First-principles study of the lattice instabilities in Mn$_2$Ni$X$ ($X =$ Al, Ga, In, Sn) magnetic shape memory alloys

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Abstract
Using first-principles based density functional theory, we have investigated the structural instabilities in the austenite phases of Mn$_2$Ni$X$ ($X =$ Al, Ga, In, Sn) magnetic shape memory alloys. A complete softening is observed in the acoustic TA$_2$ branches for all the materials along [$\xi\xi\xi0$] directions leading to instability in the austenite structure which effectively stabilizes into martensitic structure. The reasons behind this softening are traced back to the repulsion from the optical $T_{2g}$ branches and to the nesting features in the Fermi surfaces. The vibrational density of states, the force constants and the elastic moduli are also computed and analyzed, which reconfirm the underlying mechanism behind the instabilities. The results indicate that the phonon anomalies are related to the occurrence of possible pre-martensitic phases which can be quite complex.

Keywords: shape memory alloys, lattice dynamics, Fermi surface

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

1. Introduction
Magnetic shape memory alloys (MSMA) are excellent candidates for technological applications due to their coupling between different degrees of freedom, such as caloric, magnetic, elastic etc, that introduce multifunctionality in these materials. The magneto-structural coupling results in a phase transition between high temperature austenite structure and low temperature martensitic variants driven by magnetic field under ambient conditions. Microscopically, this martensitic transformation is merely a consequence of reshuffling of atomic planes, which is often mediated through different periodically modulated meta-stable structures called premartensitic structure.

Very often, the microscopic origin behind the martensitic phase transformation can be explained by softening of some phonon modes, related to the softness in elastic stiffness constants caused by the nesting topology between parallel Fermi surfaces due to intense electron–phonon coupling. This has been the case for almost all the ternary MSMA's crystallizing in Heusler structure. The most extensively studied ternary MSMA is Ni$_2$MnGa, which in single crystal environments and close to the stoichiometric composition, exhibit nearly 10% magnetic field-induced strains (MFIS) under a magnetic field of less than 1 Tesla [1, 2], making it a strong contender for micro-mechanical sensors and actuators. The structural instability of Ni$_2$MnGa in the austenite phase has been linked with an anomalous phonon softening of transverse acoustic TA$_2$ branch along [$\xi\xi\xi0$] direction. The softening occurs at a fractional wave vector $\xi = (0.33, 0.33, 0)$ and it becomes more prominent as one approaches towards the martensitic phase with decreasing temperature [3–6]. The phonon softening has been found to correlate with the premartensitic phase, which is anticipated by the precursor phonon softening at that wave vector. Inelastic neutron scattering experiments and elastic constants measurements on the high temperature phase corroborated the theoretical calculations of softening of the acoustic branch. A complete softening of the acoustic TA$_2$ branch along [$\xi\xi\xi0$] direction with unstable phonon modes was reported theoretically in Ni$_2$MnAl.
Later, Moya et al verified the Kohn anomaly observed in the theoretical study of the TA₂ branch in this material by performing inelastic neutron scattering experiment on nearly stoichiometric Ni₂MnAl [8]. However, the experimental softening is not complete since the phonon frequencies remain finite even at lowest temperature. This could be related to the fact that the composition needed for the martensitic phase transformation to occur in Ni₂MnAl is slightly off-stoichiometric [9]. First-principles calculations observed similar phonon softening of the same acoustic branch in Ni₂MnIn, Ni₂MnSh, and Ni₂MnSn [10, 11].

Although Ni₂MnGa near the stoichiometric composition is the first discovered ternary system in the Heusler structure exhibiting magnetic shape memory effect, and has been studied extensively revealing a lot of interesting physics, its use in practical applications is hindered due to the martensitic transformation temperature being lower than the room temperature, and poor ductility in poly-crystalline phase [12, 4]. Attempts were made to improve the functionality of the material by introducing disorder with various possibilities and replacing Ga conjointly with Al, Ge, In, Sn and Sb. However, the yield is not as fruitful as expected. Therefore, a quest for new MSMA began with higher operating temperatures and better elastic properties compared to Ni₂MnX. Recently, Mn₂NiGa has been reported to be a MSMA with promising functional properties [13–16]. It has a martensitic transformation temperature close to room temperature (270 K) and much broader hysteresis loop [13]. An excellent two-way shape memory effect with strains of 1.7% and field controllable shape memory effect up to 4% has been observed experimentally in Ni₂MnIn, Ni₂MnSh, and Ni₂MnSn [10, 11].

