FIRST-PRINCIPLES STUDY OF MARTENSITIC TRANSFORMATIONS IN Ni-Mn-Ga ALLOYS

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ABSTRACT

Using first-principles calculations combined with the generalized solid state nudged elastic band method we determined the minimum energy path in Ni_2MnGa magnetic shape memory alloy starting from $L2_1$ structure of austenite and leading to the different modulated phases of martensite (4O, 10M, and 14M) and to non-modulated (NM) phase. We have found that there is no energy barrier on the path to the 10M phase. Transformation paths to other structures including NM martensite exhibit more or less significant barriers in the beginning, hindering such a transformation from austenite although these structures exhibits lower total energy. On the other hand, in off-stoichiometric alloys the barrier-less transformation was found between austenite and NM martensite

KEYWORDS: MAGNETIC SHAPE MEMORY ALLOYS, MARTENSITIC TRANSFORMATION, *AB INITIO* CALCULATIONS, PHASE STABILITY.

INTRODUCTION

Much attention has been paid to the Ni-Mn-Ga magnetic shape memory alloys because they exhibit interesting properties such as a giant magnetic field-induced strain (MFIS) [Ullakko, 1996]. The MFIS is related to the high mobility of twin boundaries in connection with a large magneto-crystalline anisotropy [Söderberg, 2006]. It occurs in martensite, below the martensitic transformation temperature at which a high-temperature cubic phase with $L2_1$ structure, austenite, transforms to a phase with lower symmetry, martensite. The martensitic transformation is associated with characteristic features in the electronic structure [Zayak, 2005]. Several types of martensites have been observed in the Ni-Mn-Ga system [Niemann, 2017]. The modulated five-layered (10M) phase observed in alloys near stoichiometric composition or seven-layered (14M) phase exhibit MFIS up to 10%. Giant MFIS has never been reported for the third martensitic phase which has a purely tetragonal lattice without modulation (NM) and is typical for compositions far from stoichiometry [Söderberg, 2006]. Recent electronic structure calculations predict also a structure with four-layered modulation (4O) as the ground state at 0 K [Zelený, 2016] but so far there is no experimental confirmation.

In this work, we compare the phase transformation paths and corresponding energy barriers between the austenite and the individual types of martensites in Ni-Mn-Ga alloys. This comparison explains why the transformation to the 4O structure is replaced by the transformation to 10M in stoichiometric Ni_2MnGa while the transformation to NM martensite is preferred for off-stoichiometric alloys.

METHODS

All computations were performed by applying the plane-wave based spin-polarized DFT method with the Vienna Ab Initio Simulation Package [Kresse, 1996]. The electron ion interaction was described with the projector augmented wave method [Blöchl, 1994; Kresse, 1999]. The electron exchange and correlation energy were treated within the generalized gradient approximation in the Perdew–Burke–Ernzerhof formalism [Perdew, 1996]. The cut-off energy of 600 eV was used. The Brillouin zone (BZ) was sampled using a Γ-point centered mesh with the smallest allowed spacing between *k*-points equal to 0.1 $Å^{-1}$. The optimization of the geometry was performed when the convergence criterion on the forces became smaller than 1 meV · $Å^{-1}$ and the energy difference was smaller than 10^{-6} eV. To determine the transformation pathways, we extend the DFT calculations by the Generalized Solid State Nudged Elastic Band (G-SSNEB) method [17].

Using the idea of nanotwinning [Kaufmann, 2010] the modulated martensites were described by monoclinic or orthorhombic structures with an alternating sequence of nanotwins comprising of NM structure twinned on (101) lattice planes. Such constructed 14M, 10M structures and theoretically predicted 4O structure are illustrated in Figure 1 together with cubic austenite, 6M premartensite and the 6M-related hypothetical 6O structure.

