Proceedings of the International Symposium on Physics of Materials (ISPMA 14), September 10–15, 2017, Prague **Ab Initio** Study of Martensitic Transition in Ni₂MnGa

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Ferromagnetic shape memory alloys are modern functional materials capable of undergoing significant reversible strains induced by moderate external magnetic fields due to diffusionless structural transitions and highly mobile twin interfaces. The subject of our work is a theoretical study of the Ni–Mn–Ga alloy, as a representative of the magnetic shape memory alloys, by means of the *ab initio* simulation methods. It has been shown that the DFT+U method (the Hubbard treatment of the strong on-site Coulomb interaction of localized electrons) used for description of transition metals, can improve quantitative agreement of theoretical and experimental data. The choice of U-parameters for both Mn and Ni atoms was proposed based on the comparison of experimental and theoretical elastic constants of cubic austenite and tetragonal non-modulated martensite. The resulting theoretical results agree with the elasticity measurements. It has been also shown that involving U-correction have strong impact on the predicted formation energies of particular phases.

DOI: 10.12693/APhysPolA.134.804

PACS/topics: magnetic shape-memory alloys, Ni–Mn–Ga, density functional theory, DFT+U, elastic constants

1. Introduction

The Ni₂MnGa alloy is one of the most intensively studied magnetic shape memory alloys (SMA) nowadays, as the 10M modulated Ni₂MnGa martensite exhibits extremely small twinning stress and high mobility of the twin interfaces [1]. These features are behind the magnetic shape memory effect and other interesting properties, which promise great industrial performance in future actuators, sensors, or magnetic refrigerators [2]. Although Ni₂MnGa has been for decades in focus of scientists, there are still important questions about this material to be answered.

One of these questions is the reason and exact conditions of formation of different martensitic structures, which can be either non-modulated with tetragonal symmetry or more complex modulated (10M, 14M) with monoclinic symmetry. Other question is very different mobility of the twin interfaces in individual martensitic structures.

First-principles calculations have already proven to be a very convenient tool for finding answers to these questions and explanation of extraordinary properties of Ni₂MnGa [2]. In this work, we perform theoretical study of elastic properties of the stoichiometric cubic austenite ($L2_1$ structure; Fm3m symmetry) and nonmodulated tetragonal martensite (I4/mmm symmetry), see Fig. 1. As the method, density functional theory with the U-Hubbard correction (DFT+U) is used. We take advantage of recently published experimental data of elasticity of both phases [3] and adjust U-parameters for both d-orbitals of Mn and Ni atoms to achieve quantitative agreement. We also discuss the influence of U-parameters to the calculated formation energy of non-modulated martensite.



Fig. 1. Ni₂MnGa $L2_1$ structure: austenitic phase (left), Ni₂MnGa tetragonal: martensitic phase (right).

2. Method

Calculations were done in CASTEP plane wave basis DFT code [4]. Spin-polarized calculations were performed with the generalized gradient approximation-type (GGA) functional PBE [5] for approximation of the exchange and correlation energy. We have optimized the

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kinetic energy cutoff and mesh of k-points by performing convergence calculations with respect to these quantities. After the convergence better than 0.001 eV per atom, we used the energy of 560 eV for the kinetic energy cutoff and the mesh of $6 \times 6 \times 6$ k-points for the representation of the Brillouin zone. All structures were calculated in the conventional cell, as depicted in Fig. 1 (comprising 4 formula units).

Since transition metals are usually inaccurately described by standard DFT, it is appropriate to employ the Hubbard DFT+U model, which corrects the wrong description of the localized *d*-electrons [6, 7]. The suitable setting of the U parameter with respect to the properties of electronic structure, atomic structure, and elastic properties is crucial. The theoretical value for Ni₂MnGa based on linear response approach was proposed as U = 5.97 eV on the *d* states of Mn [8]. To find the *U*-parameters which give the best fit of the experimental elasticity, we performed series of calculations with U from 0 eV to 6 eV for both *d*-states of Mn and Ni and found the optimal values in these bounds.

Modulus of isotropic straining B and elastic constants were determined from the evolution of the energy of equilibrated structures (equilibrium with respect to atom positions) with lattice distortion. In each case, 10 distorted structures were calculated where the step of distortion was 0.1% of the lattice constant.

3. Results and discussion

3.1. Fitting of the Hubbard U-parameter

Table I shows resulting bulk moduli B of austenite for different U parameters on d states of Mn and Ni. The dependence of B on U(Mn-d) and U(Ni-d) was then interpolated by piecewise cubic polynomials in Matlab (Fig. 2) to find values of U which give the experimentally obtained B = 134 GPa for austenite. Since there was only very small influence of U at Ni, the optimization was done finally only for Mn while U(Ni-d) was kept at zero. The resulting U(Mn-d) was 3.93 eV.

