Unified physical mechanism for martensitic phase transition and ductility in Ni–Mn-based ferromagnetic shape memory alloys: the case of Cu-doped Ni_2MnGa

Guijiang Li[1,*], Lei Xu[1], Zhenhua Cao[1]

[1]College of Materials Science and Engineering, Nanjing Tech University, Nanjing 211816, China

Supplementary materials

Atomic preferential occupation and lattice sizes in Cu-doped Ni_2MnGa

In $L2_1$-type Ni_2MnGa at ground state, the two Ni atoms occupy 8c sites. Ga and Mn atoms lie in 4a and 4b sites, respectively. To obtain the stable cubic structure, the preferential atomic occupation styles in $Ni_{2-x}Cu_xMnGa$, $Ni_2Mn_{1-x}Cu_xGa$, and $Ni_2MnGa_{1-x}Cu_x$ alloys were first investigated. For each of the three alloys series, five possible atomic occupation styles were considered herein. Considering $Ni_{2-x}Cu_xMnGa$ as representative example, the considered atomic occupation styles are as follows: (I) the newly introduced Cu atoms directly occupy Ni sub-lattices, (II) Cu atoms occupy Mn sub-lattices and original Mn atoms are forced to move to Ni sub-lattices. (III) Cu atoms occupy Ga sub-lattices and original Ga atoms are forced to move to Ni sub-lattices. (IV) Cu atoms occupy Mn sub-lattices, original Mn atoms are forced to move to Ga sub-lattices, and Ga atoms then move to Ni sub-lattices. (V) Cu atoms occupy Ga sub-lattices, and original Ga atoms are forced to move to Mn sub-lattices, and Mn atoms then move to Ni sub-lattices. Based on above-mentioned atomic configurations in these series of alloys, the calculated energy listed in Table SI indicates that newly introduced Cu atoms prefer to direct atomic occupation style, as described in style (I). In Heusler alloys, the empirical atomic occupation rule indicates that transition metal atoms with more valence electrons prefer to occupy 8c sites. However, those with less valence electrons occupy 4a and/or 4b sites [1]. In Cu-doped Ni_2MnGa alloys, Cu atom possesses the most valence electrons. Thus, following this empirical atomic occupation rule, Cu atoms then preferentially occupy 8c sites. Theoretically, atomic occupation only in $Ni_{2-x}Cu_xMnGa$ alloys agrees well with conventional rule. Atomic occupations in $Ni_2Mn_{1-x}Cu_xGa$ and $Ni_2MnGa_{1-x}Cu_x$ alloys exhibit abnormal behaviors. Herein, atomic occupation styles in Cu-doped Ni_2MnGa agree well with previous theoretical predications [2, 3]. In Heusler alloys, high-ordered atomic occupations are dominated by strong interatomic covalent hybridization strength [4-6]. When the covalent hybridization level decreases, abnormal atomic occupation can occur [5]. In $Ni_2Mn_{1-x}Cu_xGa$ and

* Corresponding author (email: guijiangli@njtech.edu.cn)

$Ni_2MnGa_{1-x}Cu_x$ alloys, the abnormal atomic occupation indicates the weakening of the covalent hybridization strength dependence of Cu content. The preferential atomic occupation in $Ni_{2-x}Cu_xMnGa$ alloys indicates that the covalent hybridization level becomes higher or remains at a higher level. The future experiments such as high-resolution neutron diffractions can help to identify the atomic occupation in $Ni_2Mn_{1-x}Cu_xGa$ and $Ni_2MnGa_{1-x}Cu_x$ alloys.

Table SI. Different atomic occupation styles in Cu-doped Ni_2MnGa alloys. Considering the energy of atomic occupation style I as reference, the relative energy difference (ΔE in mRy) was obtained to determine the stable atomic occupation.

