Investigation of the structural stability of Co$_2$NiGa shape memory alloys via ab initio methods

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Abstract

CoNiGa alloys have received considerable interest due to their high-temperature shape memory properties. Although there have been many investigations on the mechanical and magnetic behavior of these materials, little is known about the microscopic basis for the observed macroscopic behavior. In this work, we discuss the stability of Co$_2$NiGa-based structures. The austenite phase is modeled as fully ordered L$_2^1$ and as partially ordered B$_2$. The stability of the austenite phase with respect to tetragonal distortions is examined. Lattice dynamics calculations suggest that the mechanism for the transformation is different from that of the much more studied and chemically similar Ni$_2$MnGa shape memory alloy (SMA). The electronic basis for the observed metastability of the cubic Co$_2$NiGa austenite is found to be qualitatively different from that observed in other ferromagnetic SMAs, especially Ni$_2$MnGa.

Keywords: Shape memory alloys; Heusler phases; Metastable phases; $ab$ Initio electron theory; Intermetallics

1. Introduction

Ni–Mn–Ga alloys are one of the most studied ferromagnetic shape memory (SM) systems [1–4]. Despite their promise, these alloys have some limitations [3], the most important being their low ductility [5,6]. Recently, Co–Ni–Ga alloys [7–18] have emerged as an alternative to Ni$_2$MnGa shape memory alloys (SMAs) [3] since they have excellent low-temperature conventional SM properties as well as strong potential as high-temperature SMAs due to their wide stress and temperature stability ranges [17,19], high melting temperatures, good oxidation resistance, and cyclic stability [11,20]. It has also been shown that Co–Ni–Ga alloys exhibit pseudoelastic behavior up to 450 °C[12]. At high temperatures and within specific composition ranges, these alloys exhibit a composite microstructure consisting of the austenite phase (partially ordered B$_2$ [17,19] or disordered body-centered cubic (bcc) [21]) and face-centered cubic (fcc) solid solution. Through proper compositional and heat treatment design it is possible to control the formation (and dissolution) of the ductile fcc phase to enhance these alloys’ ductility [17,19].

While there have been a number of works focused on the characterization of the macroscopic properties of these alloys, there has been little effort, to the best of these authors’ knowledge, to investigate this system at the electronic structure level. In the case of Ni$_2$MnGa Heusler alloys, several $ab$ initio investigations [22–30] have resulted in a very good understanding of the basis—ultimately related to the topology of the $d$- and $p$-bands at the Fermi level [29]—for the structural instability of the austenite L$_2^1$ Ni$_2$MnGa structure and its off-stoichiometry variants. It is thus hoped that $ab$ initio calculations of the Co–Ni–Ga system can help elucidate the underlying basis for its SM behavior.

In this work, we present preliminary investigations of the structural stability of stoichiometric Co$_2$NiGa Heusler
alloys through \( ab \) initio calculations. We approach this investigation by modeling the austenite as either \( L_2^1 \) or as a partially disordered ternary \( B_2 \) structure modeled through a special quasi-random structure [31–33]. The stability of these structures with respect to tetragonal distortions is explored. Additionally, the phonon dispersion of the austenite structure is calculated and the soft vibrational modes leading to the martensitic transformations are identified. The instability of the model austenite structures are then related to their electronic structure. The new results are then compared to results obtained for \( \text{Ni}_2\text{MnGa} \) and other Heusler SMAs.

2. Methods

The electronic properties of the structures considered in this work were calculated using density functional theory (DFT) [34–36], with projector augmented-wave (PAW) pseudopotentials, as implemented in the Vienna \( ab \) initio Simulation Package (VASP) [37–39]. The calculations were performed within the GGA approximation where the PW91 corrections have been used [40]. Full relaxations were performed using the Methfessel–Paxton method [41] and a final self-consistent static calculation with the tetrahedron smearing method with Blöchl corrections [42] was performed for all the structures studied. An energy cutoff of 478 eV was used to truncate the plane wave expansion of the electronic wave functions. The reciprocal mesh used had at least 3000 \( k \)-points per reciprocal atom. All the calculations employed a \( \Gamma \)-centered \( k \)-mesh. The energy cutoff and the \( k \)-mesh density used ensure uncertainties of less than 0.1 meV. The valence calculation with the tetrahedron smearing method with Blöchl corrections [42] was performed for all the structures studied. An energy cutoff of 478 eV was used to truncate the plane wave expansion of the electronic wave functions. The reciprocal mesh used had at least 3000 \( k \) points per reciprocal atom. All the calculations employed a \( \Gamma \)-centered \( k \)-mesh. The energy cutoff and the \( k \)-mesh density used ensure uncertainties of less than 0.1 meV. The valence states considered in this work were 3\( d_4s \), 3\( p_3d_4s \) and 3\( d_4s_4p \) for Co, Ni and Ga, respectively.