In this paper, we, therefore, make an attempt to understand the physical origin behind the transformations by examining the vibrational properties of these materials in a systematic way. We compute the phonon dispersion, the vibrational density of states, the elastic constants and the Fermi surfaces in order to see whether connections to the martensitic transformations can be made for these materials. The paper is organized as follows: in section 2, we provide details of the computational methods used, in section 3, we discuss the phonon dispersion relations, the vibrational densities of states, the inter-atomic force constants, the elastic constants and the Fermi surfaces in order to ascertain the mechanisms driving the martensitic transformations and finally we summarize our results indicating their relevance for future research.

2. Computational details

The electronic structures of the systems considered were calculated using the plane-wave pseudopotential (PW-PP) formalism of the density functional theory (DFT), as implemented in QUANTUM ESPRESSO [23]. Ultrasoft pseudo potentials (USPP) [24] were used to accurately calculate the electronic ground states. The spin polarized generalized gradient approximation (GGA) scheme was used as the exchange-correlation part of the potential with Perdew–Wang 91 parameterizations (PW91) [25]. Plane waves with energies up to 544 eV were used to describe electronic wave functions. The Fourier component of the augmented charge density with cut-off energy up to 6530 eV was taken after convergence tests. The Brillouin zone integrations were carried out with finite temperature Methfessel–Paxton smearing [26] method using 12 × 12 × 12 uniform k-mesh, which effectively leads to 364 k-points in the irreducible wedge of the Brillouin zone. The value of the smearing parameter was taken as 0.27 eV. Such choices of the parameters ensure the convergence of phonon frequencies within 5%.

The phonon dispersion relations were computed using density functional perturbation theory (DFPT) [27]. The DFPT scheme is employed to accurately calculate the dynamical properties in condensed matter systems with the precision at par with the electronic structure calculations. The energy threshold value for convergence was 10⁻¹⁶ Ry in phonon calculations. Dynamical matrices were conveniently calculated in reciprocal space from the ground state charge density and from its linear response to the distortion in the ionic configurations. Fourier transform was employed thereafter to obtain the real space force constants. The dynamical matrices were calculated in a 4 × 4 × 4 q-point grid for all the structures.

Convergence of phonon frequencies within 1–2% was ensured by comparing frequencies calculated directly and frequencies obtained by the Fourier transform of the dynamical matrices. Such convergence tests ensured accuracy in elastic constants as they are calculated from the slopes of the phonon dispersion curves. The Fermi surfaces were calculated on 24 × 24 × 24 highly dense uniform k-point grid. It may be noted that the strength of the phonon anomaly is extremely sensitive to temperature. An increase in temperature can reduce the nesting features of Fermi surfaces and thus weaken the anomaly. In

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DFT based calculations, the smearing parameter $\sigma$ plays the role of fictitious electronic temperature. Therefore, to reduce the effect of finite temperature in the calculations of Fermi surfaces, we kept $\sigma = 0.01$ eV all along.

3. Results and discussions

3.1. Crystal structure and lattice parameters

Experimental measurements [13–15, 28] and theoretical calculations [18–21] have confirmed that the alloys considered here favor the Hg$_2$CuTi structure (Space group $F\overline{4}3m$), also known as the inverse Heusler structure, in the cubic austenite phase as opposed to the usual Heusler structure of Ni$_2$MnX. The latter structure is best visualized as four interpenetrating f.c.c sub-lattices at (0, 0, 0), (0.25, 0.25, 0.25), (0.50, 0.50, 0.50) and (0.75, 0.75, 0.75), where the first and the third positions are occupied by Mn atoms, second and the fourth positions by Ni and $X$ atoms, respectively (figure 1(a)). Interchanging the tetrahedral Mn atom at (0.50, 0.50, 0.50) with octahedral Ni atom at (0.25, 0.25, 0.25) keeping the remaining atoms fixed at their positions, leads to an inverse Heusler structure (figure 1(b)). Hereafter, Mn atom at (0,0,0) sub-lattice will be denoted as MnI and the one at (0.25, 0.25, 0.25) as MnII.