Calculated B values [GPa] of austenite for various setting of U parameters [eV] TABLE I

		U(Mn-d) [eV]							
		2.0	3.5	4.0	4.5	5.0	6.0		
U(Ni-d)	0.0	141.7	<u>135.3</u>	132.3	128.5	127.8	124.4		
	2.0	142.6	138.6	133.2	131.1	129.6	127.3		
	4.0	144.2	138.5	135.3	132.6	131.0	128.7		
	6.0				<u>133.0</u>	132.2	130.0		

3.2. Optimal c/a ratio

Figure 3 shows evolution of formation energy with tetragonal distortion (c/a = 1 corresponds to austen-ite) calculated with U-setting resulted from the previous optimization (U(Mn-d) = 3.93 eV, U(Ni-d) = 0.00 eV). The local energy minimum corresponding to tetragonal



Fig. 2. Dependence of bulk modulus B [GPa] of austenite on U(Mn-d) and U(Ni-d) [eV].



Fig. 3. Evolution of the formation energy with tetragonal distortion. The energy is stated per conventional unit cell (4 formula units).

phase has c/a ratio equal to 1.145, while the global energy minimum is present for c/a = 1. We can see that energy of the tetragonal phase is higher compared to the cubic phase and thus this phase is metastable. This result is in contradiction to calculations done by pure GGA (neglecting the U corrections) [8–10], where tetragonal martensite in stoichiometric Ni₂MnGa remains more stable than austenite. Our results are also qualitatively different from the previously published calculations with GGA+U with setting U(Mn-d) = 5.97 eV [8]. Under those conditions, there is only single global energetical minimum in tetragonal distortion for c/a = 1 and tetragonal martensite is neither a metastable phase.

3.3. Calculation of bulk modulus and elastic constants

Table II displays calculated elastic constants and modulus of isotropic straining B for both phases and their comparison to experiments and previously published theoretical calculations obtained by DFT.

TABLE II

Comparison of theoretical and experimental elastic constants [GPa] of austenite and tetragonal martensite of Ni₂MnGa.

	В	c_{11}	c_{33}	c_{12}	c ₁₃	c_{44}	c_{66}
cubic phase $(DFT+U)$	133.5 (fitted)	160.5		90.0		89.7	
cubic phase $(exp., [13])$	133.0	140.0		132.3		104.0	
cubic phase $(DFT, [10])$	155.6	163		151		110	
tetragonal phase $(DFT+U)$	132.90	201.3	174.5	75.3	106.7	102.7	70.7
tetragonal phase $(exp., [3])$	120.00	197.8	189.1	60.9	143.5	106.2	49.7
tetragonal phase $(DFT, [10])$	155	249	193	71	141	101	56
tetragonal phase $(DFT, [11])$	157	250.4	193.0	68.0	146.6	96.5	37.3

Table III then shows the calculated lattice constants. The parameters $c' = (c_{11} - c_{12})/2$, $(c_{11} - 2c_{13} + c_{33})/4$, c_{44} , and c_{66} were determined according to the energy profile of the corresponding volume conserving strain. The values of elastic constants are in good agreement with the experimental measurements. Let us mention that only the value of *B* of austenite was fitted by *U* parameters. For both presented structures, the requirements on the elastic stability, such as $(c_{11} - c_{12}) > 0$, or $(c_{11} - 2c_{13} + c_{33}) > 0$ are fulfilled [12]. The calculated lattice constant 5.932 Å of the cubic phase agrees with the usual overestimation of lattice constants by the GGA computational methods.

TABLE III

Comparison of theoretical and experimental lattice parameters of austenite and tetragonal martensite of $\rm Ni_2MnGa$

	a [Å]	c [Å]	c/a
cubic phase $(DFT+U)$	5.932		
cubic phase (experiment, [13])	5.825		
cubic phase (DFT, [10])	5.812		
tetragonal phase $(DFT+U)$	5.674	6.496	1.145
tetragonal phase (experiment, [14])	5.52	6.44	1.2
tetragonal phase $(DFT, [10])$	5.37	6.77	1.26

4. Conclusions

In this contribution, we have shown large effect of the Hubbard DFT+U correction in DFT calculation on prediction of elastic constants of austenite and martensite in Ni₂MnGa. Based on comparison of experimental and theoretical values, the optimal setting was found as U(Mn-d) = 3.93 eV and U(Ni-d) = 0 eV. With this setting, we have obtained very good agreement with experiments for elasticity of both austenite and martensite. The choice of U parameters influences also calculated formation energies. In our calculation, the tetragonal martensite of stoichiometric Ni₂MnGa results as a metastable phase with c/a ratio equal to 1.145.

Acknowledgments

This work has been carried out under the Advanced Materials Project funded by the Czech Science Foundation (grant No. 14-36566G). Methodical support is acknowledged of the Student Grant System of the Czech Technical University in Prague (Grant No. SGS16/245/OHK4/3T/14).

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