Structure and magnetic properties of Fe$_2$NiZ (Z=Al, Ga, Si and Ge) Heusler alloys

Y.J. Zhang, W.H. Wang, H.G. Zhang, R.K. Liu, R.S. Ma, G.H. Wu

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China

**Abstract**

Fe$_2$NiZ (Z=Al, Ga, Si and Ge) Heusler alloys have been synthesized and investigated focusing on the phase stability and the magnetic properties. The experimental and theoretical results demonstrate that covalent bonding originating from p–d hybridization plays an important role in these alloys, which dominates the stability of the ordered structure but leads to a decrease of the band splitting. The electronic structure shows that the IV group main-group elements (Si and Ge) provide a stronger covalent effect than the III group elements (Al and Ga). The variations of the physical parameters, like lattice constants, atomic-ordering temperatures, magnetic moments and Curie temperature, can be attributed differences in covalent bonding in these alloy systems.

**1. Introduction**

Heusler alloys have attracted wide attention for their various applications as well as their remarkable physical properties [1]. The Heusler alloy is also interesting for studying the ordered atomic configuration and magnetic coupling in intermetallic compounds [2]. Among the Fe$_2$-based Heusler alloys, the Fe$_2$CrZ (Z is a main-group element) alloys [3,4] and Fe$_2$MnZ alloys [5,6] exhibit very interesting shape-memory properties. For Fe$_2$NiZ systems, there are also some reports on the phase stability and the magnetic properties [3,7–9]. However, for these systems, the relationship between the phase stability and the magnetic properties has not been investigated in details.

In this paper, the structural and magnetic properties of Fe$_2$NiZ (Z=Al, Ga, Si and Ge) Heusler alloys are systematically investigated. It has been found that, selecting Al, Ga, Si and Ge for Z, four kinds of Heusler alloys with well ordered Hg$_2$CuTi-type structure can be synthesized. A series of physical parameters, such as lattice constants, magnetic moments, Curie temperature and Hg$_2$CuTi/B2 ordering temperature have been measured. In order to study the relationship between the magnetic properties and the chemical bonding, calculations of the band structure and the electron localization function have been performed. The results indicate that the covalent bonding between the atoms of main-group and 3d-elements by means of p–d orbital hybridization plays an important role in the various physical properties of Fe$_2$NiZ alloys.

**2. Experimental and computational details**

Stoichiometric Fe$_2$NiZ compounds with Z=Al, Ga, Si and Ge were prepared by arc-melting, the constituting elements with a purity higher than 99.9% and a subsequent thermal treatment (for 72 h at 1273 K) to homogenize the samples. In order to ensure high atomic order, the homogenized ingots were further annealed at 925 K for 72 h and subsequently quenched in an ice–water mixture. The crystal structure was identified by X-ray diffraction (XRD) with Cu-Kα radiation (λ=1.5418 Å). Differential scanning calorimetry (DSC) with a cooling/heating rate of 10 K/min was used to investigate the thermal stability of the samples. Magnetic measurements were performed in a SQUID magnetometer (Quantum Design). The high-temperature AC magnetic susceptibility was measured to determine the Curie temperature. Calculations of the band structure and the magnetic moments were performed by means of the KKR–CPA–LDA method [10–13]. The electron distribution was obtained by studying the Electron Localization Function (ELF) [14–16].

**3. Results and discussion**

The XRD pattern of Fe$_2$NiAl is shown in Fig. 1 and fits well with the body centered cubic (bcc) structure. The other Fe$_2$NiZ alloys have similar XRD patterns. The superlattice reflections (1 1 1) and (2 0 0) are observed, which mean that the Fe$_2$NiZ compounds have an atomically ordered structure. The inset of Fig. 1 shows the crystal structure of Heusler alloys with four equivalent lattice sites 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). The covalent bonding mainly originates from p–d hybridization [17,18].
between the main-group element and the transition metal and it greatly influences the physical properties and the atomic ordering [19]. Based on the crystal-structure types of Heusler alloys, an empirical rule has been suggested [20,21] according to which atoms with relatively many valence electrons tend to occupy the A and C sites preferentially, while those with relatively few valence electrons will occupy the B and D sites. This is consistent with this experimental finding that Fe$_2$NiZ alloys crystallize in the Hg$_2$CuTi structure, in which the A and B sites are occupied by Fe atoms, C and D sites by Ni atoms and main-group-element atoms respectively [22,23]. As expected for the ordered Hg$_2$CuTi structure, the observed intensity of (1 1 1) reflection of Fe$_2$NiAl is larger than that of the (2 0 0) in Ref. [24]. The alloys of Fe$_2$NiSn and Fe$_2$NiSb have also been synthesized and a bcc main phase could be identified from the XRD patterns, but also a quite large amount of second phase can be observed.

The lattice constants of the Fe$_2$NiZ (Z=Al, Ga, Si and Ge) compounds, obtained by refining the XRD patterns, are listed in Table 1. One can see that for Z=Al, Ga, Ge the lattice constant shows little variation whereas it is much smaller for Fe$_2$NiSi. Considering the covalent radii of the main-group atoms (Al, Ga and Ge are of around 1.21 Å and Si is of 1.11 Å), one may conclude that the lattice constants reflect the dominating covalent effect in the structure of these Heusler alloys.

