Therefore, we have calculated the $J_{ij}$ between different sublattices for the disordered structure (Mn$_2$NiGa-$D_A$) as shown in figure 2(b) to examine whether this might improve the situation. Interestingly, we find the main difference with Mn$_2$NiGa-$O_A$ is that the MnNi–MnNi interaction is ferromagnetic in the first nn (2.52 meV). Moreover, the magnitude of the first nn Mn$_{Mn}$–Mn$_{Ni}$ antiferromagnetic interaction decreases to $-16$ meV from $-34$ meV. The Mn$_{Mn}$–Ni ferromagnetic interaction increases from 5.3 to 7.8 meV, while the $J_{ij}$ of Mn$_{Ni}$–Ni also changes from $-1.3$ to $-1.6$ meV. The value of $T_C$ needs further investigation because

$T_C$ is generally overestimated in the mean field approach [33, 34] and Mn$_2$NiGa with different magnetic interactions is not strictly a Heisenberg system, this large overestimation of $T_C$ needs further investigation because
for Mn$_2$NiGa-D$_A$ turns out to be 425 K, which is a reasonable estimate that is in better agreement with the experimental value (588 K) compared to Mn$_2$NiGa-O$_A$.

Thus, our FP-SPRKKR calculations show that $T_C$ is overestimated for Mn$_2$NiGa-O$_A$, while it is underestimated for Mn$_2$NiGa-D$_A$, and similar result was obtained using ASA-SPRKKR. Previous work on Ni$_{2.25}$Mn$_{0.75}$Ga [35], which is a ferromagnet albeit with disorder, also underestimated the $T_C$: $T_C$ calculated by single site CPA was 200 K, while the experimental value is 352 K. On the other hand, Ni$_2$MnGa, which is ordered and has one type of magnetic interaction (FM), the $T_C$ reported earlier [31, 35, 36] is in much better agreement with the experimental value (376 K) [37, 38]. Thus, in the case of a disordered system, the averaging character of CPA is a possible reason for the underestimation of $T_C$. Moreover, in Mn$_2$NiGa there are both FM and AFM magnetic interactions. Besides, on the experimental front, the value of $T_C$ might depend on the sample heat treatment history as is the case of crystal structure [11], but such experimental studies do not exist in literature.

3.4. Electronic structure of Mn$_2$NiGa: effect of disorder and antisite defects

The total density of states (DOS) of Mn$_2$NiGa-O$_A$ exhibits a peak close to $E_F$ at $-0.15$ eV (indicated by arrow) that arises primarily from hybridization of Ni 3d and Mn$_{3d}$ 3d minority spin states (figure 3). The majority spin Mn$_{3d}$ 3d also contributes intensity in this region ($-0.2$ eV) that is manifested as a broad feature intermixed with Ni 3d and Mn$_{3d}$ 3d majority spin states (figure 3(b)). The most intense broad peak centered around $-1.5$ eV arises mainly from Ni and Mn$_{3d}$ 3d minority spin states, while the majority spin contribution to this peak is due to hybridization of Ni and Mn$_{3d}$ 3d states. On the other hand, the peak at $-3$ eV has primarily majority spin character and originates from Ni and Mn$_{3d}$ 3d majority spin $t_{2g}$ states. The unoccupied DOS is dominated by Mn 3d states; the peak at $0.75$ eV is due to Mn$_{3d}$ 3d majority spin states, while at $1.3$ eV the contribution is from Mn$_{3d}$ minority spin states. In the occupied DOS, the opposite spin peaks dominate: for Mn$_{3d}$ the minority spin peak is around $-2$ eV. From the energy separation of the occupied minority and unoccupied majority spin DOS peaks, we find the exchange splitting of Mn$_{3d}$ to be $2.75$ eV. For Mn$_{3d}$, the most intense minority spin peak is around $-3$ eV, and thus the exchange splitting is estimated to be about $4.4$ eV. Antiparallel local moments between Mn$_{3d}$ and Mn$_{3d}$ originate from occupancy of primarily opposite spin states below $E_F$. The exchange splitting energies and the total DOS in figure 3 are in agreement with the FPLAPW calculations [3].

