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First-principles investigations of homogeneous lattice-distortive strain and shuffles in Ni_2MnGa

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Abstract

A series of first-principles calculations were performed for ferromagnetic Ni_2MnGa using density functional theory and PAW potentials. Theoretically, a tetragonal crystal structure homogeneous lattice-distortive strain is stabilized around $c/a = 0.94$ with respect to the $L2_1$ structure when, in addition, modulation shuffles with a period of five atomic planes are taken into account. This is in agreement with the observed structures in experimental works. The modulation appears to be critically important for stability of the tetragonal structure with $c/a < 1$. Here, we report a new feature which is related to the optimum amplitudes of the modulation in different atomic planes. Related to this are systematic changes in the minority spin density of states near the Fermi surface, like in the formalism of a pseudo-gap.

1. Introduction

Ferromagnetic Ni–Mn–Ga alloys around Ni_2MnGa stoichiometry are well-known high-performance materials as regards their shape-memory properties [1, 2], which allow to realize magnetically driven shape control devices. This is based on their specific magneto-elastic properties and can be used whenever a fast mechanical response is needed or when temperature and pressure are not applicable to drive structural changes. For instance, large strains (∼5%) for single crystals, close to the maximum tetragonal distortion for the $c/a = 0.94$ structure, are measured under magnetic fields around 0.5 T [3–5]. The aim in this paper is to study the structural aspect of this distortion, which is so promising for the development of new devices.

Intensive studies of the Ni_2MnGa crystal structure and magnetic order started in 1984 [6]. Neutron and x-ray diffraction experiments showed that at room temperature Ni_2MnGa exists in a highly ordered $L2_1$ type of structure with large magnetic moments which are located on the Mn sites. A peculiar feature of this material is the martensitic transformation which occurs on cooling below a certain temperature. The low-temperature crystal structures were found to have mainly a tetragonal symmetry and sometimes a complicated martensitic pattern. Further

experimental studies revealed more details about the low-temperature martensite [7, 8]. It was found that the martensite of Ni_2MnGa can exist in one of three different structures. A detailed description of them was reported together with a sequence of phase transformations leading to these structures [7, 9, 10]. Experiments with the ferromagnetic Ni–Mn–Ga materials show that the martensitic transformation has its origin in a tetragonal distortion of the ordered $L2_1$ structure. The high-temperature $L2_1$ structure has a lattice parameter of $a = 5.826$ Å [6, 11], while other structures exist as martensitic variants of lower symmetry (variants are parts of the martensite with identical structure but different orientations of distortion):

(i) a tetragonal structure with a ratio $c/a < 1$ appears on lowering the temperature,
(ii) an arrangement of atoms resembling an orthorhombic structure is formed under compression of the phase (i) along [110] axes or under tension along [100] axes, and
(iii) another tetragonal structure with $c/a > 1$ is formed under further stress of the phase (ii) [7, 10, 12].

In cases (i) and (ii) an important detail is that these structures have a slightly distorted order due to a specific shuffling of atomic planes [7]. These low-symmetry structures can exhibit shuffling of the [110] planes with a modulation of five or seven atomic planes, called 5M and 7M structures, respectively [7, 13] (modulated structures with other periods were observed as well [14]). In this work we report results of zero-temperature ground state calculations for Ni_2MnGa martensite possessing a tetragonal symmetry with ratio $c/a = 0.94$ and the modulation.

The central question is whether the modulations 5M and 7M are somewhat distinctive phases among all tetragonal structures with $c/a < 1$. Theoretical works so far based on first-principles calculations for Ni_2MnGa did not take into account the shuffling of atoms [15–17]. We believe that this is one possible explanation of why the variant with $c/a = 0.94$ was not found to be stable. Further mechanisms which might also influence stability of this variant are atomic disorder and non-collinearity of magnetic moments, but this is not considered here. In this context we would like to draw attention to a recent work in which full-potential calculations with extremely high precision also yielded a minimum of energy for $c/a = 0.94$ [18]. However, this minimum is not deep enough compared to the $L2_1$ ground state. Therefore, we propose that, in addition, modulated structures with the shuffling of atoms should be discussed in more detail in order to find the right ordering of experimentally observed martensite structures of Ni_2MnGa.

