Driving force for martensitic transformation in Ni$_2$Mn$_{1+x}$Sn$_{1-x}$

Soumyadipta Pal,$^{1,2}$ Sagar Sarkar,$^{1}$ S K Pandey,$^{1}$ Chhayabrita Maji,$^{1,3}$ and Priya Mahadevan$^{1,*}$

$^1$Department of Condensed Matter Physics and Material Sciences, S N Bose National Centre for Basic Sciences, Block-JD, Sector-III, Salt Lake, Kolkata - 700106, West Bengal, India.
$^2$Department of Physics, Calcutta Institute of Technology, Banitabla, Uluberia, Howrah - 711316, West Bengal, India.
$^3$Department of Materials Science, Indian Association for the Cultivation of Science, 2A & 2B Raja S.C. Mullick Road, Jadavpur, Kolkata - 700032, West Bengal, India.

Abstract

The martensitic transformation in Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ alloys has been investigated within ab-initio density functional theory. The experimental trend of a martensitic transition happening beyond $x = 0.36$ is captured within these calculations. The microscopic considerations leading to this are traced to increased Ni-Mn hybridization which results from the Ni atom experiencing a resultant force along a lattice parameter and moving towards the Mn atoms above a critical concentration. The presence of the lone pair electrons on Sn forces the movement of Ni atoms away from Sn. While band Jahn Teller effects have been associated with this transition, we show quantitatively that at least in this class of compounds they have a minor role.
INTRODUCTION

The interest in shape memory alloys has been driven by the enormous potential these materials represent in various fields ranging from medicine [1] to robotics [2] to aeronautics [3]. This is because one has a diffusionless structural transition which involves the rearrangement of the position of the atoms in the solid. This process is entirely reversible and has been the driving force in using shape memory alloys in wide ranging applications. The microscopic mechanism that drives the transition is therefore of interest which would help us to identify which materials would undergo this martensitic structural transition (MST). Fermi surface nesting [4] and soft phonon modes [5] have often been invoked to explain the MST, with the microscopic origin usually being associated with a band Jahn Teller effect [6]. These reasons however do not seem to be valid across all systems. Examples among Heusler alloys are seen, where despite a soft phonon mode being found in the calculations, no MST has been observed [7]. We consider the example of compounds given by \( \text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x} \).

The unusual feature of this class of compounds is that the martensitic transition is seen only for off-stoichiometric compositions where \( x \) ranges from 0.36 to 0.80 in contrast to other martensites such as \( \text{Ni}_2\text{MnGa} \) where the transition is seen for stoichiometric members. The martensitic transition in \( \text{Ni}_2\text{MnGa} \) has been explained by Jahn-Teller effects [6]. On the other hand the usual explanation offered in the case of \( \text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x} \) is the increased hybridization between the Ni and Mn \( d \) states being responsible for the observed martensitic transition [8]. This effect should be present in the stoichiometric composition also, and these ideas do not explain why one doesn’t have a martensitic transition there.

