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First-principles study of martensitic transformation and magnetic properties of carbon doped Ni–Mn–Sn Heusler alloys

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ABSTRACT

The magnetic properties, structural stabilities and martensitic transformation of carbon doped Ni–Mn–Sn Heusler alloys are investigated by means of ab initio calculations in framework of the density functional theory. The results of calculations have shown that the martensitic transformation can be realized in all series of carbon doped $Ni_2Mn_{1.5}Sn_{0.5-x}C_x$ alloys with tetragonal ratio of 1.34, 1.40,1.42 and 1.44, respectively for $x = 0.125, 0.25, 0.375$ and 0.5. The DOS peak at the Fermi level almost disappearing in the tetragonal phase near the Fermi level is the evidence of triggering martensitic transformation which is due to the structural Jahn–Teller effect. We have also found that the difference between the austenitic and martensitic phases increases with increasing carbon content, which implies an enhancement of the martensitic phase transition temperature (T_M). Besides, the electron density difference shows the enhancement of bonding between Mn and carbon atoms with the distortion taken place.

1. Introduction

Since reports on a large magnetic field-induced strain in the Ni_2MnGa Heusler alloy, Ni–Mn-based ferromagnetic shape memory alloys have attracted huge interest due to the unique properties as magnetic smart materials for technological applications [1–4]. The other functional properties, such as magnetocaloric effect [5–7], giant magnetoresistance [8–10], and exchange bias effect [10–12], have also been investigated extensively. In recent years, most of the Heusler alloys (e.g. Ni–Mn–X (X = Sn, In, Sb)) depending on chemical composition undergo a diffusionless martensitic phase transformation (MPT) from a high-temperature austenitic phase to a low-temperature martensitic phase with low symmetry, and that transition is often accompanied by a sharp change in magnetization and resistivity [13–15]. In addition, many previous investigations have shown that the MPT temperature, T_M, is sensitive to chemical composition [14–17], and it could therefore be fine-tuned by varying the alloying elements. It is important to understand the effect of T_M composition-dependence for future material design and practical applications. As the references reported that the martensitic temperature increases or decreases linearly with alloy valence electron concentration [18,19]. In fact, theoretical study is required to improve our understanding of how alloying elements change the stability of the austenitic and martensitic phases and T_M. Carbon as a potential dopant for Heusler alloys has the smaller ionic radius, which incorporating in alloys will decrease the cell volume and result in the more decreasing of bond distance [20,21], and as a consequence, tune both the martensitic transformation temperature (T_M) [20] and magnetization [20–22]. So far there were few reports about carbon incorporation in NiMn based alloys. By doping the different carbon content into the supercell interstitial site, Zhang et al. make the T_M increase from 196 to 249 K, and it also enhances a large magnetic entropy change [20]. While with C doped in substitution site for NiCoMnIn system, a large magnetocaloric properties can be expected [21,22]. In this present work, in order to extend our knowledge of a carbon substitution on properties of $Ni_2Mn_{1.5}Sn_{0.5}$ alloys, we use first-principle calculations to investigate the structural, electronic and magnetic properties in dependence on different substitutions content of carbon for main group element Sn atom.

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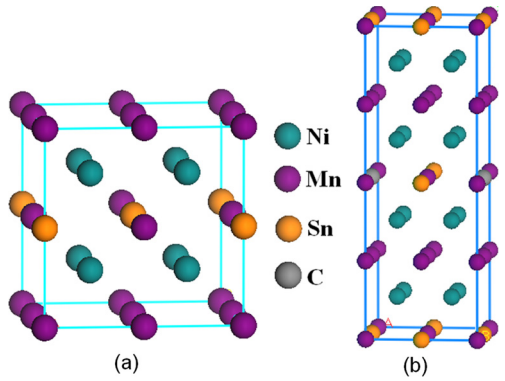

Fig. 1. Crystallographic structure in cubic phase of the $Ni_2Mn_{1.5}Sn_{0.5}$ alloy (a) and tetragonal phase of $Ni_2Mn_{1.5}Sn_{0.375}C_{0.125}$ (b).

2. Computational details

Ab initio spin-polarized pseudopotentials calculations have been performed based on the density functional theory (DFT) as is implemented the castep code [23]. For the exchange and correlation effects, the Perdew–Burke–Ernzerhof (PBE) [24] of generalized gradient approximation (GGA) was employed with the valence electron configurations for the Ni, Mn, Sn and C alloy atoms are $3d^84s^2$, $3d^54s^2$, $5s^25p^2$ and $2s^22p^2$, respectively. In the calculations, the electron–ion interactions were described by nonlocal ultra-soft pseudopotentials [25]. The integration over the first Brillouin zone has been performed with a k-mesh grid of $4 \times 4 \times 4$ for the cubic case using a Monkhorst–Pack [26], while for the tetragonal phase, we set a k-point with parameters of $5 \times 5 \times 2$ (for $x = 0.125, 0.375$) and $5 \times 5 \times 3$ (for $x = 0.25, 0.50$), respectively. The valence electron wave functions were expanded in a plane-wave basis set to a kinetic energy cutoff of 350 eV. This converged total energy difference that was set as 10^{-6} eV/atom. In the geometry optimization, all the structural parameters are relaxed with the force convergence criterion less than 0.03 eV/Å, the convergence tolerance of energy criterion set as lower than 5×10^{-6} eV/atom. The maximum ionic displacement was set within 1×10^{-3} Å, and the maximum stress within 0.03 GPa.