2. Computational details

We use the Vienna *ab initio* simulation package (VASP) [19, 20] with the implemented projected augmented-wave formalism [21]. Within density functional theory (DFT) the electronic exchange and correlation are treated by using the generalized gradient approximation (GGA). Further details: the 3d electrons of Ga are included as valence states; the plane-wave cut-off energy is 241.6 eV; the Monkhorst–Pack k-points generation scheme is used with a grid of $9 \times 7 \times 2$ points in the full Brillouin zone for a long orthorhombic supercell, which means 36 inequivalent k-points. A smearing parameter of 0.2 eV is used (after a careful test) which is the default value of VASP.

A straightforward way to proceed is to start from the five-layered structure obtained by Martynov and Kokorin [7]. We took a tenfold chain of bct primitive cells, similar to those used in [16], in order to incorporate the full period of modulation in the supercell. The construction of the supercell is explained in figure 1. The basal plane is spanned by $[1\bar{1}0]$ and [110] of the $L2_1$ structure with the modulation along [110]. Altogether we use ten atomic planes

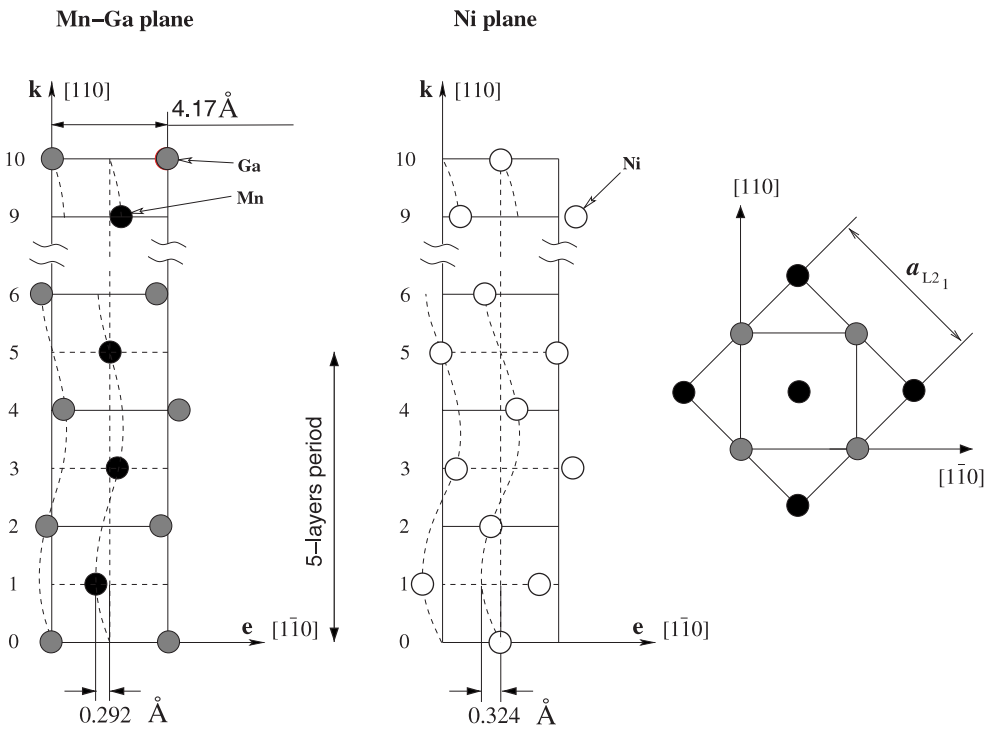

Figure 1. Calculational results for the modulation of two different atomic planes (001) in Ni_2MnGa after structural relaxation.

perpendicular to [110] to form the supercell. The modulation is generated by displacing these atomic planes along the [1$\bar{1}$0] direction. By this construction, two full five-layered periods fit into the supercell. The initial magnitude of the displacements, both for Ni and Ga–Mn layers, was chosen to be 0.175 Å (the different magnitudes shown in figure 1 will be discussed below). In this way we obtain a supercell with modulation which resembles as closely as possible the experimentally observed structure [7]. This constrained supercell has an orthorhombic symmetry with lattice parameters related to the $L2_1$ lattice parameter $a = a_{L2_1} = 5.82$ Å, (see [15–17]) by $a' = a/\sqrt{2.0} = 4.11$ Å, $b' = 5a/\sqrt{2.0} = 20.58$ Å, $c' = c = a = 5.82$ Å. In addition, we allow for a small tetragonal distortion, $c/a < 1$, in order to facilitate convergence in the calculations towards the structure which we want to stabilize. The final supercell parameters are then $a' = a \times 0.709 \approx 4.127$ Å, $b' = 5 \times a' \approx 20.630$ Å, $c' = a \times 0.974 \approx 5.669$ Å, with a starting tetragonality ratio of $c/a \approx 0.971$.