Composition	Atomic occupation	ΔE
$Ni_2(Mn_{1-x}Cu_x)Ga$ x=0.0625	I. $Ni_2(Mn_{1-x}Cu_x)Ga$	0
	II. $(Ni_{2-x}Cu_x)(Mn_{1-x}Ni_x)Ga$	2.18
	III. $Ni_2(Mn_{1-x}Ga_x)(Ga_{1-x}Cu_x)$	0.82
	IV. $(Ni_{2-x}Cu_x)(Mn_{1-x}Ga_x)(Ga_{1-x}Ni_x)$	3.07
	V. $(Ni_{2-x}Ga_x)(Mn_{1-x}Ni_x)(Ga_{1-x}Cu_x)$	9.82
$Ni_{2-x}Cu_xMnGa$ x=0.0625	I. $Ni_{2-x}Cu_xMnGa$	0
	II. $(Ni_{2-x}Mn_x)(Mn_{1-x}Cu_x)Ga$	5.28
	III. $(Ni_{2-x}Ga_x)Mn(Ga_{1-x}Cu_x)$	7.65
	IV. $(Ni_{2-x}Ga_x)(Mn_{1-x}Cu_x)(Ga_{1-x}Mn_x)$	8.17
	V. $(Ni_{2-x}Mn_x)(Mn_{1-x}Ga_x)(Ga_{1-x}Cu_x)$	6.06
$Ni_2Mn(Ga_{1-x}Cu_x)$ x=0.0625	I. $Ni_2Mn(Ga_{1-x}Cu_x)$	0
	II. $(Ni_{2-x}Cu_x)Mn(Ga_{1-x}Ni_x)$	2.2
	III. $Ni_2(Mn_{1-x}Cu_x)(Ga_{1-x}Mn_x)$	0.48
	IV. $(Ni_{2-x}Cu_x)(Mn_{1-x}Ni_x)(Ga_{1-x}Mn_x)$	2.61
	V. $(Ni_{2-x}Mn_x)(Mn_{1-x}Cu_x)(Ga_{1-x}Ni_x)$	7.52

Based on stable atomic occupation styles in $Ni_{2-x}Cu_xMnGa$, $Ni_2Mn_{1-x}Cu_xGa$, and $Ni_2MnGa_{1-x}Cu_x$ alloys, the lattice parameters of cubic phase were obtained by geometry optimization, as presented in Fig. S1. Theoretically, the lattice sizes of cubic phase in both $Ni_2Mn_{1-x}Cu_xGa$ and $Ni_2MnGa_{1-x}Cu_x$ decreased with the doping of Mn and Ga atoms by Cu atoms. In contrast, the lattice size expanded with the doping of Cu for Ni atoms in $Ni_{2-x}Cu_xMnGa$ alloys. Figs. S1(a–c) demonstrate that the variation tendencies of dependence of lattice sizes on Cu content in these three series alloys agree well with experimental observations [7-11]. The consistency between theoretical calculations and experimental results verify that current calculation method and atomic occupation styles are valid. In $Ni_{2-x}Cu_xMnGa$ alloys with strong covalent hybridization strength, the larger covalent radius of Cu (1.32 Å) than that of Ni (1.24 Å) was found to be responsible for the increase of lattice size [3]. When covalent hybridization strength decreases, the metallic bonding becomes prevalent. Owing to the volume effect of metallic bonding, materials tend to crystallize in relatively close packed structures. The

closer the arrangement of atoms, the lower the Coulomb energy and the more stable the binding. Thus, the increased metallic bonding in $Ni_2Mn_{1-x}Cu_xGa$ and $Ni_2MnGa_{1-x}Cu_x$ alloys resulted in the contraction of lattice sizes.