The phonon calculations were performed using the direct approach [43–48]. The atoms in the crystal are displaced with respect to their equilibrium positions, subject to constraints imposed by the crystal symmetry, and the resulting Hellman–Feyman forces are obtained through DFT calculations [47,49,50]. The forces are then related to atomic displacements through the force constant matrix, whose eigenvalues (after Fourier transformation) are directly related to the frequencies of the normal modes of oscillation (phonons) for a given point in the Brillouin zone. To avoid spurious forces resulting from interactions between an atom and its periodic images, a supercell is often necessary. In this work, we used the Phonon [49], Phonopy [50] as well as the ATAT [47] packages to ensure consistency of the calculations.

3. Structures under study

3.1. Experimental evidence

To date, few reports exist on the phase stability of the Co–Ni–Ga system [16,19,51]. These studies indicate that at high temperatures the central region of the ternary composition triangle is dominated by a high-symmetry phase (\( \beta \)), which has the \( B_2 \) [19] structure and which transforms to \( L_1_0 \) (tetragonal) martensite (\( \beta' \)). It is worth noting that in both Ni–Ga [52] and Co–Ga [53] phase diagrams the \( B_2 \) phase is highly non-stoichiometric. Older studies by Mikula et al. [54] also suggest that the \( B_2 \) structure extends into the ternary Gibbs triangle over a wide composition range.

3.1.1. Austenite phase

Recently, Brown et al. [21] reported a neutron diffraction study on the \( \text{Co}_{1.8}\text{Ni}_{0.92}\text{Ga}_{1.28} \) composition. At 350 K, they report that the diffraction pattern observed can be indexed on a bcc lattice with lattice parameter \( a = 2.87 \AA \) and confirmed that the composition corresponded to a single phase. Although no reflections with \( h+k+l \) consistent with \( B_2 \)-type ordering were observed, their analysis of the differences in scattering lengths at the corner and body-centered sites does not rule out this type or ordering. Chernenko et al. [8] studied the martensitic transformation in \( \text{Co}_{49}\text{Ni}_{22}\text{Ga}_{29} \). X-ray diffraction (XRD) studies allowed them to identify the austenite phase as cubic with \( B_2 \)-type ordering and lattice parameter \( a = 2.86 \AA \). Their analysis does not yield \( L_2^1 \)-type ordering, possibly due to the closeness of the atomic ordering factors [8].

\( L_2^1 \) is a bcc superstructure of stoichiometry \( A_2BC \) with atoms A, B and C split onto three distinct sublattices [55]. At high temperatures, thermal excitations lead to fully disordered bcc solid solutions. At lower temperatures, the alloy may undergo full ordering in the three sublattices simultaneously, leading to \( L_2^1 \). This transformation can also occur through an intermediate stage in which the solution undergoes a partial ordering to \( B_2 \), leading to the majority element A occupying one of the B2 sublattices while atoms B and C occupy the remaining sites. As the temperature is lowered, B and C partition into separate sublattices [55]. In Heusler alloys, the actual ordering path taken and the temperature for the order/disorder transitions depends on the relative strengths of the chemical interactions among the constituents [55]. While the absence of \( L_2^1 \) can be explained by experimental difficulties (i.e. constituents have similar scattering factors), it is also possible that further ordering of the \( B_2 \) structure could be precluded by the onset of the martensitic transformation.

3.1.2. Martensite phase

Brown et al. [21] investigated the martensite phase in \( \text{Co}_{1.8}\text{Ni}_{0.92}\text{Ga}_{1.28} \) through neutron powder diffraction. At 200 K, they established that the austenite phase had undergone partial transformation to a body-centered tetragonal (bct) structure, with \( c = 3.116 \AA \) and \( e = 2.749 \AA \). Comparing the intensity of the still-existing cubic peaks to samples characterized at higher temperature, they determined that this transformation was not complete and that 30% of the sample remained in the cubic structure. At lower temperatures (150 and 10 K), the transformation had progressed to
completion. Through analysis of peak broadening they
determined that the martensitic transformation resulted
from shears in (1 1 0) planes, in an analogous fashion to
Ni$_2$MnGa [56]. Brown et al. [21] did not observe either a lay-
ering of the martensitic structure or the existence of an inter-
mediate pre-martensitic phase observed in Ni$_2$MnGa
[57,58]. Using electron diffraction, Chernenko et al. [8] inves-
tigated the martensitic phase in Co$_{49}$Ni$_{22}$Ga$_{29}$ single crystals.
The diffraction patterns observed could be indexed to a face-
centered tetragonal (fct) structure (L1$_0$) with lattice param-
eters $a = 3.8$ Å $c = 3.2$ Å or to a bct structure (after rotating the $x$–$y$ plane by 45°) with $a = 2.7$ Å, $c = 3.2$ Å. Very
recently, Dai et al. [59] investigated the structure and mag-
etic properties of highly ordered and nearly stoichiometric
Co$_2$NiGa alloys. From powder diffraction analysis of previ-
siously annealed samples, they proposed a highly ordered structure with prototype Pt$_3$FeCu with $P4/mmm$ space group
with lattice parameter $a = 3.58$ Å. Dai et al. note that the
synthesis of the highly ordered fct martensite was only possible through high-energy ball milling of powder samples, sug-
gest that this ordered state was metastable with respect to
configurational disorder.