Interesting modifications are observed in the DOS for Mn$_2$NiGa-D$_A$. In the occupied part, the peak at $-0.15$ eV in the DOS is replaced by a smoothly increasing feature that is nearly flat at $E_F$ (figure 3(a), top panel). The minority spin Mn$_{3d}$ 3d PDOS peak broadens and shifts closer to $E_F$ and appears at about $-1.5$ eV. In the unoccupied part, the peak at $0.75$ eV that is related to Mn$_{3d}$ 3d majority spin states is drastically modified; it decreases in intensity and flattens out into a broad plateau over the energy range of $-1$ to $1$ eV merging with the peak at $-0.15$ eV. These changes imply a sizable decrease in the exchange splitting of Mn$_{3d}$ to about $2.2$ eV. The Ni 3d minority spin states that hybridize strongly with Mn$_{3d}$ 3d minority spin states also broaden and shift by $0.25$ eV toward $E_F$ from $-1.7$ to $-1.56$ eV. In contrast, none

![Figure 3](image-url)
of the PDOS peaks of Mn0.3Ni0.7Ga-3d exhibits any shift, although broadening is clearly observed. This explains why the MnNi spin moment changes in presence of disorder, while MnMn moment is unaffected (table 4). The exchange splitting of MnMn also remains unchanged, while MnNi exchange splitting shows large decrease from 2.8 to 2 eV due to disorder.

Inclusion of Mn–Ga antisite defect in the disordered structure (Mn2NiGa-DwA) causes subtle modifications in the DOS. The broadening increases in general: for example, broadening of the $-1.5$ and $-3$ eV peaks fills up the valleys around $-2$ and $-2.6$ eV (marked by red ticks in figure 3(a), top panel). This is caused by the broadening of the minority spin Ni 3d-MnNi 3d states. Interestingly, although the Ni 3d-MnMn 3d majority spin states have sizable contribution to these peaks, these states hardly exhibit any broadening. In the unoccupied states also, it is the minority spin states that broaden, see for example the peak at $-3$ eV originating from MnMn 3d states (figure 3(b), top and third panel). Thus, inclusion of antisite defects marginally broadens the minority spin PDOS, while majority spin PDOS is hardly affected in both occupied and unoccupied states.

### 3.5. Electronic structure of Mn2NiGa-DwA across the martensite transition

Lattice constant optimization through total energy minimization showed that Mn2NiGa-O is stabilized in the martensite phase through a tetragonal distortion of $c/a = 1.25$ [3], which was in agreement with XRD ($c/a = 1.21$). The DOS calculated for the two phases by FPLAPW method showed a peak at $-0.1$ eV (a corresponding peak at $-0.15$ eV is also observed in figure 3 for O$_\alpha$). The shift of this peak to lower energy in the martensite phase was related to its stabilization (see figure 3 of [3]).

Although we use the same lattice constants as in [3], the above mentioned peak near $E_F$ is absent due to disorder (figure 3(a)). So, it is an important question how the states near $E_F$ behave in the realistic Mn2NiGa-DwA structure, since this will provide a clue to the stability of the martensite phase. From the top panel of figure 4(a), we note that the total DOS at $E_F$ in the martensite phase (3.1 states/eV f.u.) is clearly reduced in comparison to the austenite phase (4.0 states/eV f.u.). In fact, a suppression of the DOS in the martensite phase is observed between $-0.35$ eV to $E_F$, while, in contrast, the DOS between $-1.0$ and $-0.4$ eV is enhanced (see the circled region in figure 4(a), top panel). Thus, there is an unambiguous evidence of transfer of electron states from higher to lower energies that would stabilize the martensite phase. Such transfer of electron states to lower energy is also observed for Mn2NiGa-D (figure 5(a), top panel). In fact, the total DOS for both Mn2NiGa-DwA and -D structures not only shows the transfer of states in the energy range of $-1$ eV to $E_F$, but also in the $-2.8$ to $-1.5$ eV region.