Due to the unavailability of experimental results on the lattice constants of Mn$_2$NiAl and Mn$_2$NiIn, we have calculated the equilibrium lattice constants of all the four materials with the GGA exchange-correlation functional and used them here. The total energies as a function of lattice parameters were correlated with the precursor phenomenon prior to the martensitic phase when the systems are cooled from high temperatures. The wave vectors corresponding to the imaginary phonon frequencies indicated shuffling of atomic planes which stabilize the $(c/a) < 1$ phases compared to the parent phase ($(c/a) = 1$). The occurrence of 3M, 5M and 7M modulated structures and even incommensurate structures were confirmed experimentally. Possibilities of such modulated structures can be inferred from the anomalies in our calculated dispersion relations for Mn$_2$NiX systems. A modulated structure with a periodicity of 8 atomic planes (2M structure) can be associated with an instability at $\xi = 0.25$, one with a periodicity of 6 atomic planes (3M structure) can be associated with an instability at $\xi = 0.33$ and one with a shuffling of 14 atomic planes (7M structure) can be associated with an instability at $\xi = 0.29$. For Mn$_2$NiAl, the unstable mode occurs for $\xi = 0.0–0.35$ with the maximum of the dip at $\xi = 0.25$. This suggests the possibilities of occurrence of several modulated phases. The commensurate wave vector closest to the maximum of the dip in the TA$_2$ branch of of Mn$_2$NiGa occurs at $\xi = 0.33$ which can be related to the occurrence of the 3M structure. Since, in Mn$_2$NiGa, the imaginary frequencies extends up to $\xi = 0.50$, in addition to aforementioned modulated structures 5M, modulation can also be observed at $\xi = 0.43$ which stabilizes with the shuffling of 10 atomic planes. In cases of Mn$_2$NiIn and Mn$_2$NiSn, the maximum in the dip of the TA$_2$ branch occurs at $\xi = 0.5$, which cannot be connected to the known modulated structures mentioned above, but the extent of the instabilities in these systems can be connected to the 3M and 5M

3.2. Phonon dispersions

The phonon dispersion spectra calculated at those lattice constants along $[\xi \xi 0]$ highly symmetric direction in the irreducible segment of the Brillouin zone (IBZ) are shown in figure 2. The main interest lies in the transverse acoustic TA$_2$ branch, which exists due to the atomic displacements $[\xi \xi 0]$ perpendicular to the propagation direction $[\xi \xi 0]$. For all Heusler systems exhibiting martensitic transformation, this branch shows an anomalous behavior. Therefore, our aim is to investigate the behavior of acoustic TA$_2$ branch along $[\xi \xi 0]$ direction. The most important features in the dispersion curves are the anomalous dips of the acoustic TA$_2$ branches where the phonon frequencies become imaginary, suggesting instabilities in the cubic austenite structures which usher in a phase transition to stable martensitic phases in all four materials. In Mn$_2$NiGa and Mn$_2$NiAl, the acoustic TA$_2$ branches have negative slopes at $\Gamma$ point, indicating a pure elastic instability in their parent structure. The range of this instability extends up to $\xi = 0.50$ for Mn$_2$NiGa and up to $\xi = 0.35$ for Mn$_2$NiAl. The maximum of the dip occur at wave vectors $\xi = 0.35$ and $\xi = 0.25$ for Mn$_2$NiGa and Mn$_2$NiAl, respectively. For Mn$_2$NiIn, the instability of the TA$_2$ branch starts from $\xi = 0.3$ producing maximum of the dip at wave vector $\xi = 0.50$. For Mn$_2$NiSn, unlike the other materials, the softening extends up to the wedge of the Brillouin zone with the maximum of the dip at $\xi = 0.50$.
modulations. These suggest possibilities of occurrence of new kinds of modulations leading to precursor phenomena in these materials or that there may be more complicated structures with co-existence of multiple modulated phases. Signatures of 7 M modulated phases have been observed experimentally in Mn2NiGa, but the occurrences of these were either dependent on the amount of stress in the system or on the sublattice occupancies. Thus, no definite conclusion on the kind of modulation in this system and the resulting pre-martensitic structures can be made from the available experimental results. Detailed systematic calculations on the non-cubic variants for these systems are to be carried out in order to settle the issue. However, this is beyond the aim and scope of the present study.

