Electronic structure and possible martensitic transformation in Ni_2FeIn alloy

YUNGAO GU¹, FANG XUE¹, GUOQING ZHAO¹, GUODONG LIU², YANG LIU³, SONGTAO LI^{3*}

¹Department of Physics and Electrical Engineering, Handan College,
Handan, 056005, P.R.China

²School of Material Science and Engineering, Hebei University of Technology,
Tianjin 300130, P.R. China

³School of Mathematics and Physics, North China Electric Power University,
Baoding 071003, P.R. China

The electronic structure and magnetic properties of Heusler alloys (Ni_2FeIn) have been studied by first principle calculations. The possible tetragonal martensitic transformation has been predicted and the structure optimization was made on cubic austenitic Ni_2FeIn in Cu_2MnAl type. The equilibrium lattice constant of austenitic Ni_2FeIn is 6.03 Å. In tetragonal phase, the global energy minimum occurs at $c/a = 1.29$. The corresponding equilibrium lattice constants for martensite Ni_2FeIn are $a = b = 5.5393$ Å and $c = 7.1457$ Å, respectively. In the austenitic phase, E_F is located at the peak in the minority DOS for $c/a = 0.96$ to 1.20, but in the martensitic phase, E_F moves to the bottom of the valley in the minority DOS, reducing the value of $N(E_F)$ effectively. Both austenitic and martensitic phases are ferromagnetic and the Ni and Fe partial moments contribute mainly to the total moments. Therefore, the martensitic transformation behavior in Ni_2FeIn is predicted.

Keywords: *electrical structure; martensitic transformations; first principle calculations*

© Wrocław University of Technology.

1. Introduction

In 1996 K. Ullakko et al. [1] reported that the large magnetic-field-induced strains were found in Ni_2MnGa alloy. Since then, Ni-based Heusler alloys [2–4] have received considerable attention for their potential application as ferromagnetic shape-memory alloys (FSMAs) in many technical fields, such as magnetic actuators or magnetocaloric materials. FSMAs are magnetic materials that exhibit a martensitic transformation together with large magnetic-field-induced strains. The alloys have not only large strain but also high response frequency because the shape memory effect can be controlled by applying magnetic field – in addition to conventional controls – by temperature and stress.

Until now, the most common FSMAs among the Heusler alloys are Ni–Mn based alloys. The Ni–Mn–Z (Z = Ga, In, Fe, Al, Sn) [5–9] alloys

have been predicted to be FSMAs by experimental and theoretical studies. Moreover, Ni–Co–Mn–In Heusler alloys exhibiting shape memory effect have been reported by R. Kainuma et al. [10]. Stresses of over 100 MPa are generated in the materials under the application of a magnetic field of 70 kOe. Such stress levels are approximately 50 times larger than that generated in a previous ferromagnetic shape-memory alloy [11]. In recent years a large amount of Heusler alloys [12–14] have been predicted to be FSMAs.

In this paper we have studied the electronic structure and magnetic properties of Heusler alloys Ni_2FeIn by first principle calculations. The possible tetragonal martensitic transformation has been predicted. We observed that Ni_2FeIn alloy has a ferromagnetic character in both austenitic and martensitic phases, and – to a great extent – the Ni and Fe partial moments contribute to the total moments. Theoretical calculations show that Ni_2FeIn is probably a ferromagnetic shape-memory alloy.

*E-mail: songtaoli2001@126.com

2. Computational methods

The electronic structure of Ni_2FeIn alloy was calculated by means of CASTEP (Cambridge Sequential Total Energy Package) code based on pseudopotential method with a plane-wave basis set [15, 16]. The interactions between the atomic core and the valence electrons were described by the ultrasoft pseudopotential [17]. The electronic exchange-correlation energy was treated with the generalized-gradient-approximation (GGA) [18]. For all cases, a plane-wave basis set cut-off of 500 eV was used. A mesh of $15 \times 15 \times 9$ k-points was employed for Brillouin zone integrations. These parameters ensured good convergences for total energy. The convergence tolerance for the calculations was selected as a difference of the total energy within 1×10^{-6} eV/atom.

3. Results and discussion

3.1. Electronic structure in austenitic and martensitic phase

Fig. 1. The austenite and martensite structures of Ni_2FeIn alloy.