3.2. ab Initio calculations of structural, magnetic and
thermodynamic parameters in Co$_2$NiGa alloys

3.2.1. Structures used to simulate the Co$_2$NiGa austenite
phase

In order to investigate the structural stability of Co$_2$Ni-
ga alloys through ab initio methods, it is first necessary
to have the appropriate models for the structures observed
experimentally. Calculations of non-stoichiometric struc-
tures are impractical unless one resorts to mean-field
approaches such as the KKR-CPA method [60]. This
approach, while useful at determining the energetics and
structural parameters of non-stoichiometric phases, is not
suitable to investigate phenomena that depend on local
interatomic interactions, such as atomic relaxations [32],
vibrational behavior, etc.

This work is therefore limited to the study of stoichio-
metric Co$_2$NiGa alloys. The properties of the austenite phase
and its stability with respect to martensitic transformations
are investigated through the use of two structures. First,
the austenite is modeled as an L2$_1$ Heusler alloy. Since
L2$_1$ is just the result of further ordering of a partially
ordered B2 structure [35], some of the mechanisms leading
to the phase transformation of L2$_1$ can be considered to be
analogous, to first order, to those involving B2-type
ordered structures.

The model for the austenite can be improved by consider-
ing configurational disorder in the two sublattices of L2$_1$
occupied by Ni and Ga. Use of large supercells to simulate
disorder is impractical since the computational effort in
DFT calculations scales as $O(N^3)$ at best [61]. This problem
can be partly overcome by employing special quasi-random
structures (SQSs) [31], which are small periodic supercells
that are designed to mimic the statistics of a truly random
configuration within a certain range. Within the context of
lattice algebra, we can assign a spin value ($\pm 1$) to each site

$$k = (1/2, 1/2, 1/2),$$

$$m = (1/2, 1/2, 1/2),$$

where $k$ stands for the number of vertices in the figure, while $m$ stands for the maximum distance within a given figure.

Table 1

<table>
<thead>
<tr>
<th>Atomic positions (in relative coordinates)</th>
<th>Lattice vectors (relative to lattice parameter $a$ of B2 structure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>$-a/2$     $a/2$     $-a/2$</td>
</tr>
<tr>
<td>0.75</td>
<td>$a/2$     $-a/2$     $a/2$</td>
</tr>
<tr>
<td>0.50</td>
<td>$-a$     $-a$     $0$</td>
</tr>
</tbody>
</table>

Correlation functions for perfectly random alloy at $x(Ga) = x(Ni) = 0.25$, $(\Pi_{4,4,m}) = 0^a$. Deviations from zero in the correlations below measure error with respect to a random alloy.

<table>
<thead>
<tr>
<th>1st shell</th>
<th>2nd shell</th>
<th>3rd shell</th>
<th>4th shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pair</td>
<td>$\Pi_{4,4} = 0$</td>
<td>$\Pi_{4,4} = 0$</td>
<td>$\Pi_{4,4} = 0$</td>
</tr>
<tr>
<td>Triple</td>
<td>$\Pi_{4,4} = 0$</td>
<td>$\Pi_{4,4} = 0$</td>
<td>$\Pi_{4,4} = 0$</td>
</tr>
<tr>
<td>Tetrahedron</td>
<td>$\Pi_{4,4} = -0.333, 0.1^b$</td>
<td>$\Pi_{4,4} = -0.333, 0.1^b$</td>
<td>$\Pi_{4,4} = -0.333, 0.1^b$</td>
</tr>
</tbody>
</table>

$^a$ Note that $k$ stands for the number of vertices in the figure, while $m$ stands for the maximum distance within a given figure.

$^b$ The 2nd shell tetrahedron has three correlation functions due to multiplicity.
In this work, we used the ATAT package [48] to create a 16-atom SQS of a ternary B2 \( \text{Co}_2\text{NiGa} \) structure in which Ni and Ga mix randomly in one sublattice. Table 1 shows the lattice vectors, atomic positions (in fractional coordinates), as well as the pair, triangle and tetrahedron correlation functions for the SQS structure \((\text{Co})_2(\text{Ni,Ga})_2\). This structure is orthorhombic with space group \( \text{Cmmm} \). Table 1 shows that the pair correlation functions match those of a random alloy up to third-nearest neighbors, while the triple correlation functions are “random like” at least within a radius equivalent to twice the lattice parameter of a bcc lattice. Table 1 shows that the tetrahedron correlation functions differ from those of a random alloy even for the tetrahedra of the smallest radius. This is not considered problematic since it is to be expected that structure properties are dominated by low-order figures.