In the present work we consider several compositions of \( \text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x} \). Our calculations find a transition for \( x = 0.375, 0.50, 0.625, 0.75 \) and 0.875, but find no transition for \( x = 0.0 \) and 0.25, consistent with experiment. As our calculations are able to capture the experimental trend, we went on to examine the microscopic origin of the transition. Considering the \( x = 0.50 \) composition, we have calculated the band structure and fit this to a microscopic tight binding model. This analysis was performed for the cubic structure as well as the martensitic structure and allows us to quantify the changes in the electronic structure. If the origin was Jahn-Teller distortions, one expects a change in the onsite energies as a result of the distortion. One however finds very small changes indicating that we must discard this model.
Short Mn-Ni (Mn1-Ni) bonds equal to 2.624 Å are found in the parent compound Ni₂MnSn. When Mn replaces Sn atoms (referred to as Mn2) one has the same Mn2-Ni bond length in the unrelaxed structure. However it is found that the system lowers its energy with Ni atoms moving towards the Mn2 atoms while there is a smaller decrease in the Ni-Mn1 bond length. This seems surprising at first as all Mn-Sn bond lengths are the same to start with and so are the bond angles leading to similar matrix elements for the hopping between Mn and Ni. This is traced to the fact that while the exchange splitting on Mn1 and Ni are in the same direction, that on Mn2 is opposite. This results in a larger energy gain when Mn2 and Ni interact. At larger doping concentrations one gains energy from Mn1 and Ni interactions also. The increased Mn-Ni hybridization is not the driving force of the martensitic transition as, at $x = 0.25$ one has shortened bonds, but no martensitic transition. As $x$ is increased, the interactions between Mn2 and the neighboring Mn1 leads to substantial deviation from a perfectly $d^5$ character on Mn1 that one finds otherwise. This then allows for energy gain from Mn1-Ni hybridization also. So a Ni atom moves towards both Mn1 and Mn2 and this is achieved by moving along the resultant force which is along a lattice parameter. Further energy lowering is possible by an elongation of that lattice parameters which results in the martensitic transition. The question that follows is why would the Ni atom move towards some of its neighbours over a centrosymmetric situation. This is traced to the presence of the lone pair on Sn. The system gains energy with Ni moving away from the Sn atoms resulting in reduced repulsion felt by the electrons on Ni from those on Sn. Hence a combination of Mn-Ni enhanced hybridization and reduced repulsion from the lone pair on Sn drive the martensitic transition. The lone pair electrons are not only present in Sn, but are also present in other elements like In and Sb. So, the mechanism proposed here should be valid for those systems also.

METHODOLOGY

*Ab-initio* electronic structure calculations are carried out using density functional theory (DFT) as implemented in the Vienna *Ab-initio* Simulation Package (VASP) [9]. We use the projected augmented wave implementation and work with the generalized gradient approximation (GGA) Perdew-Wang [10] for the exchange correlation functional. This has been seen to give a better description of the magnetism in Heusler compounds [11] and we also
see 22-24% enhanced magnetic moments in our GGA calculations compared to the LDA calculations. In off-stoichiometric $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$ ($x = 0.25, 0.375, 0.50, 0.625, 0.75, 0.875$) the Mn at parent site is labelled Mn1 while the Mn doped at Sn site has been labelled Mn2. The magnetic interaction between Mn1 and Mn2 is antiferromagnetic, while that between Ni and Mn1 is ferromagnetic. Monkhorst-Pack k-points mesh of $10 \times 10 \times 10$ for 16 atom unit cell and $10 \times 5 \times 10$ for 32 atom supercell were used to perform the k space integrations and a cut-off energy of 340 eV was used to determine the plane-waves used in the basis. The lattice parameters of the unit cell as well as the ionic positions have been optimised in each of the cases considered and the optimised value is mentioned in the text. An analysis of the electronic structure has been carried out in terms of the band dispersions as well as the partial density of states (PDOS) calculated using spheres of radii $\sim 1.3$ Å around each atom. The magnetic moments have been reported within the same spheres. Additionally an analysis of the electronic structure has been carried out using an interface of VASP to WANNIER90 [12,13]. A basis consisting of Ni $s$ and $d$, Mn $s$ and $d$ as well as Sn $p$ states. A mapping of the Bloch states is made onto Wannier functions, localized on the respective atoms with their angular parts given by the relevant spherical harmonics, via a unitary transformation. A unique transformation is obtained with the requirement of minimizing the quadratic spread of the Wannier functions. The criterion of convergence was that the spread changed by less than $10^{-6}$ between successive iterations. Once the transformation matrices are determined, one has a tight binding representation of the Hamiltonian in the basis of the maximally localized Wannier functions.

