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Study on structural, electronic and magnetic properties of Ni-Mn-Ga and Ni-Mn-In ferromagnetic shape memory alloy systems

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Abstract

Ferromagnetic shape memory alloys (FSMAs) are novel smart materials which exhibit magnetic field induced strains of up to 10 %. As such they have potential for many technological applications. Also, the strong magnetostructural couplings of the FMSM effect make the phenomenon very interesting from a scientific point of view. In the present work, a series of first-principles calculations have been performed within the framework of the Density Functional Theory (DFT) using the Vienna *Ab initio* Software Package (VASP).

In the stoichiometric Ni_2XY ($\text{X}=\text{Mn, Fe, Co}$; $\text{Y}=\text{Ga, In}$) alloys, lattice parameters, atomic separations, total and partial magnetic moments decrease gradually with the increase in the X atomic number; whereas the bulk modulus displays an opposite tendency. The formation energy indicates a destabilization tendency if Mn is substituted by Fe or Co, or Ga is replaced by In. The strong bond between neighboring Ni atoms in Ni_2MnGa is replaced by the bond between Ni and X atoms in other alloys.

For the off-stoichiometric Ni_2XY ($\text{X}=\text{Mn, Fe, Co}$; $\text{Y}=\text{Ga, In}$), the formation energies of several kinds of defects (atomic exchange, antisite, vacancy) were calculated. For most cases of the site occupation, the excess atoms of the rich component directly occupy the site(s) of the deficient one(s), except for Y-rich Ni-deficient composition. In the latter case, the defect pair ($\text{Y}_\text{X} + \text{X}_\text{Ni}$) is energetically more favorable. The value of Ni magnetic moment sensitively depends on the distance between Ni and X atoms.

The effects of Co addition on the properties of $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ ($x=0-2$) FSMAs were systematically investigated. The added Co atoms preferentially occupy the Ni sites. The calculated formation energies indicate a structural instability with the increase in the Co content for both paramagnetic (PA) and ferromagnetic austenite (FA). The total energy difference between PA and FA increases, which results in the rise of T_c when Ni is replaced by Co.

Insights into fundamental aspects such as crystallography, phase stability, and electronic structure in Ni-X-Y ($\text{X}=\text{Mn, Fe, Co}$; $\text{Y}=\text{Ga, In}$) FSMAs are of great significance to improve the functional performances and to design new promising FSMAs.

Keywords: ferromagnetic shape memory alloys (FSMAs); DFT calculation; Ni-Mn-Ga; Ni-Mn-In; structure stability; magnetic properties; density of states; defect formation energy; site occupation

Résumé

Les Alliages à Mémoire de Forme Ferromagnétiques (AMFF) sont de nouveaux matériaux intelligents qui présentent des déformations induites par l'application d'un champ magnétique pouvant aller jusqu'à 10%. Ainsi, ils ont un fort potentiel pour de nombreuses applications technologiques. En outre, les couplages forts entre le champ magnétique et la structure dans ces matériaux rendent le phénomène « mémoire » très intéressant d'un point de vue scientifique. Ce travail présente une investigation de ces matériaux via des calculs *ab initio* effectués en utilisant la théorie de la fonctionnelle de la densité (DFT) à l'aide du logiciel VASP.

Dans les alliages stœchiométriques du type Ni_2XY ($\text{X} = \text{Mn, Fe, Co}$, $\text{Y} = \text{Ga, In}$), les paramètres structuraux, les distances interatomiques, les moments magnétiques partiels et totaux augmentent graduellement avec le nombre d'électrons de valence de l'élément X alors que le module de compressibilité varie en sens inverse. Les énergies de formation des composés indiquent une tendance à la déstabilisation de l'alliage si les atomes de Mn sont substitués par des atomes de Fe ou de Co mais également si les atomes de Ga sont remplacés par des atomes d'In. La liaison forte entre les atomes de Ni dans Ni_2MnGa est remplacée par des liaisons entre les atomes de Ni et de X dans les autres alliages.

Pour les alliages non-stœchiométriques Ni_2XY ($\text{X} = \text{Mn, Fe, Co}$, $\text{Y} = \text{Ga, In}$), des énergies de formation de plusieurs types de défauts (permutations atomiques, enrichissement et appauvrissement en un ou plusieurs éléments, lacunes) ont été calculés. Dans la plupart des cas, les atomes en excès occupent les sites de l'atome déficient, sauf dans le cas d'un composé pauvre en Ni et riche en Y. Dans ce dernier cas, la paire de défauts ($\text{Y}_\text{X} + \text{X}_{\text{Ni}}$) est énergétiquement plus favorable. La valeur du moment magnétique dépend de manière très sensible de la distance entre les atomes de Ni et X.

Les effets de l'addition de Co sur les propriétés de l'alliage $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ ($x=0-2$) ont été étudiés. Les atomes de Co occupent préférentiellement les sites Ni. Les énergies de formation calculées indiquent une instabilité structurale augmentant avec la teneur en Co pour les deux phases : austénite paramagnétique (AP) et ferromagnétique (AF). La différence d'énergie totale entre ces 2 phases AP et AF augmente également avec la teneur en Co, qui se traduit par une élévation de la température de Curie T_c quand le Ni est substitué par le Co.

La complémentarité et le couplage des aspects fondamentaux tels que la cristallographie, la stabilité de phase, et la structure électronique dans les AMFF de type Ni-X-Y ($\text{X} = \text{Mn, Fe, Co}$, $\text{Y} = \text{Ga, In}$) ont une grande importance pour améliorer les performances fonctionnelles et permettront de concevoir de nouveaux AMFF prometteurs.

Mots-clés: alliages à mémoire de forme ferromagnétiques (AMFF); *ab initio*, DFT; Ni-Mn-Ga; Ni-Mn-In; stabilité des structures; propriétés magnétiques; densité d'états; énergie de formation; défauts.

摘 要

磁致形状记忆合金是新型的智能材料，具有高达 10% 的磁诱导应变。这类合金具有优良的物理特性和巨大的开发潜力，可作为驱动器、传感器、磁微机电系统等，从而成为目前国际金属材料和凝聚态物理研究的热点之一。本论文使用 VASP 量子力学计算软件包，在密度泛函理论(DFT)的框架下展开一系列的第一原理计算。

首先，我们系统地计算了磁致形状记忆合金 Ni_2XY ($\text{X} = \text{Mn, Fe, Co}$; $\text{Y} = \text{Ga, In}$) 立方母相的平衡晶格常数，磁结构，形成能以及电子态密度。晶格常数、原子间距、总磁矩以及原子磁矩均随着 X 原子序数的增大而减小；体积模量的变化趋势则相反。形成能的计算结果表明，用 Fe 或 Co 替换 Mn，或者用 In 替换 Ga，均会导致母相结构不稳定。在四方畸变的过程中，总能的变化给出了奥氏体和马氏体的结构信息以及两相之间的能量差；而磁矩随着四方性 c/a 的变化曲线可以有效预测四方马氏体转变过程中磁矩的变化。 Ni_2XY 合金的电子分波态密度由费米面之下的 Ni-3d 态和 X-3d 态成键支配；而费米面之上的反键区则由自旋向下的 X-3d 态占优。在 Ni_2MnGa 合金中，大量的自由电荷聚集在相邻 Ni 原子之间成键；而研究范围内其他合金的自由电荷则聚集在 Ni 和 X 原子之间，差别在于化学键的强度有所不同。

对于近化学当量比 Ni_2XY ($\text{X} = \text{Mn, Fe, Co}$; $\text{Y} = \text{Ga, In}$) 合金，我们计算了不同类型点缺陷(原子交换，反位，空位)的形成能和原子磁矩变化。大多数情况下，过量的原子将直接占据贫乏原子的位置，除了 Y 富余 Ni 贫乏的情况：过量的 Y 原子将占据 X 原子的位置，而 X 原子则移向空余的 Ni 亚晶格位置，形成反位缺陷对($\text{Y}_\text{X} + \text{X}_\text{Ni}$)。Ni 原子磁矩主要取决于 Ni 原子与最近邻 X 原子之间的距离。距离越小，Ni 和 X 原子的 3d 轨道电子的交互作用越强，Ni 的原子磁矩就越大。

另外，我们研究了 $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ ($x=0-2$) 中掺杂合金元素 Co 对性能的影响。合金化的第四组员 Co 优先占据合金中 Ni 的亚晶格格点。形成能的计算结果显示，用 Co 取代 Ni 会导致顺磁奥氏体和铁磁奥氏体两相的结构不稳定性增加。随着 Co 含量的增加，顺磁奥氏体与铁磁奥氏体之间的总能量差升高，这也是添加 Co 可以有效提高合金居里温度的根本原因。

对 Ni-X-Y ($\text{X} = \text{Mn, Fe, Co}$; $\text{Y} = \text{Ga, In}$) 磁致形状记忆合金诸如晶体结构、相稳定性、电子结构及磁结构等基础问题进行研究对提高 Ni-X-Y 磁致形状记忆合金的功能行为和开发新型先进磁致形状记忆合金具有重要的指导意义。

关键词: 磁致形状记忆合金; DFT 计算; Ni-Mn-Ga; Ni-Mn-In; 结构稳定性; 磁性能; 态密度; 缺陷形成能; 原子占位

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Chapter 1 Introduction

1.1 Outline

With the rapid development of science and technology, the demand for high-performance materials with multi-functional properties has been increasing. Modern technologies need transducing materials, also referred to as smart materials that undergo a substantial change in one or more properties in response to a change in external conditions. Distinctly from structural materials, smart materials possess physical and chemical properties that are sensitive to a change in the environment such as temperature, pressure, electric field, magnetic field, optical wavelength, humidity, and pH. All of the smart materials are transducer materials as they transform one form of energy into another, and hence they have wide applications as both actuators and sensors in various fields such as medical, defense, aerospace and marine industries.

Smart materials can be categorized according to the type of response and type of activation. Among the large numbers of smart materials, the electrically driven piezoelectric materials, magnetically controlled magnetostrictive materials and thermally activated shape memory alloys are most widely explored because of their numerous potential applications [1]. However, each of these materials has its own advantages and drawbacks. Piezoelectric materials can be deformed under the application of an electric field because of the electro-mechanical coupling in these materials. Likewise, these materials can generate an electric field in response to an external strain field. Piezoelectric devices are known for their high frequency capability, on the order of tens of kHz. Nevertheless, the induced strain in these materials is relatively small; the best piezoelectric ceramics only exhibit a strain of about 0.19% [2]. Magnetostrictive materials, such as Terfenol-D, can generate induced strain under magnetic fields. They can operate at high frequencies up to 10 kHz, but they also have the same drawbacks of small output strain. The maximum observed strain in single crystals is about 0.2% [3]. Moreover, the magnetostrictive materials are relatively expensive to produce and highly brittle. Shape memory alloys, like NiTi, have the ability to recover large plastic strain up to 8% [4] as a result of a thermally activated reversible martensitic transformation. However, the working frequency for these alloys is quite low (less than 1 Hz) because of the

slow process of heating and cooling that control the martensitic transformation and the reverse transformation. The respective drawbacks of the above-mentioned smart materials have greatly limited their practical applications in certain fields. The development of high-performance smart materials with both large output strain and fast response has become imperative.

Recently, a new class of smart materials called Ferromagnetic Shape Memory Alloys (FSMAs), also referred to as Magnetic Shape Memory Alloys (MSMAs), was developed. These FSMAs combine the properties of ferromagnetism with those of a diffusionless, reversible martensitic transformation. The field-induced strain in these materials results from the rearrangement of martensitic variants under applied magnetic fields. Thus they integrate the advantages of both thermally controlled shape memory alloys and magnetostrictive materials, showing giant magnetic shape memory effect and fast dynamic response. The reported magnetic-field-induced strain is as high as 9.5% [5], which is an order of magnitude higher than the strains generated in piezoelectric and magnetostrictive materials. Meanwhile, the working frequency of the FSMAs is very high, on the order of kHz [6, 7]. Inspired by the merits of these materials, considerable efforts have been devoted to the investigation on various aspects of these FSMAs in the past few decades [5-26].

Up to now, several alloy systems have been confirmed to exhibit the characteristics of FSMAs, including Ni-Mn-Ga [5-11], Co-Ni-Ga [12], Co-Ni-Al [13, 14], Ni-Fe-Ga [15, 16], Ni-Mn-Al [17], Fe-Pd [18-20] and Fe-Pt [21]. Among these alloys, Ni-Mn-Ga alloys with chemical compositions close to the stoichiometric compound Ni_2MnGa are the most promising FSMAs. There are several key characteristics that make Ni-Mn-Ga alloys unique and remarkable, attracting a high degree of research interest. First, they are the only known ferromagnetic intermetallic compounds that undergo a thermoelastic martensitic transformation from a cubic L_{21} -ordered Heusler structure to a complex martensitic structure [22, 23]. Second, the martensitic transformation in these alloys exhibits several active properties that are of great interest to the smart materials society, including the two-way shape memory effect [24, 25], super-elasticity [26] and magnetic-field-induced strain [8, 9]. Finally, and the most importantly, the largest magnetic-field-induced strain is only observed in Ni-Mn-Ga alloys [5]. Consequently, Ni-Mn-Ga alloy, which is one of the focus of this thesis,

become the most extensively studied FSMAs in the past ten years.

1.2 Ni-Mn-Ga ferromagnetic shape memory alloys

Ni-Mn-Ga alloys have already been investigated for more than 40 years. At the very beginning, Ni_2MnGa together with other alloys were demonstrated as Heusler alloys having the formula X_2YZ [27-32]. Soltys was the first to concentrate only on the Ni-Mn-Ga alloy system [33, 34]. The martensitic transformation and magnetic order were later investigated in detail by Webster *et al.* [22] in 1984. More systematic studies by Kokorin *et al.* [35] and Chernenko *et al.* [36] were initiated in the early 1990s when Ni-Mn-Ga alloys were studied as potential shape memory alloys. The novel idea of rearranging martensitic variants by a magnetic field and thus generating a field-induced strain was relatively newly developed and received attention only in recent years. In 1996, Ullakko *et al.* [8] firstly demonstrated a magnetic-field-induced strain of 0.2% in a Ni_2MnGa single crystal with a magnetic field of 8kOe applied at 265K. After that, a totally new era of investigations started. Extensive researches were carried out both experimentally and theoretically on various properties of Ni-Mn-Ga FSMAs. Theoretical models on the field-induced rearrangement of martensitic variants were established by O'Handley *et al.* [37] and James *et al.* [18] in 1998. In 2000, Murray *et al.* have succeeded in the observation of a large magnetic-field-induced strain of 6% in the five-layered martensitic phase [9, 38]. More recently, a much larger strain close to 10% was observed by Sozinov *et al.* [5] in the seven-layered martensite, which is, heretofore, the largest magnetic-field-induced strain obtained in FSMAs. Up to now, numerous studies have been performed on many aspects of Ni-Mn-Ga alloys, including crystal structure, phase transformation, magnetic properties, magnetic shape memory effect, mechanical behavior, martensite stabilization and alloying, and a lot of interesting phenomena have been revealed.

1.2.1 Crystal structure of Ni-Mn-Ga alloys

1.2.1.1 Crystal structure of parent phase

The crystal structure of Ni-Mn-Ga alloys with chemical compositions close to stoichiometric compound Ni_2MnGa have been extensively studied mostly by means of X-ray or electron diffraction and, less commonly, by means of neutron diffraction. However, it is

worth noting that it is very difficult to accurately determine the crystal structure of Ni-Mn-Ga alloys by X-ray diffraction technique, as the X-ray scattering factors of Ni, Mn and Ga atoms are similar to each other. In contrast, neutron diffraction is a more powerful tool to precisely characterize the detailed crystal structure of Ni-Mn-Ga alloys due to the significantly different neutron scattering factors of the constituent atoms.

Webster *et al.* [22] were the first to study the crystal structure of the stoichiometric Ni_2MnGa by neutron diffraction technique. They revealed that Ni_2MnGa has a cubic, $L2_1$ Heusler structure above martensitic transformation temperature. The lattice parameter was reported to be around $5.823\text{\AA}$. A more systematic neutron diffraction study was recently carried out by Brown *et al.* [39]. It was shown that the crystal structure of the parent phase in Ni_2MnGa belongs to the space group $\text{Fm}\bar{3}\text{m}$ (No. 225). Ni atoms occupy $8c$ (0.25, 0.25, 0.25) Wyckoff sites, while Mn and Ga atoms occupy $4a$ (0, 0, 0) and $4b$ (0.5, 0.5, 0.5) sites, respectively. It was demonstrated that the lattice parameter of the parent phase is temperature dependent [39]. In addition to the temperature dependency, the lattice parameters of the Ni-Mn-Ga alloys also depend on the chemical composition and heat treatment.

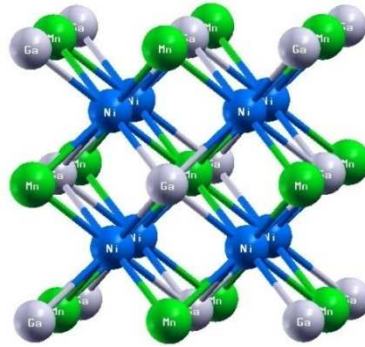


Fig. 1-1 $L2_1$ structure of Ni_2MnGa .

1.2.1.2 Crystal structure of martensite

The crystal structure of martensite in Ni-Mn-Ga alloys is an important factor because it affects their magnetic anisotropy [41-43], mechanical properties [42, 44] and chemical behavior [45, 46] that ultimately determines the functional performances of these alloys. The Ni-Mn-Ga alloys have different martensitic structures. Depending on composition and temperature, three types of martensitic structures are commonly observed, i.e. five-layered tetragonal martensite (5M), seven-layered near-orthorhombic martensite (7M) and

Non-Modulated Tetragonal martensite (NM or T). Among the three types of martensites, the NM martensite is the most stable one while 5M martensite is the most unstable one [42, 47-49], as shown in Fig. 1-2 (a). Therefore, if the 5M structure is to be observed it is transformed directly from the parent phase while the NM martensite can be a final transformation product of intermartensitic transformations from 7M or 5M martensites [50]. The first martensite transformed directly from parent phase depends on composition and there exists an empirical correlation between the martensitic transformation temperature and the first martensitic structure [49], as shown in Fig. 1-2 (b). The alloys transforming directly to the NM martensite typically have martensitic transformation temperatures that can be higher than their Curie temperatures [51, 52] and the 7M martensite appears first only in a narrow temperature range [49]. Thus, NM martensite is the only martensite that can exist both at very low temperatures as an intermartensitic transformation product and at elevated temperatures above Curie temperature as a first martensite transformed directly from parent phase.

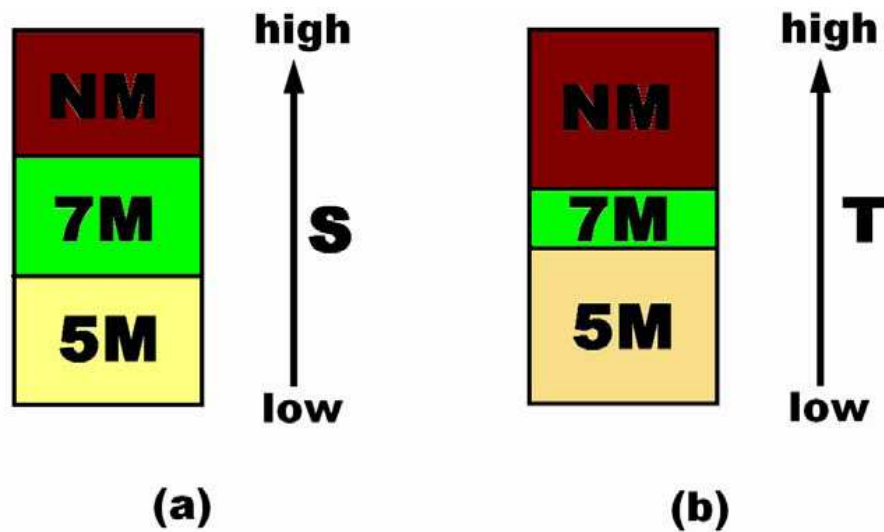


Fig. 1-2 (a) The stability (S) of the three types of martensites; (b) Relation between the first martensitic structure and the martensitic transformation temperature (T) [49].

Prior to the detailed description of the above-mentioned crystal structures of martensites in Ni-Mn-Ga alloys, it is necessary to clarify the different coordinates with respect to which the martensitic structures are expressed. There are two different cases in which the martensitic structure are expressed with respect to (i) the orthorhombic martensite coordinate system constructed from the martensitic principal axes and (ii) the cubic parent phase coordinate

system constructed from the cubic axes of the parent phase, respectively. The choice of (i) is crystallographically reasonable as it involves a smaller unit cell volume and it is also convenient to use this coordinate system to describe the crystal lattice modulation in the layered structure as a long-period superstructure. However, for a simple description of the strain values induced by stress or magnetic field, the choice of (ii) is more practical [32], as it is directly related to the change of lattice parameters, in the cubic coordinate system, after martensitic transformation. Since the cubic coordinate system is commonly accepted in the literature, for consistency the description of the literature work (unless specified) will also use this coordinate system in this chapter. A subscript “C” will be added to the lattice parameters and crystallographic planes and directions, denoting that they are expressed in the cubic parent phase coordinate system. However, in the other chapters of this thesis, the tetragonal martensite coordinate system that is more crystallographically reasonable to analyze the crystallographic features of these FSMA s will be used. One should keep in mind that the lattice parameters expressed with respect to the two coordinates are different from each other.

(1) Five-layered martensite (5M)

The 5M martensite of the low-temperature phase was observed by means of electron diffraction and X-ray diffraction in single crystals of $\text{Ni}_{51.5}\text{Mn}_{23.6}\text{Ga}_{24.9}$ (saturation magnetization $M_S=293\text{K}$) [47, 53, 54], $\text{Ni}_{49.2}\text{Mn}_{26.6}\text{Ga}_{24.2}$ ($M_S\sim 180\text{K}$) [55, 56], $\text{Ni}_{52.6}\text{Mn}_{23.5}\text{Ga}_{23.9}$ ($M_S=283\text{K}$) [55], $\text{Ni}_{52}\text{Mn}_{23}\text{Ga}_{25}$ ($M_S=227\text{K}$) [57], etc. The crystal structure is modulated by a transverse displacive wave along the $[110]_C$ direction [53, 56] and it may be presented as a periodic shuffling along $(110)_C[110]_C$ system or a long-period stacking of $\{110\}_C$ close-packed planes [40, 47]. Modulation occurs in such a way that each fifth $(110)_C$ plane does not undergo displacements, while the other four are displaced from their regular positions. The modulation can be observed in electron or X-ray diffraction as four additional spots between the main diffraction reflections [58, 59]. The average lattice is approximately tetragonal or slightly monoclinic with a short c_C axis, i.e. $c_C/a_C<1$ (in the cubic coordinates). The tetragonality of the 5M martensite was found to increase with decreasing temperature and saturate at very low temperatures [58].

(2) Seven-layered martensite (7M)

The 7M martensite was observed in single crystals of $\text{Ni}_{52}\text{Mn}_{25}\text{Ga}_{23}$ ($M_S=333\text{K}$) [53], $\text{Ni}_{48.8}\text{Mn}_{29.7}\text{Ga}_{21.5}$ ($M_S=337\text{K}$) [5] and so on. Having a modulation mechanism similar to the case of 5M martensite, modulation in 7M martensite occurs in such a way that each seventh $(110)_C$ plane does not undergo displacements, while the other six are displaced from their regular positions. X-ray and electron diffractions show that, in the diffraction pattern, the distance between the main reflection along the $[110]^*_C$ direction in reciprocal space is divided into seven parts by six additional spots [56, 60, 61]. The average lattice is approximately orthorhombic with $c_C/a_C < 1$ and a monoclinic distortion of less than 0.4° was observed by Sozinov *et al.* [62]. Martynov [53] interpreted the crystal structure of $\text{Ni}_{52}\text{Mn}_{25}\text{Ga}_{23}$ as monoclinic with the lattice parameters $a_C=6.14\text{\AA}$, $b_C=5.78\text{\AA}$ and $c_C=5.51\text{\AA}$ and with $\gamma=90.5^\circ$, while Sozinov *et al.* [5] reported that the crystal structure of the 7M martensite in $\text{Ni}_{48.8}\text{Mn}_{29.7}\text{Ga}_{21.5}$ is nearly orthorhombic and has lattice parameters of $a_C=6.19\text{\AA}$, $b_C=5.80\text{\AA}$ and $c_C=5.53\text{\AA}$.

(3) Non-modulated martensite (NM)

The NM martensite was found in single crystal samples and thin films of the alloys such as $\text{Ni}_{53.1}\text{Mn}_{26.6}\text{Ga}_{20.3}$ ($M_S=380\text{K}$) [63, 64] and $\text{Ni}_{52.8}\text{Mn}_{25.7}\text{Ga}_{21.5}$ ($M_S=390\text{K}$) [65]. No modulation occurs in this type of martensite. The crystal structure of the NM martensite was confirmed to be tetragonal with a long c_C axis. The NM martensite is the only type of martensite with $c_C/a_C > 1$. Liu *et al.* [66] reported that the lattice parameters of $\text{Ni}_{46.4}\text{Mn}_{32.3}\text{Ga}_{21.3}$ are $a_C = b_C = 5.517\text{\AA}$, $c_C=6.562\text{\AA}$ and $c_C/a_C = 1.189$ while those of $\text{Ni}_{51.7}\text{Mn}_{27.7}\text{Ga}_{20.6}$ are $a_C = b_C = 5.476\text{\AA}$, $c_C=6.568\text{\AA}$ and $c_C/a_C = 1.199$. Lanska *et al.* [67] systematically studied the composition and temperature dependence of the crystal structure and lattice parameters of Ni-Mn-Ga alloys with different types of martensite; a correlation between the martensitic crystal structure, martensitic transformation temperature and electron concentration was established [67].

1.2.2 Phase transformation in Ni-Mn-Ga alloys

1.2.2.1 Transformation sequence

As the magnetic shape memory effect due to the rearrangement of martensitic variants occurs in the ferromagnetic martensitic state in Ni-Mn-Ga FSMA, the phase transformation sequence and transformation temperature determine the service temperature range of these

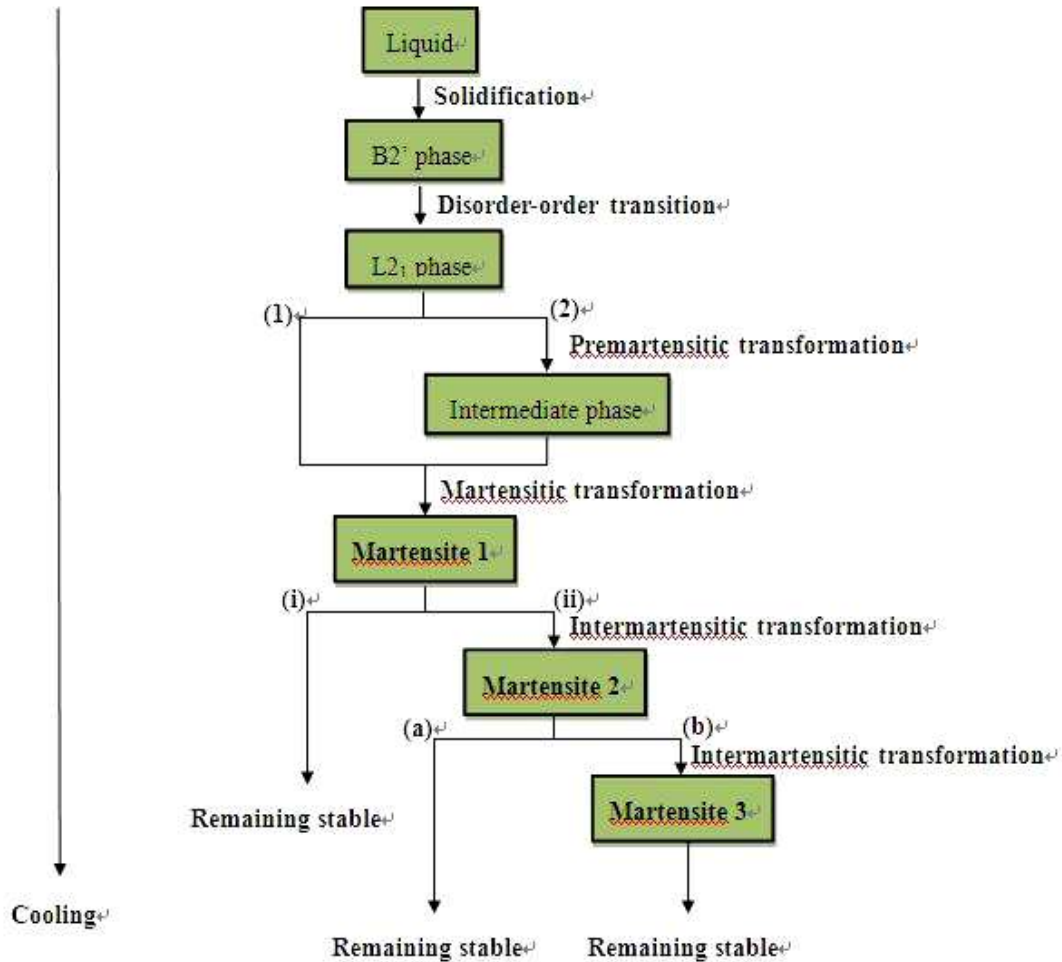


Fig. 1-3 Schematic illustration of phase transformation sequence in Ni-Mn-Ga alloys. The numbers (1) and (2), (i) and (ii), and (a) and (b) in the scheme denote that in each case there are two possible transformation paths from high-temperature phase to low-temperature phase.

alloys. Hence, it is important to study the details of phase transformation process in these alloys in order to get a good understanding of the materials behavior. The phase transformation in Ni-Mn-Ga alloys is actually quite complex and different transformation behaviors can occur, depending on the chemical composition and thermal history of the alloys. A schematic illustration of the phase transformation sequence in Ni-Mn-Ga alloys is given in

Fig. 1-3. At high temperatures, the melting alloys undergo a solidification process leading to a partially disordered B2' phase, followed by the occurrence of a disorder-order transition from B2' phase to L2₁ ordered Heusler phase upon cooling. After cooled to lower temperatures, some Ni-Mn-Ga alloys undergo firstly a premartensitic transformation and then a martensitic transformation, while the other alloys directly transform from the Heusler parent phase into martensite. Subsequently, the martensites in some alloys remain stable upon further cooling to very low temperatures whereas those in the other alloys undergo one or more intermartensitic transformations which produce more stable martensites existing at low temperatures. The detailed description of the different phase transformation in Ni-Mn-Ga alloys is presented in the following subsections.

1.2.2.2 Solidification and disorder-order transition

The Ni-Mn-Ga alloys solidify into a partially disordered intermediate B2' phase at a certain composition-dependent temperature. Overhosler *et al.* [69] reported that the solidification temperatures of the Ni₅₀Mn_xGa_{50-x} (x=15-35) alloys are in the range of 1340-1400K and Söderberg *et al.* [70] confirmed that the Ni_{50.5}Mn_{30.4}Ga_{19.1} and Ni_{53.7}Mn_{26.4}Ga_{19.9} alloys solidify at 1386K and 1392K, respectively. The B2' phase experiences a disorder-order transition into the L2₁ ordered Heusler phase upon further cooling. The B2'- L2₁ transition was confirmed to be a second order transition [71] and the transition temperature is between 800-1100K, depending on the chemical composition of the alloys [69, 70]. The difference between the B2' and L2₁ structures is that in B2' structure the Ni atoms form the frame of the lattice while Mn and Ga atoms occupy arbitrary positions, whereas in L2₁ structure Mn and Ga atoms are strictly ordered as well as Ni atoms.

1.2.2.3 Premartensitic transformation

Prior to the martensitic transformation at low temperatures, premartensitic transformation can occur in some Ni-Mn-Ga alloys. The premartensitic transformation in Ni-Mn-Ga system is not directly related to the magnetic shape memory effect of these alloys, but, scientifically, it offers various opportunities to investigate the coexisting interactions of electro-phonon, magnetoelastic and Jahn-Teller mechanisms. The physical nature of the

premartensitic transformation in Ni-Mn-Ga alloys has been the topic of both theoretical [72, 73] and experimental work by means of neutron diffraction [39, 74-76], transport [77], magnetic [78, 79], mechanical [80], acoustic [81] and ultrasonic [82] measurements, and electron microscopy [80, 83, 84].