Fig. 2 presents the DSC curves for Fe$_2$NiGa. Two sets of endothermic and exothermic peaks can be seen at about 785 K and 960 K. The inset of Fig. 2 shows spontaneous-magnetization behavior observed in an AC-susceptibility measurement. Therefore, the heat effect at 785 K can be associated with the Curie Temperature ($T_C$) of Fe$_2$NiGa. The more distinct peaks around 960 K correspond to the ordering temperature ($T_{\text{order}}$) for atomic ordering, at which Fe$_2$NiGa transforms between the Hg$_2$CuTi and

![Fig. 1. XRD pattern of Fe$_2$NiAl. The inset shows the crystal structure of Heusler alloys.](image)

![Fig. 2. Heating and cooling DSC curves of Fe$_2$NiGa. The rate of heating and cooling is 10 °C/min. The inset shows the magnetic transition in the AC susceptibility at the Curie temperature $T_C$.](image)

![Fig. 3. Total DOS of Fe$_2$NiZ (Z=Al, Ga, Si and Ge) (a) and partial DOS of p- and d-electrons (b-e).](image)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Lattice constant (a), atomic-ordering temperature ($T_{\text{order}}$) and Curie temperature ($T_C$) of Fe$_2$NiZ compounds.</th>
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</thead>
<tbody>
<tr>
<td>Fe$_2$NiZ</td>
<td>a (Å)</td>
</tr>
<tr>
<td>Al</td>
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<tr>
<td>Ga</td>
<td>5.776</td>
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<tr>
<td>Si</td>
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<tr>
<td>Ge</td>
<td>5.761</td>
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<tr>
<th>Table 2</th>
<th>The moments per formula unit of Fe$<em>2$NiZ alloys obtained by experimental measurements ($M</em>{\text{exp}}$) and calculations ($M_{\text{calc}}$) and the atomic moments (all in $\mu_B$).</th>
</tr>
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<tbody>
<tr>
<td>Z</td>
<td>$M_{\text{exp}}$</td>
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<tr>
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</tr>
<tr>
<td>Ga</td>
<td>4.89</td>
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<tr>
<td>Si</td>
<td>4.10</td>
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<tr>
<td>Ge</td>
<td>4.38</td>
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</table>
the B2 structure, in agreeing with the result in Ref. [7]. The values of \( T_c \) and \( T_{\text{order}} \) of the four alloys listed in Table 1 show that \( T_{\text{order}} \) depends strongly on the Z element. Fe₂NiGa has the lowest \( T_{\text{order}} \) of 960 K, while Fe₂NiSi has the highest one of 1095 K. Also the \( T_c \) values of Fe₂NiZ listed in Table 1 exhibit a distinct behavior: Fe₂NiGa has the much higher \( T_c \) than Fe₂NiSi.

Generally, \( T_{\text{order}} \) reflects the phase stability of the system, that is, the relatively high \( T_{\text{order}} \) corresponds to the strong covalent bonding. This is because that the atomic ordering originates from the p–d hybridization between the main-group atoms and the transition-metal atoms [19,25]. In the light of this consideration, the covalent-bonding effect of group-III elements (ZIII) should be weaker than that of group-IV elements (ZIV), and the strength of the covalent bonding should tend to decrease in the sequence Si > Ge > Al > Ga approximately. Additionally, it has been reported that the magnetic moments and internal fields in Heusler alloys are weakened by the covalent bonding [19,26], which mean that, in the case of strong covalent bonding, a system should have a low \( T_c \). This explains why the trend of \( T_c \) is opposite to that of \( T_{\text{order}} \).

The magnetic moment per formula unit and atomic moments obtained by experimentally and by means of calculations are presented in Table 2. Experimentally, moments per formula unit of 4.10–4.89 \( \mu_B \) have been obtained for the four alloys. The calculated moments per formula unit agree well with the experimental ones. It can be seen that these results do not agree with the Slater–Pauling rule of \( M=Z-24 \), as observed in Co₂Fe-based Heusler alloys, although the moments per formula unit of Co₂FeAl and Co₂FeSi are about 5\( \mu_B \) and 6\( \mu_B \), respectively [27,28]. However, as shown in Table 2, in the Fe₂NiZ system the moments of the alloys with ZIV are found to be smaller than those of the alloys with ZIII.

Table 2 shows FeA and FeB are the main contributors to the ferromagnetic structure of Fe₂NiZ. In the present four alloys, the atomic moments of the Fe atoms at the A site range from 1.61 to 1.83\( \mu_B \) whereas they range from 2.58 to 2.67\( \mu_B \) at the B site. The smaller moment of Fe in A site can be attributed to hybridization with Z atoms [26]. Experimentally, we have observed that, without annealing below \( T_{\text{order}} \), the homogenized Fe₂NiGa sample has a quite low moment of about 4.16\( \mu_B \). This implies that the magnetic moment is quite sensitive to the atomic order. Based on the calculation results listed in Table 2, the disorder between FeB and NiC is the only possible way to decrease the magnetization. It makes that FeB (2.6\( \mu_B \)) becomes FeC (1.7\( \mu_B \)), because the FeA is equivalent to the FeC and they have the same moments.