Energetically lowest optical $T_{2g}$ branch is Raman active in nature with $[\bar{\xi}00]$ polarization and the other optical branches are infrared active with $T_{1u}$ symmetry. It is known that phonon branches with same symmetry would repel each other. Since the acoustic $T_{2g}$ branch also has same state of polarization; it would be repelled by the $T_{2g}$ branches. In a previous theoretical study, Zayak et al. [29] argued that due to this repulsion the $T_{2g}$ branch is pushed downward and becomes unstable. To prove this, they compared the position of $T_{2g}$ branches at $\Gamma$ point of some stable Heusler alloys at cubic phase like Co$_2$MnGa and Co$_2$MnGe to unstable systems like Ni$_2$MnX ($X$ = Ga, Ge, In, Al) and illustrated that energetically lowered $T_{2g}$ branches in the unstable alloys compared to those alloys with stable cubic phases, produce the necessary repulsive thrust to the lowest vibrational branch. The results in figure 2 suggest the same explanation for the phonon instabilities in Mn$_2$NiX. The repulsion due to the already low lying $T_{2g}$ modes at the $\Gamma$ point for all four materials push the $T_{2g}$ frequencies down setting up the unstable modes. In [29], the authors attributed the occurrence of anomalous unstable modes in Ni$_2$MnGa to the inversion of modes of Ni and Ga. They showed that the contributions to the $T_{2g}$ branches come from the dynamics of Ni atoms and due to the inversion of optical modes, the Ni atoms vibrate at lower frequencies making the frequencies of the $T_{2g}$ mode lower. The repulsion of $T_{2g}$ modes by these $T_{2g}$ modes pull the frequencies of the former down making them imaginary. For the materials investigated here, an analysis of the vibrational amplitudes show that the $T_{2g}$ modes are dominated by the vibrations from Ni and MnI atoms who occupy crystallographic equivalent sites, and in fact the same ones as the two equivalent Ni atoms in Ni$_2$MnGa. Therefore, it would be interesting to examine whether such an inversion of optical mode is also happening for these materials. In the next subsection, we explore this by looking at the vibrational density of states (VDOS).

3.3. Vibrational density of states (VDOS)

In what follows, the atom projected VDOS for Mn$_2$NiAl, Mn$_2$NiGa, Mn$_2$NiIn and Mn$_2$NiSn are presented in figure 3.
Figure 3. Atom projected vibrational density of states (VDOS) showing contributions from different constituent atoms for (a) Mn$_2$NiAl, (b) Mn$_2$NiGa, (c) Mn$_2$NiIn and (d) Mn$_2$NiSn over the frequency range.

It is observed that the vibrational contributions from two Mn atoms occupy different frequency regions in the VDOS plots. This occurs mainly because of the following reasons: the two Mn atoms have different crystallographic symmetry; the atom occupying (0 0 0) sub-lattice, labeled as MnI, have tetrahedral symmetry and the other one at (0.25, 0.25, 0.25), labeled as MnII, sub-lattice have octahedral symmetry. As a consequence of this, their nearest neighbor environments are different leading to different bond stiffness’s (force constants) for the bonds connected to the Mn atoms. A comparison of all the VDOSs show that the VDOSs of Mn$_2$NiIn and Mn$_2$NiSn materials are quite similar and are very different from the VDOSs of the other two materials in the series. Figure 3 suggests that for Mn$_2$NiIn and Mn$_2$NiSn, vibrations of MnI atoms are prominent between 6 THz to 7 THz, whereas contributions from MnII atoms are predominantly lie between 4.5 THz to 6 THz. Due to the slightly larger atomic mass than Mn atom, Ni vibrations occur mostly between 2.5 THz to 4.5 THz. As expected, the lower frequency regions are dominated by In and Sn because they have larger atomic masses than Ni and Mn. For Mn$_2$NiGa, vibrations in the range 7–8 THz are mainly dominated by MnI atom, while vibrations from 5.5 THz to 7 THz have contributions from MnII atoms. A strong peak originated from MnI vibrations coinciding with a peak originating from vibrations of MnII atoms is also observed at 6 THz. In the frequency range 3–5 THz, vibrations of Ni atoms are predominant and the lowermost part of the spectrum is dominated by the vibrations of the Ga atoms. The features in the VDOS of Mn$_2$NiAl is different from the other three. The modes due to the vibrations of Al atoms occur at around 10 THz due to extremely light mass of Al. The Ni modes also occur at lower frequencies, similar to the cases of the other three. The vibrations of MnI and MnII atoms dominate the middle of the spectrum with their respective peaks at 6.25 THz and 7.3 THz. In case of Ni$_2$MnGa, Zayak et al [29] showed that the positions of Ga and Ni contributions to the VDOS were “inverted”, that is, the vibrations of the lighter Ni atoms were at frequencies lower than those of heavier Ga atoms. They connected this anomalous mode inversion to the instability of the TA$_2$ modes of Ni$_2$MnGa. In case of the systems studied here, the overall features in the VDOSs of all four materials suggest that there is no signature of inversion of Ni (MnI) modes with those of the modes from the element X. Thus the occurrence of unstable TA$_2$ modes cannot be associated to this.