From the PDOS (figure 4(b)), we find that the Ni 3d-MnNi 3d minority spin states are primarily responsible for such redistribution of the electron states, as shown by the red ellipses in figure 4(b). This can be related to the tetragonal distortion ($c/a = 1.25$) in the martensite phase because the Ni–MnNi distance decreases to 2.70 Å from 2.93 Å in the austenite phase resulting in stronger hybridization.

The majority spin MnGa 3d states appear around $-1.3$ and $-2.5$ eV. The minority spin PDOS of MnGa above $E_F$ shows a substantial shift toward $E_F$ in the martensite phase, thus causing an increase of states at $E_F$. Although the behavior of MnGa 3d PDOS is opposite to the behavior of Ni 3d-MnNi.
3d states, its contribution is an order of magnitude small (figure 4(b)). The exchange splitting of MnGa 3d states is about 3.3 eV, which is somewhat smaller than MnMn 3d states.

The occupied DOS is dominated by the majority spin PDOS, while the unoccupied DOS is dominated by the minority spin PDOS for both MnGa and MnMn 3d states. This is the reason that their moments are positive and parallel (table 5). In contrast, the occupied (unoccupied) DOS is dominated by the minority spin PDOS, while the unoccupied (occupied) DOS is dominated by the minority spin PDOS for MnMn (MnNi) 3d states leading to antiparallel orientation.

3.6. The electronic structure of Mn$_{1+x}$Ni$_{2−x}$Ga as a function of composition

In order to understand the role of disorder on the electronic structure of Mn$_{1+x}$Ni$_{2−x}$Ga, we have calculated the total and partial density of states (PDOS) for the series 1 ➝ x ➝ 0 (figure 5). Here, x quantifies MnNi in the formula unit (f.u.) and thus as x decreases, the disorder also decreases. Since martensite transition is observed for the whole series [2, 37], the austenite and martensite total DOS are compared to understand the origin of the stability in the latter (figure 5(a)). The Mn–Ga antisite defects are not considered since this has not been experimentally studied for the whole series. Transfer of electron states to lower energies in the range −0.8 eV to $E_F$ similar to that of Mn$_2$NiGa is noticed for all the compositions, indicating similar origin of the martensite transition in this series.

An interesting change in the DOS near $E_F$ as disorder i.e. x decreases is the appearance of a sharp peak below $E_F$ in the austenite phase at −0.16 eV for $x = 0.75 - 0.25$. This peak is primarily related to Ni 3d $e_g$ minority spin states with sizable admixture of MnNi 3d states 0.35 eV. This peak also broadens out as disorder increases and is hardly present in Mn$_2$NiGa (figure 5(a)). In figure 5(a) top panel, the peak observed at −0.15 eV in Mn$_2$NiGa-O-A disappears in Mn$_2$NiGa-D-A. Thus, it is evident that this peak close to $E_F$ arising from Ni 3d $e_g$ minority spin states is strongly affected by disorder. This peak near $E_F$ has not been observed in the photoemission spectrum of Mn$_2$NiGa [3], and it is evident from the present work that it’s absence is related to disorder. The energy separation between the occupied majority and the unoccupied minority peaks of Mn$_{1+x}$Ni$_{2−x}$Ga PDOS exhibits a small increase in the exchange splitting energy from about 4.5 eV ($x = 1$) to 4.7 eV ($x = 0.25$). On the other hand, the MnNi PDOS shows a decrease in the exchange splitting from 2.3 eV ($x = 1$) to 2.0 eV ($x = 0.25$).