Premartensitic transformation has been observed in $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}_{1-y}$ alloys with relatively small deviations from stoichiometry and martensitic transformation temperature (T_m) lower than 270K [85]. The premartensitic transformation of Ni-Mn-Ga alloys was confirmed to be a weakly first order transformation [72] and it occurs in the stoichiometric Ni_2MnGa ($T_m \sim 220\text{K}$) at around 260K [74]. Khovailo *et al.* [77] found from the anomalies in the temperature dependence of electrical resistivity that the premartensitic transformation temperature of $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ alloys is only weakly dependent on the substitution of Mn for Ni. By means of neutron diffraction experiments, Brown *et al.* [39] reported that the premartensitic phase in Ni_2MnGa has an orthorhombic (with space group of Pnnm, No.58) three-layered structure. In this structure, the modulation mechanism is similar to the cases of 5M and 7M martensites [39].

It should be noted that the premartensitic transformation only occurs in Ni-Mn-Ga alloys with relatively low T_m . Zheludev *et al.* [74] suggested that the premartensitic transformation emerges because of nesting singularities in the Fermi surface. Since the premartensitic transformation temperature is weakly dependent on deviations from stoichiometry and such a transformation is observed only in $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}_{1-y}$ alloys with $T_m < 270\text{K}$ [80], variations in valence electron concentration probably only have a slight effect on the nesting section of the Fermi surface [85]. In the alloys with $T_m > 270\text{K}$, martensitic transformations, accompanied by a radical transformation of the Fermi surface, occur even before the nesting singularities in the parent phase have time to manifest themselves and thus no premartensitic transformation is observed in these alloys [85].

Landau models for the premartensitic transformation have been proposed [73] and successfully explain that (i) the electron-phonon coupling results in a first order premartensitic transformation from the parent phase to a micromodulated intermediate phase in Ni-Mn-Ga alloys and (ii) the magnetoelastic coupling enables the existence of a commensurate premartensitic phase prior to martensitic transformations. The in-depth

investigation to understand the intrinsic nature of premartensitic transformation in Ni-Mn-Ga alloys is still needed.

1.2.2.4 Martensitic transformation

The martensitic transformation is a diffusionless, displacive solid state phase transformation of the first order type, in which the atomic displacements are done within a short range in an organized manner relative to their neighbors [1, 85]. It occurs in a certain temperature region usually showing hysteresis between the forward and reverse transformations. The chemical composition of the alloy does not change after transformation and there usually exists a clear correspondence between the crystal structure of the parent austenitic phase and that of the product martensitic phase [32]. The kinetics and morphology are dictated by the strain energy arising from shear displacements. The characteristic transformation temperatures are defined by the martensitic transformation start temperature M_s , the martensitic transformation finish temperature M_f , the austenitic transformation start temperature A_s and the austenitic transformation finish temperature A_f .

As mentioned earlier in Section 1.1.1.2, the martensitic transformation in Ni-Mn-Ga alloys may result in three different types of martensites, i.e. 5M, 7M and NM martensites. The NM martensite, if emerging as a first martensite, usually occurs in the alloys with a higher M_s , while the 7M martensite occurs only in the alloys with an M_s within a narrow temperature region (Fig. 1-2 (b)). In contrast, the 5M martensite usually occurs in the alloys with a lower M_s . The M_s of the example alloys showing different martensitic structures is also given in Section 1.1.1.2.

The martensitic transformation temperatures in Ni-Mn-Ga alloys are highly dependent on the chemical composition of the alloys [86-89]. It is generally recognized that the martensitic transformation temperatures increase with the increasing of the average number of valence electrons per atom (also called electron concentration) e/a , which is defined as follows:

$$e/a = \frac{10Ni_{at\%} + 7Mn_{at\%} + 3Ga_{at\%}}{Ni_{at\%} + Mn_{at\%} + Ga_{at\%}} \quad (1-1)$$

where $X_{at\%}$ ($X = Ni, Mn, Ga$) denotes the atomic percentage of X . In the equation, the value of

10 is applied for Ni, in which the outer electron shells are occupied as $3d^84s^2$, while for Mn the value becomes 7 from $3d^54s^2$ and for Ga 3 from $4s^24p^1$ [86].

Chernenko *et al.* [87] investigated the composition dependence of martensitic transformation temperatures of Ni-Mn-Ga alloys and concluded that (i) at a constant Mn content, Ga addition lowers M_s , (ii) Mn addition (instead of Ga) at a constant Ni content increases M_s , and (iii) substitution of Ni by Mn at a constant Ga content lowers M_s . Wu *et al.* [88] further quantified the relation between M_s and chemical composition, and derived the following equation:

$$M_s(K) = 25.44Ni_{at\%} - 4.86Mn_{at\%} - 38.83Ga_{at\%} \quad (1-2)$$

which can be used to empirically determine the M_s of the alloys from their chemical composition. The empirical relation between the martensitic transformation temperature T_m and e/a was established by Jin *et al.* [89] as follows:

$$T_m(K) = 702.5(e/a) - 5067 \quad (1-3)$$

It should be noted that T_m can be generally defined as $(M_s + M_f + A_s + A_f)/4$ [32]. The investigations on the composition dependence of martensitic transformation temperatures can serve as the guides for the development of high-temperature Ni-Mn-Ga FSMA for practical applications by composition design.

In addition to chemical composition, the atomic order of the parent phase also has a great influence on the martensitic transformation temperatures. Kreissl *et al.* [90] found that the disorder existing between Mn and Ga atoms in Ni_2MnGa alloy substantially suppresses the martensitic transformation by about 100K. Tsuchiya *et al.* [91] and Besseghini *et al.* [92] confirmed that with the ordered $L2_1$ structure obtained from the correct annealing procedure the martensitic transformation temperature region is narrower. Thus, proper thermal treatments are necessary for obtaining high-performance FSMA with good stability. Therefore, systematic study on the different kinds of point defects such as antisites, exchange of atoms, and vacancies, is crucial to the understanding of the composition and atomic order dependence of their properties.

1.2.2.5 Intermartensitic transformation

Aside from premartensitic and martensitic transformations, first order intermartensitic transformation from one martensite to another may occur in certain Ni-Mn-Ga alloys [93-105], due to the different stability of the three types of martensites as shown in Fig. 1-2 (a). A typical transformation path is 5M-7M-NM or 7M-NM, depending on the chemical composition and thermal history of the alloys. As well as being an interesting issue from a fundamental point of view, the occurrence of intermartensitic transformation has a certain influence on the applicability of the FSMAs. In this regard, it means that the working range of the utilization of FSMAs could be restricted to a temperature range where intermartensitic transformation are not observed, i.e. the intermartensitic transformation may set the lower limit for the service temperature of the magnetic shape memory effect [93].

The intermartensitic transformation is usually accompanied by anomalies in the calorimetric [63, 94, 95], mechanical [95-97], magnetic [95, 98-104] and electrical resistivity [95, 99-103] measurements, both on cooling and heating. Fig. 1-4 displays the typical temperature dependence of low field ac susceptibility in a Ni-Mn-Ga alloy showing Heusler-7M martensitic and 7M-NM intermartensitic transformations. The abrupt change in the value of the susceptibility at $\sim 355\text{K}$ is attributed to the paramagnetic-ferromagnetic transformation of the Heusler parent phase, while the abrupt change during cooling at $\sim 275\text{K}$ indicates the start of the martensitic transformation from Heusler phase to 7M martensite. Upon further cooling to $\sim 100\text{K}$, another abrupt change of the susceptibility occurs, indicating the start of the 7M-NM intermartensitic transformation. During heating both structural phase transformations occur in reverse order and show some temperature hysteresis. The intermartensitic transformation in Ni-Mn-Ga alloys was also confirmed by transmission electron microscopy (TEM) observations [63, 95, 105].

1.2.3 Magnetic properties of Ni-Mn-Ga alloys

1.2.3.1 Curie temperature

The Curie temperature (T_C), or Curie point, is defined as the temperature at which a ferromagnetic material becomes paramagnetic by losing the long-range magnetic order. This magnetic transition is one of the main limits when considering the service temperatures of the

magnetic shape memory effect. The T_C can be clearly observed from the magnetic susceptibility measurement as the susceptibility changes abruptly in the ferromagnetic to paramagnetic transition, as shown in Fig. 1-4. The T_C of the stoichiometric Ni_2MnGa was reported to be 376K [10, 22]. In contrast to the martensitic transformation temperatures, the T_C of Ni-Mn-Ga alloys is less sensitive to the chemical composition [87], having a value of around 370K for a wide range of compositions [67, 87]. Interestingly, it is possible to develop alloys with a magnetostructural transformation, i. e. $T_C = T_m$, by composition adjustment [51, 52, 106], in which some specific effects may occur due to the magnetoelastic coupling.

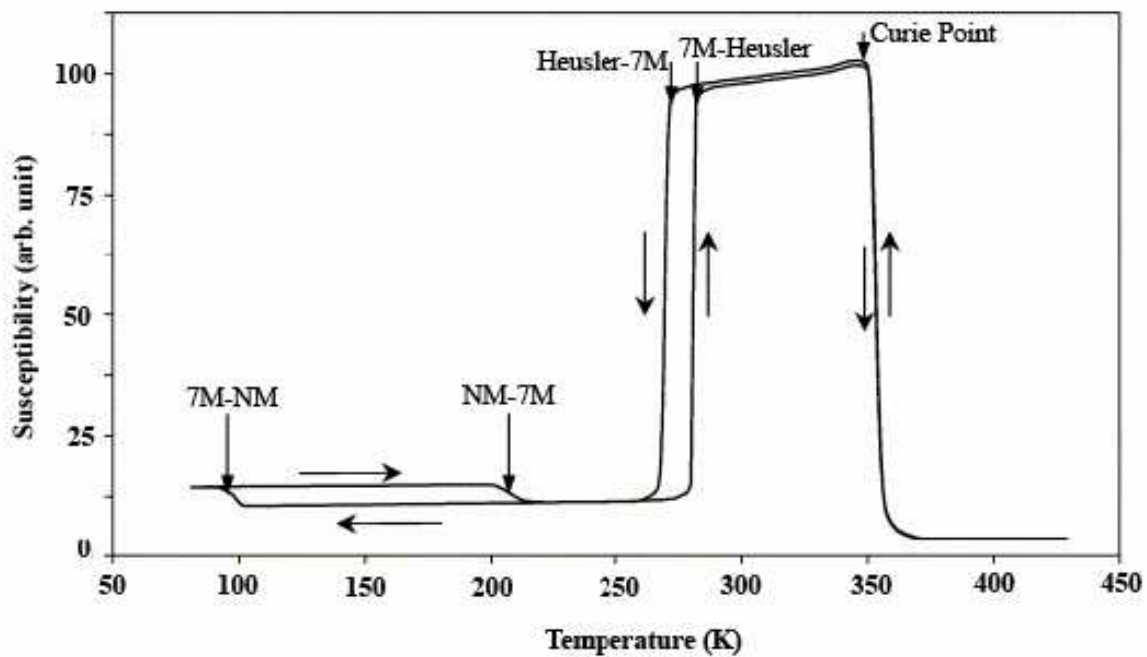


Fig. 1-4 Temperature dependence of low field ac magnetic susceptibility measured during cooling and heating in a Ni-Mn-Ga alloy showing Heusler-7M martensitic and 7M-NM intermartensitic transformations.

1.2.3.2 Magnetic moment

The magnetic moment in Ni-Mn-Ga alloys is mainly localized on the Mn sites, as confirmed by both experiments [22, 107, 108] and theoretical calculations [109]. From magnetization measurements, Webster *et al.* [22] reported that the total magnetic moment of the cubic Heusler phase of Ni_2MnGa is $4.17 \mu_B$ per formula unit, and it is primarily carried by Mn atoms while Ni atoms only carry a small magnetic moment. On the other hand, from

polarized neutron scattering and magnetization studies, Brown et al. [107] reported $0.36\mu_B$ for Ni, $2.80\mu_B$ for Mn and $-0.06\mu_B$ for Ga at 100K in the martensitic phase of Ni_2MnGa . By means of *ab initio* calculations, Ayuela *et al.* [109] reported that the magnetic moments for Ni, Mn and Ga are $0.36\mu_B$, $3.43\mu_B$ and $-0.04\mu_B$, respectively, in the parent Heusler phase and $0.40\mu_B$, $3.43\mu_B$ and $-0.04\mu_B$ in the martensite of Ni_2MnGa . For the off-stoichiometric Ni-Mn-Ga alloys, the localization of the magnetic moments on constituent atoms becomes more complex, due to the substitutive occupation of the extra atoms. Recently, Ahuja *et al.* [108] have investigated in great detail the magnetic moments of off-stoichiometric Ni-Mn-Ga alloys by using magnetic Compton scattering technique. It was found that the total magnetic moment of Ni-rich $Ni_{2.25}Mn_{0.75}Ga$ ($3.38\mu_B$) is much smaller than that of the stoichiometric Ni_2MnGa ($4.13\mu_B$ in their study), which is thought to be attributed to the substitution of Ni with a small moment ($0.25\mu_B$) for Mn with a large moment ($3.26\mu_B$) [108].

1.2.4 Magnetic shape memory effect in Ni-Mn-Ga alloys

1.2.4.1 Prerequisite

The magnetic shape memory effect (MSME) in Ni-Mn-Ga alloys, which manifest itself in terms of magnetic-field-induced strain (MFIS), originates from the rearrangement of the martensitic variants under applied magnetic fields. The prerequisite for the MSME in Ni-Mn-Ga alloys is listed as follows:

(i) The alloys must have the ferromagnetic twinned martensitic microstructure in the working temperature range. This means that the MSME is possible only at temperatures below the Curie temperature T_C and below the reverse transformation start temperature A_s .

(ii) The magnetic-field-induced stress must exceed the twinning stress of these alloys. In this context, the twinning stress σ_{tw} is the stress needed for the rearrangement of the twin variants. It can be determined from the stress-strain curve of single crystals. Since the magnetic-field-induced stress σ_{mag} cannot exceed the saturation value given by the ratio of the magnetic anisotropy (K_U) and the theoretical maximum MFIS (ϵ_0), i.e. K_U/ϵ_0 [32, 111], where the value for the strain ϵ_0 can also be evaluated from the stress-strain curve of single crystals with a single variant as the maximum strain of the detwinning, the above-mentioned prerequisite can be formulated as

$$\sigma_{mag} = \frac{K_U}{\varepsilon_0} > \sigma_{tw} \quad (1-4)$$

It is worth noting that both σ_{mag} and σ_{tw} strongly depend on the type of martensite. It was reported that the twinning stress σ_{tw} in compression varies from less than 2 MPa for the 5M and 7M martensites to 18-20 MPa for the NM martensite [32].

1.2.4.2 Mechanism

In Ni-Mn-Ga FSMA, the formation of twin boundaries accommodates the stress generated by the diffusionless martensitic transformation from the high-temperature, high-symmetry austenite to the low-temperature, low-symmetry martensite. The magnetic moment in martensite is aligned to the easy axis of magnetization by the high magnetic anisotropy and the preferred direction of magnetization changes across the twin boundary, as illustrated in Fig. 1-5. When a magnetic field is applied parallel to the easy axis of magnetization of one of the variants, the energy of the variant with the easy axis parallel to the field will be different from that of others. This energy difference exerts a stress σ_{mag} on the twin boundary and provides the driving force for the twin boundary motion. If this magnetic-field-induced stress σ_{mag} is larger than the twinning stress σ_{tw} needed for the rearrangement of the twin variants, the twin boundary will move and the variant with easy axis of magnetization parallel to the field direction will grow at the expense of the other variants, leading to the macroscopic shape change of the sample, namely MFIS. Ideally, with the magnetic field increasing to a certain critical value, all martensitic variants align themselves along the magnetic field direction and the MFIS reaches its maximum value. The schematic illustration of the rearrangement of martensitic variants under a magnetic field is shown in Fig. 1-5. In fact, the rearrangement of the martensitic variants under an applied magnetic field has already been directly observed by optical observations [110]. It should be noted that the macroscopic shape change remains even after the magnetic field is removed.

Thus, alternating magnetic field direction or simultaneous application of external stress and magnetic fields is needed to obtain reversible MFIS in such FSMAAs [32, 85].

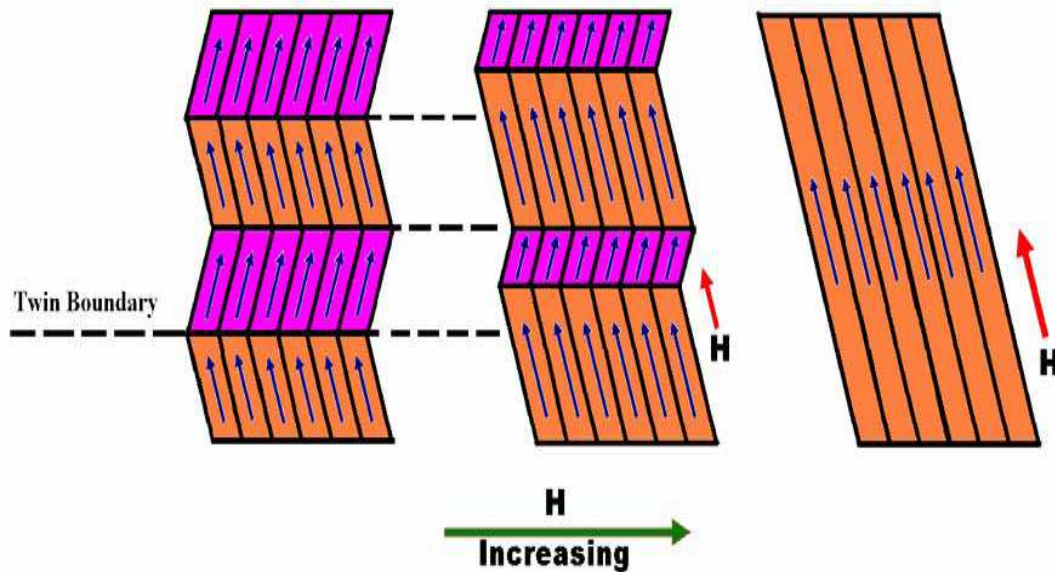


Fig. 1-5 Schematic illustration of the rearrangement of martensitic variants under a magnetic field in ferromagnetic shape memory alloys (FSMAAs).

1.2.5 Alloying of Ni-Mn-Ga alloys

Although Ni-Mn-Ga FSMAAs have a lot of advantages (as mentioned in Section 1.1), they also have some problems for practical applications. The Curie temperature of Ni-Mn-Ga alloys is around 370K, which is not high enough for some applications. The twinning stress of the alloys showing NM martensitic structure is too high and consequently large MFIS has not been observed in these alloys heretofore. On the other hand, the martensitic transformation temperatures of the alloys that show 5M and 7M martensitic structures and display large MFIS are generally too low for practical applications. Another problem, perhaps the most important, is the high brittleness of Ni-Mn-Ga alloys [115]. In recent years, great efforts have been devoted to the modification of the properties of these alloys and it is found that alloying can be an effective way to overcome some of these problems.

The effect of substitution of Fe for Ni or Mn on the martensitic transformation temperature, Curie temperature, MFIS and mechanical behaviors has been investigated by several groups [116-122]. Kikuchi *et al.* [116] found that by substituting a small amount of

Mn with Fe, the martensitic transformation temperature decreases linearly with Fe content. This is due to the fact that Fe stabilizes the parent austenitic phase and makes transition to the martensitic state more unlikely. The Curie temperature increases with Fe content because doping with Fe leads to a stronger exchange interaction between the electron spins [116]. After a systematic study on the alloys with Fe additions up to 11.6%, Koho *et al.* [117] found that the martensitic phases formed depend on the e/a ratio in the same way as in ternary Ni-Mn-Ga alloys. Liu *et al.* [118] found that when Fe substitutes Mn, the lattice parameter of the parent phase and the magnetic moment of martensite decrease, due to the smaller magnetic moment and atomic diameter of Fe, compared with Mn. Nevertheless, the reduction of magnetic moment does not impede the occurrence of large MFIS by variant rearrangement; in the $\text{Ni}_{49.9}\text{Mn}_{28.3}\text{Ga}_{20.1}\text{Fe}_{1.7}$ single crystal showing the 5M martensitic structure, Koho *et al.* [117] found a very good MFIS of 5.5%. Moreover, the doping with Fe is reported to enlarge the temperature interval where good MFIS takes place. A maximum strain of 1.15% is obtained at 290K in a $\text{Ni}_{52}\text{Mn}_{16}\text{Fe}_8\text{Ga}_{24}$ alloy and it is still 0.75% at 170K; for the corresponding ternary alloy, the MFIS has already dropped to 0.35% when the temperature lowers to 240K [118]. From the point of view of engineering applications, another positive effect of Fe doping is the improvement of ductility and toughness of the Ni-Mn-Ga alloys [119].

The alloying of Ni-Mn-Ga alloys with other elements has also been studied [103, 112-114, 122-131]. Tsuchiya *et al.* [113] investigated the addition of 4f rare earth elements (Nd, Sm and Tb), which are known to increase the magnetic anisotropy. It was found that these elements have a very low solubility in the alloys and have a high tendency to precipitate at the grain and subgrain boundaries. The martensitic transformation temperature and Curie temperature follow the same dependency on e/a ratio as the ternary alloys. The magnetization of the martensite in the alloys doped with Sm and Tb is similar to the corresponding ternary Ni-Mn-Ga alloys, while that of the alloys containing Nd has a higher value of magnetization at the high e/a range [113]. Gao *et al.* [114] studied the effect of Gd addition on martensitic transformation temperature and found that the martensitic transformation temperature increases remarkably with increasing Gd content. Glavatskyy *et al.* [123] found that the addition of Si and In drastically reduces the martensitic transformation temperature of

Ni-Mn-Ga alloys. Söderberg *et al.* [124] found the same effect for Sn additions, while the influence of Pb, Zn and Bi on martensitic transformation temperature is much more moderate. The substitution of In for Ga and replacing Mn by V or Cu were reported to strongly decrease the Curie temperature [125, 126]. The additions of Si and Ge were found to strongly decrease the martensitic transformation temperature, while C addition only causes a slight increase of this temperature [127]. The substitution of Ni by Pt was studied by Kishi *et al.* [112] with the purpose to increase the e/a ratio and consequently the martensitic transformation temperature. Indeed, the martensitic transformation temperature is greatly increased due to the increase of the e/a ratio; the $Pt_{10}Ni_{40}Mn_{25}Ga_{25}$ alloy shows a martensitic transformation temperature of $\sim 350K$ [112], much higher than that of the stoichiometric Ni_2MnGa . However, concluded from a large amount of investigations, the martensitic transformation temperature does not always depend on the change of e/a ratio, caused by the addition of a fourth element, in the expected way. According to Tsuchiya *et al.* [128], the dependence of the martensitic transformation temperature and Curie temperature on the e/a ratio in the alloys with Al, Cu, Ge or Sn seems to deviate from that in ternary Ni-Mn-Ga alloys.

Although achievements have been made on the modification of the properties of Ni-Mn-Ga alloys by alloying, the MFIS observed in the alloyed quaternary alloys is clearly lower than that in ternary Ni-Mn-Ga alloys. Overcoming the problems of Ni-Mn-Ga alloys without degrading their MSME is of great importance to the development of high-performance FSMAs with large MSME, high martensitic transformation temperature, high Curie temperature, and high ductility. However, experimental studies have obvious limitations: long study period, limited scope, high costs, etc. The theoretical calculation can simulate substitution or addition elements with any desired compositions and accordingly select the most promising one, which can provide useful guidance for experiments.

1.3 Ni-Mn-In-(Co) ferromagnetic shape memory alloys

Over the past decade, vast amount of knowledge accumulated on the properties of Ni-Mn-Ga Heusler alloys has enabled to foresee the possibility of employing these alloys in device applications. However, the actuation output stress level of the Ni-Mn-Ga alloy is only less than 5MPa, which becomes a shortage for this alloy system. Recently, a novel type of

FSMAs Ni–Co–Mn–In Heusler alloy had been experimentally investigated [132]. It shows that the martensitic transition from the ferromagnetic austenitic phase to the antiferro- or paramagnetic martensitic phase can be reversed by a magnetic field, the so-called magnetic-field-induced reverse martensitic transition (MFIRT). MFIRT is more attractive for the practical application as magnetically driven actuator because it possesses a magnetostress level on the order of tens of MPa. An almost perfect shape memory effect associated with such phase transition is induced by a magnetic field and is called the metamagnetic shape memory effect. The Ni–Mn–In is the basic ternary alloy system of the Ni–Co–Mn–In alloy, and it owns the same metamagnetic shape memory effect [133] as Ni–Co–Mn–In, accompanying large magnetoresistance,[134, 135] large entropy change,[136, 137] giant Hall effect,[138] and large reverse magnetocaloric effects (MCEs). [139] The relationship of alloying composition-martensitic transformation temperature-crystal structure of the Ni–Mn–In alloy had been systematically studied by Thorsten Krenke et al.[140]. The effect of the atomic disorder in $\text{Ni}_{50}\text{Mn}_{36}\text{In}_{14}$ on martensitic transformation temperatures has been investigated [141].

1.4 Introduction to *ab-initio* calculations

There is little doubt that most of low-energy physics, chemistry, and biology problems can be explained by the quantum mechanics of electrons and ions. The ability of quantum mechanics to predict the total energy of a system of electrons and nuclei, enables one to reap a tremendous benefit from a quantum-mechanical calculation. The quantum-mechanics approaches, or Hamiltonians, have provided the rules for calculating the energies of complex systems. So far, this expectation has been confirmed time and time again by experiments.

Nearly all physical properties are related to total energies or to differences between total energies. For instance, the equilibrium lattice constant of a crystal is the lattice constant that minimizes the total energy; surfaces and defects of solids adopt the structures that minimize their corresponding total energies. If total energies can be calculated, any physical property that can be related to a total energy or to a difference between total energies can be determined computationally. For example, to predict the equilibrium lattice constant of a crystal, a series of total-energy calculations are performed to determine the total energy as a

function of the lattice constant. As seen in Fig. 1-6, the results are then plotted on a graph of energy versus lattice constant, and a smooth curve is constructed through the points. The theoretical value for the equilibrium lattice constant is the value of the lattice constant at the minimum of this curve. Total-energy techniques also have been successfully used to predict with bulk moduli, phonons, phase-transition pressures and temperatures, and so on [142]-[143].

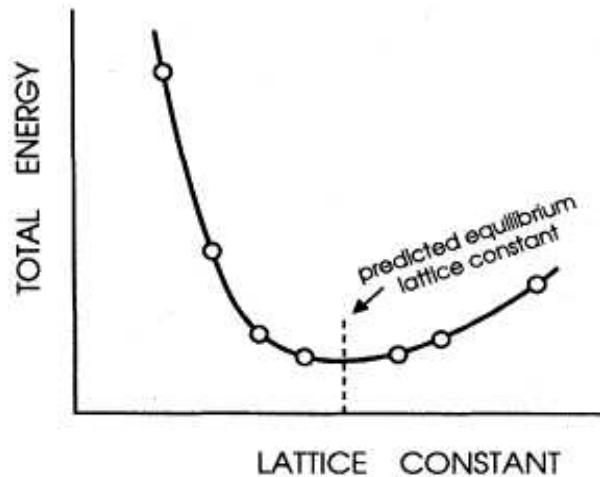


Fig. 1-6 Theoretical determination of an equilibrium lattice constant. Calculations (open circles) at various possible lattice constants are performed and a smooth function is fitted through the points. The predicted lattice constant is determined by the minimum of the curve.

Physicists have developed many methods that can be used to calculate a wide range of physical properties of materials, such as lattice constants and elastic constants. These methods, which require only a specification of the ions present, are usually referred to as parameter-free *ab initio* methods. All the *ab initio* methods have been continuously refined over recent years and all have benefited from the availability of increasingly powerful computers.

1.5 Fundamentals of a quantum theory of materials

1.5.1 Many-body problem

The determination of the properties of solid state systems from basic quantum mechanics is desirable. The wave function contains all the information about the system. In principle, it can be obtained by solving the Schrödinger equation

$$\mathbf{H}\Psi = E\Psi \quad (1-5)$$

where $\mathbf{H}$ is the Hamiltonian operator and E is the total energy of the N-particle system. However, the wave function depends on the coordinates and the velocities of all the particles so that is a function of $6N$ variables. As the number of particles in condensed matter systems is of the order of 10^{23} , an exact solution of Eq. (1-5) is not possible. Therefore some approximations have to be introduced in order to solve the many-body problem.

First, the adiabatic or Born-Oppenheimer approximation decouples the nuclear and electronic degrees of freedom. The nuclei are several orders of magnitude heavier than the electrons, so electrons respond quickly to the motions of the nuclei. Therefore the nuclei can be considered as an external potential for the electronic subsystem and the electronic part is solved as a function of the nuclear positions. Even though the Schrödinger equation is solved only for the electrons, the number of particles is still too large in most cases and one has to introduce further approximations.

There are basically two different approaches to the problem. In the first one, some approximate wave function is constructed, as for example in the Hartree and the Hartree-Fock approximations. These methods express the full many-body wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$ in terms of single-particle wave functions $\Psi(\mathbf{r}_1), \Psi(\mathbf{r}_2), \dots, \Psi(\mathbf{r}_n)$. In the Hartree approximation [144] a product of the single-particle wave functions is used which leads to N single particle equations. However, this many-body wave function does not obey the Pauli Exclusion Principle which makes the theoretical foundation of the Hartree approximation unsound. The Hartree-Fock approach [145, 146] fulfills the Pauli Exclusion Principle by expressing the many-body wave function as a Slater determinant of the single-particle wave functions. However, the ensuing equations are much more difficult to solve than the corresponding Hartree equations, while important physics is still missing from the Hartree-Fock approximation. Wave functions beyond the Hartree-Fock approximation can be constructed for example as a series of Slater determinants but the computational burden increases very rapidly so that only very small systems can be studied.

An alternative approach to the many-body problem was initiated by Thomas [147] and Fermi [148] who formulated the problem in terms of the electron density instead of the wave function. Since the density is a function of three space coordinates only, the number of

degrees of freedom is reduced drastically. The ideas of the Thomas-Fermi approximation are elaborated in the density functional theory which will be introduced below.

1.5.2 Exchange and correlation

The most difficult problem in any electronic structure calculation is posed by the need to take account of the effects of the electron-electron interaction. Electrons repel each other due to the Coulomb interaction between their charges. The Coulomb energy of a system of electrons can be reduced by keeping the electrons spatially separated, but this has to balance against the kinetic-energy cost of deforming the electronic wave functions in order to separate the electrons. The effects of the electron-electron interaction are briefly described below.

The wave function of a many-electron system must be anti-symmetric with exchange of any two electrons because the electrons are fermions. The anti-symmetry of the wave function produces a spatial separation between electrons that have the same spin and thus reduces the Coulomb energy of the electronic system. The reduction in the energy of the wave function is called the exchange energy. It is straightforward to include exchange in a total-energy calculation, and this is generally referred to as the Hartree-Fock approximation.

The Coulomb energy of the electronic system can be reduced below its Hartree-Fock value if electrons that have opposite spins are also spatially separated. In this case the Coulomb energy of the electronic system is reduced at the cost of increasing the kinetic energy of the electrons. The difference of the many-body energy of an electronic system and the energy of the system calculated in the Hartree-Fock approximation is called the correlation energy [149]. It is extremely difficult to calculate the correlation energy of a complex system, although some promising steps are taken in this direction using quantum Monte Carlo simulations of the electron-gas dynamics [150]-[151]. At present these methods are not tractable in total-energy calculations, and alternative methods are required to describe the effects of the electron-electron interaction.

1.5.3 Density-functional theory

Density functional theory, developed by Hohenberg and Kohn (1964) [152], Kohn and Sham (1965) [153], provided hope of a simple method for describing the effects of exchange

and correlation in an electron gas. Hohenberg and Kohn proved that the total energy, including exchange and correlation, of an electron gas (even in the presence of a static external potential) is a unique functional of the electron density. The minimum of the total-energy functional is the ground-state energy of the system, and the density that yields this minimum is the exact single-particle ground-state density. Kohn and Sham then showed how it is possible, formally, to replace the many-electron problem by an exactly equivalent set of self-consistent one-electron equations. These theorems imply that all the ground state properties can be calculated on the basis of the density alone.