3.4. Inter-atomic force constants

In order to understand the features in the VDOS, we analyze the behavior of the real space inter-atomic force constants. In figure 4, we plot the longitudinal component of nearest neighbor force constants of Mn$_2$NiX systems. The transverse components of force constants are not shown in the plot, since their contributions compared to the longitudinal ones are negligible. The force constants between any pair of nearest neighbor atoms are nearly equal for Mn$_2$NiAl with Mn$_2$NiGa. The same is true for Mn$_2$NiIn with Mn$_2$NiSn. However, substantial changes in the force constants between any pairs are observed as one moves from Mn$_2$NiGa to Mn$_2$NiIn. Due to the increase in the inter-atomic distances, as
Figure 4. Longitudinal component of nearest neighbor inter-atomic force constants between MnI, MnII, Ni and X atoms of Mn$_2$NiX materials.

a result of expansion in their equilibrium lattice constants from 5.850 Å to 6.162 Å the MnI–MnII and MnII–Ni longitudinal force constants become softer in Mn$_2$NiIn and Mn$_2$NiSn in comparison to Mn$_2$NiGa. On the other hand, the force constants related to X elements, i.e. MnI-X and Ni-X become harder in Mn$_2$NiIn and Mn$_2$NiSn as compared to Mn$_2$NiGa and Mn$_2$NiAl. This opposite behavior is observed since the sizes of the X elements for the former two alloys are larger than those in the latter two, and thus are able to overcome the expansion of the inter-atomic distances occurring in the former two as compared to the latter two. The nearest neighbor force constants associated to MnII atom, the MnII–Ni and the MnII–MnI, become softer as one moves from Mn$_2$NiGa to Mn$_2$NiIn and Mn$_2$NiSn. Therefore, vibration frequencies corresponding to MnII atoms would be lower in the latter two materials, which agree with the features in the VDOS. In Mn$_2$NiGa, vibrations of MnII extend from 5.5 THz to 7 THz, which in case of Mn$_2$NiIn and Mn$_2$NiSn shift to lower frequencies, around 5.5 THz. The dynamical behaviour of MnI and Ni atoms are more complicated. For both of the atoms, two sets of inter-atomic force constants behave opposite to one another. For Ni, the Ni-X nearest neighbor force constants harden, as one goes from Ga to In and Sn. This should force Ni atoms to vibrate at higher frequencies as one goes from Mn$_2$NiGa to Mn$_2$NiIn and Mn$_2$NiSn. However, the vibrations of Ni atom remain more or less around the same frequency for all the materials, since the previous effect is compensated by increasing softening of the MnII–Ni bonds as one goes from Mn$_2$NiGa to Mn$_2$NiIn and Mn$_2$NiSn. Similarly, hardening of MnI-X force constant does not affect MnI vibrations, as this is compensated by the softening of MnI–MnII inter-atomic force constants.