Fig. 1 shows the structures used to simulate the martensite and austenite phases in \( \text{Co}_2\text{NiGa} \) Heusler alloys. In Fig. 1, Co–Co bonds are the only ones depicted in order to highlight the similarities between all structures. Table 2 shows the calculated and experimental structural, thermodynamic and magnetic properties of several structures in \( \text{Co}_2\text{NiGa} \) alloys. The B2 structure is calculated using the 16-atom SQS shown in Table 1. In order for this structure to retain the underlying bcc lattice, the total volume of the structure was the only degree of freedom allowed to relax during the structural optimization. In Table 1 it can be seen that the calculated lattice parameter is remarkably similar to the measurements by Brown et al. [21] and Chernenko et al. [8]. The martensite phase derived from this partially ordered B2, labeled in Table 1 as \( \text{BCT}_a \), was obtained by allowing all the degrees of freedom of the 16-atom SQS to relax. The structure labeled as \( \text{BCT}_b \) corresponds to a fully relaxed, tetragonally distorted \( \text{L}_{21} \) structure.

As mentioned above, Brown et al. [21] suggested that the phase transition in the alloys they investigated were related to \((1\ 1\ 0)\) shears. They found that they could relate the lattice parameters of the cubic austenite and tetragonal martensite using \(a_{\text{tet}} = a_{\text{cub}}(1 - \sigma)\) and \(c_{\text{tet}} = a_{\text{cub}}(1 + 2\sigma)\) with \(\sigma \approx 0.02\). Within experimental error, the deformation along the c axis was found to be twice as large as that along the a axis. The strain parameter derived from the comparison between B2 and \( \text{BCT}_a \) (disordered \( \text{L}_{10} \)) are \(\sigma_c = 0.036\) and \(\sigma_a = 0.081\). While these microstrains are twice as large as those measured experimentally, the ratio between them is calculated to be around 2.2. The fact that this ratio is close to two suggests that the SQS structure is also unstable with respect to shear of \((1\ 1\ 0)\) planes, just as is suggested for the alloys investigated experimentally.

Table 2 shows that there is very good agreement between the calculated and experimental [8,21] lattice parameters for the disordered austenite and martensite phases, with the maximum difference (~4%) corresponding to the \( \text{L}_{10} \) phase characterized by Chernenko et al. [8]. The lattice parameters for the fully ordered \( \text{L}_{21} \) structure (5.68 Å) were not compared to experiments since this phase has not been observed experimentally. However, this lattice parameter corresponds to a cubic lattice parameter for a B2 structure of 2.84 Å, which is very close to the lattice parameter of the partially ordered B2 austenite phase [8,21]. The calculated fully ordered \( \text{L}_{10} \) structure exhibits tetragonality, with \(c/a \sim 1.06\), contrary to the results by Dai et al. [59]. This discrepancy may be reconciled if this compound reduces its tetragonality as temperature increases. In
Table 2
Calculated and experimental structural, magnetic and thermodynamic parameters of structures in Co<sub>2</sub>NiGa alloys. Calculations correspond to 0 K.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Prototype/space group</th>
<th>Lattice parameters (Å)</th>
<th>Magnetic moment (µB/Co atom)</th>
<th>Formation enthalpy (10&lt;sup&gt;-2&lt;/sup&gt; eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partially ordered structures</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>CsCl/P6&lt;sub&gt;3&lt;/sub&gt;mc</td>
<td>(a = 2.60 ) (2.61&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>1.083</td>
<td>-3.20</td>
</tr>
<tr>
<td>BCT&lt;sub&gt;a&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt;</td>
<td>P4&lt;sub&gt;3&lt;/sub&gt;33</td>
<td>(a = 2.84 ) (2.86&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>1.333 (0.97&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>-5.35</td>
</tr>
<tr>
<td>Fully ordered structures</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L2&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;MnGa/Fn-3m</td>
<td>(a = 5.68 )</td>
<td>1.626</td>
<td>-8.67</td>
</tr>
<tr>
<td>L10</td>
<td>Pt&lt;sub&gt;2&lt;/sub&gt;FeCu/P4&lt;sub&gt;3&lt;/sub&gt;3m</td>
<td>(a = 3.52 ) (3.58&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>1.474 (1.528&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>-10.65</td>
</tr>
<tr>
<td>BCT&lt;sub&gt;b&lt;/sub&gt;</td>
<td>I4&lt;sub&gt;3&lt;/sub&gt;32</td>
<td>(a = 3.59 )</td>
<td>1.395</td>
<td>-11.35</td>
</tr>
</tbody>
</table>

+ = This structure was obtained by full relaxation of a tetragonally distorted L2<sub>1</sub> structure.

a Brown et al. [21]: alloy composition: \(x_{Co} = 0.45, x_{Ni} = 0.23, x_{Ga} = 0.32\).
b Chernenko et al. [8]: alloy composition: \(x_{Co} = 0.49, x_{Ni} = 0.22, x_{Ga} = 0.29\).
c Dai et al. [59]: alloy composition: \(x_{Co} = 0.50, x_{Ni} = 0.25, x_{Ga} = 0.25\).
d This structure was calculated from the proposed SQS, allowing only volume to relax.
e This structure was derived from the proposed SQS. In this case, all degrees of freedom were relaxed during structural optimization.