The calculated electronic structure indicates that, in these systems, the p electrons of the Z element (Al, Ga, Si and Ge) hybridize with the d electrons of the transition metals. Fig. 3a presents the total electronic density of states (DOS) of Fe₂NiZ (Z=Al, Ga, Si and Ge) and Fig. 3b–d the partial DOS of the p and d electrons. The bands are formed mostly of d-states of Fe and Ni, while p-states of the Z elements participate in the hybridization [29] [30,31]. It seems to be that, if alloys are with the same main-group elements, their total DOS would become very similar. As can be seen in Fig. 3a, all peaks shift to the lower energies upon changing the Z elements from ZIII to ZIV. This shift is more apparent in spin-down states, which implies a decline of the band splitting.

As seen in Fig. 3b–e, the overlapping of p and d peaks below \( E_F \) at about –3.2 eV (for Z=ZIII) and –4.2 eV (for Z=ZIV) demonstrate the typical p–d hybridization. One can see that the p-DOS of the ZIV compounds apparently have shifted to lower energy, showing a stronger hybridization effect than in the ZIII compounds. So, the experimentally observed weakness of the magnetic coupling should be attributed to the p–d hybridization [31]. These band-structure calculations reveal the competition between covalent bonding and magnetic coupling, which is the physical mechanism

![Fig. 4. 3D ELF diagrams of Fe₂NiGa (a) and Fe₂NiSi (b) with constant ELF value of 0.006, and the 2D ELF of the alloys with ZIII (c) and ZIV (d) atoms in the (1 1 0) crystal plane. The color scale extends from 0 (blue) to 0.012 (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
that explains why moments of these alloys disobey the Slater–Pauling rule.

The Electron Localization Function (ELF) is usually used as an efficient method to represent the nature of chemical bonding in intermetallic compounds visually [14,15,32,33]. Fig. 4 presents three-dimensional (3D) and two-dimensional (2D) visualizations of ELF for Fe₂NiGa and Fe₂NiSi and shows the different distributions in alloys with Z₁₇ and Z₁₈ elements. In the 3D diagrams, the surfaces correspond to ELF values of 0.006. The regions around the main-group atoms Ga and Si can be considered as paired electrons [15], including covalent bonds or lone pairs. There, the ELF value is relatively low but may play a role in determining the atomic configuration in the intermetallic compounds. Usually, the covalent bonds are located on the line between Z–FeA and Z–NiC while lone pairs appear on the Z–FeB line [34]. The 3D ELF shapes of the alloys with Ga and Si reflect the different strengths of covalent bonds.

The high- and low-ELF values in the 2D ELF graphs correspond to areas of localized electrons and area around these maxima, respectively [34]. The regions of the highest ELF in Fig 4c and d are located around the main-group element atom and along the Z–FeA and Z–NiC bond axes, confirming their significant sharing character and the occurrence of the covalent bond. It illustrates that the covalent bonding of Si is stronger than that of Ga. This matches the sequence of covalent bonds strength mentioned above. There is a noticeable difference in the spatial configuration of the ELF: the basin of the alloys with Z₁₇ show a hexagonal shape, while it is almost sphere for those containing Z₁₈ (Fig. 4c and d). This phenomenon is clearer in the 3D ELF where Fe₂NiGa shows a hollow-type iso-ELF-surface, but Fe₂NiSi has the closed diamond-type iso-ELF-surface at the same ELF value (Fig. 4a and b). This distinction means that the electrons of the Z₁₈ element have more isotropic space configuration. One can see that a series of physical parameters presented in the present work, like lattice constants, Mₛ, Tᵣₑₒᵈ and the moment variation of FeA, NiC, as shown in Tables 1 and 2, vary according to the strength of the covalent bonding.

4. Conclusions

The structural and magnetic properties of Fe₂NiZ (Z=Al, Ga, Si and Ge) Heusler alloys have been systematically investigated by the experimental and theoretical methods. All these alloys possess the ordered Hg₂CuTi structure with the lattice constants dominated by the covalent radii of the main-group element Z. They have quite high magnetic-ordering temperature Tᵣₑₒᵈ and a moment per formula unit of more than 4μᵣ. The calculations indicate that the FeB atoms are the main magnetic contributors, having much larger moments than the FeA atoms. The covalent behavior and the sequence of its strength in Fe₂NiZ alloys have been established by the calculations and experiments. It is found that the variations of the physical parameters observed in the present work, like the lattice constants, Tᵣₑₒᵈ, the moments per formula unit, the atomic moments and Tᵣₑₒᵈ precisely follow the variation of the covalent character. This indicates an important role of covalent bonding in the structural and magnetic properties of Fe₂NiZ Heusler alloys.

Acknowledgments

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References