Physica B 462 (2015) 93–96

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

The structural and magnetic properties of $Fe_{2-x}NiGa_{1+x}$ Heusler alloys

Y.J. Zhang (张玉洁)[b,*], X.K. Xi (郗学奎)[a], F.B. Meng (孟凡斌)[b], W.H. Wang (王文洪)[a], E.K. Liu (刘恩克)[a], J.L. Chen (陈京兰)[a], G.H. Wu (吴光恒)[a]

[a] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
[b] School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300401, China

ARTICLE INFO

Available online 20 January 2015

Keywords:
Heusler alloys
Atomic-order
Transition temperature

ABSTRACT

The structural and magnetic properties of $Fe_{2-x}NiGa_{1+x}$ ($x=0\sim1$) Heusler alloys have been investigated by experimental observation and calculation. In this system, a structural transition is found as a function of composition. A higher Ga content leads to an atomic-order transformation from Hg_2CuTi to B2. The magnetization decreases due to the dilution effect and the competition between the magnetic interactions and enhanced covalent bonding. The calculation of electronic structure indicates that adding Ga enhances the *p–d* orbital hybridization between the transition-metal and main-group-element atoms at nearest-neighbor distance. A magnetic and a structural phase diagram have been obtained in which the composition dependences of the lattice constant, the ordering temperature and the Curie temperature show cusps at a critical composition of $x=0.32$.

1. Introduction

Heusler alloys have the chemical formula X_2YZ, where X and Y are transition-metal elements and Z is a main-group element [1]. By combining almost all transition-metal elements and many main-group elements, many kinds of Heusler alloys have been synthesized. Among them, there are typical examples of the magnetic-field-induced transformation [2], half-metallic magnetism [3, 4] and the influence of magnetic coupling on the atomic configuration [5, 6]. In recent years, Fe_2NiZ (Z=Al, Ga, Si and Ge) Heusler alloys have been synthesized and investigated systematically [5, 7]. After Co_2FeZ, Co_2MnZ and so on, these alloys are ferromagnetic Heusler alloys with high magnetization. In accordance with an empirical occupation rule [8–10], Fe_2NiZ alloys the Hg_2CuTi structure in which Fe atoms occupy the *A* and *B* sites, Ni atoms the *C* site and Ga the *D* site. This occupation rule is also valid when the alloys are off-stoichiometric [6].

In addition, Heusler alloys with chemical formula XYZ_2, such as $NiMnGa_2$ [11] and $CoMnGa_2$ [12, 13] have been investigated. Special for these alloys is the strong covalent bonding which arises from its Z-rich composition. If the FeNiGa alloy with Ga-rich composition can be synthesized to obtain a series of intermediate alloys between Fe_2NiGa and $FeNiGa_2$, many interesting structural and magnetic properties can be expected. The experimental results will be very helpful for understanding the competing behavior between the magnetism and the covalent bonding [6].

After the Fe_2NiZ alloys were developed, however, the structural and magnetic properties of Fe_{2-x} $NiGa_{1+x}$ alloys have not been reported.

In the present work, a series of $Fe_{2-x}NiGa_{1+x}$ ($x=0\sim1$) alloys have been synthesized and their structural and magnetic properties have been investigated systematically. The results reveal that the covalent bonding, which comes from the *p–d* orbital hybridization, dominates the atomic order and the magnetization. It is found that there is a critical composition, $x=0.32$, at which the concentration dependencies of the lattice constant, the order-disorder temperature and the Curie temperature have cusps. The calculations indicate a competition between the *p–d* and *d–d* orbital hybridization which are determining for the atomic and the magnetic order in the different composition ranges.