3. Results and discussions

Generally, stoichiometrical Heusler alloys have the chemical formula X_2YZ, where X and Y are transition metal elements, and Z is a main group element. They crystallize in a highly ordered cubic structure, in which four interpenetrating face-centered cubic lattices locate at the $A(0, 0, 0)$, $B(0.25, 0.25, 0.25)$, $C(0.5, 0.5, 0.5)$, and $D(0.75, 0.75, 0.75)$ in Wyckoff coordinates. In this work, we focus on the non-stoichiometrical alloys $Ni_2Mn_{1.5}Sn_{0.5}$ and present a calculation with C-doping, in which excess Mn prefers to occupy the Sn site basing on the lower formation energy in agreement with previous studies [15,16].

The crystallographic structure of $Ni_2Mn_{1.5}Sn_{0.5}$ alloy in cubic phase and $Ni_2Mn_{1.5}Sn_{0.375}C_{0.125}$ in tetragonal phase is depicted in Fig. 1(a) and (b). In order to determine the stability of magnetic configuration, we take into account the two situations that the magnetic moment of the excess Mn atoms at the Sn sites (Mn_{Sn}) are parallel or antiparallel alignment to Mn at the normal sites (Mn_{Mn}). Here we use "AFM" and "FM" to represent the antiparallel and parallel magnetic interactions of Mn_{Sn}–Mn_{Mn}, respectively.

The calculated total energies as a function of lattice constants of $Ni_2Mn_{1.5}Sn_{0.5-x}C_x$ for the cubic phase with Mn_{Sn} and Mn_{Mn} parallel and antiparallel alignment are plotted in Fig. 2(a), (b), (c) and (d), respectively. It can be seen from the Fig. 2 that the total energies of the "AFM" states are lower on the energies scales compared to those of the "FM" states around the equilibrium lattice parameter, which indicates the "AFM" states are more stable.

The equilibrium lattice parameters and spin configurations of the cubic austenite and tetragonal martensite phases for $Ni_2Mn_{1.5}Sn_{0.5-x}C_x$ alloys are presented in Table 1. Here, we can see that the addition of carbon results in decrease obviously of lattice parameter in austenite from 5.92 Å to 5.68 Å because of the smaller ionic radius of carbon. The decrease of the lattice constant would change the Mn_{Sn}–Mn_{Mn} distance, and as a consequence, it would tune the martensitic transformation temperature (T_M) [27,28]. Here we should note that the tetragonal ratio c/a in martensite phase increases gradually from 1.34 to 1.44 due to the carbon content increasing. With respect to the total magnetic moment, it is seen from Table 1 that the magnetic moment of austenite phase is almost about 2.0 μ_B/f.u. However, for the martensite phase, the magnetic moment just stays near a range of 1.70∼1.81 μ_B/f.u. Moreover, for the distributions of atomic magnetic moment, one can find that Mn_{Sn} atoms always interact with Mn_{Mn} atoms antiferromagnetically in both austenite and martensite. We would also like to note that the magnetic distribution of carbon should be concerned seriously. One can see a very small value about −0.02∼−0.05 μ_B/f.u., meaning nonmagnetic state of carbon in austenite phase, but when the martensitic transformation occurs, magnetic moment of carbon is spin polarized

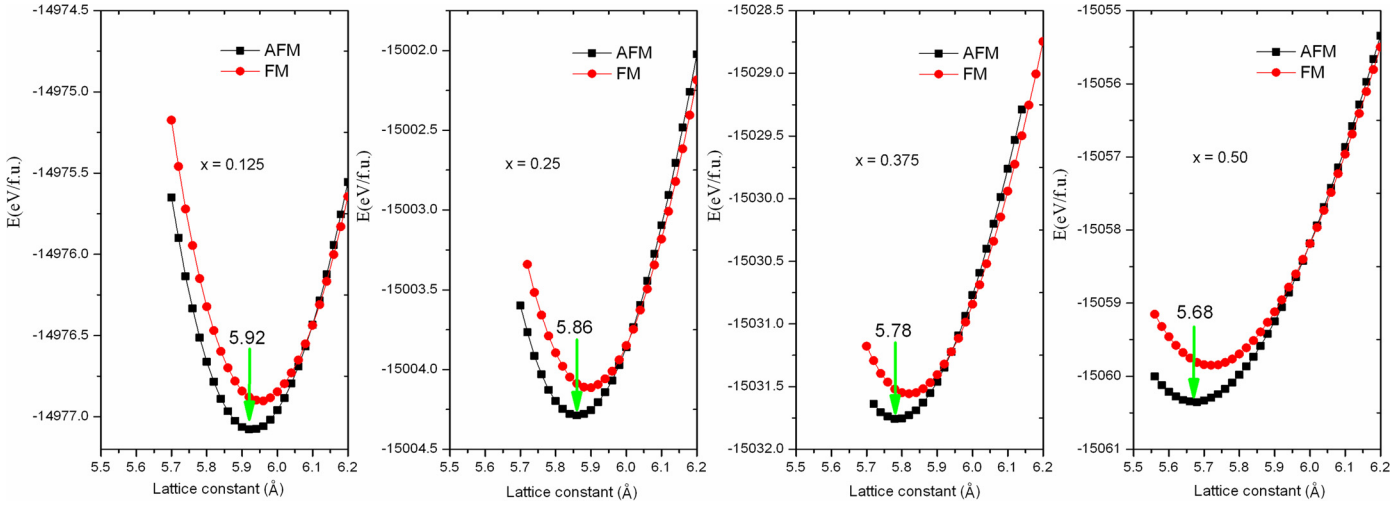

Fig. 2. Total energy as a function of lattice constants of $Ni_2Mn_{1.5}Sn_{0.5-x}C_x$ for cubic phases with FM and AFM magnetic configurations of Mn_{Mn}–Mn_{Sn} interaction (a) $x = 0.125$, (b) $x = 0.25$, (c) $x = 0.375$, and (d) $x = 0.5$, respectively.