Heusler alloys crystallize in a highly-ordered cubic structure and have a stoichiometric composition of X_2YZ , where X and Y atoms are transition metal elements, and Z atom is a main group element, which is arranged in four interpenetrating face-centered-cubic (fcc) lattices. There are two possible structures in austenitic phase: Hg_2CuTi type and Cu_2MnAl type. In Hg_2CuTi type structure, the X atoms occupy the A (0 0 0) and B (1/4

1/4 1/4) sites, and the Y atom enters the C (1/2 1/2 1/2) site, whereas Z atom occupies the D (3/4 3/4 3/4) site in Wyckoff coordinates. In contrast, in Cu_2MnAl type structure the X atoms occupy the A and the C sites, and Y atom enters the B site, leaving the D site to Z atom. As an example, Fig. 1 presents the general structure of the Heusler alloys. According to the previous studies, for 3d transition metal elements, the site preference is determined by the number of valence electrons of transition metal elements; the elements with less electrons prefer to occupy the B site, while others prefer to enter the (A, C) sites [19]. So, in Ni_2FeIn , the two Ni atoms occupy the (A, C) sites and Mn enters the B site, forming the Cu_2MnAl type structure. The same type of structure is also observed in Ni_2FeGa alloy [20].

Fig. 2. The calculated total energies as a function of the lattice parameters for austenitic Ni_2FeIn in Cu_2MnAl type structure.

First, we investigated the electronic structure of austenitic Ni_2FeIn and made structure optimization on cubic austenitic Ni_2FeIn of Cu_2MnAl type by using first principle calculations. Both paramagnetic and ferromagnetic coupling between Ni atoms at A and C sites have been considered in calculations. Fig. 2 shows the calculated total energies as a function of the lattice parameters for austenitic Ni_2FeIn in Cu_2MnAl type structure. The equilibrium lattice constant of austenitic Ni_2FeIn was derived by minimizing the total energy. The lattice constant is 6.03 Å, which is much larger than the

5.74 Å in Ni₂FeGa alloy [20] and a bit smaller than the 6.07 Å in Ni₂MnIn alloy [21]. It follows from the fact that the radius of the main group element, In atom, is much larger than that of Ga atom and the radius of transition metal element, Fe atom, is a bit smaller than that of Mn atom.

Fig. 3. The calculated total energy as a function of the c/a ratio for Ni₂FeIn alloy in the martensitic phase.

The structural phase transition is nearly volume conserving [22], which is a characteristic feature of a shape memory alloy. In the optimization of the martensitic phase, for convenience sake, it has been assumed that there is no volume difference between the austenitic and martensitic phases. In Fig. 3 the calculated total energy as a function of the c/a ratio for Ni₂FeIn alloy in the martensitic phase is shown, and the zero of total energy E_{tot} is the energy in austenitic phase. It is clear that there are two local energy minima in the $E_{tot} = f(c/a)$ curve: a shallow one at $c/a = 1.00$ (austenite), and a deep one at $c/a = 1.29$. Around $c/a = 1.00$ the energy of Ni₂FeIn changes a little, which means a very small tetragonal distortion. The energy from $c/a = 0.94$ to 1.05 is nearly constant, and for $c/a = 1.00$ there is a metastable minimum. At $c/a = 1.29$ there is the lowest energy in the whole curve indicating the most stable structure. So, in the possible martensitic transformation, the c -axis lattice will expand and a , b -axes in the lattice will contract. The corresponding equilibrium lattice constants for martensite Ni₂FeIn are

$a = b = 5.5393$ Å and $c = 7.1457$ Å, as listed in Table 1.

Fig. 4. Calculated spin-projected total and partial DOS of Ni₂FeIn in austenitic and martensitic phases.

3.2. DOS and PDOS in austenitic and martensitic phases

The calculated spin-projected total and partial density of states (DOS) for Ni₂FeIn in austenitic and martensitic phases are presented in Fig. 4. For both austenitic and martensitic phases it is found that the majority spin DOS is mainly below E_F , and the bonding peak at -3.5 eV comes from the covalent hybridization between d electrons of Ni and Fe atoms. The anti-bonding peak in the minority spin state around 0.5 eV is mainly contributed by the Fe atom. It has been reported that the covalent hybridization between the lower-energy d states of the higher-valence transition metal atom, like Ni, and the higher-energy d states of the lower-valence transition metal atom, like Fe, can be strong and lead to the formation of bonding and antibonding bands [23].

For austenite and martensite, the total DOS from -3 eV to 0 eV, in both majority spin and minority spin states, mainly consists of Ni atoms at A and C sites. The covalent hybridization between d electrons of Ni and Fe atoms forms the DOS around -3.5 eV in the majority spin state and 0.5 eV in the minority spin state. Below -5 eV the contribution is mainly from In atom at D site. The difference of total DOS between austenite and martensite

Table 1. The calculated lattice parameters a , b , c and magnetic moments for austenitic and martensitic Ni_2FeIn .