1.5.3.1 The Kohn-Sham energy functional

The Kohn-Sham total-energy functional for a set of doubly occupied electronic states ψ_i can be written

$$E\{\psi_i\} = 2 \sum_i \int \psi_i \left[-\frac{\hbar^2}{2m} \nabla^2 \psi_i \right] d^3\vec{r} + \int V_{ion}(\vec{r}) n(\vec{r}) d^3\vec{r} + \frac{e^2}{2} \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r} d^3\vec{r}' + E_{xc}[n(\vec{r})] + E_{ion}\{\vec{R}_I\} \quad (1-6)$$

where E_{ion} is the Coulomb energy associated with interactions among the nuclei (or ions) at positions $\{\vec{R}_I\}$, V_{ion} is the static total electron-ion potential, $n(\vec{r})$ is the electronic density given by

$$n(\vec{r}) = 2 \sum_i |\psi_i(\vec{r})|^2 \quad (1-7)$$

and $E_{xc}[n(\vec{r})]$ is the exchange-correlation functional.

Only the minimum value of the Kohn-Sham energy functional has physical meaning. At the minimum, the Kohn-Sham energy functional is equal to the ground state energy of the system of electrons with the ions at positions $\{\vec{R}_I\}$.

1.5.3.2 Kohn-Sham equations

It is necessary to determine the set of wave functions ψ_i that minimize the Kohn-Sham energy functional. These are given by the self-consistent solutions to the Kohn-Sham equations [153]:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ion}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}) \right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (1-8)$$

where $\psi_i(\vec{r})$ is the wave function of electronic state i , ε_i is the Kohn-Sham eigenvalue, and V_H is the Hartree potential of the electrons given by

$$V_H(\vec{r}) = e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' \quad (1-9)$$

The exchange-correlation potential, V_{xc} , is given formally by the functional derivative

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})} \quad (1-10)$$

The Kohn-Sham equations represent a mapping of the interaction many-electron system onto a system of non-interacting electrons moving in an effective potential. If the exchange-correlation energy functional were known exactly, then taking the functional derivative with respect to the density would produce an exchange-correlation potential that included the effects of exchange and correlation exactly.

The Kohn-Sham equations must be solved self-consistently so that the occupied electronic states generate a charge density that produces the electronic potential that was used to construct the equations. The Kohn-Sham equations are a set of eigenequations, and the terms within the brackets in Eq (1-8) can be regarded as a Hamiltonian. The bulk of the work involved in a total-energy calculation is the solution of this eigenvalue problem once an approximation expression for the exchange-correlation energy is given.

1.5.3.3 Local density approximation

The Hohenberg-Kohn theorem provides motivation for using approximate methods to describe the exchange-correlation energy as a function of the electron density. The first practical approximation is local density approximation (LDA; Kohn and Sham, 1965 [153]). In local density approximation, the exchange-correlation energy of an electronic system is constructed by assuming that the exchange-correlation energy per electron at a point $\vec{r}$ in the electron gas, $\varepsilon_{xc}(\vec{r})$, is equal to the exchange-correlation energy per electron in a homogeneous electron gas that has the same density as the electron gas at point $\vec{r}$. Thus,

$$E_{xc}[n(\vec{r})] = \int \varepsilon_{xc}(\vec{r}) n(\vec{r}) d^3\vec{r} \quad (1-11a)$$

$$\text{and} \quad \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})} = \frac{\partial [n(\vec{r})\epsilon_{xc}(\vec{r})]}{\partial n(\vec{r})} \quad (1-11b)$$

$$\text{with} \quad \epsilon_{xc}(\vec{r}) = \epsilon_{xc}^{\text{hom}} n(\vec{r}) \quad (1-11c)$$

The relaxation of the constraint of an equal occupation of spin-up and spin-down states and the minimization of the total energy with respect to spin occupancy leads to the local spin-density approximation (LSDA) which allows magnetic properties of atoms, molecules and solids to be treated [154].

The LDA is generally very successful in predicting structures and macroscopic properties, but some shortcomings are notorious as well. These concern in particular: (i) energies of excited states, and in particular band gaps in semiconductors and insulators are systematically underestimated. This is after all not so surprising since DFT is based on a theorem referring to the ground state only. (ii) There is a general tendency to overbinding, i.e. cohesive energies are significantly overestimated and lattice parameters are underestimated by up to 3%. (iii) The wrong ground state is predicted for some magnetic systems (the most notable example is Fe which is predicted to be hexagonal close packed and non-magnetic instead of body-centered cubic and ferromagnetic) and for strongly correlated systems (e.g. the Mott insulators NiO and La_2CuO_4 are predicted to be metallic in the LDA). (iv) Van der Waals interactions are not appropriately described in the LDA, although there are some recent suggestions for overcoming this problem [155-157].

1.5.3.4 Generalized gradient approximation

Attributing the limitations of the local description to the neglect of the dependence of the exchange-correlation functional on the local variations of the electron density, generalized-gradient approximations (GGA) have been introduced. In the GGA, there is an explicit dependence of the exchange-correlation functional on the gradient of the electron density. For solid-state applications, the GGAs proposed by Perdew and co-workers [158-162] have been widely used and have proved to be quite successful in correcting some of the deficiencies of the LDA: the overbinding is largely corrected (the GGAs lead to larger lattice constants and lower cohesive energies) [163, 164] and the correct magnetic ground state is

predicted for ferromagnetic Fe [165] and antiferromagnetic Cr and Mn [166, 167] (this also includes a greatly improved prediction of magnetovolume and magnetostructural effects). However, there are also cases where the GGA overcorrects the deficiencies of the LDA and leads to an underbinding. The most notable examples are noble-gas dimers and N₂ molecular crystals which according to the GGA would not be bound [168]. A further limitation of some of the GGAs is to incorrectly estimate the strength of hydrogen bonds, leading, e.g. to a wrong estimate of the freezing point of water.

1.5.4 Basis functions

In practice, the wave functions $\psi_i(\vec{r})$ must be represented as a linear combination of a finite number of basis functions. The choice of the basis determines the achievable accuracy and computational efficiency.

Methods applicable to complex systems employ mostly one of three types of basis sets, namely: (i) linear combinations of atomic orbitals (LCAOs); (ii) linearized augmented plane waves (LAPWs); or (iii) plane waves (PWs) in combination with pseudopotentials for describing the electron-ion interaction. In the present work, the calculations are implemented using Vienna Ab-initio Simulation Package (VASP) [169-171], VASP is a complex package for performing ab-initio quantum-mechanical simulations using ultra-soft pseudopotentials or the projector-augmented wave method with a plane wave basis set. The interaction between ions and electrons is described by ultra-soft Vanderbilt pseudopotentials (US-PP) [172, 173] or by the projector-augmented wave (PAW) [174, 175] method. Both of them allow for a considerable reduction of the number of plane waves per atom for transition metals and first row elements. Forces and the full stress tensor can be calculated with VASP and used to relax atoms into their instantaneous ground-state.

1.5.4.1 Pseudopotential approximation

Although Bloch's theorem states that the electronic wave functions can be expanded using a discrete set of plane waves, a plane wave basis set is usually very poorly suited to

expanding electronic wave functions because a very large number of plane waves are needed to expand the tightly bound core orbitals and to follow the rapid oscillations of the wave functions of the valence electrons in the core region. An extremely large plane wave basis set would be required to perform an all-electron calculation, and a vast computational time would be required to calculate the electronic wave functions. The pseudopotential approximation allows the electronic wave functions to be expanded using a much smaller number of plane wave basis.

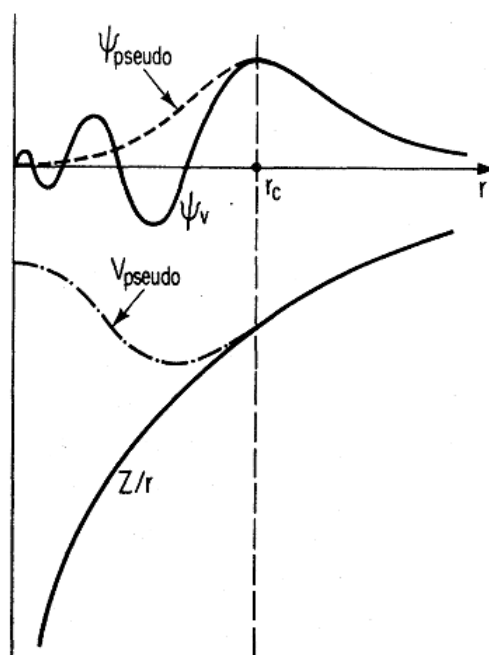


Fig. 1-7 Schematic illustration of all-electron (solid lines) and pseudoelectron (dashed lines) potentials and their corresponding wave functions. The radius at which all-electron and pseudoelectron values match is designated r_c .

It is well known that most physical properties of solids are dependent on the valence electrons to a much greater extent than on the core electrons. The pseudopotential approximation exploits this by removing the core electrons and by replacing them and the strong ionic potential by a weaker pseudopotential that acts on a set of pseudo wave functions rather than the true valence wave functions. An ionic potential, valence wave functions and the corresponding pseudopotential and pseudo wave function are illustrated schematically in Fig. 1-7.

The valence wave functions oscillate rapidly in the region occupied by the core electrons due to the strong ionic potential in this region. The pseudopotential is constructed, ideally, so that its scattering properties or phase shifts for the pseudo wave functions are identical to the scattering properties of the ion and the core electrons for the valence wave functions, but in such a way that the pseudopotential wave functions have no radial nodes in the core region. Outside the core region the two potentials are identical, and the scattering from the two potentials is indistinguishable. Without a smooth, weak pseudopotential it becomes difficult to expand the wave functions using a reasonable number of plane wave basis set.

In total-energy calculations, the exchange-correlation energy of the electronic system is a function of the electron density. If the exchange-correlation energy can be desired accurately, it is necessary that outside the core regions the pseudo wave functions and real wave functions be identical, not just in their spatial dependences but also in their absolute magnitudes, so that the two wave functions generate identical charge densities. Adjustment of the pseudopotential to ensure that the integrals of the squared amplitudes of the real and pseudo wave functions inside the core regions are identical guarantees the equality of the wave function and pseudo function outside the core region. This is the so-called norm conservation.

1.5.4.2 Plane waves in combination with Pseudopotentials

Plane-wave (PW) basis sets offer several advantages: (i) convergence with respect to the completeness of the basis set is easily checked by extending the cut-off energy (i.e. the highest kinetic energy in the PW basis); (ii) fast-Fourier-transforms (FFT) facilitate the solution of the Poisson equation; and (iii) forces on the atoms and stresses on the unit cell may be calculated directly via the Hellmann-Feynman theorem, without applying Pulay corrections for the site-dependence of the basis set [176]. The drawback is that in order to achieve convergence with a manageable size of the basis set, the strong electron-ion interaction must be replaced by a sufficiently weak pseudopotential. The basic idea of the pseudopotential approach is to project the Schrödinger equation for the valence electrons onto the subspace orthogonal to the core orbitals [177, 178], eliminating the nodal structure of the valence orbitals close to the core without modifying them in the region where chemical

bonding occurs. Much effort has been spent in constructing pseudopotentials designed to satisfy the conflicting requirements of accuracy, transferability and computational efficiency. For the s,p-bonded main-group elements a variety of pseudopotentials that work well have been proposed [179-182], but the difficult cases are the first-row elements and the transition and rare-earth elements with nodeless 2p, 3d and 4f orbitals where the usual concepts fail. For these elements the so-called ultra-soft pseudopotentials (US-PP) supplementing a PW representation of the smooth part of wavefunctions, charge densities and potentials with localized augmentation functions are by far the most efficient solution [172, 173]. Recently, the close correlation between US-PPs and the FLAPW method has been established [183], a one-to-one correspondence between US-PPs and the projector-augmented-wave (PAW) method proposed by Blöchl [174] has been demonstrated by Kresse and Joubert [175]. To date modern FLAPW, PAW and US-PP techniques provide the most accurate DFT calculations. Differences between the US-PP approach and the all-electron PAW or FLAPW approaches exist only in those cases where the linearization of the valence-core exchange interaction becomes problematic (some ferro- and antiferromagnetic systems, early 3d elements, . . .) [175, 184].

The last two decades have witnessed important theoretical and algorithmic advances in the theory of condensed matter and in quantum chemistry. Together with the revolution that has occurred in computer technology, these advances enable us to tackle problems of practical importance. As a result, atomistic computational technologies (computational quantum mechanics, molecular simulations and molecular mechanics) begin to bridge the gap between fundamental materials science and materials engineering.

1.6 Motivation and objectives

During the past decade, extensive experimental investigations have been devoted to various aspects of Ni-Mn-Ga alloys. However, experimental studies have limitations: long study period, limited scope, high costs, etc. The theoretical calculation can simulate

(1) substitution or addition elements with any desired compositions and accordingly select the most promising one, which can provide useful guidance for experiments;

(2) several kinds of point defect such as antisites, exchange of atoms, and vacancies, which is crucial to the understanding of the composition and atomic order dependence of the properties.

Based on this background, the present work has been orientated to the investigation on *the fundamental aspects, with emphasis on the crystal structure, magnetic properties and electronic properties of the Ni-Mn-Ga and Ni-Mn-In ferromagnetic shape memory alloys*.

The main contents of this work can be summarized as follows:

(1) Optimize the lattice parameters, the bulk modulus, the total and partial magnetic moments in cubic Ni_2XY ($\text{X}=\text{Mn}$, Fe and Co , $\text{Y}=\text{Ga}$, In) from first-principles calculations. Meanwhile, the formation energy of the cubic phase of Ni_2XY is estimated. The spin-resolved electronic density of states and difference charge density are calculated.

(2) Investigate in detail on the formation energy of the several kinds of the point defect such as antisites, exchange of atoms, and vacancies in defective Ni_2XY ($\text{X}=\text{Mn}$, Fe and Co , $\text{Y}=\text{Ga}$, In). The preferred site occupations and the magnetic properties in various situations are discussed.

(3) Study the effect of alloying with Co element on the crystal structure, thermal stability and magnetic properties of Ni-Mn-Ga ferromagnetic shape memory alloys, aiming at developing new promising ferromagnetic shape memory alloys with optimal properties.

The objective of the present work is to bridge the gap between the experimental observation and theoretical calculations; provide direct evidence for the explanation of the experimental results of the Ni-Mn-Ga and Ni-Mn-In alloys; reveal the physical nature of the properties; lay a solid foundation for the improvement of the performances of the present alloys and for the design of new promising ferromagnetic shape memory alloys.

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Chapter 2 Investigation on crystal, magnetic and electronic structures of ferromagnetic shape memory alloys Ni_2XY (X=Mn, Fe, Co; Y=Ga, In) by first-principles calculations

2.1 Outline

As a kind of newly developed materials, Ni-Mn-Ga and Ni-Mn-In FSMA have many fundamental issues remaining unclear. This has significantly impeded the improvement of the functional performances of these alloys. Full information on crystal, magnetic and electronic structures of these alloys are of great fundamental importance to the design of high-performance FSMA with optimal properties. However, experimental studies have limitations: long study period, limited scope, high costs, etc. The theoretical calculation can simulate substitution or addition elements with any desired compositions and accordingly select the most promising one, which can provide useful guidance for experiments.

In this chapter, the crystal, magnetic and electronic structures of the ferromagnetic shape memory alloys Ni_2XY (X=Mn, Fe and Co, Y=Ga, In), are systematically investigated by means of the first-principles calculations within the framework of density functional theory (DFT) using the Vienna *ab initio* software package (VASP). Mn, Fe and Co are nearby elements in the same periodicity, whereas Ga and In are in the same group in the periodic table. Investigation on these alloy systems together can provide us the evolution of the crystal, magnetic and electronic structures when the X or Y constituent element is substituted by others. In order to investigate the effect of the substitution of Mn atom by Fe or Co on the phase stability, formation energy of cubic Ni_2XY has been calculated. The spin-resolved Densities Of States (DOS) are computed by the tetrahedron method with Blöchl corrections and gives rise to the nature of the magnetic properties

2.2 Ni_2XGa (X= Mn, Fe, Co) ferromagnetic shape memory alloys

2.2.1 Introduction

Since large magnetic field induced strains (MFIS) were discovered in the ferromagnetic

martensitic phase of near-stoichiometric Ni_2MnGa alloys [1], there has been an increasing interest in research and development of such alloys, due to its potential application as a magnetically driven shape memory alloy which is more efficient than temperature or stress driven shape memory devices. Our group is involved in determining the crystal structure [2] and the twinning relationship between martensitic variants [3, 4] in Ni-Mn-Ga alloys. Furthermore, theoretical prediction of martensitic transformation crystallography by crystallographic phenomenological theory in such material has been proposed [5]. Nevertheless, the high brittleness of Ni-Mn-Ga alloy restricts its practical applications; therefore, addition of other elements could be a potential alternative to overcome this disadvantage. So the study of the substitution of one element by another and the addition of the fourth element have been experimentally started. Many new types of ferromagnetic shape memory alloys have been developed in order to increase toughness, for example Ni-Fe-Ga [6, 7], Co-Ni-Ga [8, 9], etc. Near-stoichiometric Ni_2FeGa alloys seem to be a promising system as they undergo, on cooling, a martensitic transformation (MT) from L_{21} -Heusler-structure to ferromagnetic martensite with layered structures (i.e. five-layered, 5M, or seven-layered, 7M [6, 7]), which are good candidates to show large MFIS. Recently intermetallic Co-Ni-Ga alloys are recognized as new ferromagnetic shape memory materials due to their good ductility [10], magnetic-controlled two-way shape memory effect [11] and high martensitic starting transformation temperatures [12]. However, experimental studies have limitations: long study period, limited scope, high costs, etc. The theoretical calculation can simulate substitution or addition elements with any desired compositions and accordingly select the most promising one, which can provide useful guidance for experiments.

The detailed information of the crystallographic, magnetic and electronic structures of the stoichiometric Ni_2XGa ($\text{X} = \text{Mn, Fe, Co}$) are crucial for the understanding the essence of the shape memory effect associated with the martensitic transition. Therefore, the purpose of the present section is to disclose the change tendency of the substitution of Mn atom by Fe or Co in stoichiometric Ni_2XGa , X denotes Mn, Fe and Co atom, which can provide theoretical evidence for experimental phenomenon.

2.2.2 Calculation method

The *ab initio* calculations have been performed based on the density functional theory (DFT), using Vienna *ab initio* software package [13-15] (VASP). The interaction between ions and electrons is described by ultra-soft pseudopotentials [16, 17] (USPP) and also by the projector-augmented wave (PAW) [18, 19] method. Both USPP and PAW pseudopotentials in VASP code allow for a considerable reduction of the number of plane-waves per atom for transition metals. The generalized gradient approximation (GGA) in Perdew and Wang parameterization [20] is used to describe the exchange-correlation energy and up to now it is the best approach to describe magnetic materials. For the pseudopotentials used, the electronic configurations are Ni ($3d^8 4s^2$), Mn ($3d^6 4s^1$), Fe ($3d^7 4s^1$), Co ($3d^8 4s^1$), and Ga ($4s^2 4p^1$), respectively. In this work, the kinetic energy cutoff is 275 eV for PAW and 250eV for USPP. A Monkhorst-Pack [21] grid is employed to sample the Brillouin zone. The k-points in the Brillouin zone for self-consistent field cycles and density of states (DOS) calculations are generated with $10 \times 10 \times 10$ and $14 \times 14 \times 8$ meshes for austenite and non-modulated (NM) martensitic phases. We use different k-point meshes for different phases to ensure the same k-points density for all the phases in our calculations. The calculation is semi-relativistic and the spin polarization is taken into account for all the cases. Both ferromagnetic and non-magnetic states have been considered for Ni_2MnGa . All structures considered in this paper have been relaxed using the conjugate gradient algorithm and both the atomic position and the volume have been optimized. From these calculations, total energies, magnetic moments, and relaxed structures at ground state have been analyzed.

2.2.3 Results and discussion

2.2.3.1 Structure optimization of stoichiometric Ni_2XGa

First we optimized the lattice parameters of both the austenitic and the martensitic phase of Ni_2MnGa alloy with USPP and PAW pseudopotentials. The space groups for the austenitic and the non-modulated martensitic phase are Fm-3m and I4/mmm, respectively, and the geometric structures are shown in Fig. 2-1 (a) and (b).

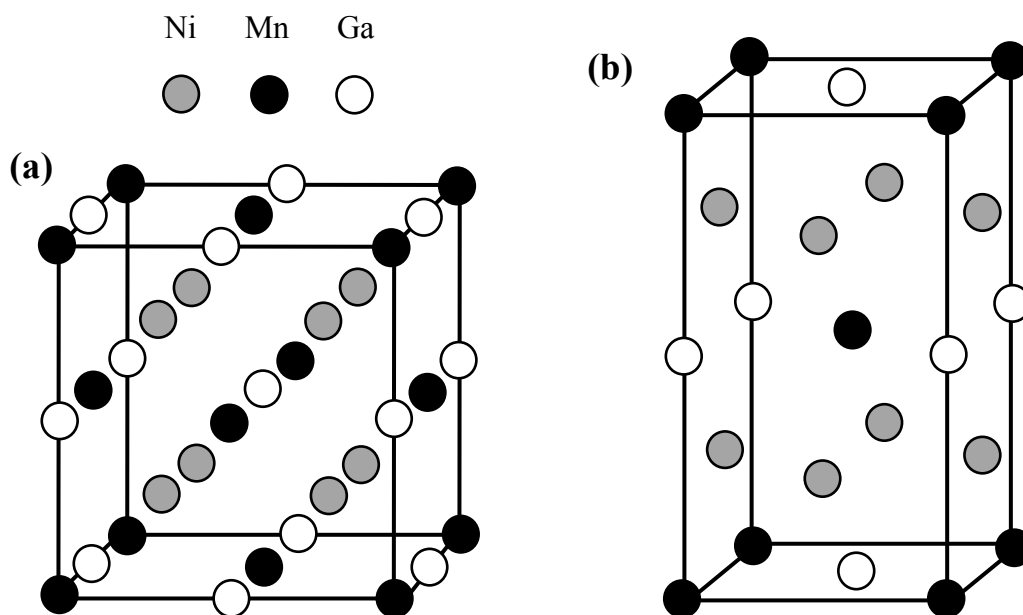


Fig. 2-1 Geometric structures of Ni_2MnGa (a) cubic L_{21} austenitic phase; (b) tetragonal non-modulated martensitic phase.

Table 2-1 Optimized lattice parameters of both austenitic and martensitic phases in Ni_2MnGa . Both ferromagnetic and non-magnetic states with USPP and PAW pseudopotentials have been considered. Experimental values [2, 22] are also listed for comparison.

		L ₂₁ cubic austenite		non-modulated martensite	
		a (Å)	a(Å)	c(Å)	c/a
USPP	ferromagnetic	5.805	3.853	6.612	1.716
	non-magnetic	5.711	3.634	6.641	1.827
PAW	ferromagnetic	5.774	3.840	6.520	1.698
	non-magnetic	5.692	3.672	6.513	1.774
Experimental values		5.823 ^a	3.852 ^b	6.580 ^b	1.708 ^b

a Reference²²

b Reference²

For each phase the ferromagnetic and non-magnetic states have been considered. The results are listed in Table 2-1. To verify our calculation, some experimental results [2, 22] are chosen and listed in Table 2-1 for comparison. It can be seen from Table 2-1, the

ferromagnetic US-PP configuration has the best agreement with the values measured from neutron diffraction experiment [2, 22] for both phases. The relative differences compared with the experimental values are within 0.5%. Therefore, we select ferromagnetic USPP scheme for all the following calculations.

Table 2-2 Optimized lattice parameters (a), bulk moduli (B), total and partial magnetic moments in cubic Ni₂XGa. Available experimental values and calculated results from other calculations [22-28] are also listed for comparison.

Ni ₂ XGa	a	B	M ^{tot}	M ^{Ni}	M ^X	M ^{Ga}
	(Å)	(GPa)	(μ _B)	(μ _B)	(μ _B)	(μ _B)
Ni ₂ MnGa	5.805	151	4.20	0.35	3.52	-0.06
	5.823 ^a	146 ^b 155 ^f	4.17 ^{c,g} 4.27 ^f	0.33 ^g 0.36 ^c	3.84 ^g 3.43 ^c	-0.04 ^c
Ni ₂ FeGa	5.752	164	3.41	0.28	2.91	-0.04
	5.741 ^d		3.04 ^d			
Ni ₂ CoGa	5.699	171	1.80	0.14	1.58	-0.02
	5.405 ^e	169 ^e	1.78 ^e	0.16 ^e	1.55 ^e	-0.02 ^e

^a Reference [22]

^b Reference [23]

^c Reference [24]

^d Reference [25]

^e Reference [26]

^f Reference [27]

^g Reference [28]

The equilibrium lattice parameters, bulk modulus, total and partial magnetic moments in Ni₂XGa (X=Mn, Fe, Co) alloy systems, as listed in Table 2-2, and also compared the values obtained with experimental and calculated values from the literature [22-28]. As it can be seen from Table 2-2, our computational results are in fair agreement with the literature.

In Ni₂MnGa, the relative difference of lattice constant compared with the neutron

diffraction result [22] is 0.31%, and that of the total magnetic moment is 0.72%. From Table 2-2, we conclude that the lattice parameters, total and partial magnetic moment decrease gradually with the increase in the atomic number of X, whereas the bulk modulus displays an inverse tendency. The atomic radius of each X atom had been calculated by E. Clementi *et al.* [29]. The radii of Mn, Fe and Co are 1.61 Å, 1.56 Å and 1.52 Å, respectively. Therefore, the decreasing lattice parameters mainly result from the decreasing X radius. The decrease in the total magnetic moments, resulting in the gradual weakening of ferromagnetism mainly depends on the 3d electronic states of X atoms. The moment from the 3d Ni is substantially low as compared with the X moment. The magnetic moment of Ga atoms are also listed in Table 2-2. The direction of the induced spin polarization at Ga site is opposite to the direction of the X atoms, and this feature reveals the strong hybridization of the X-d states with the Ga sp states. The magnitude of the Ga moment decrease with the increase of the X atomic number, as the weakened X atomic moment reduces the hybridization and therefore the induced moment. The difference of the magnetic moment between Ni_2MnGa and Ni_2FeGa is close to $0.8 \mu_B$; whereas that between Ni_2FeGa and Ni_2CoGa is close to $1.6 \mu_B$. The effect of the substitution of Mn atom by Fe or Co is not just limited to the crystal structures, but it also affects magnetic properties.

Heusler alloys are considered to be ideal local moment systems. In the Ni_2XGa Heusler alloys ($\text{X} = \text{Mn, Fe, Co}$), the magnetic moment is mainly localized on the X atom. The localized character of the magnetization results from the exclusion of minority spin electrons from the X 3d states. The occupied d states of X are delocalized by their strong interaction with the Ni-atom d states [30]. Since the X-X distances are all $\geq 4 \text{ Å}$ for $\text{X} = \text{Mn, Fe, Co}$, there is no significant direct interaction between the X atoms. The indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) [31-33] type exchange interaction gives rise to magnetism in these materials. In Ni_2MnGa , which is ferromagnetic, the Mn-Mn interaction is mediated by the Ni conduction electrons [30]. Webster *et al.* [28] reported the total magnetic moment of Ni_2MnGa to be $\approx 4.17 \mu_B$ with $\approx 3.84 \mu_B$ localized on Mn and $\approx 0.33 \mu_B$ on Ni from magnetization and neutron diffraction studies, which are in good agreement with our prediction.

2.2.3.2 Energetic stability of cubic Ni_2XGa

In order to investigate the effect of the substitution of Mn atom by Fe or Co on the stability of the cubic phase, formation energy of cubic Ni_2XGa has been calculated. The formation energy E_f is a measure of the phase stability in solid states and is defined as the total energy of the compound minus the total energies of the related pure elements in their reference states [34, 35]:

$$E_f = E_{\text{tot}}(\text{Ni}_2\text{XGa}) - 2E_{\text{tot}}^0(\text{Ni}) - E_{\text{tot}}^0(\text{X}) - E_{\text{tot}}^0(\text{Ga}) \quad (2-1)$$

Here X represents Mn, Fe and Co, $E_{\text{tot}}(\text{Ni}_2\text{XGa})$ is the total energy of the unit cell of Ni_2XGa , $E_{\text{tot}}^0(\text{Ni})$, $E_{\text{tot}}^0(\text{X})$ and $E_{\text{tot}}^0(\text{Ga})$ are the total energies per atom of the pure Ni, X, and Ga in their reference states, respectively.

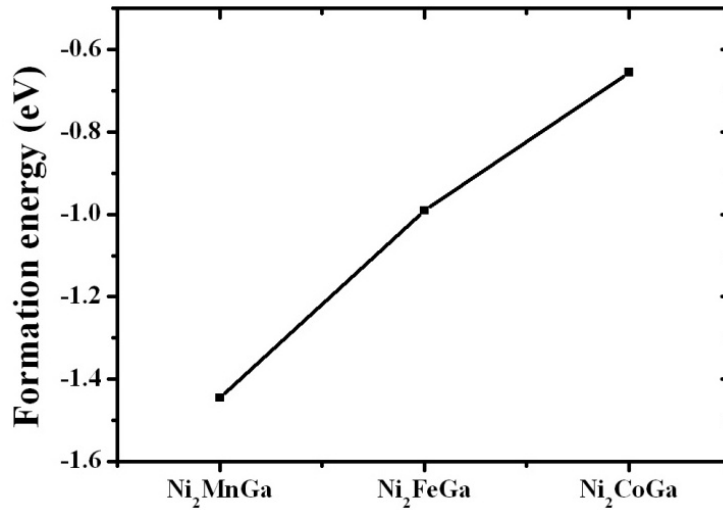


Fig. 2-2 Formation energy of the Ni_2XGa (X=Mn, Fe, Co).

The calculated results E_f of the Ni_2XGa in the cubic phase are shown in Fig. 2-2. The formation energies of the cubic phases are negative for all the three alloy systems; however the results show a destabilization tendency of the cubic structure if Mn atom is substituted by Fe or Co, since the formation energy of the compound increases.

2.2.3.3 Effect of c/a ratio on the total energy and magnetic properties in Ni_2XGa

Using the optimized structure parameters obtained from US-PP approach, keeping the volume of unit cell as a constant, we calculated the variation of the total energies, partial and total magnetic moments with the tetragonal distortion (c/a ratio) of three ferromagnetic shape

memory alloys Ni_2XGa ($\text{X} = \text{Mn, Fe, Co}$) at absolute zero temperature ($T=0\text{K}$). The total energy as a function of the tetragonal c/a ratio of the three alloy systems is shown in Fig. 2-3. Each alloy has two local energy minima, within the c/a ratio range from 0.80 to 1.45.

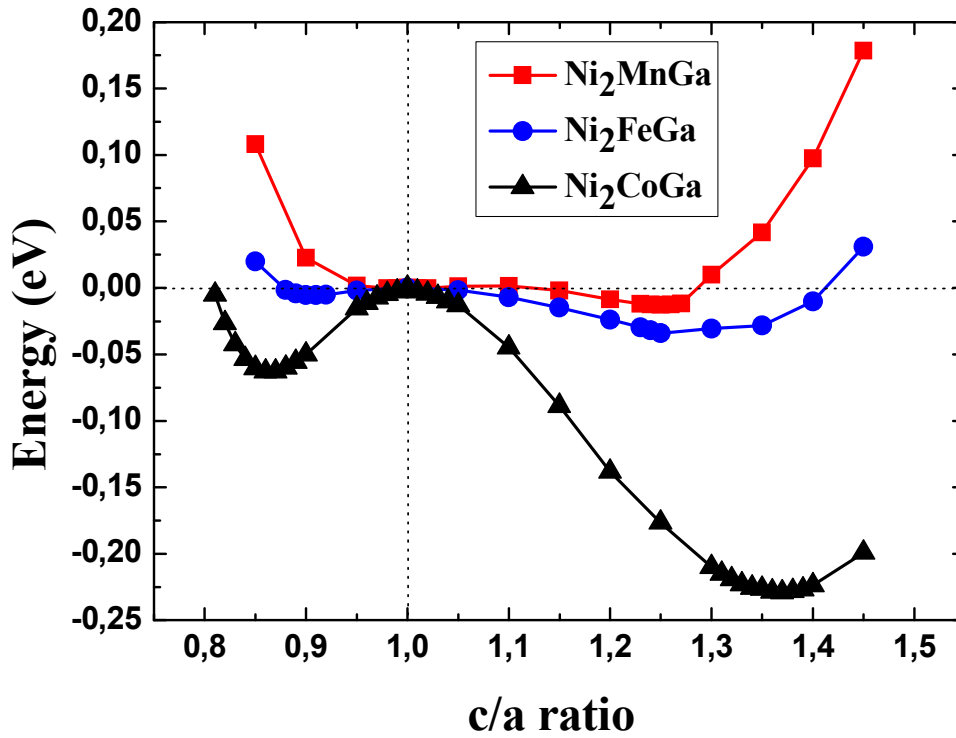


Fig. 2-3 Relative variation of the total energy as a function of the tetragonal distortion (c/a ratio) in three ferromagnetic alloy systems: Ni_2MnGa , Ni_2FeGa and Ni_2CoGa . Zero energy corresponds to the energy of the L2_1 structure in each case.