Table 2, it is also shown that the structure labeled as BCT<sub>b</sub> is slightly lower in energy than L1<sub>0</sub> (by 7 meV/atom). These two structures are related as BCT<sub>b</sub> is essentially L1<sub>0</sub> with an inversion center.

Table 2 shows that there is relatively good agreement between the calculated and experimental magnetization for the partially disordered B2 phase. In experiments and calculations, the martensitic transformation results in larger total magnetic moments. Furthermore, by comparing the calculated magnetic moments of the disordered (BCT<sub>a</sub>) and fully ordered structures, the martensite phase is about 20–25% more stable than the partially ordered ones by about 3.59 meV/atom. In the case of the partially disordered B2 phase. In experiments and calculations, the martensitic transformation results in larger total magnetic moments. Furthermore, by comparing the calculated magnetic moments of the disordered (BCT<sub>a</sub>) and ordered L1<sub>0</sub> structures, it is evident that ordering leads to an increase in magnetism of about 25%. The experiments by Dai and collaborators [59] suggest that ordering leads to an increase of 30%, in good agreement with the calculations.

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4. Stability with respect to tetragonal distortions

In the case of Ni<sub>2</sub>MnGa and other related SMAs, it has been shown that the cubic austenite phase is metastable (or unstable) with respect to tetragonal distortions [29]. In one of the first published related works, Ayuela et al. [62] investigated the stability of different L2<sub>1</sub> structures with respect to tetragonal distortions through DFT calculations. Their results showed that Fe-, Ni- and Co-based Heusler compounds were unstable with respect to tetragonal distortions, while Mn-based compounds were stable. In the case of Ni<sub>2</sub>MnGa, the minimum along the Bain path occurred at \(c/a \sim 1.22\), which is a result also reproduced by Zayak and collaborators [29,63]. In the case of Ni<sub>2</sub>CoGa, the minimum in energy was located at \(c/a = 1.39\) [62]. In systems based on Co, this kind of instability had not been previously observed [29]. In order to investigate the stability of cubic Co<sub>2</sub>NiGa alloys with respect to tetragonal distortions, we calculated the energy as the cubic structures were deformed along a Bain path:

\[\varepsilon = \begin{bmatrix} e_1 & 0 & 0 \\ 0 & e_1 & 0 \\ 0 & 0 & \frac{1}{(1+e_1)^2} - 1 \end{bmatrix}\] (2)

The structures studied were the L2<sub>1</sub> as well as the partially disordered B2 structure (SQS). Fig. 2 depicts the total energy difference with respect to the minimum energy for L2<sub>1</sub>. From Fig. 2, it can be seen that the B2 structure is higher in energy than L2<sub>1</sub> by about 50 meV/atom through-
out the entire transformation path. Since the behavior is qualitatively the same, this suggests that configurational effects due to disorder do not change the stability of the cubic phase upon tetragonal distortions.

In the case of the L21 austenite phase, it can be seen that the $E/vs. c/a$ ratio curve is essentially flat at $c/a \sim 1$, indicating that this structure is marginally stable at best. This curve also shows that there is no noticeable local maximum between the cubic structure and the true minimum along this transformation path. Along this path, there is essentially no barrier for the cubic-to-tetragonal transformation of this Heusler alloy. This is qualitatively different from what is observed in the Ni$_2$MnGa system [63]. For Co$_2$NiGa, the global minimum along this path corresponds to a $c/a \sim 1.39$ (very close to $\sqrt{2}$), which is very similar to the $c/a$ ratio corresponding to the minimum energy for the Ni$_2$CoGa Heusler alloy reported by Ayuela et al. [62] but very different from Ni$_2$MnGa.

In the case of the B2 austenite phase, the structure at $c/a \sim 1$ does not seem to “sit” at a local minimum. The structure is unstable with respect to tetragonal distortions. The calculations seem to suggest that the local minimum for this structure is located at $c/a < 1$. Zayak [63] investigated non-stoichiometric Ni$_2$MnGa alloys through supercell calculations and found that there was a local minimum at $c/a \sim 0.94$. While the location of the local minimum in the Co$_2$NiGa is not precisely at the same $c/a$ ratio, the possibility of a local tetragonal (meta)stabilization at $c/a < 1$ due to configurational disorder warrants further investigation. As in the case of L21, the global minimum (along this transformation path) for the B2 structure corresponds to a $c/a \sim 1.39$ [62]. The elastic constants of the cubic (L21 and B2) austenite phases were calculated by imposing strains on the structure and calculating the resulting internal stresses [64]. Table 3 shows the elastic constants for both cubic structures. In Table 3 it is shown that the $C_{11} - C_{12}$ shear constant is very small (L21) or even slightly negative (B2). These calculations are in agreement with the Bain path calculations presented in Fig. 2.