Ni_2FeIn	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	c/a	$M_{\text{tot}}(\mu_B)$	$M_{\text{Ni}}(\mu_B)$	$M_{\text{Fe}}(\mu_B)$	$M_{\text{In}}(\mu_B)$
Austenite	6.03	6.03	6.03	1.00	3.52	0.32	2.86	0
Martensite	5.5393	5.5393	7.1457	1.29	3.56	0.40	2.76	-0.02

is small but tetragonal distortion impacts the DOS around E_F in minority spin state.

Fig. 5. The calculated total DOS of Ni_2FeIn for $c/a = 0.90$ to 1.40 .

In order to investigate the influence of tetragonal distortion, the total DOS of Ni_2FeIn for $c/a = 0.90$ to 1.40 have been calculated and shown in Fig. 5. The insets in Fig. 5 show the enlarged area around the E_F . The shape of the total DOS remains substantially unchanged with c/a rising from 0.90 to 1.40 , and the majority spin DOS is mainly below E_F . The bonding peak and the anti-bonding peak are located at -3.5 eV and 0.5 eV, respectively. It should be noted that E_F is located at the peak in the minority spin DOS from $c/a = 0.96$ to 1.20 because the energy around $c/a = 1.00$ changes a little. However, in the martensitic phase, E_F moves to the bottom of the valley in the minority DOS reducing the value of $N(E_F)$ effectively. The total DOS decreases with c/a increasing due to the tetragonal distortion. It is known as the Jahn-Teller effect, in which the DOS

peak at E_F in the austenitic phase is divided into two peaks – below and above E_F , with tetragonal distortion – resulting in a dropping of the total energy and causing the martensitic transformation [24]. This indicates that the tetragonal phase is more stable and that a martensitic transformation may occur at lowering temperature.

3.3. Magnetic properties

The total DOSs in majority spin and minority spin states are asymmetric in Fig. 4. It means that the Ni_2FeIn alloy is magnetic. In the PDOS of Fe at B site, the spin splitting of Fe atom is large, resulting in a large local moment. The PDOS of Ni atom has a better symmetry and the spin moment is smaller than that of Fe atom. For austenitic phase and martensitic phase, In atom is nearly paramagnetic and its moment is 0 and $-0.02 \mu_B$, respectively. The calculated magnetic moments for Ni_2FeIn of austenitic and martensitic phases are listed in Table 1. Ni_2FeIn is a ferromagnetic material, which is mainly determined by the parallel aligned Ni and Fe atom spin moments.

The variation of the martensitic moment in Ni_2FeIn alloy is related to the partial moments of Ni(A, C) and Fe(B). In Fig. 6 the total and partial spin moments of Ni_2FeIn as a function of c/a ratio are presented. The total moment around $c/a = 1.00$ changes a little corresponding to the metastable structure of austenite. For the part of $c/a > 1$ the total moment increases and drops with the increase in c/a ratio. It is strongly related to the increasing trend of Ni(A, C) atom spin moment and the decreasing trend of Fe(B) atom spin moment. The possible martensitic transformation appears at the point of $c/a = 1.29$. The total moment of martensite at $c/a = 1.29$ is a little larger than that of the austenite at $c/a = 1.29$. In Fig. 6, with c/a increasing, the Ni_2FeIn alloy becomes ferromagnetic

Fig. 6. Total and partial spin moments as a function of the c/a ratio for Ni_2FeIn .

because the spin moments of Ni and Fe atoms keep parallel aligned in the tetragonal distortional process.

4. Conclusions

The electronic structure and magnetic properties of Heusler alloys Ni_2FeIn have been studied theoretically. We investigated the electronic structure of austenitic Ni_2FeIn and made structure optimization on cubic austenitic Ni_2FeIn of Cu_2MnAl type by using first principle calculations. The equilibrium lattice constant of austenitic Ni_2FeIn is 6.03 Å. In the tetragonal phase, the global energy reaches minimum at the point of $c/a = 1.29$. The corresponding equilibrium lattice constants for martensite Ni_2FeIn are $a = b = 5.5393$ Å and $c = 7.1457$ Å, respectively. However, the energy difference between the martensitic and austenitic phases is only 18.38 meV/cell. E_F is located at the peak in the minority DOS for $c/a = 0.96$ to 1.20. On the other hand, in martensitic phase, E_F moves to the

bottom of the valley in the minority DOS reducing the value of $N(E_F)$ effectively. This indicates that the tetragonal phase is more stable and that a martensitic transformation may occur at lowering temperature. The spin moments of Ni and Fe atoms keep parallel aligned in the tetragonal distortional process, so they contribute greatly to the total moments. Both austenitic and martensitic phases are ferromagnetic.