For the stoichiometric Ni_2XGa ($\text{X} = \text{Mn, Fe, Co}$), the first local minimum is $c/a = 1.00$, 0.91 and 0.86 respectively and the second local minimum is $c/a = 1.25$, 1.25 and 1.37 respectively. The point $c/a = 1.00$ corresponds to the structure of the parent austenite phase, space group Fm-3m ; $c/a = 1.25$ corresponds to a kind of martensite. According to the results of A. T. Zayak and P. Entel *et al.* [36], a non-modulated martensite of Ni_2MnGa with c/a ratio ≈ 1.2 is the most stable phase at the extremely low temperature, which is consistent with our calculation results in this case. Therefore, at the absolute zero temperature, the $c/a = 1.25$ tetragonal non-modulated martensitic phase has been predicted. With the gradual increase of temperature, the metastable 5M , 3M , L2_1 structure will appear one after another [22].

In Ni_2FeGa and Ni_2CoGa compounds, we can find a local maximum at $c/a = 1.00$ (whereas $c/a=1.00$ is a minimum of energy in the Ni_2MnGa compound). Due to the different structure stability ($c/a < 1.00$, $c/a = 1.00$ and $c/a > 1.00$) of the Ni_2XGa (X=Mn, Fe, Co), when the temperature increases, the transition sequence will be different. Moreover, it is known that there is a strong competition between intermetallic compound and a disordered FCC second γ phase precipitation in the experiments. Thus it is difficult to form pure Ni-Fe-Ga intermetallic compounds in as-cast alloys, except using the melt-spinning technique [37]. The Ni_2CoGa alloy has the deepest energy minima, so the martensitic phase of this alloy is the most stable one. However, since the inverse martensitic transformation is driven by a thermal field in Ni_2XGa , the deepest energy difference between austenite and martensite in Ni_2CoGa also means that it is the most difficult one to drive its conventional shape memory effect.

The calculated total magnetic moments and contributions associated with individual atoms in Ni_2XGa , as a function of the c/a ratio are shown in Fig. 2-4.

It can be seen that the principal contribution to the total magnetic moment is mainly given by X atom (X=Mn, Fe, Co). Since the contribution of Ga to the total magnetic moment is very small, we ignored the contribution of Ga to the total variation of magnetic moment. The shape of the total magnetic moment curve is given by Ni atom except for Ni_2FeGa , because there are two Ni atoms contributing to the total magnetic moment change. With X=Mn, as shown in Fig. 2-4 (a), the evolution of Ni moment is wavelike and follows the variation of total magnetic moment, whereas Mn moment uniformly decreases after the maximum point at $c/a=1.00$. In Ni_2FeGa , shown in Fig. 2-4 (b), the shape of Ni moment curve is parabolic with only one single minimum, differing from the case of Ni_2MnGa . So the variation tendency of total magnetic moment for Ni_2FeGa is determined by strong combined effect of Ni and Fe atomic magnetic moments. The situation for Ni_2CoGa differs from the first two types, as shown in Fig. 2-4 (c), the variation of total magnetic moment is similar to the Ni moment, but the curve is parabolic, not wavelike. Through the investigation of the variation of the total magnetic moment with the tetragonality (c/a ratio), we can effectively predict the magnetic moment change during the martensitic transition.

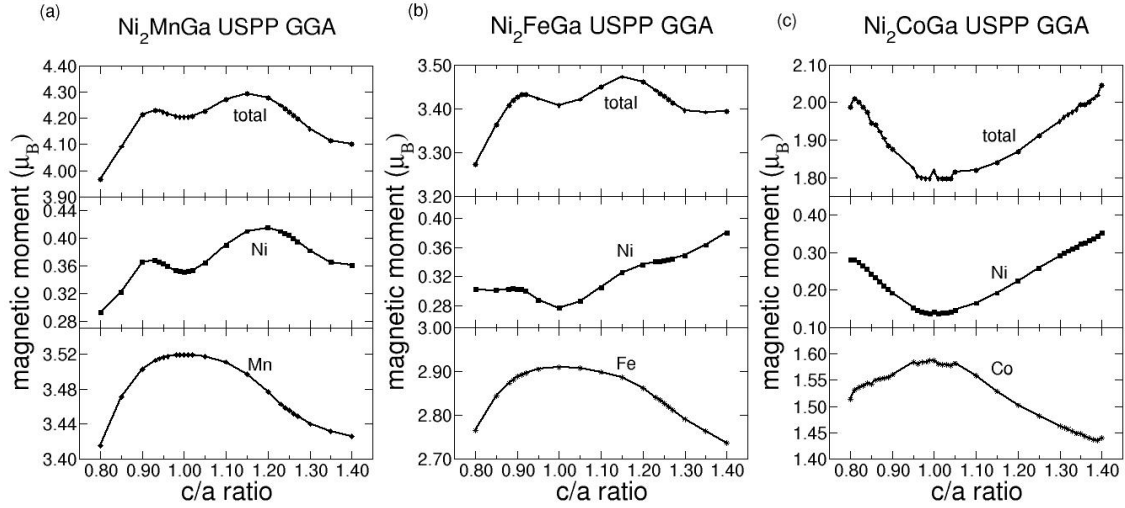


Fig. 2-4 Evolution of the total and partial magnetic moments with the c/a ratio in ferromagnetic Ni_2XGa : (a) $\text{X} = \text{Mn}$; (b) $\text{X} = \text{Fe}$; (c) $\text{X} = \text{Co}$.

2.2.3.4 Density of states and charge distribution

To further investigate the nature of the magnetic properties, the spin-resolved Densities Of States (DOS) are computed by the tetrahedron method with Blöchl corrections [38]. The DOS for the three cubic Ni_2XGa ($\text{X} = \text{Mn, Fe, Co}$) are calculated at their equilibrium lattice constants and optimized internal parameters.

Fig. 2-5 (a)-(c) show the computed total densities of states for Ni_2XGa ($\text{X} = \text{Mn, Fe, Co}$) alloys, respectively. The total DOS of Ni_2MnGa around Fermi level had been studied well by A. T. Zayak *et al.*[36], and our present calculation result on Ni_2MnGa is in fair agreement with theirs, as displayed in Fig. 2-5(a). As it can be seen, for all the systems, there are three regions: the lowest valence band, the upper valence band and the conduction band. The lowest valence band is almost symmetric. For the upper valence band, the up spin and down spin components from -6 eV to -2 eV in the total density of states are quite similar for each case. Therefore we mainly focus our attention on the variation of the density of states near the Fermi level. Comparing the total up and down densities, we note that the differences of the magnetic moments of these materials are determined by the difference of the up and down electron number at the Fermi level. From Ni_2MnGa to Ni_2CoGa , the down spin electron DOS at Fermi level is gradually increasing, whereas those of the up spin part remains almost

unchanged. This is the main origin of the differences of the magnetic moments in these alloys.

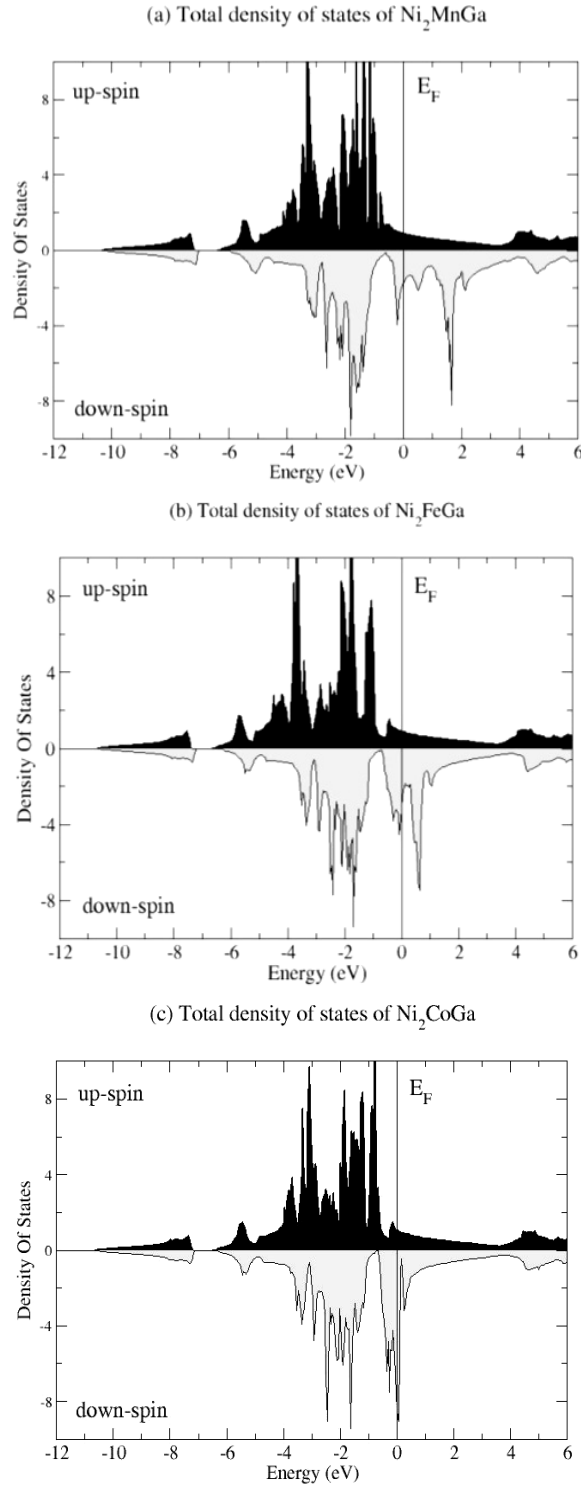


Fig. 2-5 Calculated spin-resolved total DOS for (a) Ni_2MnGa , (b) Ni_2FeGa , and (c) Ni_2CoGa .

Fig. 2-6 shows the spin-resolved partial DOS for the three Ni_2XGa alloys. For each case, the 3d orbits of the Ni and X atoms are shown separately.

The partial DOS is dominated by the Ni and Mn 3d states in the bonding region below E_F .

From the upper panels of Fig. 2-6 (a)-(c), the up spin Ni 3d states extend from -5 eV to above

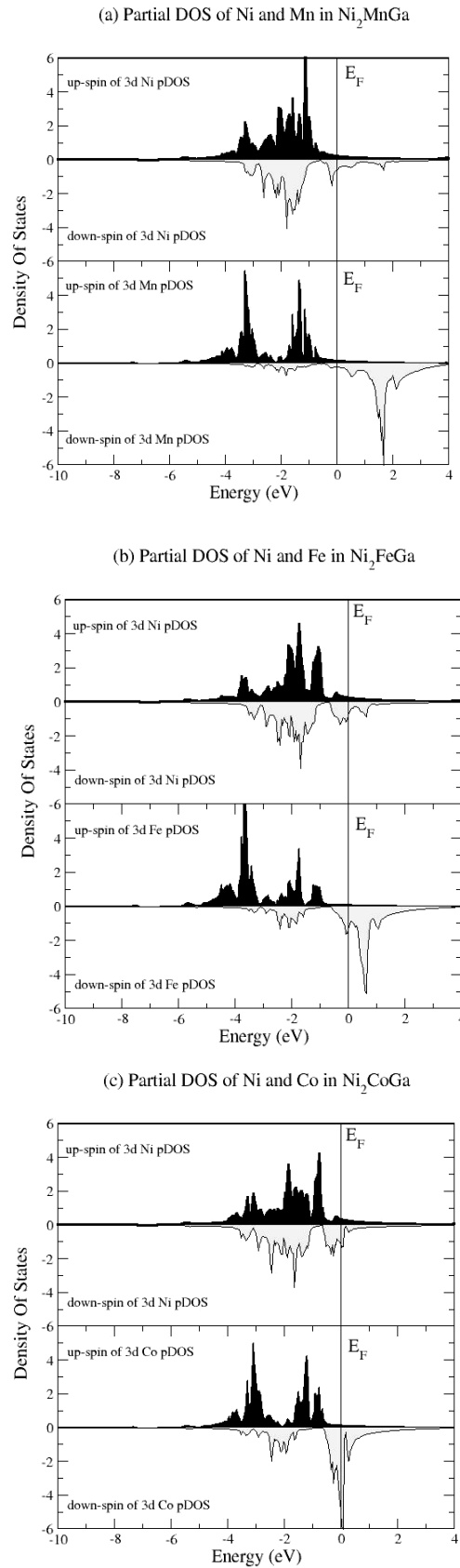


Fig. 2-6 Calculated spin-resolved partial DOS of Ni and X 3d states for cubic phase of

(a) Ni_2MnGa , (b) Ni_2FeGa , and (c) Ni_2CoGa .

E_F . The down spin Ni 3d t_{2g} states are centered around on -1.7 eV and the down spin Ni 3d pDOS has a sizable contribution near E_F for the three alloys, which is the e_g character. The main difference of the Ni pDOS appears around the Fermi level. With the substitution of Mn by Fe or Co, we must consider that one or two electron(s) more than the Ni_2MnGa compound in a unit cell. These substitutions create the displacement of the Fermi level gradually in the down spin density of Ni.

From the lower panels of Fig. 2-6 (a), the down spin Mn 3d states dominate the antibonding region above E_F with the peak around 1.8 eV and have a small contribution below E_F . The up spin Mn 3d states are almost fully occupied and the t_{2g} and e_g states are clearly separated appearing at -3.1 and -1.2 eV, respectively. With the substitution of Mn by Fe or Co, from the lower panels of Fig. 2-6 (a)-(c), there are three main differences of the X pDOS, and all of them appear in the down-spin part. The first one is the intensity of the peak centered on -2 eV is increased with this effect; the second one is the antibonding region above E_F is narrowed and the last one is also a displacement of E_F . Now we can conclude that the effect of substitution of Mn by Fe or Co on electronic DOS is mainly in the down-spin part, especially around the Fermi level.

In order to investigate the nature of the bonds in these three ferromagnetic systems, the difference charge density has been calculated at the isosurface $0.035 \text{ e}/\text{\AA}^3$, as shown in Fig. 2-7. Golden represents electron gain, and blue electron loss. There are two different bond characters : in Fig. 2-7 (a), there is strong bond between neighboring Ni atoms in Ni_2MnGa whereas in Ni_2FeGa and Ni_2CoGa alloys, as shown in Fig. 2-7 (b) and (c), the bond exists between Ni and X atoms. The intensity of the bond in Ni_2CoGa alloy is much stronger than that in Ni_2FeGa .

2.2.4 Conclusions

The optimized lattice parameters of both austenitic and martensitic phases of the Ni_2MnGa , the equilibrium lattice parameters, bulk moduli, total and partial magnetic moments, the formation energy, density of states and difference charge density of the cubic

phase of the stoichiometric Ni_2XGa ($\text{X} = \text{Mn, Fe, Co}$) have been systematically calculated.

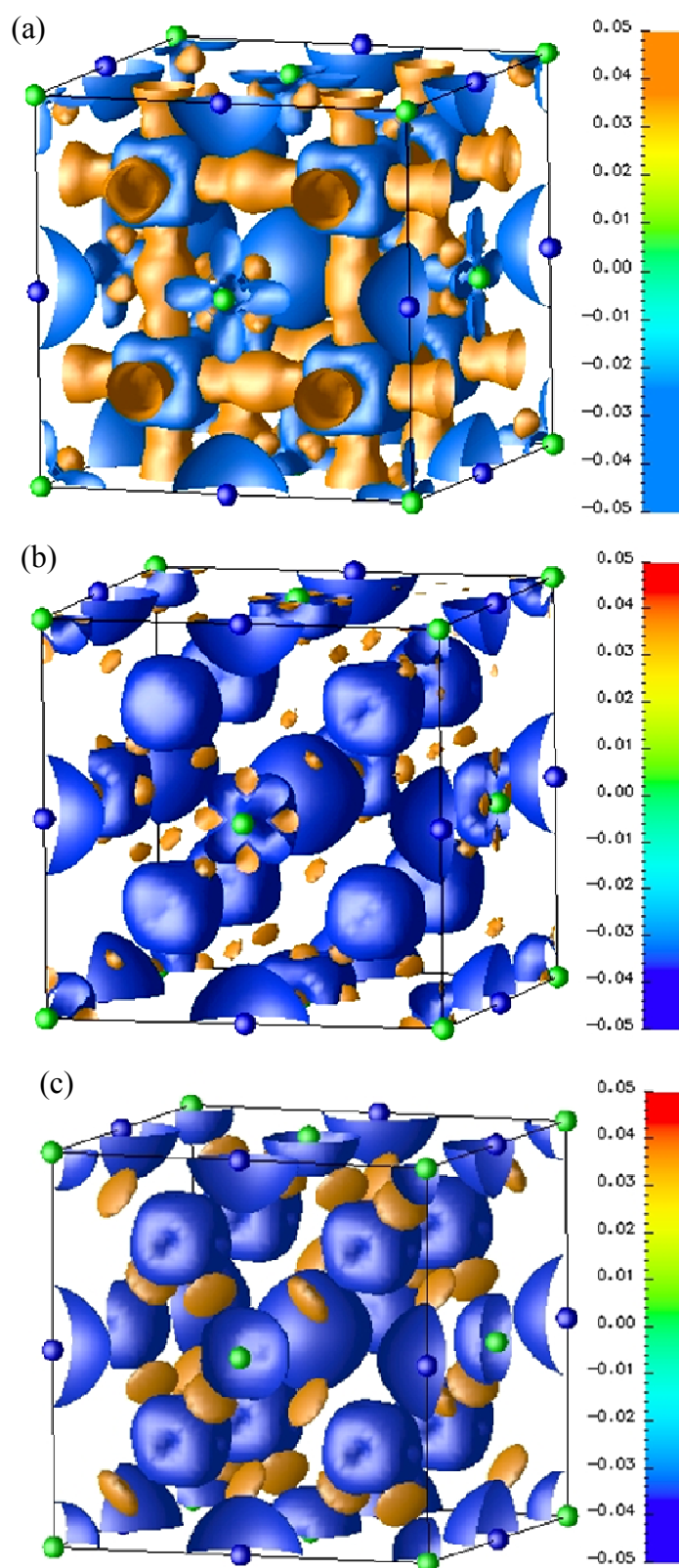


Fig. 2-7 Isosurface plots of the difference charge density at $0.035 \text{ e}/\text{\AA}^3$ for

(a) Ni_2MnGa ; (b) Ni_2FeGa and (c) Ni_2CoGa .

The lattice parameters, total and partial magnetic moments decrease gradually with the increase in the atomic number of X; whereas the bulk modulus displays an opposite tendency. The formation energies of the three cubic systems are all negative and show a destabilization tendency if Mn atom is substituted by Fe or Co. During the tetragonal deformation, for the stoichiometric Ni_2MnGa , Ni_2FeGa and Ni_2CoGa compounds, the first local minimum is $c/a=1$, 0.91 and 0.86, and the second local minimum is $c/a=1.25$, 1.25 and 1.37 respectively. The shape of the total magnetic moment curve with the c/a ratio variation is normally given by the Ni atom, but not for Ni_2FeGa . From Ni_2MnGa to Ni_2CoGa , the down spin total density of states at the Fermi level is gradually increasing, whereas those of the up spin part remains almost unchanged, which is the essential difference of the magnetic moment in these alloys. The partial DOS is dominated by the Ni and X 3d states in the bonding region below the Fermi level. The down spin X 3d states dominates the antibonding region above the Fermi level. The strong bond between the Ni atoms in the Ni_2MnGa is replaced by the bond between Ni and X atoms in Ni_2FeGa and Ni_2CoGa compounds.

2.3 Ni_2XIn (X= Mn, Fe, Co) ferromagnetic shape memory alloys

2.3.1 Introduction

Research on shape memory alloys have received significant attention after the discovery of the shape memory (MSM) effect in Ferromagnetic shape memory alloys (FSMAs) Ni-Mn-Ga [1]. This effect arises from a magnetic-field-induced reorientation of the martensitic variants through their high magnetocrystalline anisotropy. The driving force is provided by the difference between the Zeeman energies of the neighboring martensitic variants [39]. Giant strains up to 10% had been reported for off-stoichiometric Ni-Mn-Ga single variant crystal with the 14M modulated martensitic structure [40]. Over the past decade, vast amount of knowledge accumulated on the properties of Ni-Mn-Ga Heusler alloys has enabled to foresee the possibility of employing these alloys in device applications [41]. However, the actuation output stress level of the Ni-Mn-Ga alloy is only less than 5MPa, which restricts its practical applications. Recently, a novel type of FSMAs Ni-Mn-In-Co

Heusler alloy has been experimentally investigated [42]. It shows that the martensitic transition from the ferromagnetic austenitic phase to the antiferro- or paramagnetic martensitic phase can be reversed by a magnetic field, the so-called magnetic-field-induced reverse martensitic transition (MFIRT). MFIRT is more attractive for the practical application as magnetically driven actuator because it possesses a magnetostress level on the order of tens of MPa. An almost perfect shape memory effect associated with such phase transition is induced by a magnetic field and is called the metamagnetic shape memory effect. The Ni–Mn–In is the basic ternary alloy system of the Ni–Co–Mn–In alloy, and it owns the same metamagnetic shape memory effect [43], accompanying large magnetoresistance [44, 45], large entropy change [46, 47], giant Hall effect [48], and large reverse magnetocaloric effects (MCEs) [49]. The relationship of alloying composition-martensitic transformation temperature-crystal structure of the Ni-Mn-In alloy had been systematically studied by T. Krenke *et al.* [50].

The purpose of the present work is to investigate the basic physical properties of the stoichiometric Ni_2XIn and the change tendency with the substitution of Mn atom by Fe or Co.

2.3.2 Results and discussion

2.3.2.1 Structure optimization of stoichiometric Ni_2XIn

The lattice parameters of the parent austenitic L_{21} phase of Ni_2MnIn alloy with US-PP and PAW pseudopotentials have been calculated. The space group for austenitic phase is Fm-3m . Both the ferromagnetic and the non-magnetic states have been considered. The results are listed in Table 2-3. To verify our calculation, experimental result [50] is chosen and listed in Table 2-3 for comparison. It can be seen from Table 2-3, the ferromagnetic US-PP scheme has the best agreement with the value measured from the X-Ray diffraction experiment [50]. The relative difference compared with the experimental value is 0.30%. Therefore, we select ferromagnetic US-PP scheme for all the following calculations of Ni-X-In alloys.

In addition, from Table 2-3, the theoretical lattice constants of the four computational schemes are all slightly smaller than the experimental value, which may be in part due to the fact that the experimental lattice constant was measured at elevated temperature.

Table 2-3 Optimized lattice parameter of parent austenitic L2_1 phase of Ni_2MnIn . Both ferromagnetic and non-magnetic states with the US-PP and PAW pseudopotentials have been considered. Experimental value [50] and the relative difference between the calculated and experimental lattice parameter of the austenite L2_1 phase are also listed for comparison.

Computational		L2_1 austenite	Relative difference
schemes		a (Å)	(%)
US-PP	ferromagnetic	6.053	0.30
	non-magnetic	5.952	1.96
PAW	ferromagnetic	6.036	0.58
	non-magnetic	5.943	2.11
Experimental values		6.071 ^a	

^a Reference [50].

Then we optimized the lattice parameters, atomic separation, bulk moduli, total and partial magnetic moments of Ni_2XIn (X=Mn, Fe, Co) alloy systems, as listed in Table 2-4, and also compared with the data obtained either by experiments or by calculations from the literature [50-52]. As it can be seen from Table 2-4, our computational results are in fair agreement with those from the literature.

From Table 2-4, the lattice parameters, atomic separation, total and partial magnetic moments decrease gradually with the increase in the atomic number of X, whereas the bulk modulus displays an inverse tendency. As seen from Fig. 2-1 (a), from crystallographic geometry, the atomic separation of the neighboring Ni and X atoms equals to that of the neighboring Ni and In atoms; they have the same distance between the neighboring Ni-Ni and Mn-In atoms, which is nearly half of the lattice parameter. The atomic radius of each X atom had been calculated by E. Clementi *et al.*[29]. The radii of Mn, Fe and Co are 1.61Å, 1.56Å and 1.52Å, respectively. Therefore, one reason for the decreasing lattice parameters and atomic separation is the decreasing X radius, the other may be caused by the change of the intensity of the ionic bond, which will be discussed in section 2.3.2.4. The decrease of the

total magnetic moments, resulting in the gradual weakening of the ferromagnetism mainly depends on the 3d electronic states of X atoms. The moment from the 3d Ni is substantially low as compared to the Mn moment. The magnetic moment of In atoms are also listed in Table 2-4. The direction of the induced spin polarization at In site is opposite to the direction of the X atoms, and this feature reveals the strong hybridization of the X-d states with the In sp states. The magnitude of the In moment decrease with the increase of the X atomic number, as the weakened X atomic moment reduces the hybridization and therefore the induced moment. The difference of the total magnetic moment between Ni₂MnIn and Ni₂FeIn is close to 0.85 μ_B ; whereas that is 1.53 μ_B between Ni₂FeIn and Ni₂CoIn. The effect of the substitution of Mn atom by Fe or Co is not just limited to the crystal structures, but it also affects the magnetic properties.

Table 2-4 Optimized lattice parameters (a), atomic separation, bulk moduli (B), total and partial magnetic moments (M) in cubic Ni₂XIn. Available experimental data and results from other calculations ^{a-d} are also listed for comparison.

Ni ₂ XIn	a (Å)	Atomic separation (Å)		B (GPa)	Magnetic properties (μ_B)			
		Ni-X (Ni-In)	Ni-Ni (X-In)		M ^{tot}	M ^{Ni}	M ^X	M ^{In}
Ni ₂ MnIn	6.053	2.62	3.03	127	4.33	0.33	3.69	-0.08
	6.036 ^a 6.071 ^b	2.61 ^a	3.02 ^a	133 ^a 138 ^d	4.14 ^a 4.22 ^c	0.32 ^a	3.49 ^a	-0.08 ^a
Ni ₂ FeIn	5.992	2.59	3.00	140	3.49	0.28	3.00	-0.06
	5.978 ^a	2.59 ^a	2.99 ^a	143 ^a	3.31 ^a	0.26 ^a	2.84 ^a	-0.06 ^a
Ni ₂ CoIn	5.944	2.57	2.97	145	1.90	0.15	1.68	-0.04
	5.941 ^a	2.57 ^a	2.97 ^a	160 ^a	1.77 ^a	0.15 ^a	1.53 ^a	-0.03 ^a

^a PAW calculation

^b Reference [50]

^c Reference [51]

^d Reference [52]

2.3.2.2 Energetic stability of cubic Ni_2XIn

In order to investigate the effect of the substitution of Mn atom by Fe or Co on the stability of the cubic phase, the formation energy of the cubic Ni_2XIn has been calculated. The formation energy E_f is a measure of the phase stability in solid states and is defined as the total energy of the compound minus the total energies of the related pure elements in their reference states [34, 35]:

$$E_f = E_{tot}(Ni_2XIn) - 2E_{tot}^0(Ni) - E_{tot}^0(X) - E_{tot}^0(In) \quad (2-2)$$

Here X represents Mn, Fe and Co, $E_{tot}(Ni_2XIn)$ is the total energy of the unit cell of Ni_2XIn , $E_{tot}^0(Ni)$, $E_{tot}^0(X)$ and $E_{tot}^0(In)$ are the total energies per atom of the pure Ni, X, and In in their reference states, respectively.

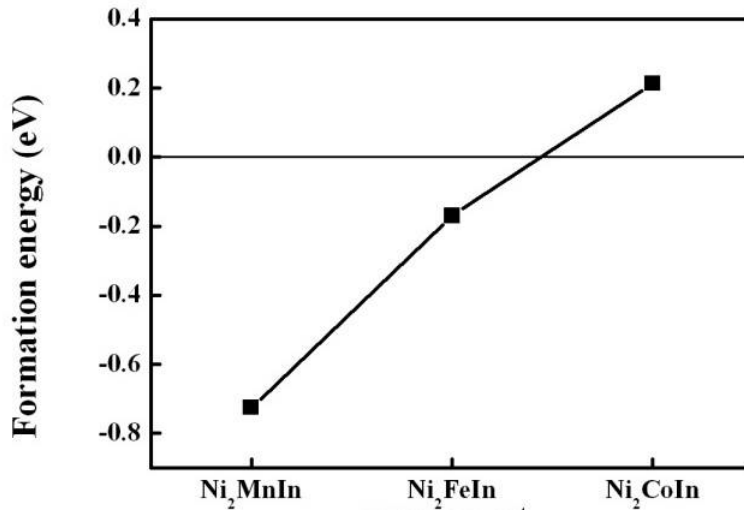


Fig. 2-8 Formation energy of the Ni_2XIn (X=Mn, Fe and Co).

The calculated results E_f of the Ni_2XIn in the cubic phase are shown in Fig. 2-8. The results show a destabilization of the cubic structure if Mn atom is substituted by Fe or Co, since E_f increases with such substitution. The value of E_f for Ni_2FeIn is just below zero, whereas that for Ni_2CoIn is quite above zero, indicating the structural instability of this alloy and a strong tendency of martensitic transformation.

2.3.2.3 Effect of c/a ratio on the total energy and magnetic properties in Ni_2XIn

The martensitic phase is a low-temperature phase, and its total energy at temperature near zero should be lower than that of the high-temperature austenitic phase. The transformation deformation has been studied by introducing a tetragonal distortion to the L_{21} structure. Using the optimized structure parameter and keeping the volume of the unit cell constant, we calculated the variation of the total energies, partial and total magnetic moments with the tetragonal distortion (c/a ratio) of the three ferromagnetic shape memory alloys Ni_2XIn ($\text{X} = \text{Mn, Fe and Co}$) at absolute zero temperature ($T=0\text{K}$). The total energy as a function of the tetragonal c/a ratio ranging from 0.80 to 1.60 of the three alloy systems is plotted in Fig. 2-9.

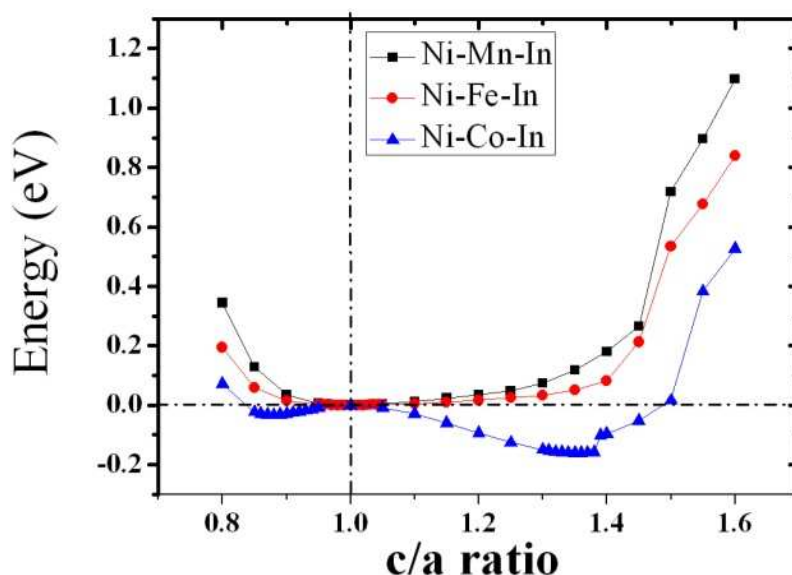


Fig. 2-9 Relative variation of the total energy as a function of the tetragonal distortion (c/a ratio) in three ferromagnetic alloy systems: Ni_2MnIn (black line), Ni_2FeIn (red line) and Ni_2CoIn (blue line). Zero energy corresponds to the energy of the L_{21} structure in each case.

For the stoichiometric Ni_2MnIn and Ni_2FeIn , there is only one energy minimum at $c/a=1.00$ as seen from Fig. 2-9. It corresponds to the structure of the parent austenite phase. That means the austenite phase possesses the absolute stability in these two stoichiometric alloys. According to the research results of Thorsten Krenke et al. [50], when the concentration of the

indium component is higher than 16%, no structural transformation was observed in Ni-Mn-In alloy system, which is consistent with our computational result. It is known that for Ni-X-In systems, the shape memory effect is obtained by magnetic field induced reversible austenite-martensite phase transformations. If there are no such transformations, no shape memory can be realized. Thus the stoichiometric Ni_2MnIn and Ni_2FeIn can not be used as magnetic shape memory alloys. Composition modification could be an alternative to obtain martensitic transformation and thus the shape memory effect.