RESULTS

In stoichiometric Ni_2MnGa alloy there is no energy barrier on the minimum energy path to the 10M phase and the energy decreases with a large negative slope (blue curve in Figure 1) [Zelený, 2018]. Geometry of the lattice in the initial part of the path confirms that this transformation is driven by a softening of the TA_2 [$\xi\xi$0] phonon branch [Zayak, 2005] corresponding to the shift of (110) planes. In later part of the path individual NM nanotwins are

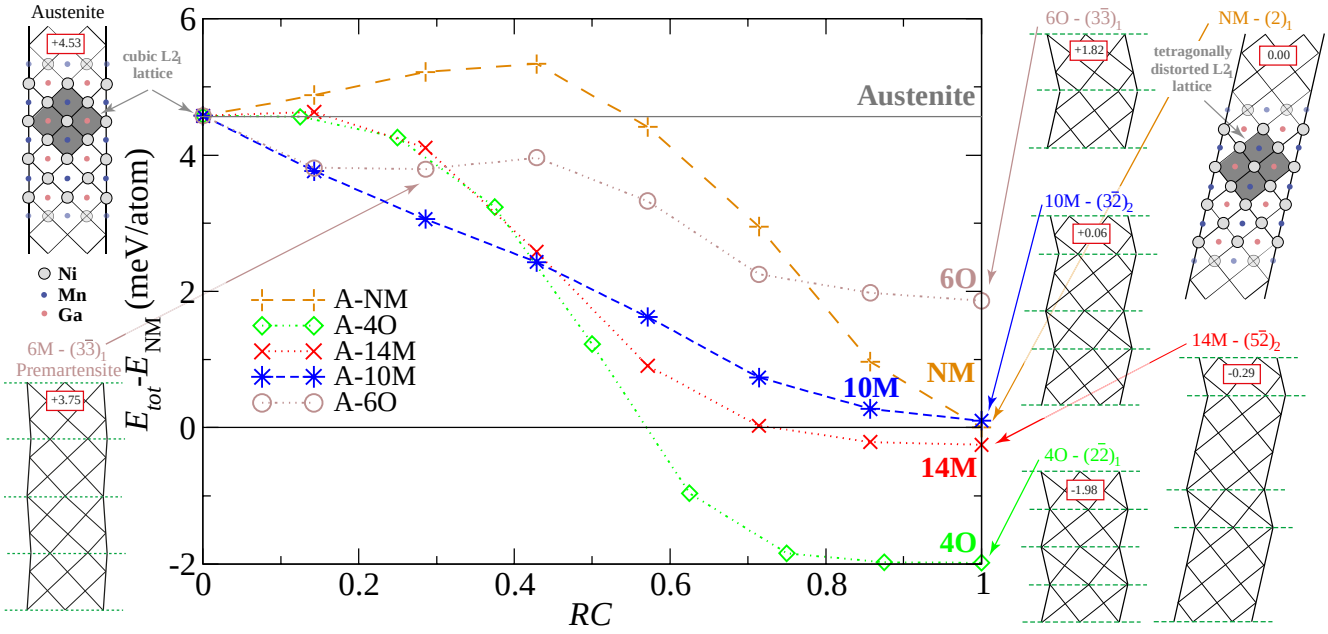

Figure 1: Calculated minimum energy path of Ni_2MnGa along the reaction coordinate RC for the transformation starting from austenite to fully transformed martensite and schematic illustration of the austenite, premartensite 6M and martensite structures: 6O, NM, 10M, 14M and 4O. Gray filling in the austenite and NM identify the original and tetragonally distorted $L2_1$ cell; the green dashed lines mark nanotwin boundaries; numbers in red boxes correspond to total energy differences in meV/atom. All energies are relative to the total energy of NM martensite. Adapted from [Zelený, 2018].

stabilized by band Jahn-Teller effect. Moreover, a similar negative slope in the beginning of path is found also for the transformation to the 6M premartensite. Paths to other structures including NM martensite exhibit more or less significant barriers in the beginning, hindering such a transformation from austenite although these structures exhibits lower total energy. On the other hand, in off-stoichiometric alloys with concentration of excess Mn 3.125 and 6.250 at. % the barrier-less transformation was found between austenite and NM martensite corresponding to tetragonal distortion of the lattice due to Jahn-Teller effect. Increasing concentration of Mn instead of Ga also further stabilize NM martensite with respect to austenite.

CONCLUSION

Our theoretical finding obtained with help of electronic structure calculations demonstrates that the kinetics of the martensitic transformation in Ni-Mn-Ga alloy represented by energy barrier along the transformation path is decisive for the selection of the particular low-symmetry structure of martensite.

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