RESULTS AND DISCUSSIONS

The experimentally reported unit cell of $\text{Ni}_2\text{MnSn}$ is cubic with a lattice parameter of 6.05 Å[15]. Carrying out an optimization of the lattice parameter within our calculations, the theoretical lattice parameter is found to be 6.06 Å and the structure remains cubic. The distances between Ni and Mn as well as between Ni and Sn are found to be 2.62 Å. In contrast to what we find in $\text{Ni}_2\text{MnSn}$, $\text{Ni}_2\text{MnGa}$ is found to undergo a structural transformation and favors a tetragonal phase at low temperature. This suggests that an important role is played by the p-element in inducing the martensitic transformation. In order to understand this further we examine the atom and orbital projected partial density of states. This is shown
in Fig. 1. Ni \(d\) states are found to contribute in the energy window -4 to 2 eV, which is also the energy window in which Mn \(3d\) states contribute. Sn \(5p\) states are found to have a low weight in the same energy window. Sn \(5s\) states are localized and are found to contribute -8 to -10 eV below the Fermi level, with low weight in the unoccupied part. These states have been referred to as lone pair states as they are not involved in any bonding with the neighboring atoms. This indicates that the electronic structure of \(\text{Ni}_2\text{MnSn}\) emerges from the bonding of the Ni \(3d\) and Mn \(3d\) states. Examining the Mn \(d\) PDOS, one finds that the majority spin states are completely filled while the minority spin states are empty, indicating a \(d^5\) configuration at the Mn site. The exchange splitting of the Mn \(d\) states and the Ni \(d\) states are found to be in the same direction.

Now when one of the Sn atoms is replaced by Mn, corresponding to the composition \(\text{Ni}_2\text{Mn}_{1.25}\text{Sn}_{0.75}\), we find that despite allowing for changes in the cell shape upon optimization, the structure remains cubic. The optimized lattice constant is found to 5.99 Å as against 6.06 Å that was found for the parent compound. The absence of a tetragonal transition at this composition, which is usually associated with the existence of a martensitic transition, is consistent with experiment. There is also a volume contraction found when we replace...
Sn with Mn. This is expected as the ionic radius of Mn is smaller than that of Sn. The bond lengths between Ni-Mn1, Ni-Mn2 and Ni-Sn are found to be 2.57 Å, 2.52 Å and 2.62 Å as against the bond lengths of 2.59 Å found before the atomic relaxations. There is a reduction in the Ni-Mn bond lengths, with a larger reduction in the Ni-Mn2 bond lengths.

We then consider the composition \( x = 0.375 \) in the formula \( \text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x} \). This is close to the composition \( x = 0.36 \) at which point one finds the onset of the martensitic transitions in experiment. This can be realized in a 32 atom supercell. Starting with a cubic unit cell one finds that a tetragonal unit cell is favored at the end of the unit cell optimization with lattice parameters \( a = 6.83 \) Å, \( b \approx c = 5.55 \) Å, resulting in a tetragonality \( a/c \approx 1.23 \). However, the tetragonality reported in experiment \([15,17]\) is \( \sim 1.10 \). This might be due to structural disorder which are not accounted for in the theoretical calculation. The difference in the lattice parameters by GGA based DFT and the experiment has been also reported for Ni-Mn-Ga system \([18]\). Moreover, one finds a reduction in some of the Ni-Mn bond lengths. These are found to be in the range 2.50-2.64 Å for Ni-Mn1, 2.53-2.54 Å for Ni-Mn2. Additionally there is a substantial increase of the Ni-Sn bond lengths from the stoichiometric compound. The question that follows is whether this aids the tetragonality and how. Understanding this would help us to explain the observed martensitic phase transition.

We then continue the discussion by considering the composition \( x = 0.50 \). Here again one finds that there is a reduction in Ni-Mn1 and Ni-Mn2 bond lengths. Additionally there is a tetragonal unit cell which is found to be favored for different combinations of \( x = 0.50 \) which is the indicator of the martensitic transition.