Being different from the previous two cases, there are two energy minima located at $c/a=0.88$ and $c/a=1.36$, and a local maximum at $c/a = 1.00$ for Ni_2CoIn . Because of the large energy difference between the austenite and the martensite of the Ni_2CoIn alloy, together with the positive formation energy of the cubic phase, we can deduce that the martensitic phase of this alloy is the more energetically stable.

The calculated total magnetic moments and the magnetic moments carried by the individual atoms in Ni_2XIn , as a function of the c/a ratio are shown in Fig. 2-10. It can be seen that the principal contribution to the total magnetic moment is given by X atom (X=Mn, Fe, Co). The influence of In atom can be neglected for its limited contribution. The shape of the total magnetic moment curve is similar to that of the Ni moment except for Ni_2FeIn , because there are two Ni atoms contributing to the variation of the total magnetic moment.

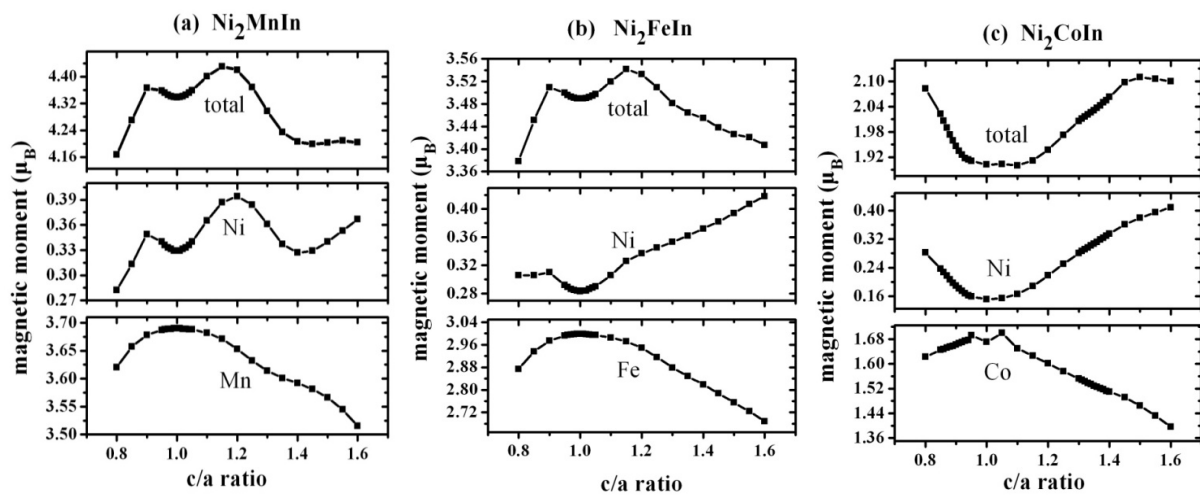


Fig. 2-10 Evolution of the total and partial magnetic moment with the c/a ratio in Ni_2XIn :

(a) X= Mn ; (b) X= Fe ; (c) X= Co.

The variation of the total magnetic moment is similar for Ni_2MnIn and Ni_2FeIn compounds, it is wavelike. In both cases, $c/a = 1.00$ corresponds to the local magnetic moment minimum. The two local maxima are located at $c/a = 0.90$ and $c/a = 1.15$ for both cases. For Ni_2CoIn compound, the magnetic moment variation with c/a is mainly parabolic with a flat region from 1.00 to 1.10. Beyond this range, the total magnetic moment increases monotonously with the increase of the tetragonal deformation. Through the investigation of the variation of the total magnetic moment with the tetragonality (c/a ratio), we can effectively predict the magnetic moment change during the martensitic transition.

2.3.2.4 Density of states and charge distribution

To further investigate the nature of the magnetic properties, the spin-resolved Density Of States (DOS) are computed by the tetrahedron method with Blöchl correction. [38] The DOS for the three cubic Ni_2XIn ($\text{X} = \text{Mn, Fe and Co}$) compounds are calculated at their equilibrium lattice constants and optimized internal parameters.

Fig. 2-11 (a)-(c) show the computed total DOS for the three cubic stoichiometric alloys, respectively. As it can be seen, for all the systems, there are three regions: the lowest valence band, the upper valence band and the conduction band. The lowest valence band is almost symmetric. For the upper valence band, the up spin and down spin components from -6 eV to -1 eV in the total density of states are quite similar for each case. Therefore we mainly focus our attention on the variation of the total DOS near the Fermi level. Comparing the total up and down densities, we note that the differences of the magnetic moments of these materials are determined by the difference of the up and down electron number at the Fermi level. From Ni_2MnIn to Ni_2CoIn , the down spin electron DOS at Fermi level is gradually increasing, whereas those of the up spin part at Fermi level remains almost unchanged (fully occupied). Therefore, the total magnetic moment from Ni_2MnIn to Ni_2CoIn (being $4.33\mu_B$ for Ni_2MnIn , $3.49\mu_B$ for Ni_2FeIn and $1.90\mu_B$ for Ni_2CoIn) decreases. Partial density of states has also been calculated, and it indicates that such a variation comes from the contribution of the 3d states of the X ($\text{X} = \text{Mn, Fe, Co}$) element. This is the main origin of the differences of the magnetic

moments in these alloys.

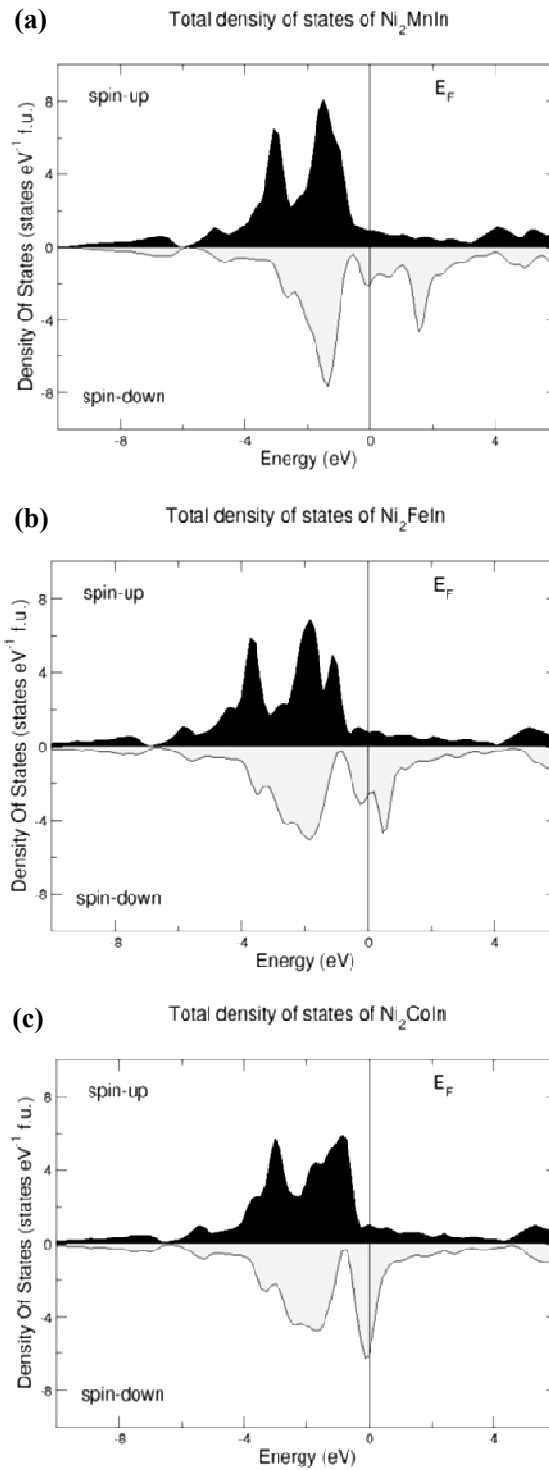


Fig. 2-11 Calculated spin-resolved total density of states for (a) Ni_2MnIn ; (b) Ni_2FeIn ; and (c) Ni_2CoIn .

Fig. 2-12 shows the spin-resolved partial DOS for the three Ni_2XIn alloys. For each case, the 3d orbits of the Ni and X atoms are shown separately. The partial DOS is dominated by

the Ni and Mn 3d states in the bonding region below Fermi level.

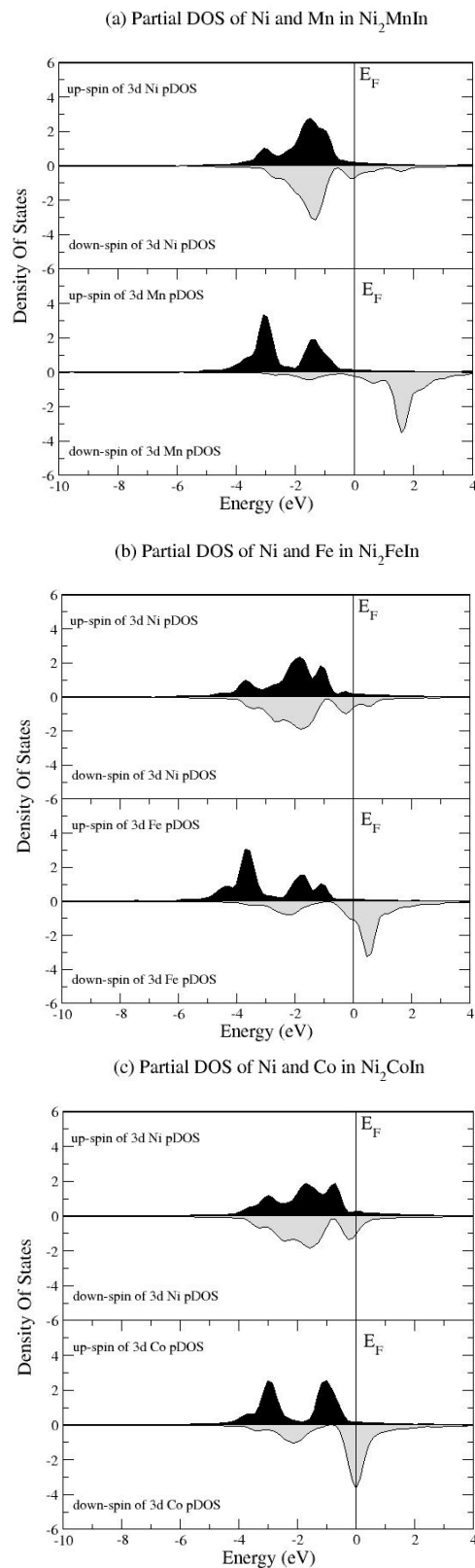


Fig. 2-12 Calculated spin-resolved partial DOS of Ni and X 3d states for cubic phase of

(a) Ni_2MnIn , (b) Ni_2FeIn , and (c) Ni_2CoIn

From the upper panels of Fig. 2-12 (a)-(c), the up spin Ni 3d states extend from -4 eV to

the Fermi level. The main difference of the down spin Ni pDOS appears around the Fermi level. With the substitution of Mn by Fe or Co, the peak intensity at Fermi level gradually increases. From the lower panels of Fig. 2-12 (a), the down spin Mn 3d states dominate the antibonding region above E_F with the peak around 1.8 eV and have a small contribution below E_F . The up spin Mn 3d states are almost fully occupied and the t_{2g} and e_g states are clearly separated appearing at -3 and -1.3 eV, respectively. With the substitution of Mn by Fe or Co, from the lower panels of Fig. 2-12 (a)-(c), there are two main differences of the X pDOS, and both of them appear in the down-spin part. One is the intensity of the peak centered on -2eV is increased with this effect; the other is a displacement of E_F . Now we can conclude that the effect of substitution of Mn by Fe or Co on electronic DOS is mainly in the down-spin part, especially around the Fermi level.

In order to investigate the nature of the bonds in these three ferromagnetic systems, the difference charge density has been calculated at the isosurface $0.03 \text{ e}/\text{\AA}^3$, as shown in Fig. 2-13. Golden represents electron gain, and blue electron loss. We can see that there is only one bond type exists in Ni_2XIn series, which is located between the Ni and the X (X= Mn, Fe, Co) atoms. According to section 2.2.3.4, there is very strong bond between neighboring Ni atoms in Ni_2MnGa , but we can not found this character in Ni_2MnIn . The weakest bond is in Ni_2MnIn , whereas the strongest in Ni_2CoIn . The different bond intensity also contributes partially to the change of the lattice parameter and atomic separation in these alloys. The stronger the bond is, the smaller the lattice parameter and atomic separation will be.

2.3.3 Conclusions

The optimized structural parameters, the total and partial magnetic moment, the formation energy, the density of states and the charge distribution of the cubic phase of the stoichiometric Ni_2XIn (X= Mn, Fe and Co), and the effect of the tetragonal c/a ratio on the total energy and the magnetic properties in Ni_2XIn have been systematically calculated. The results show that the lattice parameters, atomic separations, total and partial magnetic moments decrease gradually with the increase of the atomic number of X; whereas the bulk

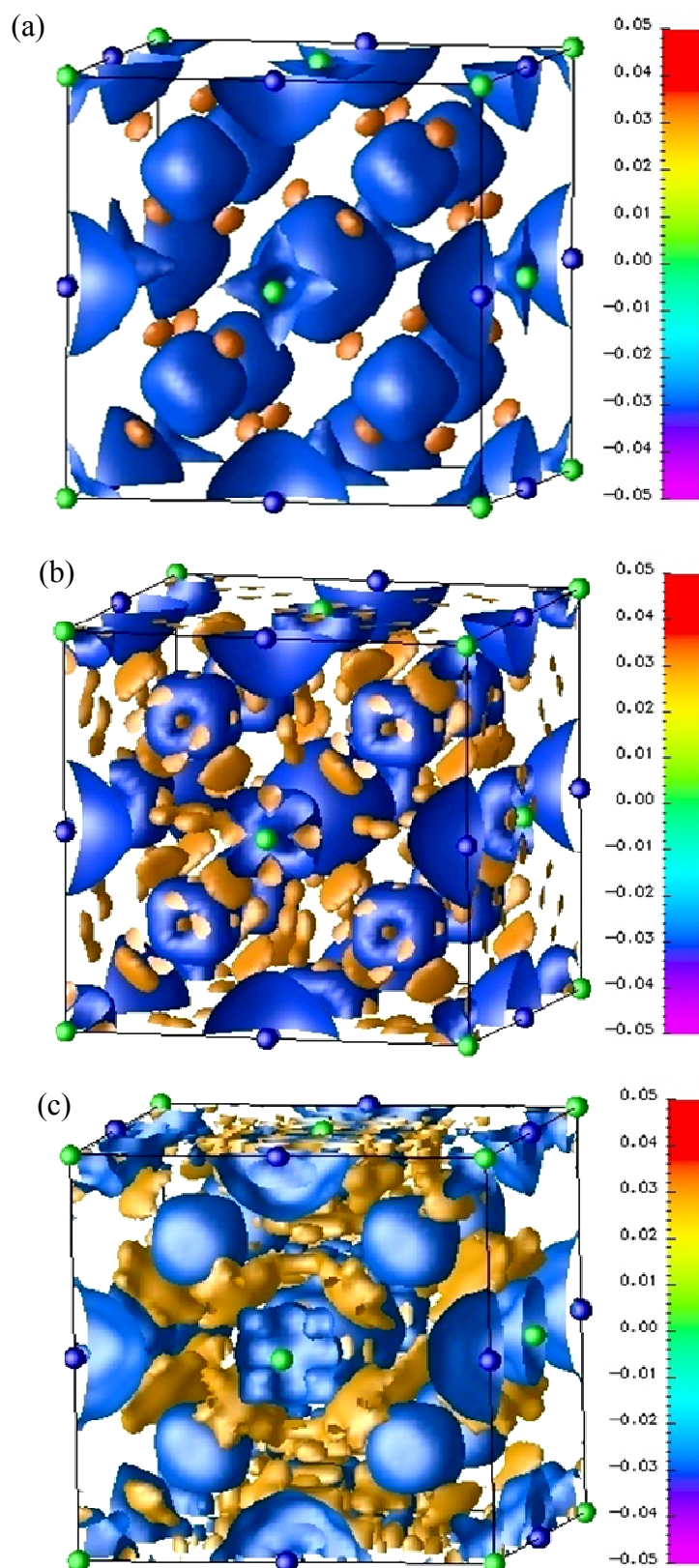


Fig. 2-13 Isosurface plot of the charge density at $0.03 \text{ e}/\text{\AA}^3$ for
(a) Ni_2MnIn ; (b) Ni_2FeIn and (c) Ni_2CoIn .

modulus displays an opposite tendency. The calculated formation energies of the three cubic systems show a destabilization of the cubic structure if Mn atom is substituted by Fe or Co. The value of E_f for Ni_2FeIn is just below zero, whereas it is quite above zero for Ni_2CoIn . During the tetragonal deformation, only one energy minimum appears at $c/a= 1.00$ for the stoichiometric Ni_2MnIn and Ni_2FeIn , whereas two energy minima appear at $c/a=0.88$ and $c/a=1.36$, and a local maximum at $c/a = 1.00$ for Ni_2CoIn . The martensitic Ni_2CoIn alloy is the most energetically stable phase. The investigation of the variation of the total magnetic moment with the tetragonal c/a ratio can effectively predict the change of the magnetic moment during the tetragonal martensitic transition. From Ni_2MnIn to Ni_2CoIn , the down spin total DOS at the Fermi level is gradually increasing, whereas those of the up spin part remains almost unchanged, which is the essential difference of the magnetic moment in these alloys. The partial DOS is dominated by the Ni and X 3d states in the bonding region below the Fermi level. The down spin X 3d states dominates the antibonding region. With the substitution of Mn by Fe or Co, there are two main differences of the X pDOS, one is the intensity of the peak centered on -2eV is increased with this effect; the other is a displacement of E_F . There is only one bond type exists in Ni_2XIn alloys, which is located between Ni and X atoms (X= Mn, Fe and Co), however the bonding intensity is different. In conclusion, all the results of the present paper provide important evidence for further understanding of the thermal stability from the formation energy calculation and magnetic properties from the spin-polarized DOS of the three alloy systems Ni_2XIn (X= Mn, Fe and Co).

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Chapter 3 Defect formation energy and magnetic structure of ferromagnetic shape memory alloys Ni-X-Y (X=Mn, Fe, Co; Y=Ga, In) by first-principles calculations

3.1 Outline

As is well known, the preferred site occupation and atomic disorder of the FSMAs plays an important role in determining the performances of these materials. The effect of the different point defects on the crystallographic and magnetic structures in FSMAs is of great significance to the martensitic temperature control and thus the performance optimization of these materials. Nevertheless, no systematic investigation has been devoted to these aspects heretofore.

Furthermore, the individual magnetic property on this new kind of materials is still insufficient. The governing factor of the individual magnetic moment has rarely been studied. As a matter of fact, insight into the preferred site occupation and magnetic features of the defective Ni_2XY (X=Mn, Fe and Co, Y=Ga, In) alloys is of both theoretical interest and practical guidance to the development of the promising FSMAs with optimal properties.

Based on the crystal structure information obtained in Chapter 2, the formation energies of the several kinds of defects (atomic exchange, antisite, vacancy) which are formed in stoichiometric Ni_2XY (X=Mn, Fe and Co, Y=Ga, In) are estimated. The effects of different constituent element on the structural stability have been analyzed. The atomic occupation status has been discussed in detail when composition adjusting procedure is carried out. The individual magnetic moment in the defective Ni_2XY has been determined in the self-defining magnetic characteristic rectangle.

3.2 Defect formation energy and magnetic structure of Ni-X-Ga (X=Mn, Fe and Co)

3.2.1 Introduction

The ferromagnetic Heusler alloys have been studied intensively for the last decade due

to their interesting magneto-elastic properties, in particular, shape memory effect, magnetic field induced superelasticity, etc. They are very attractive for applications as different kinds of actuators, sensors, magnetic micro-electro-mechanical systems, for recording and storage of information. These alloys undergo a martensitic transformation (MT) from a high-temperature cubic $L2_1$ phase to a low-symmetry martensite phase with several possible structures depending on the composition. The most experimentally and theoretically investigated Heusler alloy is Ni_2MnGa system. The different martensitic structures of Ni_2MnGa with different c/a ratio have been calculated [1]. Numerous experiments have shown that MT temperature (T_M) is very sensitive to the composition and atomic order of the alloy. The T_M linearly increases with the Ni content, whereas the Curie temperature (T_C) displays an opposite tendency in $Ni_{2+x}Mn_{1-x}Ga$ alloys [2]; when quenching temperature is increased from 800°C to 1000°C, the T_M has changed by 100°C [3]. The role of atomic disorder in Ni-Mn-Ga magnetic shape memory alloy had been investigated by first principle calculation [4]. The off-stoichiometry could be realized by introducing different kinds of defects into an ideal crystal. Therefore, systematic study on the different kinds of point defects such as antisites, exchange of atoms, and vacancies, is crucial to the understanding of the composition and atomic order dependence of their properties.

In this work, the formation energies of different kinds of point defects: exchange of atoms, antisites (one type of atom occupies the sublattice of the other type), and vacancies in three Heusler alloy systems Ni-X-Ga (X=Mn, Fe, Co) have been calculated systematically. We also analyzed the variation in the magnetic structure when a point defect is introduced into an ideal crystal.

3.2.2 Computational method

The basic computational methods are the same as section 2.2.2.

The defect formation energy is estimated using following equations [5]:

$$\Delta H_f = \Delta E + n_{Ni}\mu_{Ni} + n_X\mu_X + n_{Ga}\mu_{Ga} \quad (3-1)$$

$$\Delta E_f = E_{def} - E_{id} + n_{Ni}\mu_{Ni}^0 + n_X\mu_X^0 + n_{Ga}\mu_{Ga}^0 \quad (3-2)$$

where ΔH_f and ΔE_f are the defect formation enthalpy and defect formation energy, respectively; E_{def} and E_{id} are the total energies of the defective and ideal unit cell, respectively; n_i is the number of atom of the type i which is transferred to or from a chemical reservoir; μ_i^0 is the corresponding chemical potential of the pure element; and μ_i is the chemical potential of each atom in the Ni_2XGa alloy, corresponds to the energy variation of an atom transfer to or from a chemical reservoir, which is not necessary in the solid ground state.

For the stoichiometric Ni_2XGa (X=Mn, Fe, Co) with cubic L2_1 structure (Space Group: $\text{Fm}\bar{3}\text{m}$, No. 225), Ni atoms occupy the (8c) sites: (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75), X atoms locate on the (4a) sites at (0, 0, 0) and Ga atoms occupy the (4b) sites: (0.5, 0.5, 0.5), as shown in Fig. 3-1 (a).

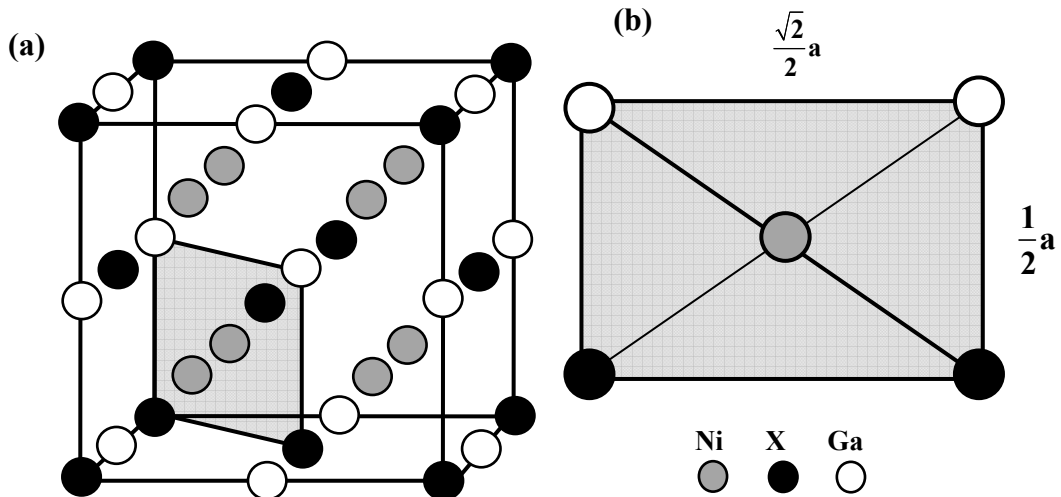


Fig. 3-1 (a) Geometric structure of cubic L2_1 Ni_2XGa , X denotes Mn, Fe, Co and (b) The rectangular cell in the (110) plane used to analyze the magnetic properties.

In order to investigate the variation in the magnetic moments around the point defects, we define a rectangle in the cubic structure. For that we choose the coordinates (0,0,0) and (0.5,0.5,0) of X atoms, (0,0,0.5) and (0.5,0.5,0.5) of Ga atoms as well as the (0.25,0.25,0.25) of the Ni atom to constitute a rectangle. We call it magnetic characteristic rectangle, as shown in Fig. 3-1 (b). Such a rectangle that allows displaying the variation in the magnetic moments at various point defects and their nearby atoms will be discussed in detail in section 3.2.3.2.

3.2.3 Results and discussion

3.2.3.1 Defect formation energy

In order to adjust the martensitic transformation temperature T_M and Curie temperature T_C to be suitable for practical application, we have to adjust the composition around the stoichiometric Ni_2XGa (X=Mn, Fe, Co). The process of the composition adjustment will be sure to generate a variety of point defects, such as excess atoms of one element occupying the sublattice of the deficient one (antisite), vacancies, or exchange of the neighbor atoms (exchange). The aim of calculating the defect formation energy is to estimate an order of defect stability in the parent phase.

The calculated formation energies of introducing different kinds of defects into ideal Ni_2XGa series X= Mn, Fe, Co, are given in Table 3-1 for a defect concentration of 6.25%. Since the calculations are based on the structure of parent cubic phase, so during the process of composition adjustment, the positive defect formation energy obtained means that such defect can make the cubic structure metastable, and therefore such material has a strong tendency to transform into a martensitic phase, corresponding martensitic transformation temperatures will increase. At this defect concentration, the negative defect formation energy means the type of defect can exist steadily in the initial cubic structure. At lower defect concentration (1.6 at.%), the same tendency is also observed.

As seen from Table 3-1, the Ga antisite on the X sublattice has the lowest formation energy in the investigated series, and the second lowest is the Ni antisite on the X sublattice. These two defects are more likely to form in the parent cubic phase during synthesizing process. Among all the antisite defects, the atomic substitutions on the Ga sublattice (Ni_{Ga} and X_{Ga}) correspond to the highest formation energy. Normally, from the experimental results, the Ni-rich or Mn-rich, Ga-deficient Ni-Mn-Ga alloys have higher MT temperatures than the stoichiometric one. Excess Ni and/or Mn components, and deficient Ga, are the usual composition designs for Ni-Mn-Ga alloy, due to the fact that they have appropriate martensitic transformation temperatures and Curie temperatures for practical applications. So maybe when these two kinds of defects (Ni_{Ga} and X_{Ga}) form in the alloy, the result is an instable austenitic phase, so they have strong tendency to transform to a stable martensitic one.

The formation energies of Ni and X vacancy are lowest in the Ni_2CoGa compound. The highest vacancy formation energies are obtained at the Ga sublattice as seen in Table 3-1. It is confirmed that the Ga atom is dominant for the stability of parent phase. In addition, some other types of defects are also energetically favorable, for instance the Ni-X exchange in Ni_2FeGa and Ni_2CoGa systems.

Table 3-1 Formation energies ΔE_f (in eV) of point defects in Ni_2XGa (X = Mn, Fe, Co).

Types of defects	exchange					antisite				vacancy		
	X-Ga	Ni-X	Ni-Ga	Ni_X	X_{Ni}	Ni_{Ga}	Ga_{Ni}	X_{Ga}	Ga_X	V_{Ni}	V_X	V_{Ga}
Ni_2MnGa	0.59	1.15	1.48	0.27	0.63	1.23	0.80	1.05	-0.24	0.93	1.17	2.55
Ni_2FeGa	0.54	-0.10	1.32	-0.18	-0.01	0.99	0.76	1.35	-0.67	0.81	0.72	2.23
Ni_2CoGa	0.22	-0.35	1.03	-0.48	0.06	1.16	0.25	1.37	-1.06	0.75	0.33	2.24

The degree of the atomic long-range order in the off-stoichiometric Ni_2MnGa shape memory alloys is of particular interest because it influences both the martensitic transformation temperature and the Curie temperature [6]. Furthermore, the site occupancy in the off-stoichiometric Ni_2MnGa is critical to the modulated structure of the martensite [7]. Therefore, fundamental knowledge of the site occupancy is essential to further understanding of the martensitic transformation behavior of the Ni_2MnGa based alloys. In most cases within our investigated series, the excess atoms of the rich component would occupy the site(s) of the deficient one(s), which is called “normal” site occupancy. However, we cannot rule out the other possibilities. It is very important to notice that the formation energies of Ga antisite at the X sublattice are all negative in the series (in Table 3-1). It means that when adjusting the composition of an alloy, this kind of defect forms in priority in order to reduce the total energy of the system under condition to keep the structure constant. We can deduce that in the Ga-rich X-deficient off-stoichiometric Ni_2XGa (X=Mn, Fe, Co) alloys, excess Ga atoms directly occupy the sites of the deficient X sublattice, forming the “normal” site occupation.

The point defect of Ga antisite at the Ni site can be formed in two ways (direct and indirect) in Ga-rich Ni deficient Ni-Mn-Ga alloy. The direct way is that the excess Ga atoms

directly occupy the sublattice of the deficient Ni sites. However, the formation energy of such Ga_{Ni} defect is quite high (as seen from Table 3-1). The indirect way is that the excess Ga atoms occupy the X sites (Ga_X) and the X atoms have to move to the free Ni sites (X_{Ni}), so that the result is the defect pair ($\text{Ga}_X + \text{X}_{\text{Ni}}$). From the energy point of view, the latter path is more favorable. For example in the Ni_2MnGa compound, without considering the interaction between defects, the energy of forming a ($\text{Ga}_{\text{Mn}} + \text{Mn}_{\text{Ni}}$) antisite defect pair is $(-0.24+0.63) = 0.39$ eV that is only half of the formation energy of the Ga_{Ni} defect in Ni_2MnGa (0.80 eV, as shown in Table 3-1). Therefore, the so called “indirect” site occupation is more common in the Ga-rich Ni-deficient alloys.

The site occupancy in off-stoichiometric Ni_2XGa alloys has rarely been addressed in the literature. Among the few publications, the excess Mn atoms occupy the sites of Ga sublattice in $\text{Ni}_2\text{Mn}_{1+x}\text{Ga}_{1-x}$ alloy [6]. The “normal” site occupation is favorable for most of the off-stoichiometric Ni_2MnGa [8], all in line with our theoretical prediction.

3.2.3.2 Magnetic structure of the defective Ni-X-Ga

In this part, we mainly analyze the magnetic moments of the most energetically favorable antisite-type defects. The atomic magnetic moments and the corresponding change rates in different types of antisite point defects in Ni-Mn-Ga alloys are listed in Table 3-2. The change rate of the atomic moment has been established using equations below:

$$\text{Change rate} = \frac{M_{\text{Ni/X}}(\text{defective}) - M_{\text{Ni/X}}(\text{ideal})}{M_{\text{Ni/X}}(\text{ideal})} \times 100\% \quad (3-3)$$

As seen from Table 3-2, The Ga atom only carries a small magnetic moment, so in the following discussion we will not consider its contribution. It can be seen from Table 3-2 that the range of variation in Ni moments is much larger than that of Mn when introducing an antisite defect into an ideal crystal. Therefore, we mainly focus on the change of Ni moments. In stoichiometric Ni_2MnGa , the magnetic moments of Ni and Mn are $0.36 \mu_B$ and $3.52 \mu_B$, respectively. When a Ni atom occupies a Ga site, namely creates a Ni antisite at Ga site, Ni_{Ga} , the magnetic moments of eight normal-Ni atoms ranges within $0.40\text{-}0.43 \mu_B$. The change rates of Ni atoms are from +11 to +19 % compared with the Ni moment in the stoichiometric alloy. The extra-Ni carries a very small magnetic moment of $0.11\mu_B$, only about one-third of

the normal value ($0.36 \mu_B$). After the relaxation, the optimized volume of one unit cell with a Ni_{Ga} antisite defect becomes smaller ($193.39 \text{ \AA}^3$) by about 1.15% as compared with the stoichiometric structure ($195.64 \text{ \AA}^3$). The atomic positions have changed as well and although the extra-Ni and normal-Ni remained unchanged, the Mn and Ga atoms have moved close to the center of the unit cell, resulting in the reduction of the unit cell volume. From the calculation results we can see, when a Ga is replaced by Ni atom, the distance between normal-Ni and its nearest Mn neighbor is $2.47 \sim 2.48 \text{ \AA}$, instead of $2.49 \text{ \AA}$ in the ideal structure. The distance becomes smaller, thus enhancing the interaction between 3d electrons of Ni and Mn, therefore the magnetic moments of normal-Ni atoms have increased. Oppositely the distance between extra-Ni and its nearest Mn neighbor is $2.86 \text{ \AA}$, much higher than $2.49 \text{ \AA}$, resulting in the weakened interaction of 3d electrons between extra-Ni and Mn. This is the reason for the sharp decrease of extra-Ni moment.