2. Experimental and calculation methods

$Fe_{2-x}NiGa_{1+x}$ ($x=0\sim1$) alloys were prepared by arc-melting high-purity Fe, Ni and Ga under argon atmosphere. The as-cast ingots were annealed at 1073 K for one day to homogenize and then annealed at 900 K for two days to ensure atomic order. X-ray diffraction (XRD) with Cu-Kα radiation ($\lambda=1.5418$ Å) was carried out to characterize the crystal structure. The magnetic measurements were performed in a superconducting quantum interference device magnetometer (SQUID-Quantum Design). Differential scanning calorimetric (DSC) was used to determine the magnetic- and structural-transition temperatures with heating

* Corresponding author.
E-mail address: ghwu@aphy.iphy.ac.cn (Y.J. Zhang (张玉洁))

http://dx.doi.org/10.1016/j.physb.2015.01.022
0921-4526/

and cooling rates of 10 K/min. The electron-localization function (ELF) and density of states (DOS) electronic structure and magnetic moments were calculated by the pseudopotential method with plane-wave-basis set based on density-functional theory with the local spin density approximation (LSDA) [14, 15]. Plane-wave cut-off energy of 550 eV and $13 \times 13 \times 13$ k-points in the irreducible Brillouin zone were used.

3. Results and discussion

The series of $Fe_{2-x}NiGa_{1+x}$ alloys crystallizes in a body-centered-cubic (bcc) structure. Fig. 1 shows the indexed XRD reflections of stoichiometric Fe_2NiGa and $FeNiGa_2$. The compound Fe_2NiGa, which has been reported to order in the Hg_2CuTi structure [5, 7], has a lattice constant of 5.776 Å. It is seen in Fig. 1 that the (100) and (200) superlattice reflections are absent for Fe_2NiGa The (100) reflection emerges and becomes more distinct with increasing Ga content *x* This indicates that $FeNiGa_2$, which has a lattice constant of 5.760 Å, has the ordered B2 (CsCl) structure (Pm-3m space-group). The atomic mixing mostly occurs between *A*/*C* or *B*/*D* sites and results in the B2 structure with a lower degree of atomic order than L21 [16, 17]. The B2 structure is the same as that of NiGa [18] in contrast with the L21 structure of other $XYGa_2$ alloys [12]. This structure means the Fe and Ni atoms occupy the *A*/*C* sites randomly in $FeNiGa_2$. Thus, the results indicate that, with increasing Ga content, the structure of $Fe_{2-x}NiGa_{1+x}$ alloys changes from Hg_2CuTi to B2.

The lattice constants of all $Fe_{2-x}NiGa_{1+x}$ alloys, obtained by refining the XRD patterns, are shown in Fig. 2. It is seen that the composition dependence of lattice constants is not monotonous. Adding Ga leads to a lattice expansion in the range $x=0\sim0.32$ and, when *x* becomes larger, to a contraction. A maximum is found at $x=0.32$. The final alloy of $FeNiGa_2$ in the series is also in F-43m space group [19].

The atomic radius of Ga (1.38 Å) is larger than that of Fe (1.25 Å) [20], which explains the initial increase of the lattice constant upon Ga substitution for Fe. However, the decrease for $x > 0.32$ implies there must be another, competing, physical mechanism which dominates at higher Ga contents.

Fig. 3 shows the calculated ELFs of Fe_2NiGa (a) and $FeNiGa_2$ (b). As reported in previous work, significant *p*–*d* hybridization exists in Fe_2NiGa alloys [5]. This means that covalent bonding is an important factor in determining the structure and other physical properties of alloys.

The ELF is an effective means of visualizing the bond interactions [21]. The color of ELF in Fig. 3 varies from blue via yellow to red if the ELF value changes from 0 to 0.02 and qualitatively indicates the strength of the covalent bonding built up by *p*–*d* hybridization. The red regions are all dispersed around Ga atoms, indicating the *p*–*d* orbital hybridization between the main-group element and its neighboring transition-metal atoms. There are four Ga atoms and four transition metal atoms surrounded each by

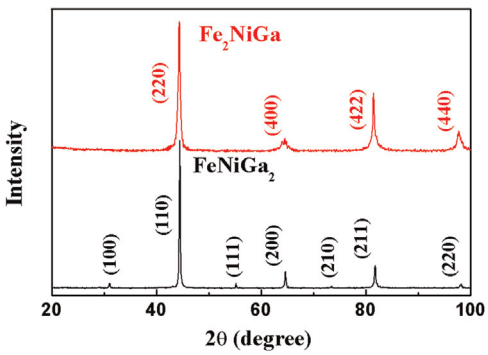

Fig. 1. XRD patterns of Fe_2NiGa and $FeNiGa_2$.