3.5. Fermi surfaces

Previous first-principles studies in Ni$_2$MnX relate the martensitic instability of those materials with Fermi surface nesting [29–33]. The anomalies in the phonon branch mainly depend on the shape of the Fermi surfaces and the electron–phonon matrix elements via the phonon wave vector $\xi$ [31, 32]. This phenomenon occurs due to strong attraction between two flat-parallel Fermi surfaces connected by a nesting vector $q$, at the expense of atomic displacements and at the wave vector where the maximum dip of the acoustic phonon branch is observed. However, this cannot be generalized for all ternary alloys showing martensitic instabilities. For Co$_2$NiGa, a newly found shape memory alloy, Stiewart et al. [34] observed that softening in TA$_2$ phonon branch was absent as a result of nonappearance of nesting features in the Fermi surfaces of Co$_2$NiGa. Here, we present Fermi surfaces corresponding to the spin-minority bands only, since most prominent features are observed in this spin channel as the systems undergo martensitic transitions [18]. The three dimensional Fermi surfaces of Mn$_2$NiGa for 18th and 19th spin-minority bands are shown in figure 5. The figure clearly exhibits flat portions of both the minority bands. However, to examine the Fermi surface in detail, to obtain clues about the nesting between different parallel Fermi surfaces and hence, to relate this novel feature to observed phonon anomaly, two dimensional (2D) projections are necessary. In figure 7 we show the two-dimensional cross-sections of Fermi surfaces with the (1 1 0) plane for the four systems (The relevant portion of the Irreducible Brillouin zone is shown in figure 6). The cross-sections for Mn$_2$NiGa, Mn$_2$NiAl and Mn$_2$NiIn bear close resemblances while that of the Mn$_2$NiSn is somewhat different. Inspite of this difference, the nesting vectors (indicated by red arrows in Fermi surfaces plots) are consistent with the wave vectors at which the phonon anomalies are observed in our phonon dispersion curves. Thus, we can conclusively associate the occurrences of unstable modes in the Mn$_2$NiX alloys with the Fermi surface nesting. We refrain from further discussions on the differences in shapes of Fermi surfaces between materials with the element X belonging to different columns in the periodic table because it is not necessary in
Mn2NiGa and shown in brackets. Surprisingly, they observed Fermi surface nesting features in the Fermi surfaces and their relations to the martensitic instabilities found in these systems. The dynamical stability of the crystalline phase implies that the strain energy changes be positive definite against all possible small deformations. This condition imposes restrictions on elastic constants. The stability criteria for cubic crystals requires  

\[ c_{44} > 0, \quad c_{11} > |c_{12}|, \quad c_{11} + 2c_{12} > 0 \]  

Therefore to introspect the kinds of instabilities present in the materials considered here and to validate our calculated phonon dispersion results, we compute the elastic constants for all the four materials from the initial slope \((\xi \to 0)\) of phonon dispersion plots along \([\xi \xi 0]\) direction. The elastic constants \(c_{44}, c'=(1/2)(c_{11} - c_{12})\) and \(c_{ij}=(1/2)(c_{11} + c_{12} + 2c_{44})\) are related to TA1, TA2 and LA acoustic modes [37]. These elastic constants are connected to ultrasound velocity via \(c_{ij} = \rho v^2\) relation [37] where \(\rho\) is the mass density. The three independent elastic constants of cubic crystal are tabulated in table 1. Our computed \(c_{12}\) and \(c_{44}\) agree quite well with the experimental results available only for Mn2NiGa, whereas in our calculation, \(c_{11}\) is underestimated [36]. Overall the agreement with experiment is good for Mn2NiGa. This, in effect, is an indirect indication to the accuracy of calculated phonon spectra. The results show that the equation (1) is satisfied by Mn2NiIn and Mn2NiSn only. This indicates that Mn2NiAl and Mn2NiGa are unstable in the cubic structure. We gain further insight into the nature of stabilities of these materials by looking at the other two parameters listed in table 1, the shear constant and the elastic anisotropy ratio. Since the acoustic TA2 branch is related to shear constant \(c'\), hence, negative \(c'\) for Mn2NiAl and Mn2NiGa is an indication of pure elastic instability which stabilizes though shear deformation across \((\xi \xi 0)\) planes in \([\xi \xi 0]\) direction. The same is not true for the other two materials. Although they satisfy equation (1) and have sizable \(c'\), their anisotropy ratios \(A\) are high enough to bring in a martensitic transformation [38]. The elastic anisotropy ratio \(A = c_{44}/c'\) is an important quantity to measure of stability of cubic structures under stress across \((\xi \xi 0)\) planes [39]. The larger the value it acquires, more unstable the structure becomes. For systems undergoing martensitic transformations, the value of \(A\) varies from 2 onward [11, 38, 40–43]. In cases of Mn2NiIn and Mn2NiSn, the values of \(A\) lie well within the limits observed in shape memory alloys. The origin of this could be rather small value of the shear modulus \(c'\). Additionally, we find that \(c_{44}\) in cases of Mn2NiIn and Mn2NiSn is much softer than those for the other two materials. The comparative softening in \(c_{44}\) for Mn2NiIn and Mn2NiSn as compared to Mn2NiGa and Mn2NiAl, indicate that the cubic Mn2NiIn and Mn2NiSn will transform to different martensitic phases compared to the other two where the transformations would be driven by softening in