Table 3-2 Atomic magnetic moments and corresponding change rate
in different types of point defects in Ni-Mn-Ga alloy.

	Ni atomic moment (μ_B)		Change rate of Ni moment (%)		Mn atomic moment (μ_B)		Change rate of Mn moment (%)	
Pure	0.36				3.52			
Ni_2MnGa								
Ni_{Ga}	Ni_{Ni}	Ni_{Ga}	Ni_{Ni}	Ni_{Ga}	$3.46 \sim 3.54$		$-2 \sim +1$	
	$0.40 \sim 0.43$	0.11	$+11 \sim +19$	-69				
Ga_{Ni}	$0.29 \sim 0.34$		$-19 \sim -6$		$3.49 \sim 3.52$		$-1 \sim 0$	
Ni_{Mn}	Ni_{Ni}	Ni_{Mn}	Ni_{Ni}	Ni_{Mn}	$3.54 \sim 3.58$		$+1 \sim +2$	
	$0.31 \sim 0.34$	0.22	$-14 \sim -6$	-39				
Mn_{Ni}	$0.24 \sim 0.35$		$-33 \sim -3$		Mn_{Mn}	Mn_{Ni}	Mn_{Mn}	Mn_{Ni}
					$3.43 \sim 3.44$	-3.05	$-3 \sim -2$	-187
Mn_{Ga}	$0.46 \sim 0.49$		$+28 \sim +36$		Mn_{Mn}	Mn_{Ga}	Mn_{Mn}	Mn_{Ga}
					$3.52 \sim 3.58$	3.67	$0 \sim +2$	$+4$
Ga_{Mn}	0.26		-28		$3.53 \sim 3.58$		$0 \sim +2$	

In the situation of Ga_{Ni} , a Ga antisite on Ni site, the Ni moments range in the interval 0.29-0.34 μ_{B} , i.e. smaller than the stoichiometric ones, and the corresponding change rate is -5~ -19 %. In the depleted Ni alloy, the distance between the Ni atoms and their first neighbor Mn atoms increases from 2.49 to 2.51 Å, resulting in the weakened interaction between the 3d electrons of Ni and Mn, therefore the decreased Ni moments. It can be concluded that in Ni-Mn-Ga ferromagnetic shape memory alloy, the value of the Ni magnetic moment sensitively depends on the distance between Ni and Mn. The smaller the distance is, the larger the Ni magnetic moment will be.

The most interesting phenomenon is that in the cases of Mn rich antisite defects Mn_{Ni} and Mn_{Ga} , the moments of extra Mn atoms are totally different. The extra Mn moment in Mn_{Ni} defect is -3.05 μ_{B} , whereas that in Mn_{Ga} defect is 3.67 μ_{B} . This difference mainly arises from the distance between the extra Mn and its nearest Mn neighbor. In the case of Mn_{Ni} , this distance is 2.52 Å; whereas in the case of Mn_{Ga} , the distance is 2.91Å. Therefore, the magnetic moment of the excess Mn is parallel or anti-parallel to that of the normal Mn atoms, depending on the distance between them. When the distance between two adjacent Mn atoms is smaller than a certain threshold, the demagnetization effect will drive the magnetic moment of the extra Mn to be anti-parallel to those of Mn at the normal sites in order to achieve a magnetic balance.

To further investigate the charge distribution in Mn-excess antisites, the charge density distribution maps at isosurface 0.035 electron/Å³ are plotted in Fig. 3-2, gold color means electron gain, and blue electron loss. We can clearly see that when extra Mn occupies one Ni site, most of the free electrons gather around the extra Mn. But when the extra Mn occupies a Ga position, the charges are regularly distributed as in the perfect Ni_2MnGa : all the charges located between two neighboring Ni atoms function as a bridge.

For Ni-Fe-Ga and Ni-Co-Ga alloys, the effect of introducing an antisite defect on atomic moments located far away from the defect within a unit cell is roughly the same as that of Ni-Mn-Ga. Here we focus on the variation in magnetic moment of the point defect and its surrounding atoms, and express them within the magnetic characteristic rectangle in the (110) plane, as seen in Fig. 3-3 and Fig. 3-4. We note that a Mn atom changes its magnetic moment when it is located at the different sites in Ni-Mn-Ga alloy: it is 3.52, -3.05, 3.67 μ_{B} , at the

sublattice site of Mn, Ni, and Ga, respectively (Table 3-2), which we have already discussed in detail. Whereas in the Ni-Fe-Ga and Ni-Co-Ga alloys, the X atomic magnetic moment is 2.91, 2.20, 2.96 μ_B for Fe and 1.59, 1.50, 1.81 μ_B for Co, when it occupies the sublattice site of X, Ni, and Ga, as shown in Fig. 3-3 (a), (d), (e) and Fig. 3-4 (a), (d), (e), respectively. Obviously, the magnetic moments of the nearest Fe or Co are aligned parallel to each other for all the cases, as expected in a ferromagnetic domain. Furthermore, when X (X=Fe, Co) atom occupies the Ga-sublattice site, X_{Ga} , the magnetic moment of excess X atom is larger than that of the normal X atom. This may be due to the fact that the replacement of a non-magnetic Ga by a ferromagnetic X atom enhances the interaction between the 3d electrons of the extra X with its surrounding 8 Ni atoms.

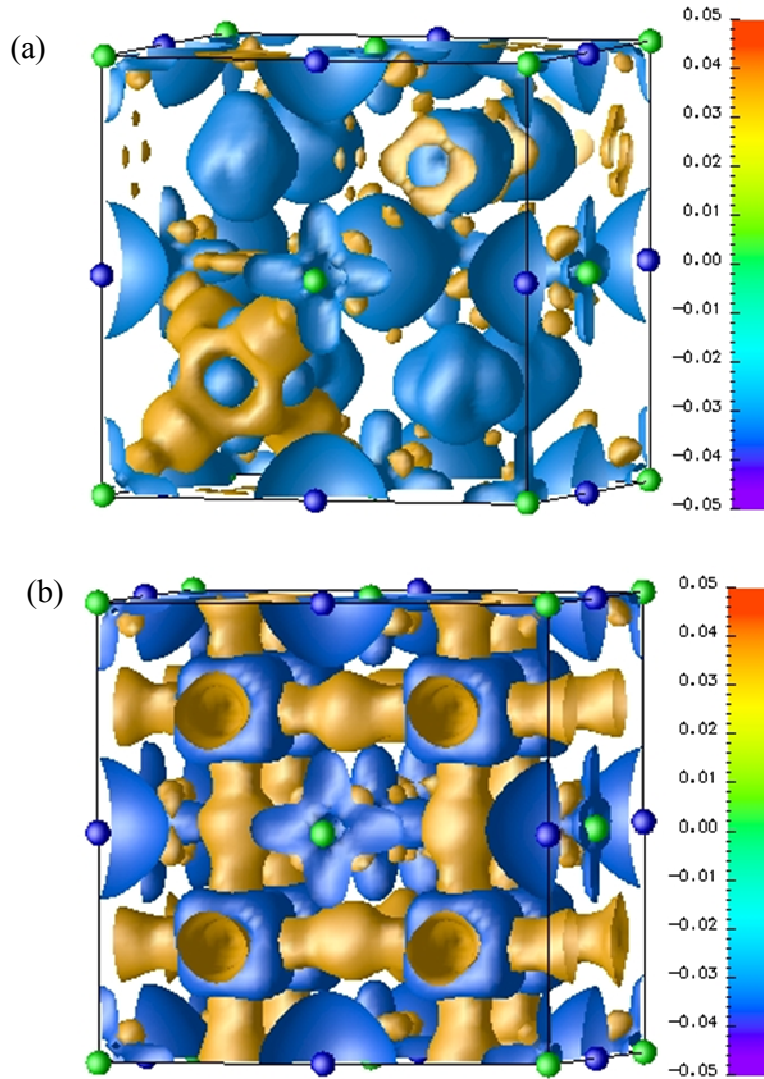


Fig. 3-2 Isosurface plots of the charge density at 0.035 electron/ $\text{\AA}^3$ in Mn rich antisite defects

(gold color means electron gain, and blue electron loss). (a) Mn_{Ni} and (b) Mn_{Ga} .

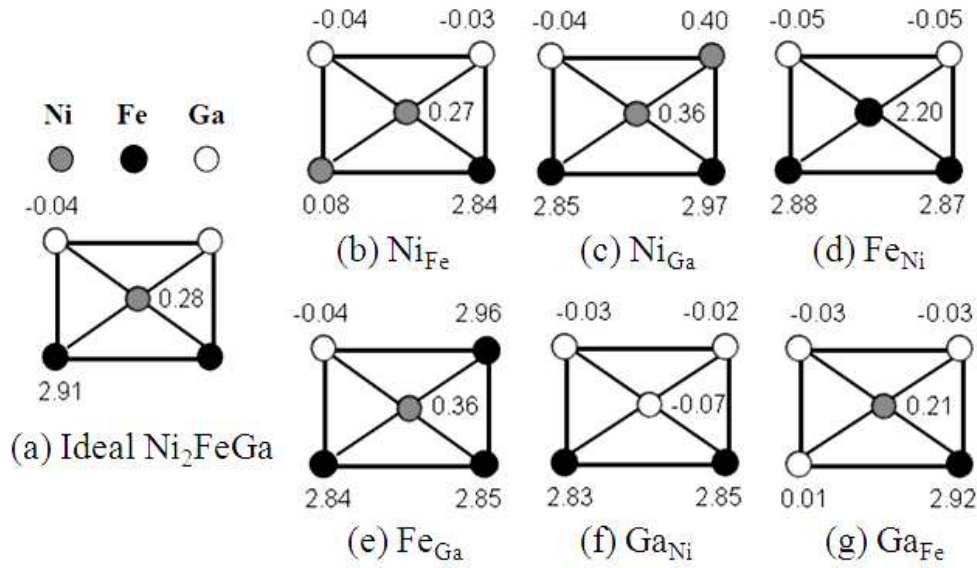


Fig. 3-3 Magnetic characteristic rectangle in the (110) plane of various antisite defects in Ni-Fe-Ga alloy (a) ideal Ni_2FeGa ; (b) Ni_{Fe} ; (c) Ni_{Ga} ; (d) Fe_{Ni} ; (e) Fe_{Ga} ; (f) Ga_{Ni} ; (g) Ga_{Fe} .

For Ni-Fe-Ga and Ni-Co-Ga alloys, the effect of introducing an antisite defect on atomic moments located far away from the defect within a unit cell is roughly the same as that of Ni-Mn-Ga. Here we focus on the variation in magnetic moment of the point defect and its surrounding atoms, and express them within the magnetic characteristic rectangle in the (110) plane, as seen in figure 3 and figure 4. We note that a Mn atom changes its magnetic moment when it is located at the different sites in Ni-Mn-Ga alloy: it is 3.52, -3.05, 3.67 μ_{B} , at the sublattice site of Mn, Ni, and Ga, respectively (Table 3-2), which we have already discussed in detail. Whereas in the Ni-Fe-Ga and Ni-Co-Ga alloys, the X atomic magnetic moment is 2.91, 2.20, 2.96 μ_{B} for Fe and 1.59, 1.50, 1.81 μ_{B} for Co, when it occupies the sublattice site of X, Ni, and Ga, as shown in Fig. 3-3 (a), (d), (e) and Fig. 3-4 (a), (d), (e), respectively. Obviously, the magnetic moments of the nearest Fe or Co are aligned parallel to each other for all the cases, as expected in a ferromagnetic domain. Furthermore, when X (X=Fe, Co) atom occupies the Ga-sublattice site, X_{Ga} , the magnetic moment of excess X atom is larger than that of the normal X atom. This may be due to the fact that the replacement of a

non-magnetic Ga by a ferromagnetic X atom enhances the interaction between the 3d electrons of the extra X with its surrounding 8 Ni atoms.

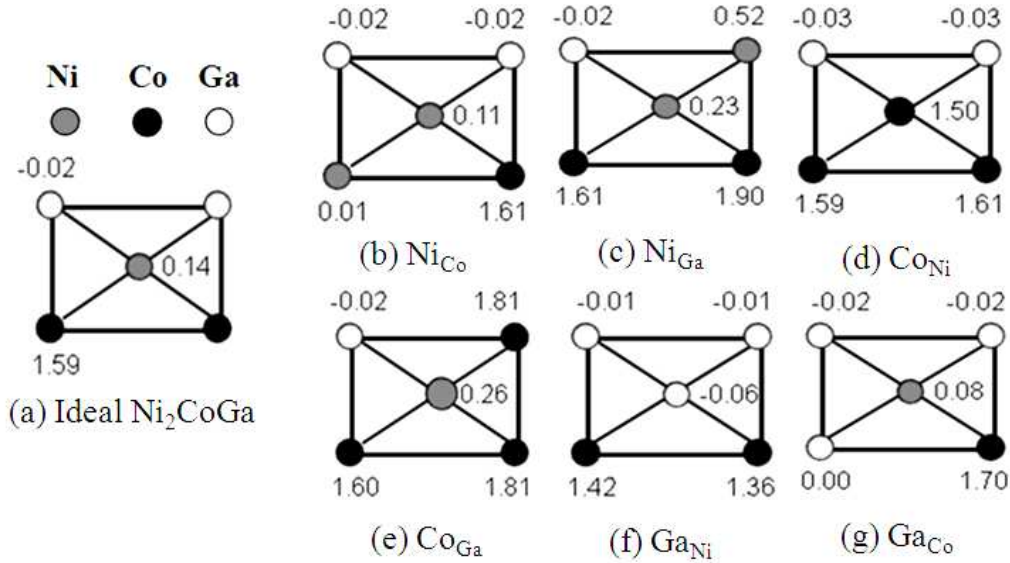


Fig. 3-4 Magnetic characteristic rectangle in the (110) plane of various antisite defects in Ni-Co-Ga alloy (a) Ideal Ni_2CoGa ; (b) Ni_{Co} ; (c) Ni_{Ga} ; (d) Co_{Ni} ; (e) Co_{Ga} ; (f) Ga_{Ni} ; (g) Ga_{Co} .

In Ni-Mn-Ga alloy, when a Ni atom occupies the sublattice site of Ni, Mn, Ga, its atomic magnetic moment is 0.36, 0.22 and $0.11\mu_{\text{B}}$, respectively (Table 3-2). It shows that the magnetic moment always decreases when extra Ni is located at the site of the sublattice of other elements. Compared with the Ni-Mn-Ga alloy, the situations for Ni-Fe-Ga and for Ni-Co-Ga alloys are different: the Ni atomic magnetic moment is 0.28, 0.08, $0.40\mu_{\text{B}}$ for Ni-Fe-Ga and that for Ni-Co-Ga is 0.14, 0.01, $0.52\mu_{\text{B}}$, when Ni occupies the sublattice site of the Ni, X, and Ga, as shown in Fig. 3-3 (a), (b), (c) and Fig. 3-4 (a), (b), (c), respectively. The magnetic moment of the extra Ni is close to 0 when a Ni atom occupies the X (X = Fe, Co) site; whereas it is much larger than the normal value when the extra-Ni atom occupies the Ga site.

In the Ga antisite defects, Ga_{Ni} and Ga_{X} , as shown in Fig. 3-3 (f), (g) and Fig. 3-4 (f), (g), the magnetic moments of extra-Ga are all almost zero, and such types of defects have little effect on the Ni and X atoms around the defects.

3.2.3.3 Conclusions

The formation energies of several different kinds of defects (atomic exchange, antisite and vacancy) and the variation in atomic magnetic moments in off-stoichiometric Ni_2XGa series (X= Mn, Fe, Co) are systematically calculated. The Ga and Ni antisites at the sites of the X sublattice have the lowest formation energies and the Ni and X antisites at the Ga sublattice sites have the highest formation energies. Therefore the Ga atoms stabilize the cubic structure, and the effect of X atoms on the structural stability is opposite. The information is of great importance to guide composition regulation during the fabrication process of these alloys. For the off-stoichiometric Ni_2XGa , in most cases the excess atoms of the rich component will directly occupy the site(s) of the deficient one(s) except in the Ga-rich Ni-deficient case. The excess Ga atoms occupy the X sites and the X atoms have to move to the free Ni sites. The magnitude of the variation in the Ni moments is much larger than that of Mn in the defective Ni_2XGa . The value of the Ni magnetic moment sensitively depends on the distance between Ni and X. The smaller the distance is, the larger the Ni moment will be. The magnetic moments of the excess Fe or Co in Ni-Fe-Ga and Ni-Co-Ga alloys are aligned parallel to each other whereas those of excess Mn could be aligned parallel or antiparallel depending on the distance between the neighboring Mn atoms.

3.3 Defect formation energy and magnetic structure of Ni-X-Ga (X= Mn, Fe and Co)

3.3.1 Introduction

Ferromagnetic shape memory alloys (FSMAs) have received much attention as high performance sensor and actuator materials, since a large magnetic-field-induced strain by the rearrangement of twin variants in the martensitic phase has been reported. Up to now, several FSMAs including Ni-Mn-Ga, Ni-Fe-Ga, Co-Ni-Ga, Fe-Pd, Ni-Mn-Al systems have been studied. Over the past decade, vast amount of knowledge accumulated on the properties of Ni-Mn-Ga Heusler alloys has enabled to foresee the possibility of employing these alloys in device applications. However, the actuation output stress level of the Ni-Mn-Ga alloy is only less than 5MPa, which represents a shortcoming of this alloy system. Recently, an unusual

type of FSMA Ni–Co–Mn–In Heusler alloy has been experimentally investigated [9]. It shows the martensitic transition from the ferromagnetic austenite phase to the antiferro- or paramagnetic martensitic phase and a magnetic-field-induced reverse martensitic transition (MFIRT), making it more attractive for practical application as magnetically driven actuator because it possesses a magnetostress level in the order of tens of MPa. An almost perfect shape memory effect associated with this phase transition is induced by a magnetic field and is called the metamagnetic shape memory effect. The Ni–Mn–In is the basic ternary alloy system of the Ni–Co–Mn–In alloy, and it shows the same metamagnetic shape memory effect as Ni-Co-Mn-In [10], accompanied by large magnetoresistance, magnetic superelasticity, and large reverse magnetocaloric effects (MCEs). The relationship of alloying composition—martensitic transformation temperature—crystal structure has been systematically studied by Thorsten Krenke et al. [11]. The effect of the atomic disorder in $\text{Ni}_{50}\text{Mn}_{36}\text{In}_{14}$ on martensitic transformation temperatures has been investigated [12]. The off-stoichiometry could be realized by introducing different kinds of defects into an ideal crystal. Therefore, systematic study on the different kinds of point defects such as antisites, exchange of atoms and vacancies, is crucial to the understanding of the dependence of their properties on composition and atomic order.

In the present work, the formation energies of different kinds of point defects: exchange of atoms, antisites (one type of atom occupies the sublattice of another type) and vacancies in three Heusler alloy systems Ni-X-In (X=Mn, Fe, Co) are calculated systematically for the first time. We also analyze the effect on the magnetic structure of a point defect introduced into the ideal crystal.

3.3.2 Computational method

The computational methods used in this section are the same as those in section 2.2.2 and section 3.2.2.

3.3.3 Results and discussion

3.3.3.1 Defect formation energy

In order to adjust that the martensitic transformation temperature T_M and the Curie temperature T_C are suitable for practical application, we have to adjust the composition around the stoichiometric Ni_2XIn . The process of the composition adjustment will surely generate a variety of point defects, such as excess atoms of one component occupying the sublattice of deficient one (antisite), vacancies, or exchange of neighboring atoms (exchange). The aim of calculating the defect formation energy is to estimate the stability of the defects in the parent phase.

The calculated formation energies of introducing different kinds of defects into ideal Ni_2XIn series $X= Mn, Fe$ and Co , are given in Table 3-3 for a defect concentration of 6.25%. Since the calculations are based on the structure of the parent cubic phase, during the process of composition adjustment, the positive defect formation energy obtained means that such defect can make the cubic structure metastable, therefore such a material has a strong tendency to transform into martensitic phase, and the corresponding martensitic transformation temperature will increase. At the same defect concentration, the negative defect formation energy means that this type of defect may exist steadily in the initial cubic structure. With lower defect concentration (1.6 at.%), the same tendency is also observed.

As seen from Table 3-3, the In antisite on the X sublattice (In_X) and the Ni antisite on the X sublattice (Ni_X) have the lowest formation energies in the investigated series. These two kinds of defects are most likely to form in the parent cubic phase during the synthesizing process. Among all the antisite defects, the In_{Ni} antisite possesses the highest formation energy. Normally, from the experimental evidence, the Mn-rich and the In-deficient Ni-Mn-In alloys are the usual composition designs, due to the fact that they have appropriate martensitic transformation temperatures and Curie temperatures for practical applications and the magnetic field drivable inverse martensitic transition. The Mn-rich, In-deficient composition will surely generate a lot of Mn antisities on the In sublattice (Mn_{In}) defects. From Table 3-3, the Mn_{In} defect has relatively low formation energy.

The formation energy of Ni vacancy (V_{Ni}) are lowest in the vacancy-type defects. The

highest vacancy formation energies are obtained at the In sublattice as seen in Table 3-3. It is confirmed that the In atom is dominant for the stability of the parent phase. In addition, some other types of defects are also energetically favorable, for instance the Ni-X exchange in Ni_2FeIn and Ni_2CoIn systems.

Table 3-3 Formation energies ΔE_f (in eV) of point defects in Ni_2XIn (X =Mn, Fe, Co).

Types of defects	exchange				antisite				vacancy			
	X-In	Ni-X	Ni-In	Ni _X	X _{Ni}	Ni _{In}	In _{Ni}	X _{In}	In _X	V _{Ni}	V _X	V _{In}
Ni_2MnIn	0.36	0.90	1.29	0.40	1.07	0.64	1.53	0.07	0.41	0.59	1.51	1.77
Ni_2FeIn	0.39	0.10	1.14	-0.13	0.15	0.39	1.46	0.49	-0.26	0.53	0.95	1.19
Ni_2CoIn	0.21	-0.26	0.74	-0.51	0.18	0.32	1.05	0.58	-0.54	0.29	0.55	0.73

The degree of the atomic long-range order in the off-stoichiometric Ni-Mn-In shape memory alloys is of particular interest because it influences both the martensitic transformation temperature and the Curie temperature¹⁷. Furthermore, the site occupancy in the off-stoichiometric Ni-Mn-In is critical to the modulated structure of the martensite. However, the site occupancy in off-stoichiometric Ni-X-In alloys has rarely been addressed in the literature. Therefore, fundamental knowledge of the site occupancy is essential to further understand the martensitic transformation behavior of the Ni_2MnIn based alloys.

In most cases in the present investigated series, the excess atoms of the rich component would occupy the site(s) of the deficient one(s), which is called “normal” site occupancy. However, we cannot rule out the other possibilities. It should be noted that the formation energies of the In antisite at the Ni sublattice (In_{Ni}) are extremely high whereas those of the In antisite at the X sublattice (In_X) are energetically favorable in the series (see Table 3-3). We make the hypothesis that the point defect of In antisite at the Ni site can be formed in two ways (direct and indirect) in In-rich Ni deficient Ni-Mn-In alloy. The direct way is that the excess In atoms directly occupy the sublattice of the deficient Ni sites. However, the formation energy of such In_{Ni} defect is quite high (as seen in Table 3-3). The indirect way is

that the excess In atoms occupy the X sites (In_X) and the X atoms have to move to the free nearby Ni sites (X_{Ni}), so that the final result should be the defect pair ($\text{In}_X + \text{X}_{\text{Ni}}$). From the energy point of view, the latter path is more favorable. We validate our assumption through ab-initio calculation, as the total energy of the direct path for each atom is -5.88eV whereas that of the indirect one is -5.90eV. Therefore, the so called “indirect” site occupation is more common in the In-rich Ni-deficient alloys than the direct one.

3.3.3.2 Magnetic structure of the defective Ni-X-In

In this part, we mainly analyze the magnetic moments of the most energetically favorable antisite-type defects. The atomic magnetic moments and the corresponding change rates in different types of antisite defects in Ni-Mn-In alloys are listed in Table 3-4. The change rates of the atomic moments of Ni (respectively Mn) have been established using eq. (3-3).

The In atom only carries a small magnetic moment, so in the following discussion we will not consider its contribution. It can be seen from Table 3-4 that the variation range of Ni moments is much larger than that of Mn when introducing an antisite defect into an ideal crystal. Therefore, we mainly focus on the change of Ni moments. In stoichiometric Ni_2MnIn , the magnetic moments of Ni and Mn are $0.33\mu_B$ and $3.67\mu_B$, respectively. When a Ni atom occupies an In site, namely creates a Ni antisite at the In sublattice, Ni_{In} , the magnetic moments of eight normal-Ni atoms range within $0.38\sim 0.41\mu_B$. The change rates of Ni atoms are from +15 to +24 % compared with that of the Ni moment in the stoichiometric alloy. The extra-Ni carries a smaller magnetic moment of $0.28\mu_B$, and the corresponding change rate is -15%. After the relaxation, the optimized volume of the unit cell with a Ni_{In} antisite defect becomes smaller ($211.90\text{\AA}^3$) by about 3.62% as compared with the stoichiometric structure ($219.85\text{\AA}^3$). The atomic positions have changed as well: the normal-Ni atoms have moved towards the center of the unit cell (extra-Ni), resulting in the reduction of the unit cell volume. From the calculation results, when a In is replaced by Ni atom, the distance between the normal-Ni and its nearest Mn neighbor is $2.55\text{\AA}$, instead of $2.61\text{\AA}$ in the ideal structure. The distance becomes smaller, thus enhances the interaction between the 3d electrons of Ni and Mn, which increases the magnetic moments of the normal-Ni atoms. On the contrary, the

distance between extra-Ni and its nearest Mn neighbor is 2.98Å, much larger than 2.61Å, resulting in the weakened interaction of 3d electrons between extra-Ni and Mn. This is the origin of the sharp decrease of the extra-Ni moment.

In the situation of In_{Ni} , an In antisite on Ni site, the Ni moments range in the interval 0.26 ~ 0.33 μ_{B} , they are smaller than the stoichiometric one, and the corresponding change rate is within the range -21 ~ 0 %. In the depleted Ni alloy, the distance between the Ni atoms and their first Mn neighbor atoms increases from 2.61 to 2.63Å, resulting in the weakened

Table 3-4 Atomic magnetic moments and corresponding change rate in different types of antisite defects in Ni-Mn-In alloy.

	Ni atomic moment (μ_{B})		Change rate of Ni moment (%)		Mn atomic moment (μ_{B})		Change rate of Mn moment (%)	
Pure Ni_2MnIn	0.33				3.67			
Ni_{In}	Ni_{Ni}	Ni_{In}	Ni_{Ni}	Ni_{In}	3.58 ~ 3.74		-2 ~ +2	
	0.38~0.41	0.28	+15~+24	-15				
In_{Ni}	0.26 ~ 0.33		-21 ~ 0		3.66 ~ 3.69		0 ~ +1	
Ni_{Mn}	Ni_{Ni}	Ni_{Mn}	Ni_{Ni}	Ni_{Mn}	3.68 ~ 3.72		0 ~ +1	
	0.29~0.31	0.19	-12 ~ -6	-42				
Mn_{Ni}	0.26 ~ 0.41		-21 ~ +24		Mn_{Mn}	Mn_{Ni}	Mn_{Mn}	Mn_{Ni}
					3.55~3.60	0.98	-3 ~ -2	-73
Mn_{In}	0.45 ~ 0.47		+36 ~ +42		Mn_{Mn}	Mn_{In}	Mn_{Mn}	Mn_{In}
					3.59 ~ 3.84	3.62	-2 ~ +5	-1
In_{Mn}	0.23		-30		3.70 ~ 3.71		+1	

interaction between the 3d electrons of Ni and Mn, therefore the decreased Ni moments. It can be concluded that in Ni-Mn-In ferromagnetic shape memory alloy, the value of the Ni magnetic moment sensitively depends on the distance between Ni and Mn. The smaller the distance is, the larger the Ni magnetic moment will be.

The most interesting phenomenon is that in the cases of Mn rich antisite defects Mn_{Ni}

and Mn_{In} , the moments of the extra Mn atoms are totally different. The extra Mn moment in the Mn_{Ni} defect is $0.98\mu_{\text{B}}$, whereas that in the Mn_{In} defect is $3.62\mu_{\text{B}}$. In order to clarify the origin of the difference of extra-Mn moment in Mn-excess antisites, the charge density maps at the isosurface $0.03 \text{ electron}/\text{\AA}^3$ are plotted in Fig. 3-5, where gold color means electron gain, and blue electron loss. We can clearly see that when the extra Mn occupies a Ni site, most of the free electrons gather around the extra Mn. But when the extra Mn occupies an In position, the charges are regularly distributed between Ni and Mn atoms.

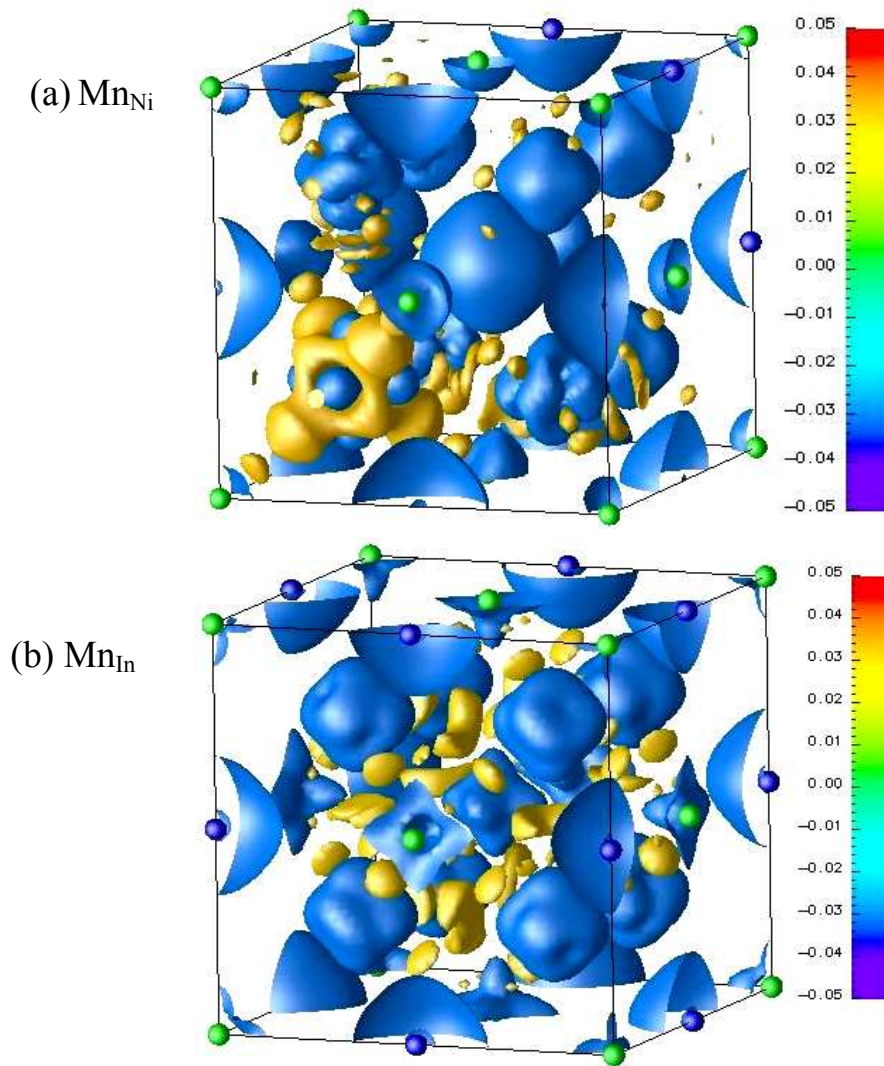


Fig. 3-5 Isosurface plots of the charge density at $0.03 \text{ electron}/\text{\AA}^3$ in Mn rich antisite defects (gold color means electron gain, and blue electron loss). (a) Mn_{Ni} and (b) Mn_{In} .