4. Conclusion

Using full potential spin-polarized scalar relativistic Korringa–Kohn–Rostocker (SPRKKR) method, we have studied the spin moments, exchange parameters, Curie temperature and the spin polarized DOS and partial DOS of Mn$_2$NiGa in structures such as ordered (O), disordered (D) and disordered with antisite defect (DWA). Moreover, the series Mn$_{1+x}$Ni$_{2−x}$Ga has been studied in the D structure. For Mn$_2$NiGa, the total spin moment increases due to disorder because of the decrease in the magnitude of the antiparallel MnNi moment.

The presence of Mn–Ga antisite defects induces ferromagnetic interaction between Mn$_{1+x}$Ni$_{2−x}$Ga atoms that enhances the total moment. For Mn$_2$NiGa, total spin moment decreases in the martensite phase for both the disordered as well as antisite defect structures compared to the austenite phase. The exchange parameters show interesting difference...
between ordered and disordered Mn$_2$NiGa. A reasonable estimate of $T_C$ (425 K) compared to the experimental value (588 K) is obtained for the disordered structure (Mn$_3$NiGa-D$_4$). Disorder influences the electronic structure of Mn$_2$NiGa through overall broadening of the PDOS and a decrease in the exchange splitting. Inclusion of antisite defects in the calculation marginally broadens the minority spin PDOS, while the majority spin PDOS is hardly affected in both the occupied and unoccupied states.

For Mn$_{1+x}$Ni$_{2-x}$Ga, as $x$ decreases, an increase in the total moment is caused by the decrease in the number of Mn$_{Ni}$ atoms that reduces the contribution of Mn$_{Mn}$–Mn$_{Ni}$ antiferromagnetic interaction. While for Ni$_2$MnGa, the total spin moment in the martensitic phase is larger than the austenitic phase, for $x \geq 0.25$ this is reversed i.e. the moment in the martensitic phase is smaller. This indicates possible occurrence of inverse magnetocaloric behavior for $x \geq 0.25$. This behavior has been observed in case of Mn$_2$NiGa. Mn$_{Mn}$ PDOS exhibits an increase in the exchange splitting energy as $x$ decreases, while the Mn$_{Ni}$ PDOS shows a decrease in the exchange splitting. A redistribution of Ni 3$d$–Mn$_{Ni}$ 3$d$ minority spin electron states near $E_F$ is primarily responsible for the stability of the martensitic phase in Mn–Ni–Ga.

Acknowledgments

H Ebert, M Meinert, J Minár, S Mankovsky, B Sanyal, and S Singh are thanked for useful discussions. SWD thanks Council of Scientific and Industrial Research, New Delhi for research fellowship. The support from the scientific computing group of the Computer Centre, RRCAT is gratefully acknowledged.