### Table 1. Calculated elastic constants and elastic anisotropy ratio for Mn2NiX materials. Experimental elastic constants are only available for Mn2NiGa and shown in brackets.

| Systems  | \(c'\) (GPa) | \(c_{11}\) (GPa) | \(c_{12}\) (GPa) | \(c_{44}\) (GPa) | \(A = c_{44}/c'\) |
|----------|--------------|-----------------|-----------------|-----------------|-----------------|
| Mn2NiAl  | -33.13       | 100.35          | 127.19          | 131.66          | -3.97           |
| Mn2NiGa  | -13.42       | 58.91           | 125.17          | 111.00          | -8.27           |
| Mn2NiIn  | 16.44        | 118.64          | 85.76           | 41.47           | 2.52            |
| Mn2NiSn  | 15.43        | 146.05          | 115.19          | 64.27           | 4.17            |

Figure 6. Illustration of the 110 cross section \((k_x + k_y = 1)\) in fcc irreducible Brillouin zone (IBZ).

the present discussion where the focus is on to establish the nesting features in the Fermi surfaces and their relations to the martensitic instabilities found in these systems.

In [35], Barman et al. also computed the Fermi surfaces of Mn2NiGa. Surprisingly, they observed Fermi surface nesting in the austenite phases along \((1 0 0)\) and \((0 1 0)\) directions only, and not along \((1 1 0)\) direction like we did. The \(q\) value for one of the nesting vectors found by them is quite close to ours (The \(q\) value found by them is 0.31 which is very close to our value, \(q = 0.35\) though. The nesting along \((1 1 0)\) direction was observed by them in the martensite phases along \((1 0 0)\) and \((0 1 0)\) directions only, and not along \((1 1 0)\) direction like we did. The \(q\) value for one of the nesting vectors found by them is 0.31 which is very close to our value, \(q = 0.35\) though. The nesting along \((1 1 0)\) direction was observed by them in the martensite phase with the \(q\) value 0.75. Though they attributed this to the possible instabilities in the TA2 phonon mode, it wasn’t substantiated by computations of the phonon spectra. Our results are qualitatively different from theirs as we found nesting along \((1 1 0)\) direction in the austenite phase of Mn2NiGa. Moreover, our results are consistent as the Fermi surface nesting along \((1 1 0)\) could be related to the computed instabilities in the TA2 phonon mode along \((1 1 0)\) with the nesting vector computed from the Fermi surfaces agreeing with the wave vector at which the maximum of the instability occurs.

### 3.6. Elastic constants

The dynamical stability of the crystalline phase implies that the strain energy changes be positive definite against all possible

\[ \text{Table 1. Calculated elastic constants and elastic anisotropy ratio for Mn2NiX materials. Experimental elastic constants are only available for Mn2NiGa and shown in brackets.} \]

| Systems  | \(c'\) (GPa) | \(c_{11}\) (GPa) | \(c_{12}\) (GPa) | \(c_{44}\) (GPa) | \(A = c_{44}/c'\) |
|----------|--------------|-----------------|-----------------|-----------------|-----------------|
| Mn2NiAl  | -33.13       | 100.35          | 127.19          | 131.66          | -3.97           |
| Mn2NiGa  | -13.42       | 58.91           | 125.17          | 111.00          | -8.27           |
| Mn2NiIn  | 16.44        | 118.64          | 85.76           | 41.47           | 2.52            |
| Mn2NiSn  | 15.43        | 146.05          | 115.19          | 64.27           | 4.17            |

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[48x328] Mn2NiGa. Surprisingly, they observed Fermi surface nesting and not along \((1 1 0)\) direction like we did. The \(q\) value found by them is 0.31 which is very close to our value, \(q = 0.35\) though. The nesting along \((1 1 0)\) direction was observed by them in the martensitic phase with the \(q\) value 0.75. Though they attributed this to the possible instabilities in the TA2 phonon mode, it wasn’t substantiated by computations of the phonon spectra. Our results are qualitatively different from theirs as we found nesting along \((1 1 0)\) direction in the austenite phase of Mn2NiGa. Moreover, our results are consistent as the Fermi surface nesting along \((1 1 0)\) could be related to the computed instabilities in the TA2 phonon mode along \((1 1 0)\) with the nesting vector computed from the Fermi surfaces agreeing with the wave vector at which the maximum of the instability occurs.