For Ni-Fe-In and Ni-Co-In alloys, the effect of the introduction of an antisite defect on the atomic moments located far away from the defect within a unit cell is roughly the same as

that observed for Ni-Mn-In. Here we focus on the variation in magnetic moment of the point defect and its surrounding atoms, and express them within the magnetic characteristic rectangular cell in the (110) plane, as seen in Fig. 3-6 and Fig. 3-7. We note that a Mn atom changes its magnetic moment when it is located at different sites in Ni-Mn-In alloy: it is 3.67, 0.98 and 3.62 μ_B , at the sublattice site of Mn, Ni, and In, respectively (Table 3-4), which we have already discussed in detail. In the Ni-Fe-In and Ni-Co-In alloys, the X atomic magnetic moment is 3.00, 2.97 and 3.00 μ_B for Fe and 1.68, 1.57 and 1.83 μ_B for Co, when it occupies the sublattice site of X, Ni, and In, as shown in Fig. 3-6 (a), (d), (e) and Fig. 3-7 (a), (d), (e), respectively. Obviously, the magnetic moments of the nearest Fe or Co are aligned parallel to each other in all the cases, as expected in a ferromagnetic domain. Furthermore, when X (X=Fe and Co) atom occupies the In-sublattice site, X_{In} , the magnetic moment of excess X atom is larger than that of the X_{Ni} in each case. This may be due to the fact that the replacement of a non-magnetic In by a ferromagnetic X atom enhances the interaction between the 3d electrons of the extra X with its 8 neighboring Ni atoms.

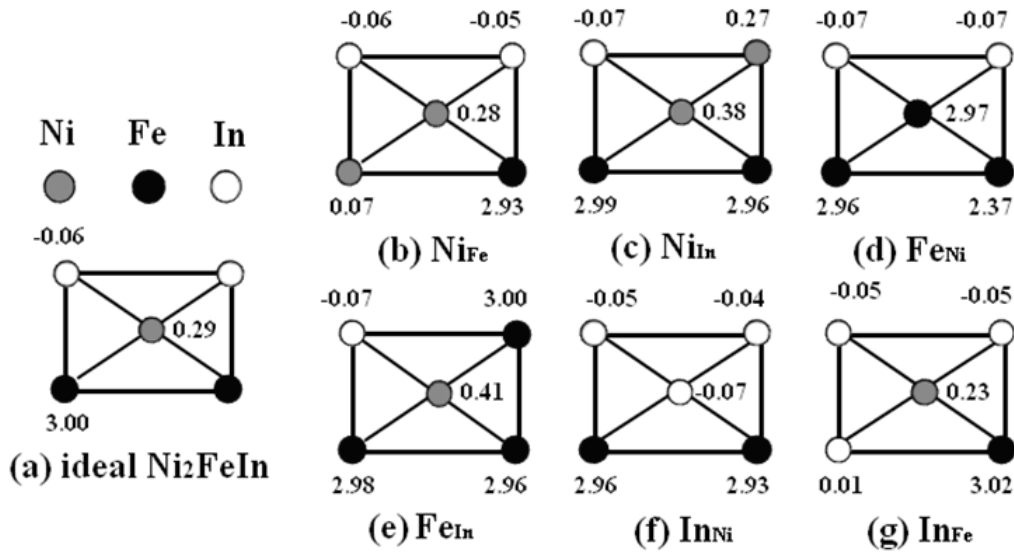


Fig. 3-6 Magnetic characteristic rectangular cell in the (110) plane of various antisite defects in Ni-Fe-In alloy (a) ideal Ni_2FeIn ; (b) Ni_{Fe} ; (c) Ni_{In} ; (d) Fe_{Ni} ; (e) Fe_{In} ; (f) In_{Ni} ; (g) In_{Fe} .

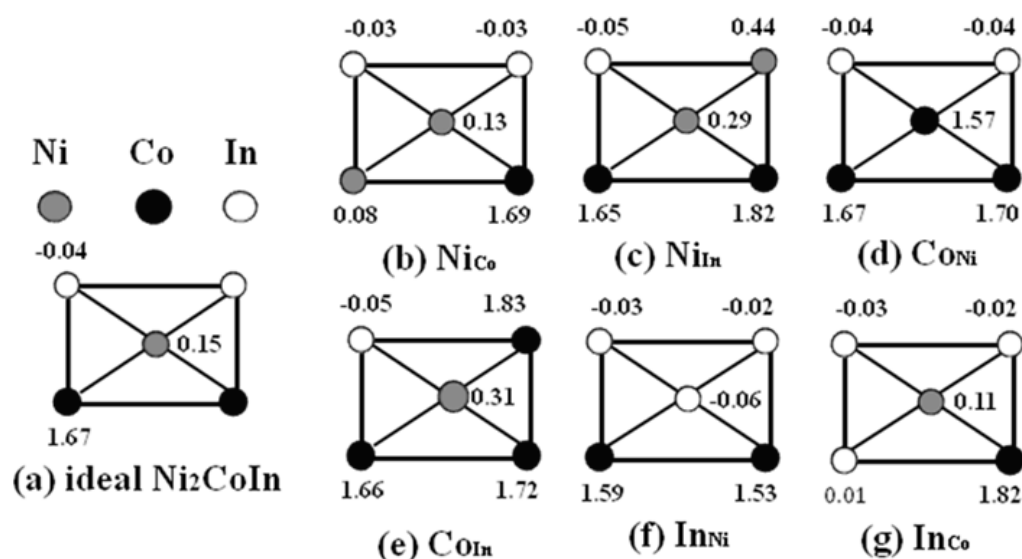


Fig.3-7 Magnetic characteristic rectangular cell in the (110) plane of various antisite defects in Ni-Co-In alloy (a) ideal Ni_2CoIn ; (b) Ni_{Co} ; (c) Ni_{In} ; (d) Co_{Ni} ; (e) Co_{In} ; (f) In_{Ni} ; (g) In_{Co} .

In Ni-Mn-In alloy, when a Ni atom occupies the sublattice site of Ni, Mn and In, its atomic magnetic moment is 0.33, 0.19 and $0.28\mu_B$, respectively (Table 3-4). It shows that the magnetic moment always decreases when extra Ni is located at the site of the sublattice of another element. Compared with the Ni-Mn-In alloy, the situations for Ni-Fe-In and for Ni-Co-In alloys are different: the Ni atomic magnetic moment is 0.29, 0.07 and $0.27\mu_B$ for Ni-Fe-In and 0.15, 0.08 and $0.44\mu_B$ for Ni-Co-In, when Ni occupies the sublattice site of Ni, X, and In, as shown in Fig. 3-6 (a), (b), (c) and Fig. 3-7 (a), (b), (c), respectively. The magnetic moment of the extra Ni is close to 0 when a Ni atom occupies the X (X = Fe, Co) site.

In the Indium antisite defects, In_{Ni} and In_{X} , as shown in Fig. 3-6 (f), (g) and Fig. 3-7 (f), (g), the magnetic moments of extra-In are all almost zero, and such types of defects have little effect on the Ni and X atomic magnetic moments around the defects.

3.3.3.3 Conclusions

The formation energies of several different kinds of defects (atomic exchange, antisite and vacancy) and the variation in atomic magnetic moments in off-stoichiometric Ni_2XIn ferromagnetic shape memory alloys were systematically calculated for the first time. The In and Ni antisites at the site of the X sublattice have the comparable low formation energies.

This information is of great importance to guide composition regulation during the fabrication process of these alloys. For the off-stoichiometric Ni_2XIn , in most cases the excess atoms of the rich component will directly occupy the site(s) of the deficient one(s) except in the In-rich Ni-deficient case. The excess In atoms occupy the X sites and the X atoms have to move to the free Ni sites. The magnitude of the variation in the Ni moments is much larger than that of Mn in the defective Ni_2XIn . The value of the Ni magnetic moment sensitively depends on the distance between Ni and X. The smaller the distance is, the larger the Ni moment will be.

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Chapter 4 Effects of alloying element Co on Ni-Mn-Ga ferromagnetic shape memory alloys from first-principles calculations

4.1 Outline

Although Ni-Mn-Ga FSMA have demonstrated superior MSME, they also have some intrinsic problems for their use in industrial applications, such as brittleness and low Curie temperature. Addition of other elements is a classical way to modify the properties of a given alloy and it has been demonstrated that alloying with a fourth element is indeed efficient in improving certain properties of Ni-Mn-Ga alloys.

From the viewpoint of practical applications, the Ni-Mn-Ga FSMA should have high martensitic transformation temperature and high Curie temperature. Due to the sensitivity of martensitic transformation temperature to the concentrations of Ni, Mn and Ga, high martensitic transformation temperature can be realized by composition design. Nevertheless, the Curie temperature of Ni-Mn-Ga alloys is not sensitive to their concentrations. Thus, the addition of a fourth element is needed to increase the Curie temperature of the Ni-Mn-Ga FSMA.

This chapter aims to study the effect of alloying element Co on Ni-Mn-Ga ferromagnetic shape memory alloys. The influence of Co addition on crystal structure, magnetic property, formation energy and Curie temperature is systematically investigated. It will be demonstrated that added Co preferentially occupies the Ni sites in Ni_2MnGa alloy; the change in crystal structure with the increase of the Co content; the difference in the magnetic properties will be explained from the electronic density of states analysis. The aim of this paper is to provide theoretical guidance for the development of new promising ferromagnetic shape memory alloys with optimized properties

4.2 Introduction

Ni-Mn-Ga ferromagnetic shape memory alloys with chemical composition close to the stoichiometric compound Ni_2MnGa have attracted great attention during the past decade, due to the large magnetic shape memory effect that originates from the rearrangement of

martensitic variants under an external magnetic field [1, 2]. The large magnetic-field-induced strain has been observed in the ferromagnetic state at temperatures below the martensitic transformation temperature. From the application point of view, high martensitic transformation temperature and high Curie temperature are very important. It has been found that a high martensitic transformation temperature in the Ni–Mn–Ga alloys could be achieved by composition adjustment [3-5], as the martensitic transformation temperature is very sensitive to the chemical composition. In contrast, the Curie temperature (T_C) of these alloys is less composition dependent and has a value around 370K for a wide range of composition [3, 6]. So far, great efforts have been devoted to alloying the ternary alloys with a fourth element to increase T_C . Recent investigations [7-11] show that the substitution of Co for Ni is an effective way to increase T_C , which leads to a slight decrease in the martensitic transformation temperature. As we know, the alloying elements influence both the crystal and electronic structures and hence the stability of the austenite and the martensite. Therefore, knowledge of the effects of Co addition is of great importance for understanding the composition dependence of T_C and the variation in the stability of the austenite phase. Actually, full information on the effect of Co on various physical properties of Ni–Mn–Ga–Co alloys with a broad range of Co addition is of great value for materials design.

The purpose of the present work is to explore the effect of Co addition on the crystal structure, the Curie temperature and the electronic structures in the $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ ($x=0, 0.5, 1, 1.5$ and 2) ferromagnetic shape memory alloys by first principles calculations, aiming at providing the theoretical data and directions for developing high performance FSMAs in this alloy system. These alloys are denoted by X0, X0.5, X1, X1.5 and X2, respectively. According to the calculated formation energy, we determine the preferential occupation site of Co atom and the effect on the phase stability. The difference between the total energies of the paramagnetic and the ferromagnetic austenite is also calculated. The correlation between this total energy difference and the Curie temperature is established. The electronic density of states is analyzed to elucidate the evolution of the magnetic properties with the increase of the Co content. Such calculations on Ni-Mn-Ga-Co ferromagnetic shape memory alloys are performed for the first time, aiming at providing the theoretical data and directions for developing high performance FSMAs in this alloy system.

4.3 Computational method

The computational methods used in this chapter are the same as those in section 2.2.2.

4.4 Results and discussion

4.4.1 Site preference of Co and equilibrium lattice parameters

The formation energies of the ferromagnetic austenite are calculated in order to study the site preference of the Co addition in the $\text{Ni}_8\text{Mn}_4\text{Ga}_4$ alloy. The formation energy E_{form} is a measure of the phase stability in solid states. We substitute one atom of the $\text{Ni}_8\text{Mn}_4\text{Ga}_4$ unit cell with one Co atom, which is corresponding to 6.25% of the Co atomic weight. The Co atom may have three possible sites: Ni site, Mn site and Ga site. For the 8 Ni atoms, their positions are equivalent by symmetry, whereas for the Mn and Ga atoms, there are two distinct sites, respectively: Mn I (0, 0, 0) and Mn II (0.5, 0.5, 0); Ga I (0.5, 0.5, 0.5) and Ga II (0.5, 0, 0), see Fig.4-1 (a).

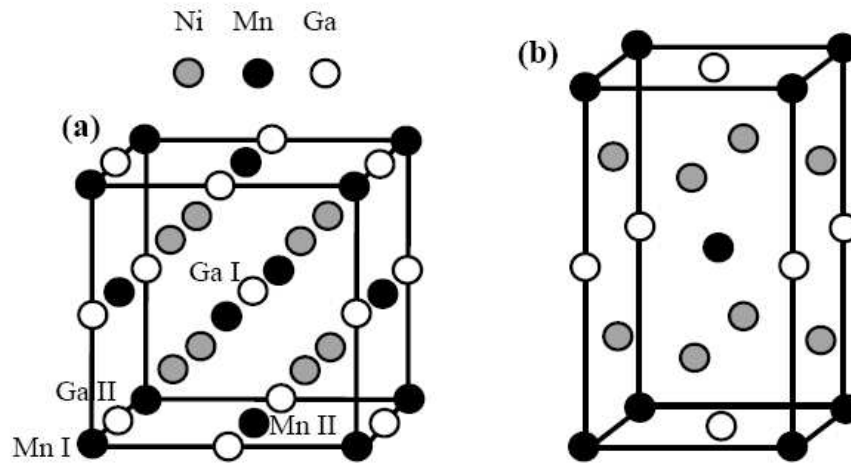


Fig. 4-1 Crystal structures of Ni_2MnGa (a) Heusler (L2_1) austenite; (b) tetragonal non-modulated martensite.

For the different possible sites of the added Co, the formation energies are different. From our calculation results, if the Co atom occupies the Ni, Mn and Ga site, the formation energy is -0.36 eV, -0.32 eV, and -0.25 eV per atom, respectively. It is known that the lowest formation energy corresponds to the preferred site occupancy. Therefore, the formation energy results indicate that the Co atoms prefer to occupy the Ni sites in the Ni_2MnGa .

Table 4-1 Equilibrium lattice parameters and magnetic moments of the ferromagnetic austenite and tetragonal martensite for $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ ($x=0, 0.5, 1, 1.5$ and 2) alloys. Cubic (Cub.) and tetragonal (Tet.) refer to the parent and the martensite phases, respectively.

x		a (Å)	c (Å)	c/a	Magnetic moment (μ_B)
0	Cub.	5.805			4.224
	Tet.	3.853	6.633	1.724	4.280
0.5	Cub.	5.803			4.331
	Tet.	3.851	6.579	1.702	4.309
1	Cub.	5.799			4.436
	Tet.	3.863	6.512	1.685	4.343
1.5	Cub.	5.796			4.534
	Tet.	3.927	6.300	1.604	4.538
2	Cub.	5.793			4.637
	Tet.	4.072	5.855	1.515	4.620

For both the austenite and martensite phases, the calculated equilibrium lattice parameters and total magnetic moments are shown in Table 4-1. In general, with the increase of the Co content, the optimized lattice parameters of the parent phase decrease regularly; whereas for the martensite, the lattice parameter a increases and c decreases, thus leading to a decrease of the c/a ratio. The total magnetic moment increases with the Co content for both phases, mainly because the ferromagnetism of Co is stronger than that of Ni (this will be discussed further in Section 4.4.3). It is very interesting to notice that many experimental observations [7-11] demonstrate that the substitution of Ni by Co results in a decrease in electron concentration e/a and a decrease in martensitic transformation temperature (T_m). Jin *et al.*[12] established an empirical linear relation between T_m and e/a . According to our calculation results, the decrease of the-tetragonality c/a ratio may contribute to the decrease of T_m with the increase of the Co content.

4.4.2 Effect of Co addition on phase stability of the paramagnetic and ferromagnetic austenite and Curie transition

In order to investigate the effect of the substitution of Ni by Co on the phase stability, the formation energies (E_{form}) of both the paramagnetic and ferromagnetic austenite of the $Ni_{8-x}Mn_4Ga_4Co_x$ ($x=0, 0.5, 1, 1.5$ and 2) alloys are calculated. The formation energy is defined as the total energy of the compound minus the total energies of the related pure elements in the reference bulk state [20, 21]. All these energies are normalized by the number of the atoms.

$$E_{form} = E_{tot}(Ni_{8-x}Mn_4Ga_4Co_x) - (8-x)E_{tot}^0(Ni)/16 - 4E_{tot}^0(Mn)/16 - 4E_{tot}^0(Ga)/16 - xE_{tot}^0(Co)/16 \quad (4-1)$$

Here $E_{tot}(Ni_{8-x}Mn_4Ga_4Co_x)$ is the total energy per atom of the $Ni_{8-x}Mn_4Ga_4Co_x$ unit cell; $E_{tot}^0(Ni)$, $E_{tot}^0(Mn)$, $E_{tot}^0(Ga)$ and $E_{tot}^0(Co)$ are the total energy per atom of the pure Ni, Mn, Ga and Co unit cell in their reference states, respectively.

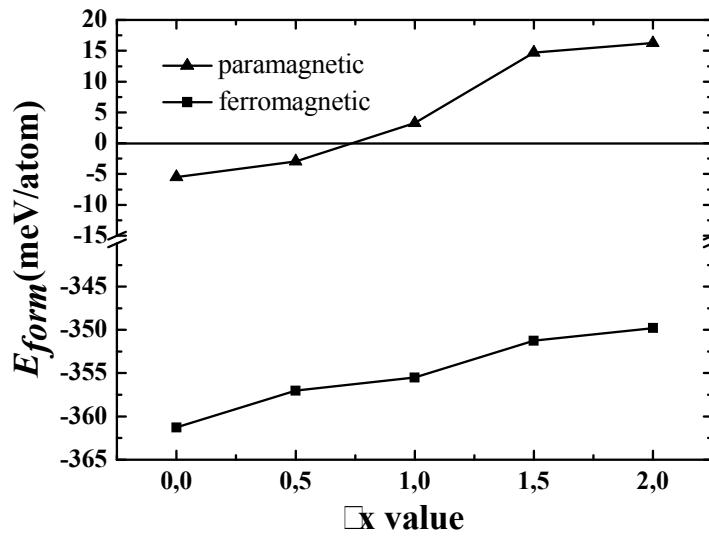


Fig. 4-2 Formation energies of the paramagnetic and ferromagnetic austenite of the $Ni_{8-x}Mn_4Ga_4Co_x$ ($x=0, 0.5, 1, 1.5$ and 2) alloys.

The calculated E_{form} of the paramagnetic and ferromagnetic austenite of the $Ni_{8-x}Mn_4Ga_4Co_x$ ($x=0, 0.5, 1, 1.5$ and 2) alloys are displayed in Fig. 4-2. It is seen that the formation energy of the paramagnetic austenite is much higher than the ferromagnetic one at

all the compositions studied, which is consistent with the fact that the paramagnetic austenite is the high temperature phase. The ferromagnetic austenite is more stable than the paramagnetic one, and the critical temperature between them is the so-called Curie Temperature (T_C). The phases become instable in both paramagnetic and ferromagnetic states when Ni is substituted by Co because the E_{form} gradually increase with the amount of Co.

According to the stoner theory [15-16], the total energy difference between the paramagnetic and the ferromagnetic state (ΔE_{tot}), can give an estimate of T_C [17]. According to the Heisenberg model and the molecular field theory, the link between ΔE_{tot} and T_C is given by:

$$\Delta E_{tot} = -k_b T_C \xi \quad (4-2)$$

where ξ represents the ratio M/M_0 of the magnetic moment M at $T \neq 0K$ and the equilibrium magnetic moment M_0 at $T=0K$. Velikokhatny and Naumov [18] have noted in Ni_2MnGa a scale factor of about ten between the predicted and experimental T_C values, 3943K and 380K respectively. In fact, the Stoner theory cannot be applied to describe high-temperature magnetic properties. Indeed, in the Stoner theory all magnetic moments vanish above T_C . Nevertheless, Chakrabarti *et al.* [19] noted that it is possible to obtain T_C by using a scale factor obtained from the experimental value of pure material and predict the relative variation of T_C with doping concentration. Recently, Brown *et al.* [20] determined by neutron diffraction a T_C value of 365K for Ni_2MnGa . With the reference value of T_C equal to 365K for X0, we can estimate the scale factor and predict the value of T_C to be 368K for X1 and 376K for X2. However, these predicted T_C values are lower than the experimentally determined values.

The average magnetization of a system becomes zero above T_C , while localized spin moments and elementary excitations in the form of spin waves can exist and contribute to T_C . [15, 16] Even so, only from the total energy difference results, we can still draw the conclusion that T_C increases with the Co content, which is in fair agreement with the experimental observations [7-11].

4.4.3 Effect of the Co addition on electronic density of states

To further investigate the effect of the Co addition on the electronic structure and the magnetic properties, the spin-resolved density of states (DOS) for X0, X1 and X2 alloys, are computed at their equilibrium lattice constants, as well as optimized internal parameters by the tetrahedron method with Blöchl corrections [21], see Fig.4-3.

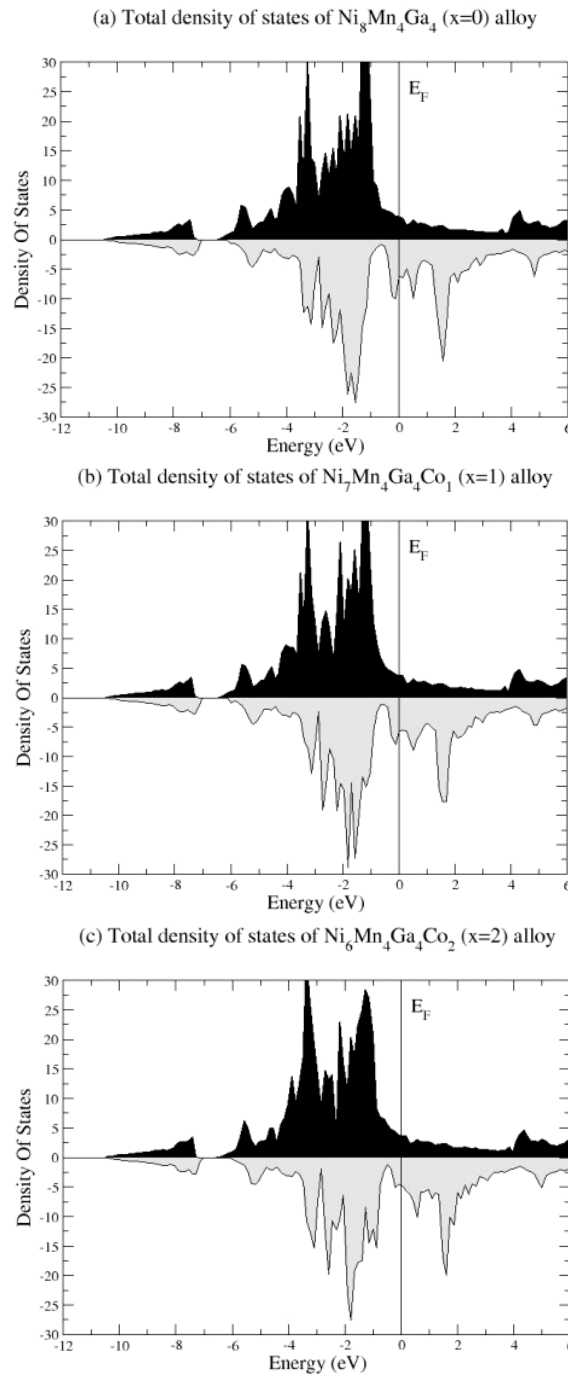


Fig. 4-3 Calculated spin-resolved total density of states for (a) X0, (b) X1 and (c) X2 alloys.

As seen in Fig.4-3 (a)-(c), with the increase of Co content, the down-spin electron DOS around the Fermi level (mainly at -0.2eV) gradually decreases, whereas those of the up spin remain almost unchanged. This gives rise to the enhancement of the total magnetic moments in these alloys. The total magnetic moments are 4.224, 4.436 and 4.637 μ_B for X0, X1 and X2 alloys, respectively (as shown in Table4-1).

Fig. 4-4 shows the spin-resolved partial density of states (pDOS) of the X1 alloy as an example of the Ni-Mn-Ga-Co alloys. The 3d states of Ni, Mn and Co are shown separately. It is seen that the pDOS is dominated by the bonding effect of the Ni, Mn and Co 3d up-spin states, which is localized between -5eV and the Fermi level. The 3d up-spin states of the Ni and Co atoms are similar (the peaks are in the same positions). This effect is a consequence of the hybridization of the electronic level between Ni and Co atoms. From the second panel of Fig. 4-4, the 3d down spin states of Mn dominates the antibonding region above the Fermi level with a peak at 1.8 eV.

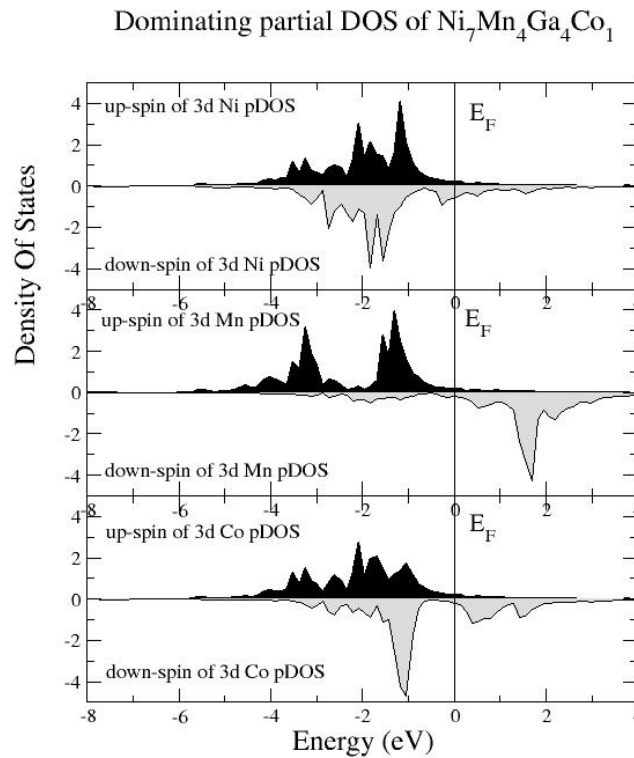


Fig. 4-4 Calculated spin-resolved partial density of states for the X1 alloy.

4.5 Conclusions

Our first principles calculations on total energy differences and electron structures of the $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ ($x=0, 0.5, 1, 1.5$ and 2) ferromagnetic shape memory alloys allow us to draw the following conclusions. The added Co atoms preferentially occupy the Ni site. With the increase of the Co content, the optimized lattice parameters for the parent phase decrease, whereas for the martensite phase, the lattice parameter a increases and c decreases, thus leading to a decrease of the tetragonality c/a ratio. The formation energy result indicates a structural instability when Ni is replaced by Co. The total energy difference between paramagnetic and ferromagnetic austenite indicates the increase of T_c with the Co content. The down spin total DOS around the Fermi level gradually decrease, whereas those of the up spin part remains almost unchanged. This gives rise to the enhancement of the total magnetic moment of these alloys. The hybridization between the Ni and Co pDOS dominates the bonding region below the Fermi level, and the Mn pDOS governs the antibonding region above the Fermi level.

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Chapter 5 Conclusions and perspectives

From the above theoretical simulations and calculations, the following important conclusions can be drawn:

Investigation on crystal, magnetic and electronic structures of ferromagnetic shape memory alloys Ni_2XY ($X=Mn, Fe, Co$; $Y=Ga, In$) by first-principles calculations

The optimized structural parameters, the total and partial magnetic moment, the formation energy, the density of states and the charge distribution of the cubic phase of the stoichiometric Ni_2XY ($X= Mn, Fe, Co$; $Y= Ga, In$), and the effect of the tetragonal c/a ratio on the total energy and the magnetic properties in Ni_2XY have been systematically calculated.

The results show that the lattice parameters, atomic separations, total and partial magnetic moments decrease gradually with the increase of the atomic number of X ; whereas the bulk modulus displays an opposite tendency. The calculated formation energies of the three cubic systems show a destabilization of the cubic structure if Mn atom is substituted by Fe or Co .

During the tetragonal deformation of the Ni_2XGa alloys, for the stoichiometric Ni_2MnGa , Ni_2FeGa and Ni_2CoGa compounds, the first local minimum is $c/a= 1, 0.91$ and 0.86 , and the second local minimum is $c/a= 1.25, 1.25$ and 1.37 respectively. Whereas in the Ni_2XIn alloys, only one energy minimum appears at $c/a= 1.00$ for the stoichiometric Ni_2MnIn and Ni_2FeIn , whereas two energy minima appear at $c/a=0.88$ and $c/a=1.36$, and a local maximum at $c/a = 1.00$ for Ni_2CoIn .

The investigation of the variation of the total magnetic moment with the tetragonal c/a ratio can effectively predict the change of the magnetic moment during the tetragonal martensitic transition. In Ni_2XGa alloy series, the shape of the total magnetic moment curve with the c/a ratio variation is normally given by the Ni atom, but not for Ni_2FeGa . The situation for Ni_2XIn alloy series is similar.

From Ni_2MnY to Ni_2CoY , the down spin total DOS at the Fermi level is gradually increasing, whereas those of the up spin part remains almost unchanged, which is the essential difference of the magnetic moment in these alloys. The partial DOS is dominated by

the Ni and Mn 3d states in the bonding region below E_F . The down spin Mn 3d states dominate the antibonding region above E_F with the peak around 1.8 eV. In the Ni_2XGa alloy series, the strong bond between the Ni atoms in the Ni_2MnGa is replaced by the bond between Ni and X atoms in Ni_2FeGa and Ni_2CoGa compounds; whereas in the Ni_2XIn alloys, there is only one bond type exists, which is located between Ni and X atoms (X= Mn, Fe and Co). The bond between neighboring Ni atoms, which is stably existed in Ni_2MnGa alloy, not appears in Ni_2XIn series.

In conclusion, all the results presented in this part provide important evidence for further understanding of the thermal stability from the formation energy calculation and magnetic properties from the spin-polarized DOS of the three alloy systems Ni_2XY (X= Mn, Fe, Co; Y= Ga, In).

Defect formation energy and magnetic structure of ferromagnetic shape memory alloys Ni_2XY (X=Mn, Fe, Co; Y=Ga, In) by first-principles calculations

The formation energies of several different kinds of defects (atomic exchange, antisite and vacancy) and the variation in atomic magnetic moments in off-stoichiometric Ni_2XY (X= Mn, Fe, Co; Y= Ga, In) have been systematically investigated.

In the Ni_2XGa alloy series, the Ga and Ni antisites at the sites of the X sublattice have the lowest formation energies and the Ni and X antisites at the Ga sublattice sites have the highest formation energies. Therefore the Ga atoms stabilize the cubic structure, and the effect of X atoms on the structural stability is opposite. This information is of great importance to guide composition regulation during the fabrication process of these alloys. For the off-stoichiometric Ni_2XGa , in most cases the excess atoms of the rich component will directly occupy the site(s) of the deficient one(s) except in the Ga-rich Ni-deficient case. The excess Ga atoms occupy the X sites and the X atoms have to move to the free Ni sites.

In the Ni_2XIn alloy series, the In and Ni antisites at the site of the X sublattice have the comparable low formation energies. For the off-stoichiometric Ni_2XIn , in most cases the excess atoms of the rich component will directly occupy the site(s) of the deficient one(s) except in the In-rich Ni-deficient case. The excess In atoms occupy the X sites and the X atoms have to move to the free Ni sites.

The magnitude of the variation in the Ni moments is much larger than that of Mn in the defective Ni_2XY . The value of the Ni magnetic moment sensitively depends on the distance between Ni and X. The smaller the distance is, the larger the Ni moment will be. In the Ni_2XGa alloy series, the magnetic moments of the excess Fe and Co in Ni-Fe-Ga and Ni-Co-Ga alloys are aligned parallel to each other whereas those of excess Mn could be aligned parallel or antiparallel depending on the distance between the neighboring Mn atoms. Whereas in the Ni_2XIn alloy series, the magnetic moments of the excess Mn, Fe and Co are all parallel aligned, presented ferromagnetic status.