In Fig. 2 fully relaxed crystal structures of initial cubic structure of composition \( x = 0.25, 0.375 \) and 0.50 of \( \text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x} \) have been shown. In each case the optimized Ni-Mn1 and Ni-Mn2 bond lengths have been indicated. Examining the structures closely, we can identify a pattern that emerges in the relaxations. Ni atoms are found to move towards Mn2 atoms, with their bond lengths with Sn increasing. Their movement towards Mn1 atoms is less though at larger concentrations they move towards those Mn1 atoms which are nearest neighbors of Mn2. This is consistent with extended x-ray absorption fine structure (EXAFS) measurements of \( \text{Ni}_2\text{Mn}_{1.4}\text{Sn}_{0.6} \) \([19]\) where one finds that Ni-Mn bond lengths decrease upon martensitic transformation. In the low temperature martensitic phase in the case of Ni K-edge, Ni-Mn and Ni-Sn bond lengths are 2.569 Å and 2.607 Å changing from 2.595
FIG. 2. (Color online) Ni-Mn1 and Ni-Mn2 bond distances in ā unit, after full relaxation of cubic structure of composition $x = 0.25, 0.375$ and 0.50 of Ni$_2$Mn$_{1+x}$Sn$_{1-x}$. The direction of magnetic moment on each atom has been indicated by arrow.

This seems surprising at first and the question we ask next is what are the underlying energetics that dictate the Ni movement. At $x = 0.25$ we find that both Mn1 and Mn2 have an almost $d^5$ configuration though their exchange splittings are opposite in direction. This results in stronger hybridization between Ni and Mn2 atoms, compared to that with Mn1. This is the reason the Ni atom moves towards Mn2. As $x$ is increased, one has Mn1 and Mn2 atoms occupying nearest neighbor sites. They interact with each other and as a result one finds a deviation of Mn1 from a $d^5$ configuration found at $x = 0.25$. This results in a smaller moment on those Mn1 atoms which are closer to Mn2 and is found to be 3.383 $\mu_B$ as against 3.486 $\mu_B$ for the stoichiometric Ni$_2$MnSn. Now one finds that Ni atoms can gain...
energy from interactions with both Mn1 (only the low moment atoms) and Mn2. This is what we find for \( x = 0.375 \) and beyond. The Ni atoms move towards both Mn1 and Mn2. The resultant movement is along a lattice parameter. Hence in each case one finds that the lattice parameter increases along the direction of movement and there is further lowering of energy. The natural question that follows is why does the Ni atom move away from a centro-symmetric position towards the Mn atoms.

In each of the structures shown in Fig. 2 one finds that the movement of the Ni atoms is away from the Sn atoms. The reason for this is apparent when we plot the line profile of the Sn 5s charge density along the Sn-Mn and Sn-Ni bonds of Ni$_2$MnSn in Fig 3. The chosen Mn atom is further away and is at 3.03 Å from the Sn atom. However, the Ni atom is at 2.62 Å from the Sn atom. If there were strong covalent interactions between the Ni and Sn atoms, one would expect the charge density to be more delocalized along the bond. Instead we find that the charge density is more localized along the Sn-Ni bond than along the Sn-Mn bond, the spread reflecting the increased separation of the pair of atoms. This verifies that the driving force of the distortions is additionally the repulsion the electrons on Ni face from those on Sn.

An alternate explanation for the martensitic transition that has been offered has been the band Jahn Teller effect. The idea is that Jahn Teller distortions lift the degeneracy of the \( d \) orbitals. This is aided by tetragonality and hence the conclusion that Jahn-Teller

![FIG. 3. (Color online) Line charge density of the Sn 5s states along the Sn-Mn and Sn-Ni bond. The respective bondlengths are indicated in parentheses.](image)
distortions drive the martensitic transition. In order to quantify this we map the \textit{ab-initio} band dispersions for \( x = 0.50 \) to a tight binding model which included \( s \) and \( d \) orbital states of Ni and Mn and \( p \) orbital states of Sn in the basis. Maximally localized wannier functions were considered for the radial parts of the wavefunction. The tight-binding bands are superposed on the \textit{ab-initio} bands of unstable cubic and fully relaxed tetragonal structure in Fig. 4(a) and (b), respectively.

In both cases, one finds an excellent mapping of the \textit{ab-initio} band structure within the tight-binding model. The relative on-site energy of Ni d states with respect to \( d_{xz} \) spin up state are listed in Table I. The changes one finds in the energies are small. This suggests that Jahn-Teller distortions cannot be the driving force for the martensitic transitions seen in this system. It is important to note that in the spin down channel reduced exchange splitting is possibly due to transfer of charge to Ni atoms. This might be from Sn s states.
Thus our analysis reveals that the lone pair effect of Sn 5s electrons is the main triggering factor for additional tetragonality.