### 3.6. Elastic constants

The dynamical stability of the crystalline phase implies that the strain energy changes be positive definite against all possible
Figure 7. 2D cross section of the Fermi surfaces with the (1 1 0) plane \( k_x + k_y = 1 \) for (a) \( \text{Mn}_2\text{NiAl} \), (b) \( \text{Mn}_2\text{NiGa} \), (c) \( \text{Mn}_2\text{NiIn} \) and (d) \( \text{Mn}_2\text{NiSn} \). The green and black lines indicate spin minority bands. The red arrows indicate nesting vectors \( \mathbf{q} = 0.25(1 1 0) \) for \( \text{Mn}_2\text{NiAl} \), \( \mathbf{q} = 0.35(1 1 0) \) for \( \text{Mn}_2\text{NiGa} \) and \( \mathbf{q} = 0.50(1 1 0) \) for \( \text{Mn}_2\text{NiIn} \) and \( \text{Mn}_2\text{NiSn} \).

\( c' \) as has been observed in cases of other shape memory alloys [38]. The results on elastic constants therefore corroborate the inferences drawn from the differences in dispersion relations for the materials studied.

The vibrational and elastic properties discussed in this work show a clear trend. \( \text{Mn}_2\text{NiGa} \) and \( \text{Mn}_2\text{NiAl} \) are quite similar in their behaviors. The same goes for \( \text{Mn}_2\text{NiIn} \) and \( \text{Mn}_2\text{NiSn} \). The vibrational and elastic properties among these two groups are significantly different. The origin of such differences can be traced back to the differences in their electronic structures [18]. The signatures of mechanical instability were reflected in electronic structures of \( \text{Mn}_2\text{NiGa} \) and \( \text{Mn}_2\text{NiAl} \), where high densities of states, as compared to \( \text{Mn}_2\text{NiIn} \) and \( \text{Mn}_2\text{NiSn} \), were found at the Fermi level. The origin of this was larger hybridizations between the Mn and Ni atoms at the octahedral positions for the former two systems. For the latter two systems, rather small densities of states at Fermi level, due to smaller hybridizations between the magnetic atoms at octahedral positions, originating from larger distances between those magnetic atoms (due to the atoms sitting in a larger lattice compared to the former two which happens as In and Sn have larger sizes than Ga and Al), signified that it would take external influences to induce instabilities into these systems.

4. Summary and conclusions

We have investigated the lattice dynamics of \( \text{Mn}_2\text{NiX} \) (\( X = \text{Al}, \text{Ga}, \text{In}, \text{Sn} \)) MSMAs in their austenite phase using first-principles based density functional theory calculations. The calculated phonon spectra show anomalous behavior of the acoustic \( \text{TA}_2 \) branch along \([\xi\xi0]\) direction for all the four materials indicating structural instability. Instabilities in the said acoustic mode can be related to the repulsion by the optical \( T_{2g} \) mode having the same symmetry as the \( \text{TA}_2 \) mode. Unlike \( \text{Ni}_2\text{MnGa} \), no inversion of optical modes could be observed, thus ruling this out as one of the possible mechanisms behind the anomalous features in phonon spectra. The features in the vibrational densities of states can be explained from the qualitative variations of the interatomic force constants across the materials. The calculated elastic constants corroborate the structural instabilities inferred from phonon dispersion relations. Negative shear constants for \( \text{Mn}_2\text{NiAl} \) and \( \text{Mn}_2\text{NiGa} \) indicate pure elastic instabilities in these materials. Finally, the nesting features in the Fermi surfaces confirm that the observed phonon anomalies are associated with them. The wave vectors at which the maximum anomaly occur indicate the possibility of formation of pre-martensitic modulated phases which are yet to be confirmed by experiments. The results also indicate that these modulated pre-martensitic phases could be quite complex and further investigations into this aspect is necessary.

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