Fig. 3 shows the calculated Bain path for the L21 structure in the Co$_2$NiGa and Ni$_2$MnGa systems as a function of volume. From Fig. 3, it can be seen that the behavior in the two systems is qualitatively different. In the case of Co$_2$NiGa, the minimum is located approximately at $c/a \sim \sqrt{2}$ for all volumes, with the Bain paths calculated at larger volumes having the energy minimum at slightly larger values. On the other hand, the Bain path of Ni$_2$MnGa shows the local minima at $c/a \sim 1.27$ in accordance with previous calculations by Zayak and collaborators [63]. In the case of the Ni$_2$MnGa L21 structure, increasing the volume of the unit cell makes the tetragonal structure less stable than the cubic structure, while the opposite effect is observed in Co$_2$NiGa. For Ni$_2$MnGa, it has been argued that the stability of the tetragonal structure is associated with a kind of Jahn–Teller distortion [63,65]. An increase in volume reduces the overlap of electron orbitals, making the tetragonal structure less favorable. In the case of Co$_2$NiGa, such a preference for reduced symmetry at smaller volumes is not observed. On the contrary, in Co$_2$NiGa larger volumes decrease the stability of the cubic phase.

The stability of the cubic phase was further studied through phonon dispersion calculations. $2 \times 2 \times 2$ periodic super cells (128 atoms), based on the cubic conventional lattice, were constructed from optimized primitive cells. The direct force constant method was chosen for calculating the phonon dispersion relations [66,67]. Displacement amplitudes of 0.005–0.01 Å were used to calculate the interatomic force constants. This amplitude was large enough to reduce noise in the calculations of the interatomic forces and small enough to prevent the system from deviating from harmonicity.

The phonon dispersion relation of Ni$_2$MnGa is shown in Fig. 4b (right). The phonon dispersion is calculated using two different amplitudes (0.005 and 0.01 Å) for the atomic displacements necessary to extract the force constants. Both displacement magnitudes essentially yield the same dispersion curve. These theoretical results, calculated at 0 K, are compared with the neutron diffraction and inelastic neutron experiment, performed at 270 K [68]. The calculated phonon dispersion shows good agreement with the experimental data for the non-soft acoustic branches. The imaginary frequency of TA2 branch along the $I–Y$ direction corresponds to the softening of the acoustic phonon branch in the experimental data. The soft TA mode corre-

Table 3
Calculated elastic constants (GPa) for austenite phases in Co$_2$NiGa system.

<table>
<thead>
<tr>
<th></th>
<th>B2</th>
<th>L21</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>186</td>
<td>197</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>187</td>
<td>187</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>139</td>
<td>120</td>
</tr>
<tr>
<td>$C_{11} - C_{12}$</td>
<td>-1</td>
<td>10</td>
</tr>
</tbody>
</table>
Corresponding to the \((1/3, 1/3, 0)\) wave vector along the \([1 1 0]\) direction shows the most pronounced instability, indicated in the calculations by negative (or imaginary) frequencies. The “freezing” of this unstable mode has been related to the formation of a pre-martensitic phase in the Ni\(_2\)MnGa system since pre-martensite has the same \((1/3, 1/3, 0)\) modulation\(^{[68,69]}\).

Bungaro et al.\(^{[70]}\) previously calculated the phonon dispersion of Ni\(_2\)MnGa in the \(L2_1\) structure using density functional perturbation theory (DFPT)\(^{[71]}\). Their calculation also shows the unstable mode at the \((1/3, 1/3, 0)\) wave vector. Contrary to our calculations, they did not encounter other imaginary modes within the Brillouin zone, in contrast to the calculations in Fig. 4b, where there is an additional soft mode along the \(Γ–W\) direction. Bungaro et al., however, predicted that the TA branch along this direction was soft, although not unstable, in accordance with experiments. The discrepancy between Bungaro et al.’s\(^{[71]}\) calculations and this work could be due to the fact that our finite displacement calculations do not have the resolution to sample the Brillouin zone adequately and as a result they overestimate the “softness” of the TA mode along the \(Γ–W\) direction.

The phonon dispersion curve of Co\(_2\)NiGa is shown in Fig. 4a (top). According to these calculations, there is no imaginary mode for this structure at the optimized lattice parameter (5.682 Å). The calculations show, however, a softening of the TA branches located at the \(X\) point of the Brillouin zone, which corresponds to the \([1 1 0]\) direction. In contrast to Ni\(_2\)MnGa, softening does not occur at the \((1/3, 1/3, 0)\) point along the \([1 1 0]\) direction, suggesting that no modulation of the martensite phase or pre-martensitic structure are present in this system\(^{[2]}\). Since no instability could be observed in the ferromagnetic Co\(_2\)NiGa \(L2_1\) structure, we performed calculations on the paramagnetic \(L2_1\) to see if magnetism played a role in the marginal stability of \(L2_1\). The paramagnetic structure was fully optimized and it was found that its lattice parameter did not change much from that of the ferromagnetic \(L2_1\) (5.657 vs. 5.682 Å). Fig. 5 displays the phonon dispersion curve for paramagnetic Co\(_2\)NiGa \(L2_1\). Apparently, all modes are shifted towards lower frequencies, compared with the magnetic structure. Anomalies of the
TA branches were examined at the $X$ symmetry point. The softening feature of TA branches reveals an instability of this structure along the [1 1 0] direction. These calculations suggest that magnetism (or its loss due to magnetic disorder at finite temperatures) may be responsible for the stability of this structure. Gruner et al. [27] recently investigated the effect of magnetism on the stability of L2$_1$ Ni$_3$MnGa and found that the decrease of magnetism initially stabilizes the structure up to a point, beyond which the structure developed other instabilities.