3. Computational results

The atomic positions in the supercell are allowed to relax as well as the volume of the cell and its shape. Using the conjugate-gradient algorithm, the structure converged to a minimum of energy which is different from the minima found in other calculations [15–17]. The period and phase of the modulation did not change with respect to the initial values. However, the ratios between the lattice parameters have changed considerably. New parameters of the supercell, after the convergence has been achieved, are $a \approx 4.17$ Å, $b \approx 20.73$ Å, $c \approx 5.633$ Å. In comparison with the cubic phase, we obtain a value for the tetragonality ratio $c/a \approx 0.955$,

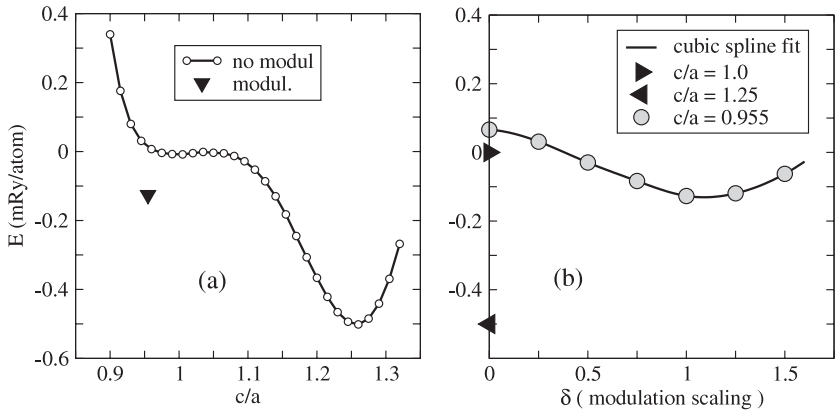

Figure 2. (a) The total energy of Ni_2MnGa as a function of the tetragonality ratio c/a for the non-modulated structure. A single point marked by a triangle shows the energy of the modulated structure. (b) The variation of the energy if we scale the modulation with a parameter δ ($\delta = 1.0$ corresponds to the optimum value found after structural relaxation while $\delta = 0.0$ means no modulation).

which is close to the experimental value of $c/a = 0.94$. A more detailed discussion shows that the structure has two different atomic (001) layers as sketched in figure 1. One of them consists of Mn and Ga atoms, while the second one consists only of Ni atoms in agreement with the experimental reference [7]. We note that the modulation amplitudes in the two atomic layers have different values: 0.292 and 0.324 Å for the Mn–Ga and Ni planes, respectively. These different amplitudes found theoretically have not yet been confirmed by experiment or mentioned in other works.

Figure 2 shows the energy landscape by comparing the results for different unmodulated and modulated structures. The dependence of the total energy on c/a for a non-modulated structure is presented in figure 2(a). Similar to results discussed in [16, 17], there are only two local energy minima. The point marked by a triangle shows the energy decrease for the relaxed structure obtained in our calculations. It is interesting to scale the modulation and to see the resulting energy changes for a fixed ratio of $c/a = 0.955$; see figure 2(b). The value $\delta = 1.0$ corresponds to the relaxed structure, while $\delta = 0.0$ corresponds to no modulation at all. It is obvious that a non-zero amplitude of modulation leads to an energy being lower than the energy for the $L2_1$ structure. For the fixed ratio $c/a = 0.955$ we find an optimum value for the amplitude of modulation. This optimum value gives the crystal a new structure which is energetically more favourable than the cubic one ($c/a = 1.0$) by about 0.15 mRyd/atom. But this energetic decrease is not enough to surpass the $c/a \sim 1.25$ structure, which is so far one order of magnitude lower in energy compared to the case $c/a = 1.0$ [18]. However, this exchange of ordering of the structures, when including the modulation, makes the theoretical results agree with experimental findings when lowering the temperature in spite of the fact that the new modulated structure is not lower in energy compared to the energy of the structure with $c/a \sim 1.25$. We tentatively assume that this could be explained by the lack of disorder or non-collinear magnetic moments as mentioned above, since at least the atomic interchange is natural for Heusler alloys. Current calculations to show this are under way.