Acknowledgements

This work has been supported by the National Science Foundation of China (11004055, 50901028), the Fundamental Research Funds for the Central Universities (11ML63, 12MS142, 13ZD23), the Beijing-funded Joint Development Program of the Central Universities in Beijing and the Program for New Century Excellent Talents in University (NCET-12-0844).

References

- [1] ULLAKKO K., HUANG J.K., KANTNER C., O'HANDLEY R.C., KOKORIN V.V., *Appl. Phys. Lett.*, 69 (1996), 1966.

- [2] ZAYAK A.T., ENTEL P., *J. Magn. Magn. Mater.*, 290 – 291 (2005), 874.
- [3] LUO H.Z., MENG F.B., LIU G.D., LIU H.Y., JIA P.Z., LIU E.K., WANG W.H., WU G.H., *Intermetallics*, 38 (2013), 139.
- [4] WUTTIG M., LI J., CRACIUNESCU C., *Scripta Mater.*, 44 (2001), 2393.
- [5] MARTYNOV V.V., KOKORIN V.V., *Ann. Phys.-Paris*, 2 (1992), 739.
- [6] ENTEL P., GRUNER M.E., ADEAGBO W.A., ECKLUND C.J., ZAYAK A.T., AKAI H., ACET M., *J. Magn. Magn. Mater.*, 310 (2007), 2761.
- [7] LIU Z.H., HU H.N., LIU G.D., CUI Y.T., ZHANG M., CHEN J.L., WU G.H., XIAO G., *Phys. Rev. B*, 69 (2004), 134415.
- [8] FUJITA A., FUKAMICHI K., GEJIMA F., KAINUMA R., ISSHIDA K., *Appl. Phys. Lett.*, 77 (2001), 3054.
- [9] SUTOU Y., IMANO Y., KOEDA N., OMORI T., KAINUMA R., ISHIDA K., OIKAWA K., *Appl. Phys. Lett.*, 85 (2004), 4358.
- [10] KAINUMA R., IMANO Y., ITO W., SUTOU Y., MORITO H., OKAMOTO S., KITAKAMI O., FUJITA A., KANOMATA T., ISHIDA K., *Nature*, 439 (2006), 957.
- [11] MURRAY S.J., MARIONI M., ALLEN S.M., O'HANDLEY R.C., LOGRASSO T.A., *Appl. Phys. Lett.*, 77 (2000), 886.
- [12] LUO H.Z., LIU G.D., MENG F.B., LI S.J., ZHU W., WU G.H., ZHU X.X., JIANG C.B., *Physica B*, 405 (2010), 3092.
- [13] DAI X.F., WANG H.Y., CHEN L.J., DUAN X.F., CHEN J.L., WU G.H., ZHU H., XIAO J.Q., *J. Cryst. Growth*, 290 (2006), 626.
- [14] LUO H.Z., JIA P.Z., LIU G.D., MENG F.B., LIU H.Y., LIU E.K., WANG W.H., WU G.H., *Solid State Commun.*, 170 (2013), 44.
- [15] PAYNE M.C., TETER M.P., ALLAN D.C., ARIAS T.A., JOANNOPOULOS J.D., *Rev. Mod. Phys.*, 64 (1992), 1065.
- [16] SEGALL M.D., LINDAN P.L.D., PROBERT M.J., PICKARD C.J., HASNIP P.J., CLARK S.J., PAYNE M.C., *J. Phys.-Condens. Mat.*, 14 (2002), 2717.
- [17] VANDERBILT D., *Phys. Rev. B*, 41 (1990), 7892.
- [18] PERDEW J.P., BURKE K., ERNZERHOF M., *Phys. Rev. Lett.*, 77 (1996), 3865.
- [19] KANDPAL H.C., FECHER G.H., FELSER C., *J Phys. D Appl. Phys.*, 40 (2007), 1507.
- [20] LIU Z.H., ZHANG M., CUI Y.T., ZHOU Y.Q., WANG W.H., WU G.H., ZHANG X.X., XIAO G., *Appl. Phys. Lett.*, 82 (2003), 424.
- [21] KRENKE T., ACET M., WASSERMANN E.F., MOYA X., MAÑOSA L., PLANES A., *Phys. Rev. B*, 73 (2006), 174413.
- [22] CHAKRABARTI A., BARMAN S.R., *Appl. Phys. Lett.*, 94 (2009), 161908.
- [23] GALANAKIS I., DEDERICH S.P.H., PAPANIKOLAOU N., *Phys. Rev. B*, 66 (2002), 134428.
- [24] FUJII S., ISHIDA S., ASANO S., *J. Phys. Soc. Jpn.*, 58 (1989), 3657.

Received 2014-04-05

Accepted 2014-06-12