According to Fig. 3, the tetragonal structure becomes more stable with respect to tetragonal distortions as the volume of the cell increases. Fig. 6 shows the effects of increasing volume on the lattice dynamic properties of L2$_1$ Co$_2$NiGa. Fig. 6a shows the softening of the TA branch at different high-symmetry points ($X$, $L$, $W$) as a function of volume. As expected, larger volumes lead to lowering of mode frequencies due to weakening of interatomic force constants [47]. While the TA frequencies at points $W$ and $L$ of the Brillouin zone show a gradual phonon softening as the volume increases, the TA branch at the $X$ point (corresponding to the [1 1 0] direction) shows a clear stable–unstable transition (whereby the frequency of this mode becomes imaginary) at a lattice expansion of about 1.5%. The softening of this phonon mode is even more evident in Fig. 6b, where the phonon dispersion of the lowest acoustic branch is plotted for different lattice expansions. Fig. 7 shows the atomic displacements corresponding to the unstable TA phonon mode at the $X$ point (along the [1 1 0] direction). As can be seen in Fig. 7, Ga and Ni move in phase along the [1 1 0] direction.

From Figs. 5 and 6 it is evident that two distinct macroscopic factors affect the stability of the L2$_1$ structure in the Co$_2$NiGa system. First, Fig. 5 shows that loss of magnetism tends to destabilize the structure. As temperature increases, magnetic disorder reduces the total lattice magnetism. As the Curie temperature is reached, complete magnetic disorder makes the L2$_1$ structure dynamically unstable. Destabilization can also be reached by increasing the volume. Again, this increase in volume can in principle be mapped to an increase in temperature (due to thermal lattice expansion). Thus, according to our calculations, the low-temperature metastable Co$_2$NiGa becomes dynamically unstable at finite temperatures due to magnetic disorder (ferromagnetic–paramagnetic transition) and/or phonon softening due to bond stretching. This seems to suggest that the high-temperature cubic phase observed in experiments is either stabilized through anharmonic contributions (i.e. phonon–phonon interactions) or that the high-symmetry phase is simply the result of averaging the tetragonal variants [72].

5. Electronic structure

In this section, we present preliminary analyses of the electronic structure features that we believe are responsible for the observed metastability of L2$_1$ Co$_2$NiGa with respect to tetragonal deformations. Fig. 8 shows the total electronic density of states (DOS) for L2$_1$ Co$_2$NiGa and Ni$_3$MnGa as well as the site-projected $d$-band for both structures. While the majority (spin-up) channel for both structures looks similar on a qualitative basis, in the case of Co$_2$NiGa, the structure sits just above the energy gap between bonding and anti-bonding spin-down states (point A in Fig. 8). In contrast, the Fermi level in Ni$_3$MnGa sits in a valley of anti-bonding
electronic states (point B in Fig. 8). As explained by Entel and collaborators [29], this highly unstable electronic configuration arises from the inability of spin-down 3d electrons from Ni to hybridize with Mn spin-down 3d electrons, since the band is very full, resulting in turn in a large magnetic moment for Mn in this structure. Ni 3d spin-down electrons are thus unable to hybridize with Mn 3d electron states unless they flip spin. Instead of hybridizing with Mn 3d spin-down electrons, Ni 3d spin-down electrons hybridize with the 4p electrons of Ga.

Given the fact that the local magnetic moment of Co and Ni are similar and lower than Mn, it is expected that in the case of Co2NiGa, hybridization between the 3d spin-down electrons of Co and Ni takes place, as evident from the fact that the site-projected electronic DOS at Co and Ni sites are very similar in Co2NiGa.

Fig. 8b shows that the observed anti-bonding valley in Ni2MnGa responsible in great part for the instability of this cubic structure is originated from Mn and Ni spin-down electronic states (mostly of d-character) that lie on opposite sides of the Fermi level (indicated in the figure with a dotted line). The staggered configuration of these anti-bonding minority states illustrates in a very graphic manner the fact that 3d spin-down electrons in Ni and Mn do not hybridize. In fact, Entel et al. [29] found that the anti-bonding Ni peak (marked as C in Fig. 8b) consists of t_{2g} states while the anti-bonding Mn peak (marked as D in Fig. 8b) consists of e_{g} states. t_{2g} anti-bonding states become dominant in Ni due to the body-centered-like crystal field “seen” by Ni ions in the L2_{1} Ni_{2}MnGa structure. Fig. 8a shows that the shape of the spin-down electronic DOS at Co and Ni sites in the cubic Co2NiGa are almost identical, suggesting a high level of hybridization between 3d spin-down Co and Ni electronic states. Fig. 8 shows that the observed metastability of Co2NiGa and instability of Ni2MnGa have fundamentally different origins.