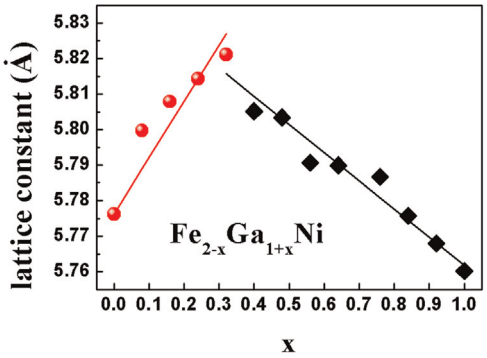

Fig. 2. Composition dependence of the lattice constant of $Fe_{2-x}NiGa_{1+x}$ alloys.

Fe or Ni atoms at the nearest-neighbor distance in Fe_2NiGa. This diversity of atomic species leads to non-equivalent lattice sites and high atomic ordering [6]. Accordingly, the ELF patterns between Ga–Fe and Ga–Ni are different.

The neighboring relationship in $FeNiGa_2$ is quite different from the Fe_2NiGa. The nearest-neighboring atoms of Fe and Ni are only Ga atoms. In Fig. 3(b), one can see that the ELF around Fe*A* and Ni*C* becomes very similar. This implies little difference of the covalent bonding between Fe and Ga and Ni and Ga, and thus gives rise to the B2 structure in which the *A* and *C* sites are randomly occupied by Fe and Ni. This is in accordance with the XRD patterns shown in Fig. 1 and disagrees with other alloys, for example $CoMnGa_2$ in which the atoms order in the L21 structure [11–13]. This observed degradation of atomic ordering suggests that, not only the covalent bonding, but also the species of the transition metal, the difference in electronegativity or the *d*–*d* hybridization probably play an important role in the atomic ordering. For example, our neutron diffraction examination reveals partly disorder in $NiMnGa_2$ where 17% of the *A* and *C* sites are randomly occupied by Mn and Ni atoms [22].

Fig. 4 shows the calculated densities of states of *p* and of *d* electrons (*p*DOS and *d*DOS) of Fe_2NiGa and $FeNiGa_2$. The visible exchange splitting of *d*DOS is the origin of the atomic magnetic moment. The corresponding peaks of the *p* and *d* partial DOSs of Fe_2NiGa, shown in Fig. 4(a) and (b), indicate the hybridization [5]. Substitution of Ga for Fe changes the bonding in the alloys. As can be seen in Fig. 4, the *p* and *d* peaks become similar in $FeNiGa_2$, which exhibits much stronger *p*–*d* interaction than in Fe_2NiGa. These results are consistent with the ELF calculations shown in Fig. 3. In $FeNiGa_2$, the exchange splitting between the spin-up and spin-down *d* states has almost disappeared. This is mainly due to the *p*–*d* hybridization, because it favors anti-parallel alignment of two spins whereas the magnetic coupling promotes parallel alignment. The covalent interaction and magnetic coupling are competing interactions [23]. Additionally, introduction of Ga atoms changes the neighboring relationship of Fe–Fe or Fe–Ni from nearest neighbors to the next-nearest neighbors, which further weakens the *d*–*d* exchange interaction between Fe and Ni.

Fig. 5 shows the composition dependence of the magnetic moment per formula unit. It should be mentioned that there is collinear alignment ferromagnetic moments in $Fe_{2-x}NiGa_{1+x}$ alloys [5], based on which is our premise in this magnetic-structure research [24]. In Fig. 5, the measured moment of $Fe_{2-x}NiGa_{1+x}$ alloys show a linear decrease with increasing Ga content, which is consistent with the calculated moments. The partial moments of Fe*A* and Ni*C* also show a linear decrease, whereas the Fe*B* moment remains almost constant. The theoretical calculation shows that the atomic moments of Fe and Ni are ferromagnetically ordered.

Substitution of Ga for Fe will dilute the concentration of magnetic atoms, which will decrease the moment per formula unit. Additionally, the competition between covalent interaction and