CONCLUSIONS

In summary, we have investigated the structural properties of Ni$_2$Mn$_{1-x}$Sn$_{1-x}$ by means of ab-initio density functional theory. We have obtained martensitic transformation for $x \geq 0.375$ which is in good agreement with the experimental value of $x \geq 0.36$. The relative on-site energies of Ni $d$ states in cubic and fully relaxed tetragonal structure of Ni$_2$Mn$_{1.5}$Sn$_{0.5}$ reveals that the changes in the energies are very small and that the Jahn-Teller effect cannot be the driving force for the martensitic transitions seen in this system. It is the Ni-Mn hybridization and Sn lone pair effect on Ni which makes the cubic structure unstable and triggers the structural transformation for Ni-Mn-Sn systems. The microscopic considerations that result in the mechanism becoming operative in non-stoichiometric compositions are discussed.

We acknowledge funding from DST Nanomission under the umbrella of the Thematic Unit of Computational Material Science and DAE. S.S acknowledges CSIR India for his fellowship.

* Corresponding author: priya.mahadevan@gmail.com

[1] N.B. Morgan, Mat. Sci. Eng. A 378, 16 (2004).
[2] T. W. Duerig, K. N. Melton, D. Stöckel, and C. M. Wayman, Engineering Aspects of Shape
Memory Alloys, Butterworth-Heinemann Ltd. (1990).

[3] D J Hartl and D C Lagoudas, Proc. IMechE Part G: J. Aerospace Engineering. 221, 535 (2007).

[4] C. P. Opeil, B. Mihaila, R. K. Schulze, L. Mañosa, A. Planes, W. L. Hults, R. A. Fisher, P. S. Riseborough, P. B. Littlewood, J. L. Smith, and J. C. Lashley, Phys. Rev. Lett. 100, 165703 (2008).

[5] M. S. Wechsler, D. S. Lieberman, and T. A. Read, J. Met. 5, 1503 (1953).

[6] P. J. Brown, A. Y. Bargawi, J. Crangle, K. -U. Neumann, and K. R. A. Ziebeck, J. Phys.: Condens. Matter 11, 4715 (1999).

[7] S. Ağduk and G. Gökoğlu, J. Alloys Compd. 511, 9 (2012).

[8] M. Ye, A. Kimura, Y. Miura, M. Shirai, Y. T. Cui, K. Shimada, H. Namatame, M. Taniguchi, S. Ueda, K. Kobayashi, R. Kainuma, T. Shishido, K. Fukushima, and T. Kanomata, Phys. Rev. Lett. 104, 176401 (2010).

[9] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).

[10] J.P. Perdew, K. Burke and Y. Wang, Phys. Rev. B 54, 16533 (1996).

[11] H. C. Kandpal, G.H. Fecher and Claudia Felser, J Phys. D 40, 1507 (2007).

[12] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comput. Phys. Commun. 178, 685 (2008).

[13] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).

[14] I. Souza, N. Marzari and D. Vanderbilt, Phys. Rev. B 65, 035109 (2001).

[15] T. Krenke, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, and A. Planes, Phys. Rev. B 72, 014412 (2005).

[16] Y. Sutou, Y. Imano, N. Koeda, T. Omori, R. Kainuma, K. Ishida, and K. Oikawa, Appl. Phys. Lett. 85, 4358 (2004).

[17] P. J. Brown, A. P. Gandy, K. Ishida, R. Kainuma, T. Kanomata, K-U Neumann, K. Oikawa, B. Ouladdiaf, and K .R. A. Ziebeck, J. Phys.: Condens. Matter 18, 2249 (2006).

[18] S. Banik, R. Ranjan, A. Chakrabarti, S. Bhardwaj, N. P. Lalla, A. M. Awasthi, V. Sathe, D. M. Phase, P. K. Mukhopadhyay, D. Pandey, and S. R. Barman, Phys. Rev. B 75, 104107 (2007).

[19] P A Bhobe, K R Priolkar, and P R Sarode, J. Phys.: Condens. Matter 20, 015219 (2008).