References

[1] Singh S et al 2012 Phys. Rev. Lett. 109 246601
[2] Liu G D, Chen J L, Liu Z H, Dai X F, Wu G H, Zhang B and Zhang X X 2005 Appl. Phys. Lett. 87 262504
[3] Barman S R, Banik S, Shukla A K, Kamal C and Chakrabarti A 2007 Europhys. Lett. 80 57002
[4] Barman S R and Chakrabarti A 2008 Phys. Rev. B 77 174401
[5] Liu G D, Dai X F, Yu S Y, Zhu Z Y, Chen J L, Wu G H, Zhu H and Xiao J Q 2006 Phys. Rev. B 74 054435
[6] Chakrabarti A and Barman S R 2009 Appl. Phys. Lett. 94 161908
[7] Luo H, Liu G, Meng F, Li S, Zhu W, Wu G, Zhu X and Jiang C 2010 Physica B 405 3092
[8] Paul S, Sanyal B and Ghosh S 2013 J. Phys.: Condens. Matter 25 236005
[9] Sánchez Llamazares J L, Sanchez T, Santos J D, Pérez M J, Sanchez M L, Hernando B, Escoda LI, Sutiol J J and Varga R 2008 Appl. Phys. Lett. 92 012513
[10] Brown P J, Kanomata T, Neumann K, Neumann K U, Ouladdiaf B, Sheikh A and Ziebeck K R A 2010 J. Phys.: Condens. Matter 22 056001
[11] Singh S, Maniraj M, D’Souza S W, Ranjan R and Barman S R 2010 Appl. Phys. Lett. 96 081904
[12] Ahuja B L, Ahmed G, Banik S, Itou M, Sakurai Y and Barman S R 2009 Phys. Rev. B 79 214403
[13] Ebert H et al The Munich SPRKKR package, version 5.4 and 6.3 (http://olymp.cup.unimuenchen.de/ak/ebert/SPRKKR)
[14] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[15] Blaha P, Schwarz K, and Luitz J 1999 WIEN97 ed K Schwarz (Wien: Technische Universität Wien)
[16] Galanakis I 2005 Phys. Rev. B 71 012413
[17] Chakrabarti A, Biswas C, Banik S, Dhaka R S, Shukla A K and Barman S R 2005 Phys. Rev. B 72 073103
[18] Ayuela A, Enkovaara J and Nieminen R M 2002 J. Phys.: Condens. Matter 14 5325
[19] Barman S R, Banik S and Chakrabarti A 2005 Phys. Rev. B 72 184410
[20] Hobbs D, Hafner J and Spisak D 2003 Phys. Rev. B 68 014407
[21] Banik S, Rawat R, Mukhopadhyay P K, Ahuja B L, Chakrabarti A, Paulose P L, Singh S, Singh A K, Pandey D and Barman S R 2008 Phys. Rev. B 77 224417
[22] Singh S, Esakki Muthu S, Senyshyn A, Rajput P, Suard E, Arumugam S and Barman S R 2014 Appl. Phys. Lett. 104 051905
[23] Von Ranke P J, de Oliveira N A, Alho B P, Plaza E Jr, de Sousa V S R, Caron L and Reis M S 2009 J. Phys.: Condens. Matter 21 056004
[24] Mañosa L, Planes A and Acet M 2013 J. Mater. Chem. A 1 4925
[25] Krenke T, Acet M, Wassermann E F, Moya X, Mañosa L and Planes A 2005 Nat. Mater. 4 450
[26] Moya X, Mañosa L, Planes A, Aksory S, Acet M, Wassermann E F and Krenke T 2007 Phys. Rev. B 75 184412
[27] Comtesse D et al 2014 Phys. Rev. B 89 184403
[28] Devarajan U, Muthu S E, Arumugam S, Singh S and Barman S R 2013 J. Appl. Phys. 114 053906
[29] Hu F, Shen B and Suna J 2000 Appl. Phys. Lett. 76 3460
[30] Liechtenstein A I, Katsnelson M I, Andreev V A and Gubanov V P 1987 J. Magn. Magn. Mater. 67 65
[31] Şaşioğlu E, Sandratskii L M and Bruno P 2004 Phys. Rev. B 70 075427
[32] Ruzs J, Bergqvist L, Kudrnovský J and Turek I 2006 Phys. Rev. B 73 214412
[33] Sabiryanov R F and Jaswal S S 1997 Phys. Rev. Lett. 79 155
[34] Pajda M, Kudrnovský J, Turek I, Drchal V and Bruno P 2001 Phys. Rev. B 64 174402
[35] Buchelnikov V D et al 2010 Phys. Rev. B 81 094411
[36] Siewert M et al 2011 Appl. Phys. Lett. 99 191904
[37] Banik S, Singh S, Rawat R, Mukhopadhyay P K, Ahuja B L, Astwathi A M, Barman S R and Sampathkumaran E V 2009 J. Appl. Phys. 106 103919
[38] Çakir A, Righi L, Albertini F, Acet M, Farle M and Aktürk S 2013 J. Appl. Phys. 114 183912