In figure 3 we present results of total energy calculations for different values of c/a for a fixed modulation. We notice that the c/a variation leads to a minimum at about $c/a = 0.94$. This is a considerable improvement with respect to other existing results.

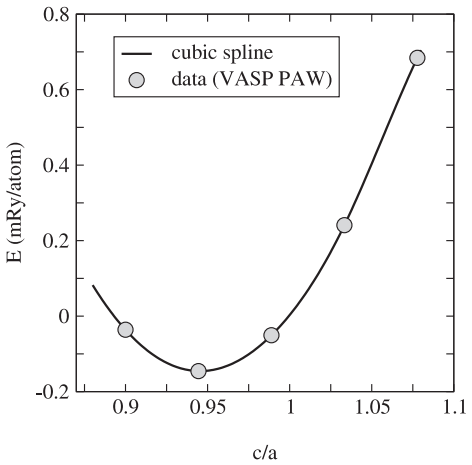

Figure 3. The dependence of the total energy on the variation of c/a for a fixed modulation obtained from relaxation. This curve shows agreement of the calculations with experiments in which structures with $c/a \approx 0.94$ are observed.

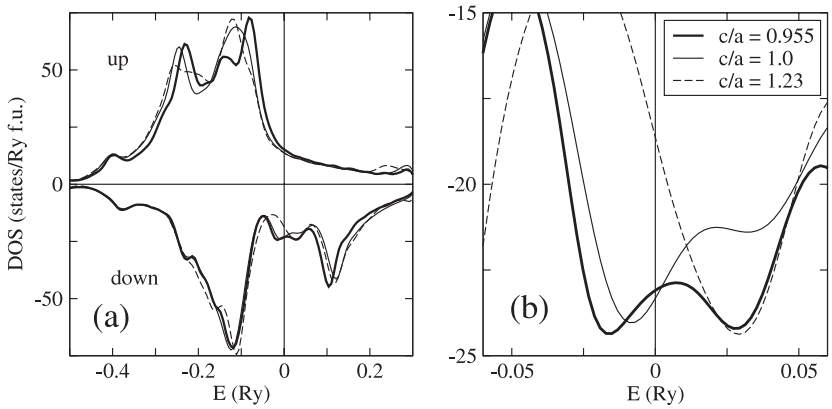

Figure 4. (a) The total DOS for three different structures of Ni_2MnGa: cubic $L2_1$, tetragonal with $c/a \approx 1.25$, and modulated tetragonal with $c/a = 0.955$. (b) An enlargement of the minority spin DOS around the Fermi level.

In figure 4 we present the density of states (DOS) for three different structures: cubic structure ($c/a = 1.0$), tetragonal structure ($c/a = 1.25$), and modulated tetragonal structure ($c/a = 0.955$). Figure 4(b) shows an enlargement of the minority spin DOS around the Fermi level. Obviously the modulated tetragonal structure with $c/a = 0.955$ shows a tendency to open a pseudo-gap close to E_F.

4. Conclusions

On the basis of first-principles calculations we have shown that the tetragonal martensite structure of Ni_2MnGa with $c/a < 1.0$ can be stabilized by allowing for shuffling of atoms corresponding here to a modulation with a well-defined period. The structural parameters used in the calculations are in agreement with the experimental ones [7, 12]. The energy of

the modulated structure is considerably lower compared to the energy for the $L2_1$ structure of Ni_2MnGa, which makes the theory agree with experimental trends. Also we found that the amplitudes of modulation are different for Mn–Ga and for Ni planes. This finding encourages and challenges further experimental work, e.g., with respect to the interpretation of x-ray results. The effect of modulation is not negligible and certainly will prompt further work—for example, with respect to the orthorhombic phases of Ni_2MnGa. Further work necessitates the including of atomic disorder and the considering of non-collinear magnetic structures.

Acknowledgments

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