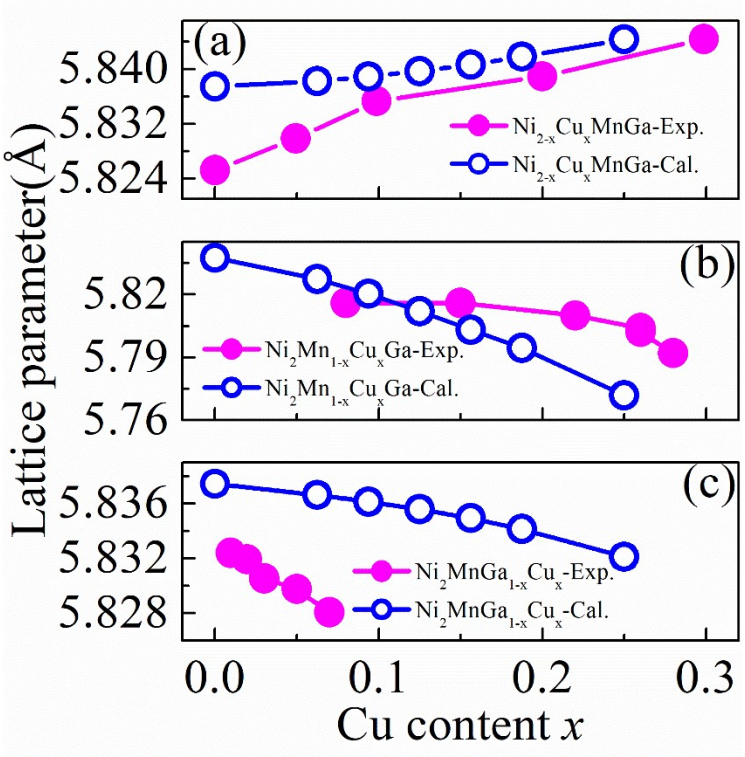

FIG. S1 Lattice parameters of (a) $Ni_{2-x}Cu_xMnGa$, (b) $Ni_2Mn_{1-x}Cu_xGa$, and (c) $Ni_2MnGa_{1-x}Cu_x$ alloys. For comparative analysis, the experimental values for $Ni_{2-x}Cu_xMnGa$ [7], $Ni_2Mn_{1-x}Cu_xGa$ [8-10], and $Ni_2MnGa_{1-x}Cu_x$ [11] are also listed. Solid circle represents values from experiments and open circle indicates theoretical data obtained in this study.

Based on theoretical atomic occupation styles and optimized lattice parameters, the elastic constants and their derived physical parameters, magnetism, and electronic structure were calculated to explore the unified physical mechanism for martensitic phase transition and ductility in Cu-doped Ni_2MnGa.

Reference

1. T. J. Burch, T. Litrenta and J. I. Budnick, *Phys. Rev. Lett.*, 1974, **33**, 421-424.
2. C. M. Li, H. B. Luo, Q. M. Hu, R. Yang, B. Johansson and L. Vitos, *Phys. Rev. B*, 2011, **84**, 024206.
3. A. Chakrabarti, M. Siewert, T. Roy, K. Mondal, A. Banerjee, M. E. Gruner and P. Entel, *Phys. Rev. B*, 2013, **88**, 174116.
4. G. J. Li, E. K. Liu, H. G. Zhang, J. F. Qian, H. W. Zhang, J. L. Chen, W. H. Wang and G. H. Wu, *Appl. Phys. Lett.*, 2012, **101**, 102402-102404.

5. G. J. Li, E. K. Liu, H. G. Zhang, Y. J. Zhang, G. Z. Xu, H. Z. Luo, H. W. Zhang, W. H. Wang and G. H. Wu, *Appl. Phys. Lett.*, 2013, **102**, 062407.
6. G. J. Li, E. K. Liu, Y. J. Zhang, Y. Du, H. W. Zhang, W. H. Wang and G. H. Wu, *J. Appl. Phys.*, 2013, **113**, 103903.
7. T. Kanomata, T. Nozawa, D. Kikuchi, H. Nishihara, K. Koyama and K. Watanabe, *Int. J. Appl. Electromagn. Mech.*, 2005, **21**, 151-157.
8. D. W. Zhao, T. Castan, A. Planes, Z. B. Li, W. Sun and J. Liu, *Phys. Rev. B*, 2017, **96**, 7.
9. S. K. Sarkar, Sarita, P. D. Babu, A. Biswas, V. Siruguri and M. Krishnan, *J. Alloys Compd.*, 2016, **670**, 281-288.
10. J. P. Guo, Z. Y. Wei, Y. Shen, Y. F. Zhang, J. Y. Li, X. L. Hou and J. Liu, *Scr. Mater.*, 2020, **185**, 56-60.
11. K. Endo, T. Kanomata, A. Kimura, M. Kataoka, H. Nishihara, R. Y. Umetsu, K. Obara, T. Shishido, M. Nagasako, R. Kainuma and K. R. A. Ziebeck, *Mater. Sci. Forum*, 2011, **684**, 165-176.