Here it is important to note the significance of this finding: up until recently, the formation of the pseudo-gap of minority electronic states was considered a necessary condition for the onset of martensitic transformations in Heusler alloys. Co2NiGa differs in a fundamental way from this condition since it is clearly at most metastable (at 0 K) with respect to tetragonal distortions, as indicated by the Bain path and lattice dynamic calculations presented above. Furthermore, the metastability in this Heusler compound is due to the fact that the Fermi level is located at the beginning of relatively low-lying spin-down anti-bonding states.

Fig. 9 shows the calculated total electronic DOS for Co2NiGa at three discrete points along the Bain Path shown in Fig. 2. As in the previous figures, the Fermi level is indicated by the dotted line at 0 eV. Fig. 9 shows that by lowering the symmetry of the initially cubic Co2NiGa, the anti-bonding spin-down states are pushed towards higher energies. Moreover, as the distortion increases, spin-down bonding states (mostly of d character) are pulled towards the Fermi level, lowering the electronic energy of the structure and making the tetragonal variant of Co2NiGa more stable than the cubic structure. The loss of symmetry also contributes to the greater localization of magnetic moments, which is consistent with experiments [8,21] as well as with calculations in this work (see Table 2) and elsewhere [59].

This analysis also suggests possible ways of increasing the driving force for the cubic-to-tetragonal martensitic transformation for this system: in order to increase the relative stability of the martensite structure one must add electrons so the Fermi level lies higher on the spin-down minority
states. In fact, in this system it has been observed experimentally [8] that increasing the electron-to-atom ratio tends to raise the martensite temperature, which is consistent with the admittedly simplistic analysis presented in this work.

Fig. 10 shows the calculated electronic DOS for L1\textsubscript{0} in both fully ordered and partially disordered states. The disordered L1\textsubscript{0} results from fully relaxing the SQS used to simulate the B2 structure. When comparing the total electronic DOS, both structures show similar behavior. In both structures the 3\textit{d}\textsuperscript{spin-up} electronic states are almost full. In both cases, hybridization of 3\textit{d}\textsuperscript{spin-up} states is relatively strong. In the case of the 3\textit{d}\textsuperscript{spin-down} states for the fully ordered L1\textsubscript{0} structure, hybridization is weaker, since the degenerate peaks that appear above and below the Fermi level in Co 3\textit{d}\textsuperscript{spin-down} DOS do not appear in Ni sites. This result is in excellent agreement with the calculations by Dai et al. [59].

Fig. 8. Upper left and right panels: total electronic structure of L2\textsubscript{1} Co\textsubscript{2}NiGa (left) and Ni\textsubscript{2}MnGa. Middle and lower panels: Site-projected \textit{d}-band for transition metals in Co\textsubscript{2}NiGa and Ni\textsubscript{2}MnGa. The Fermi level is indicated by the vertical dotted line at 0 eV.

Fig. 9. Total electronic DOS for tetragonally distorted (at constant volume) Co\textsubscript{2}NiGa.

Fig. 10. Upper left and right panels: total electronic structure of fully ordered L1\textsubscript{0} Co\textsubscript{2}NiGa (left) and disordered L1\textsubscript{0} Co\textsubscript{2}MnGa (right). Middle and lower panels: site-projected \textit{d}-band for transition metals. The Fermi level is indicated by the vertical dotted line at 0 eV.
6. Conclusions

In this work, the structural and electronic properties of the austenite and martensitic phases in the Co$_2$NiGa system have been investigated and compared to the Ni$_2$MnGa Heusler alloy. The austenite phase has been modeled as fully ordered L2$_1$ and partially ordered B2 (through the use of an SQS). These phases are unstable (metastable) with respect to tetragonal distortions, with the energy difference between the cubic and tetragonal structures being about 20 meV at 0 K.

Contrary to what has been reported for Ni$_2$MnGa and other Ni-based SMA systems in which the austenite phase has L21-type ordering, Co$_2$NiGa does not exhibit modulation consistent with the existence of layered pre-martensitic and martensitic phases. The calculations of the lattice dynamic behavior of the system shows that there is softening of the acoustic branches, although this softening occurs at the X point in the Brillouin zone, which corresponds to the [1 1 0] direction. Decrease in magnetism and increase in volume contribute to the instability of the austenite phase. In Ni$_2$MnGa increasing volume increases the stability of the cubic phase.

In contrast to what happens in Ni$_2$MnGa and other similar SMA systems, the austenite phase in the Co$_2$NiGa system exhibits strong hybridization in the spin-down d-states in the sites occupied by the magnetic elements (Co and Ni in this case). The metastability in this Heusler compound is due to the fact that the Fermi level is located at the beginning of relatively low-lying spin-down anti-bonding states. Decreasing the stability with respect to tetragonal distortions can be achieved in this system by taking the Fermi level at 3d spin-down states to higher energies, increasing the electron-to-atom ratio. The instability in Ni$_2$MnGa is radically different, having its origin in the lack of hybridization between 3d spin-down Mn and Ni states.

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