The effects of alloying element Co on Ni-Mn-Ga ferromagnetic shape memory alloys from first-principles calculations

The crystal structure, the thermal stability and the magnetic properties of the $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ ($x=0, 0.5, 1, 1.5$ and 2) ferromagnetic shape memory alloys have been systematically calculated for the first time. The added Co atoms prefer to occupy the Ni sites. With the increase of the Co content, the optimized lattice parameters for the parent phase decrease regularly, whereas for the martensite phase, the lattice parameters a increases and c decreases, thus leading to a decreased tetragonality c/a ratio. The calculated formation energies show the structural instability with the increase of the Co content for both the paramagnetic and the ferromagnetic austenite. The total energy difference between the paramagnetic and the ferromagnetic austenites increases, which results in the rise of T_c when Ni is replaced by Co. With the increased Co content, the down spin total density of states around the Fermi level gradually decrease, whereas those of the up spin part remains almost unchanged. This gives rise to the change of the total magnetic moment of these alloys. The partial density of states is dominated by the 3d states of the Ni, Mn and Co in the bonding region below the Fermi level and the 3d down spin states of the Mn dominates the antibonding region above the Fermi level.

Perspectives

Up to now, the Ni-Mn-Ga and Ni-Mn-In FSMA have been investigated extensively on many aspects. Plenty of valuable information of both theoretical significance and practical

interest has been obtained and many new phenomena have been revealed. As a kind of newly developed materials, Ni-Mn-Ga and Ni-Mn-In FSMAs show promising prospects for future applications. However, we should be aware that there is still a long way to go before the large-scale practical applications of these materials. There are still several critical issues that need to be resolved. The problems which can be explained by *ab initio* calculations are summarized as follows:

- (1) To date, the large MFIS is only observed in single crystalline 5M and 7M martensites. Therefore, simulations on modulations mechanism in 5M and 7M martensites will be a good research direction.
- (2) Since the large strains in Ni-Mn-Ga and Ni-Mn-In are induced by a magnetic field or thermal field, the effects of magnetic/thermal field on total energy, crystal structure and electronic distribution will be quite necessary.
- (3) The calculations on the mechanical properties such as elastic constants, Young's modulus using *ab initio* approach are straightforward and easy to handle.
- (4) To develop new promising ferromagnetic shape memory alloy systems with the help of first-principles calculations will open new research areas.

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Publication List

I. Publications in International Journals

1. **J. Bai**, J.-M. Raulot, Y. D. Zhang, C. Esling, X. Zhao and L. Zuo, Defect formation energy and magnetic structure of shape memory alloys Ni-X-Ga (X= Mn, Fe and Co) by first principle calculation. *Journal of Applied Physics* **108**, 064904 (2010).
2. **J. Bai**, J.-M. Raulot, Y. D. Zhang, C. Esling, X. Zhao and L. Zuo, The effects of alloying element Co on Ni-Mn-Ga magnetic shape memory alloys from first-principles calculations, *Applied Physics Letters*, **98**, 164103 (2011).
3. **J. Bai**, J.-M. Raulot, Y. D. Zhang, C. Esling, X. Zhao and L. Zuo, Crystallographic, magnetic and electronic structures of ferromagnetic shape memory alloys Ni₂XGa (X= Mn, Fe, Co) from first-principles calculations, *Journal of Applied Physics* **109**, 014908 (2011).
4. **J. Bai**, J.-M. Raulot, C. Esling, X. Zhao and L. Zuo, Structure stability and magnetic properties of Ni₂XGa (X = Mn, Fe, Co) Ferromagnetic Shape Memory Alloys by DFT approach. *Solid State Phenomena* **160**, 69-74 (2010).
5. **J. Bai**, J.-M. Raulot, Y. D. Zhang, C. Esling, X. Zhao and L. Zuo, First-principles calculations of ideal and defective Ni-X-In (X= Mn, Fe, Co) ferromagnetic shape memory alloys, *Acta Materialia*, submitted.
6. **J. Bai**, J.-M. Raulot, Y. D. Zhang, C. Esling, X. Zhao and L. Zuo, Effects of alloying element Co on Ni-Mn-In magnetic shape memory alloys by *Ab initio* calculations, submitted.
7. C. Esling, D. Y. Cong, **J. Bai**, Y. D. Zhang, J.-M. Raulot, X. Zhao, and L. Zuo, Structure and Phase Stability of NiMnGa Ferromagnetic Shape Memory Alloys by Experimental and ab-initio Techniques. *Materials Science Forum*, **638-642**: 2040-2045 (2010).
8. A. Poty, J.-M. Raulot, H. Xu, J. Bai, C. Schuman, J.-S. Lecomte, M.- J. Philippe and C. Esling, Classification of the Critical Resolved Shear Stress in the HCP materials by atomic simulation: Application to α -zirconium and α -titanium. *Journal of Applied Physics*, accepted.

II. Contributions to International Conferences

1. C. Esling, **J. Bai**, Y. D. Zhang, J.-M Raulot, X. Zhao, and L. Zuo, French – German meeting of the Texture and Anisotropy research groups of the French and German Societies for Metallurgy and Materials, University of Paris 11, Orsay, France, April 2, 2009. *[Invited Lecture]*
2. C. Esling, D. Y. Cong, **J. Bai**, Y. D. Zhang, J.-M Raulot, X. Zhao, and L. Zuo: Structure and Phase Stability of NiMnGa Ferromagnetic Shape Memory Alloys by Experimental and ab-initio Techniques. EPM Symposium, as a part of Thermec 09 Conference, Berlin, Germany, August 2009. *[Invited Lecture]*
3. **J. Bai**, J.-M. Raulot, C. Esling, X. Zhao and L. Zuo: Structure stability and magnetic properties of Ni₂XGa (X = Mn, Fe, Co) Ferromagnetic Shape Memory Alloys by DFT approach. 3rd International Conference on Texture and Anisotropy of Polycrystals (ITAP-3), Gottingen, Germany, September 2009. *[Poster Presentation]*
4. **J. Bai**, J.-M. Raulot, Y. D. Zhang, C. Esling, X. Zhao and L. Zuo: Effects of Co addition on crystal structure, thermal stability and magnetic properties of Ni-Mn-Ga ferromagnetic shape memory alloys from first-principles calculations. Thermec 2011 Conference, August 1-5, 2011, Quebec City, Canada. *[Invited Lecture]*
5. J.- M. Raulot, A. Poty, H. Xu, D. Rodney, **J. Bai**, C. Schuman, J.-S. Lecomte, M.-J. Philippe and C. Esling : Hierarchy of the dislocation glide systems in titanium alloys by atomic simulation. The 12th World conference on Titanium, 19-24 June, 2011, Beijing, China. *[oral presentation]*
6. C. Esling, **J. Bai** and J.- M. Raulot : Study on structural, electronic and magnetic properties of ferromagnetic shape memory alloys by DFT approach. 14th International conference Density Functional Theory in Chemistry, Physics and Biology, August 29-September 2, 2011, Athens-Greece. *[Invited Lecture]*

Résumé en français

1. Introduction

Avec le développement rapide des sciences et des technologies, la demande croissante de matériaux à hautes performances avec des propriétés multi-fonctionnelles a augmenté. Les technologies modernes ont besoin de matériaux à transduction, également dénommés « matériaux intelligents » ou SMART en anglais qui subissent un changement substantiel d'une ou de plusieurs propriétés en réponse à un changement des conditions extérieures. Tous les matériaux intelligents sont des matériaux transducteurs car ils transforment de l'énergie sous une forme en une autre forme d'énergie. Ils ont donc de nombreuses applications à la fois comme capteurs et comme actionneurs dans divers domaines tels que le médical, la défense, l'aérospatiale et de la marine. Les Alliages à Mémoire de Forme Ferromagnétiques (AMFFs) sont de nouveaux matériaux intelligents qui combinent les propriétés de ferromagnétisme avec des propriétés sans diffusion, comme la transformation martensitique réversible. La contrainte induite par un champ magnétique dans ces matériaux résulte du réarrangement de domaines martensitiques sous l'action d'un champ magnétique appliqué.

Ainsi, les AMFFs possèdent les avantages des alliages à mémoire de forme thermiquement contrôlés et des matériaux magnétostrictifs, offrant l'effet à mémoire de forme magnétique géant et une réponse dynamique rapide. La déformation indirecte induite par champ magnétique est plus élevée que 9,5% [1], qui est d'un ordre de grandeur plus élevé que les déformations générées dans les matériaux piézoélectriques et magnétostrictifs. En même temps, la fréquence de travail des AMFFs est très élevée, de l'ordre de quelques kHz [2, 3]. Inspiré par les mérites de ces matériaux, des efforts considérables ont été consacrés à l'étude et à la compréhension des AMFFs durant les dernières décennies [1-22].

Jusqu'à présent, plusieurs alliages présentent les caractéristiques des AMFFs, dont les alliages Ni-Mn-Ga [1-7], Co-Ni-Ga [8], Co-Ni-Al [9, 10], Ni-Fe-Ga [11, 12], Ni-Mn-Al [13], Fe-Pd [14-16] et Fe-Pt [17]. Parmi ces alliages, les alliages Ni-Mn-Ga avec des compositions chimiques proche du composé stœchiométrique Ni_2MnGa font partis des AMFFs les plus prometteurs, puisque la plus grande déformation induite par champ magnétique ($>9,5\%$) n'est observée que dans les alliages Ni-Mn-Ga [1]. Cet effet est dû à la réorientation des variants

martensitiques ou au mouvement des joints de macles causées par l'anisotropie magnéto cristalline de la martensite [23]. L'étude de l'alliage Ni-Mn-Ga est l'un des objectifs de ce travail. Cependant, la contrainte de blocage à la déformation induite par champ magnétique de l'alliage Ni-Mn-Ga est seulement d'environ 2-5 MPa [1, 24]. En conséquence, un champ de contraintes minuscules peut réduire considérablement la déformation induite par champ magnétique, conduisant à une forte dégradation de l'effet à mémoire de forme induit par champ magnétique. Récemment, un nouveau type de phase d'Heusler AMFF, Ni-Mn-Co-In, a été étudié expérimentalement [25]. Il a été montré que la transition martensitique peut être renversée par un champ magnétique, que l'on appelle transition martensitique inverse induit par champ magnétique (MFIRT). Une déformation stockée de l'ordre de 3% accompagnée d'une contrainte seuil géante d'environ 100 MPa, a été trouvée dans un premier temps dans un monocristal de Ni-Mn-Co-In sous un champ magnétique de quelques Tesla (T) [25]. Le système Ni-Mn-In est le système d'alliage ternaire de base à l'origine de l'alliage Ni-Mn-Co-In. Ces deux alliages possèdent le même effet à mémoire de forme métamagnétique [26], accompagné d'une grande magnétorésistance [27, 28], d'une grande variation d'entropie [29, 30], d'un effet Hall géant [31], et de grands effets magnétocaloriques inverses (MCE) [32]. Bien que les propriétés des alliages Ni-Mn-In aient été largement mesurées, les rapports entre les aspects fondamentaux tels que la structure électronique, structure magnétique et la structure cristalline détaillées sont encore rares. Par conséquent, l'étude des alliages Ni-Mn-In fait partie de ce travail de recherche.

Un autre inconvénient fatal de l'alliage Ni-Mn-Ga est sa haute fragilité, ce qui limite ses applications pratiques. Par conséquent, l'ajout d'autres éléments pourraient être une alternative potentielle pour pallier à cet inconvénient. Beaucoup de nouveaux types de AMFFs ont été développés afin d'augmenter la ténacité, par exemple Ni-Fe-Ga [11, 12], Co-Ni-Ga [9, 10], etc.

Toutefois, des études expérimentales ont des limites: longue période d'études, de portée limitée, les coûts élevés, etc... Le calcul théorique permet de simuler l'effet d'éléments de substitution ou d'addition proche des compositions souhaitées et, par conséquent de prédire le matériau qui sera le plus prometteur. La simulation peut fournir des indications utiles pour les expériences.

Dans le travail présenté, les alliages AMFFs Ni_2XY ($\text{X}=\text{Mn}, \text{Fe}, \text{Co}$, $\text{Y}=\text{Ga}, \text{In}$) stœchiométriques et hors-stœchiométriques ont été systématiquement étudiés par calculs ab initio. Les effets de l'addition de Co sur les propriétés de Ni_2MnGa ont été étudiés en détails.

2. Méthode de calcul

Les calculs ab initio ont été effectués sur la base de la théorie fonctionnelle de la densité (DFT), utilisant ab initio de Vienne logiciel [33-35] (VASP). L'interaction entre les ions et les électrons est décrit par des pseudopotentiels ultra-doux [36, 37] (USPP) et aussi par la méthode d'ondes augmentées projetées (PAW) [38, 39]. Les deux type de pseudopotentiels USPP et PAW dans le code VASP permettre une réduction considérable du nombre d'ondes planes par atome pour les métaux de transition. L'approximation de gradient généralisé (GGA) dans le paramétrage de Perdew et Wang [40] a été utilisé pour décrire l'énergie d'échange-corrélation et jusqu'à présent, elle est la meilleure approche pour décrire les matériaux magnétiques. Pour les pseudopotentiels utilisés, les configurations électroniques sont Ni ($3d^8 4s^2$), Mn ($3d^6 4s^1$), Fe ($3d^7 4s^1$), Co ($3d^8 4s^1$), Ga ($4s^2 4p^1$) et In ($5s^2 5p^1$) respectivement. Dans ce travail, l'énergie cinétique de coupure est de 275 eV pour PAW et 250eV pour USPP. Une grille d'échantillonnage de Monkhorst-Pack [41] est utilisée pour la zone de Brillouin. Le nombre de points k dans la zone de Brillouin pour des cycles autocohérents et le calcul de la densité d'états (DOS) sont générés avec les grilles $10 \times 10 \times 10$ et $14 \times 14 \times 8$ pour austénite et pour les phases martensitiques non modulé (NM). Nous utilisons différentes grilles de points k pour les différentes phases afin de conserver la même densité de points k pour toutes les phases dans nos calculs. Le calcul est semi-relativiste et la polarisation de spin est prise en compte dans tous les cas étudiés. Toutes les structures considérées dans ce travail ont été relaxées en utilisant l'algorithme du gradient conjugué. Les positions atomiques et le volume ont été optimisés. A partir de ces calculs, les énergies totales, les moments magnétiques, les structures relaxées de l'état fondamental ont été analysés. L'énergie de formation des défauts a été estimée en utilisant l'équation suivante [5]:

$$\Delta E_f = E_{\text{def}} - E_{\text{id}} + n_{\text{Ni}} \mu_{\text{Ni}}^0 + n_{\text{X}} \mu_{\text{X}}^0 + n_{\text{Ga}} \mu_{\text{Ga}}^0 \quad (1)$$

où ΔE_f est l'énergie de formation des défauts; E_{def} et E_{id} sont les énergies totales de la cellule

unité avec défaut et sans défaut (idéale), respectivement; n_i est le nombre d'atomes de type i qui est transféré à partir d'un réservoir chimique; μ_i^0 correspond au potentiel chimique de l'élément pur.

Les groupes d'espace pour la austénitique et la phase non modulée martensitique sont Fm-3m et I4/mmm, respectivement, et les structures géométriques sont présentées sur la Fig. 1 (a) et (b).

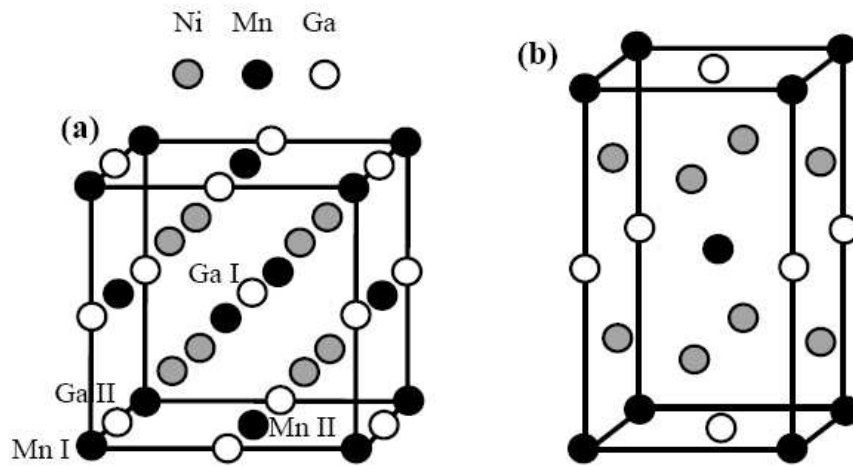


Fig. 1 Les structures de Ni_2MnGa (a) Heusler (L21) austénite; (b) martensite tétragonale non modulée.

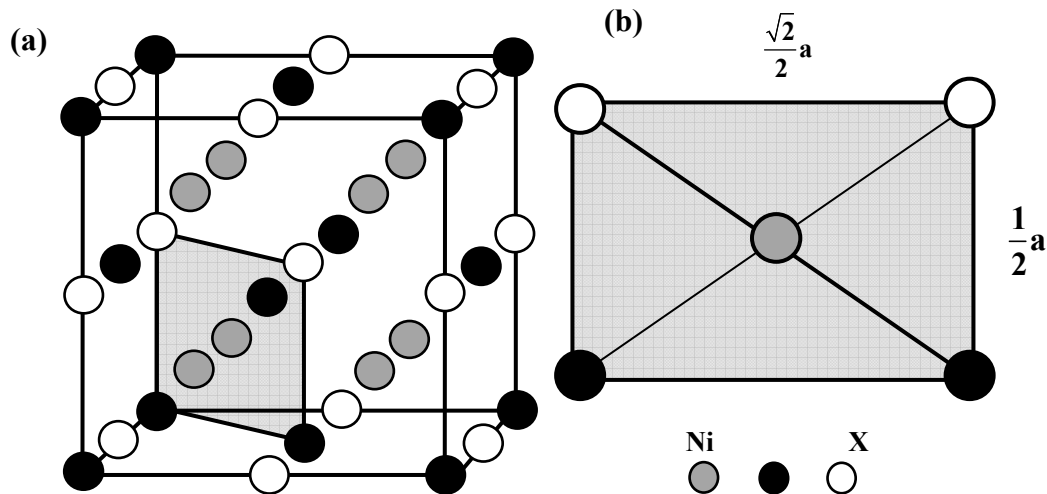


Fig. 2 (a) structure géométrique $\text{L21 Ni}_2\text{XGa}$, X désigne Mn, Fe, Co et (b) cellule rectangulaire dans le plan (110) utilisé pour analyser les propriétés magnétiques.

Afin d'étudier la variation des moments magnétiques autour des défauts ponctuels, nous

définissons un rectangle dans la structure cubique, comme le montre la Fig. 2 (a). Les coordonnées (0,0,0) et (0.5,0.5,0) sont celles de l'atome X, (0,0,0.5) et (0.5,0.5,0.5) sont les positions de l'atome de Ga et enfin la position (0.25,0.25,0.25) correspond à l'atome de Ni. Un rectangle caractéristique, comme le montre la Fig. 2 (b) a été construit afin d'étudier les propriétés magnétiques. Une telle cellule rectangulaire permet d'afficher la variation dans les moments magnétiques sur les sites du défaut et de ses atomes voisins.

3. Résultats et discussion

3.1 Ni₂XY stœchiométriques

3.1.1 Optimisation de la structure

Premièrement, nous avons optimisé les paramètres de maille à l'équilibre, calculer le module de compressibilité, les moments magnétiques total et partiels dans les alliages Ni₂XY (X = Mn, Fe, Co, Y = Ga, In), dont la liste est donnée au tableau 1 et au tableau 2. Une comparaison peut être effectuée entre les valeurs obtenus et les valeurs expérimentales et/ou calculées issues de la littérature [18, 42-50]. Comme on peut le voir à partir du tableau 1 et du tableau 2, nos résultats de calcul sont en bon accord avec ceux de la littérature.

Tableau 1 Paramètres de réseau optimisée (a), des modules en vrac (B), totale ou partielle des moments magnétiques dans les cubes Ni₂XGa. Disponible valeurs expérimentales et calculées à partir des résultats d'autres calculs [18, 42-47] sont également indiqués pour comparaison.

Ni ₂ XGa	a (Å)	B (GPa)	M ^{tot} (μ _B)	M ^{Ni} (μ _B)	M ^X (μ _B)	M ^{Ga} (μ _B)
Ni ₂ MnGa	5.805	151	4.20	0.35	3.52	-0.06
	5.823 ^a	146 ^b 155 ^f	4.17 ^{c,g} 4.27 ^f	0.33 ^g 0.36 ^c	3.84 ^g 3.43 ^c	-0.04 ^c
Ni ₂ FeGa	5.752	164	3.41	0.28	2.91	-0.04
	5.741 ^d		3.04 ^d			
Ni ₂ CoGa	5.699	171	1.80	0.14	1.58	-0.02
	5.405 ^e	169 ^e	1.78 ^e	0.16 ^e	1.55 ^e	-0.02 ^e

^a Reference [42], ^b Reference [43], ^c Reference [44], ^d Reference [45],

^e Reference [46], ^f Reference [47], ^g Reference [18].

Pour Ni₂MnGa, la différence relative du paramètre de maille calculé par rapport au résultat de diffraction des neutrons [42] est de 0,31%, et la différence sur le moment

magnétique total est de 0,72%. D'après le tableau 1 et le tableau 2, nous concluons que les paramètres de maille, et les moments magnétiques total et partiels diminuent progressivement avec l'augmentation du numéro atomique de X, alors que le module de compressibilité affiche une tendance inverse. Le rayon atomique de chaque atome X a été calculé par Clementi et al. [51]. Les rayons de Mn, Fe et Co sont 1.61Å, 1.56Å et 1.52Å, respectivement. Par conséquent, la diminution des paramètres de maille résulte principalement de la diminution du rayon atomique de l'élément X. La diminution du moment magnétique total (engendrant un affaiblissement progressif du ferromagnétisme) dépend principalement des états électroniques 3d de l'atome X. Le moment issu des états électroniques 3d de Ni est assez faible par rapport à la contribution de l'atome X. Le moment magnétique des atomes de Ga et In sont également répertoriés dans le tableau 1 et tableau 2. La direction de polarisation de spin induite sur les sites atomiques de Ga ou de In est opposée à la direction des atomes X, et cette caractéristique révèle la forte hybridation des états électroniques d de l'élément X et des états sp de l'élément Y (càd Ga ou In). L'amplitude du moment magnétique de l'élément Y diminue avec l'augmentation du numéro atomique de l'élément X, ainsi le faible moment magnétique de l'élément X réduit l'hybridation et par conséquent, le moment magnétique total. L'effet de la substitution du constituant X ou Y ne se limite pas à la structure cristalline, mais elle affecte aussi les propriétés magnétiques.

Tableau 2 paramètres de maille optimisés (a), distances inter atomiques, modules de compressibilité (B), moments magnétiques total et partiel (M) des structures cubiques Ni₂XIn. Les données expérimentales disponibles et les résultats d'autres calculs sont également indiqués pour comparaison.

Ni ₂ XIn	a (Å)	Atomic separation (Å)		B (GPa)	Magnetic properties (μ _B)			
		Ni-X (Ni-In)	Ni-Ni (X-In)		M ^{tot}	M ^{Ni}	M ^X	M ^{In}
Ni ₂ MnIn	6.053	2.62	3.03	127	4.33	0.33	3.69	-0.08
	6.036 ^a 6.071 ^b	2.61 ^a	3.02 ^a	133 ^a 138 ^d	4.14 ^a 4.22 ^c	0.32 ^a	3.49 ^a	-0.08 ^a
Ni ₂ FeIn	5.992	2.59	3.00	140	3.49	0.28	3.00	-0.06
	5.978 ^a	2.59 ^a	2.99 ^a	143 ^a	3.31 ^a	0.26 ^a	2.84 ^a	-0.06 ^a
Ni ₂ CoIn	5.944	2.57	2.97	145	1.90	0.15	1.68	-0.04
	5.941 ^a	2.57 ^a	2.97 ^a	160 ^a	1.77 ^a	0.15 ^a	1.53 ^a	-0.03 ^a

^a PAW calculation, ^b Reference [48], ^c Reference [49], ^d Reference [50].

3.1.2 Stabilité énergétique de Ni_2XY en phase cubique

Afin d'étudier l'effet de la substitution de l'élément X ou Y sur la stabilité de la phase cubique, les énergies de formation des structures cubiques Ni_2XGa et Ni_2XIn ont été calculées. L'énergie de formation E_f est une mesure de la stabilité de la phase à l'état solide et est définie comme l'énergie totale du composé, moins la somme des énergies de chaque élément constituant dans leur phase pure (état de référence):

$$E_f = E_{tot}(Ni_2XY) - 2E_{tot}^0(Ni) - E_{tot}^0(X) - E_{tot}^0(Y) \quad (2)$$

où X = Mn, Fe et Co, Y = Ga, In. $E_{tot}(Ni_2XY)$ est l'énergie totale de la cellule unité de Ni_2XY , $E_{tot}^0(Ni)$, $E_{tot}^0(X)$, $E_{tot}^0(Y)$ sont les énergies totales par atome de Ni pur, X, Y et dans leurs états de référence, respectivement.

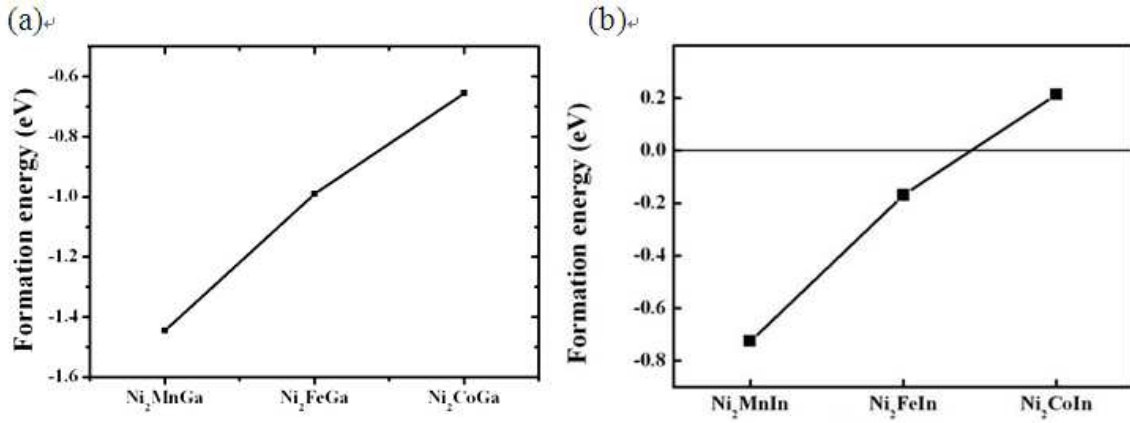


Fig. 3 Energie de Formation de Ni_2XY (X = Mn, Fe, Co, Y = Ga, In):

(a) Ni_2XGa ; (b) Ni_2XIn .

Les résultats des énergies de formation E_f calculées dans la phase cubique Ni_2XY sont présentés à la Fig. 3. A la Fig. 3 (a), les énergies de formation sont toutes négatives pour les trois alliages Ni_2XGa en phase cubique (structures stables), mais les résultats montrent une tendance à la déstabilisation de la structure cubique si l'atome Mn est substitué par un atome de Fe ou de Co (énergie plus élevée). A partir de la Fig. 3 (b), la même tendance est observée avec la substitution X dans les composés Ni_2XIn . La valeur de l'énergie de formation de Ni_2FeIn est juste en dessous de zéro, tandis que celle des Ni_2CoIn est tout à fait au dessus de zéro, indiquant l'instabilité structurelle de l'alliage Ni_2CoIn et une forte tendance de la transformation martensitique. En comparant la Fig. 3 (a) et 3 (b), les énergies de formation des alliages Ni_2XIn sont systématiquement plus élevées que ceux des alliages Ni_2XGa . Par

conséquent, nous pouvons tirer la conclusion que le remplacement de l'atome de Mn par un atome de Fe ou de Co conduira le système moins stable que le composé Ni_2MnGa .

3.1.3 Effet du rapport c/a sur l'énergie totale et les propriétés magnétiques

En utilisant les paramètres maille optimisés obtenue à partir de l'approche USPP, en gardant le volume de la cellule élémentaire un constant, nous avons calculé la variation de l'énergie totale, des moments magnétiques partiels et total avec la distorsion tétragonale (rapport c/a) de la structure cubique Ni_2XY ($X = \text{Mn, Fe, Co}$, $Y = \text{Ga, In}$) à la température du zéro absolu ($T = 0\text{K}$), comme le montre les Fig. 4, 5, 6.

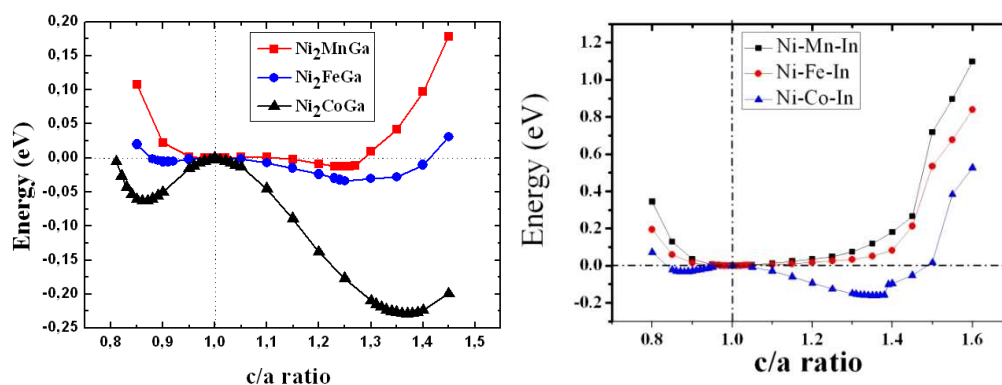


Fig. 4 Variation relative de l'énergie totale en fonction de la distorsion tétragonale (rapport c/a) (a) Ni_2XGa ; (b) Ni_2XIn ($X = \text{Mn, Fe, Co}$). Le zéro d'énergie correspond à l'énergie de la structure $L2_1$ dans chaque cas.

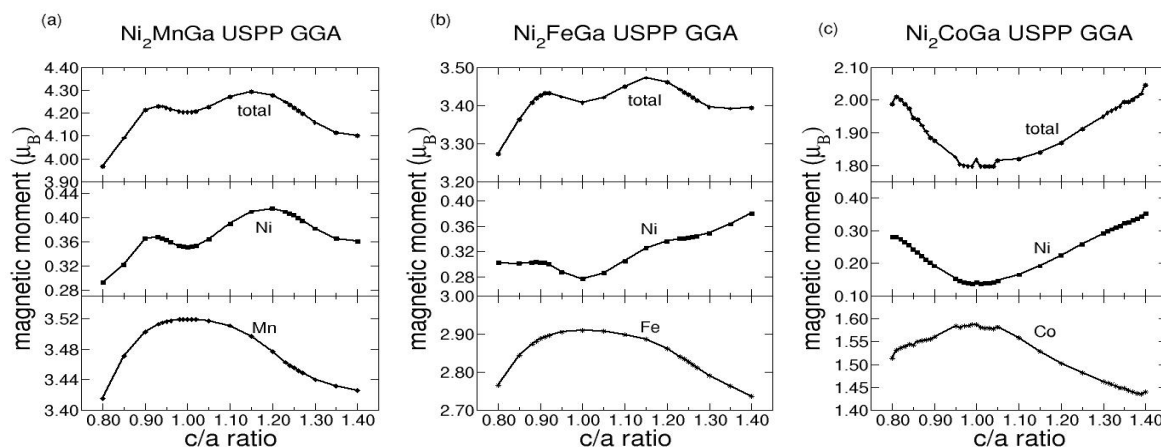


Fig. 5 Evolution des moments magnétiques total et partiels avec le rapport c/a dans les composés Ni_2XGa ferromagnétiques: (a) $X=\text{Mn}$, (b) $X=\text{Fe}$; (c) $X=\text{Co}$.

Au cours de la déformation tétragonale, l'énergie totale en fonction du rapport (c/a) donne les informations sur les structures de l'austénite et de la martensite, ainsi que la différence d'énergie entre elles. L'étude de la variation du moment magnétique total avec le rapport c/a prédit efficacement les modifications du moment magnétique au cours de la transition martensitique.

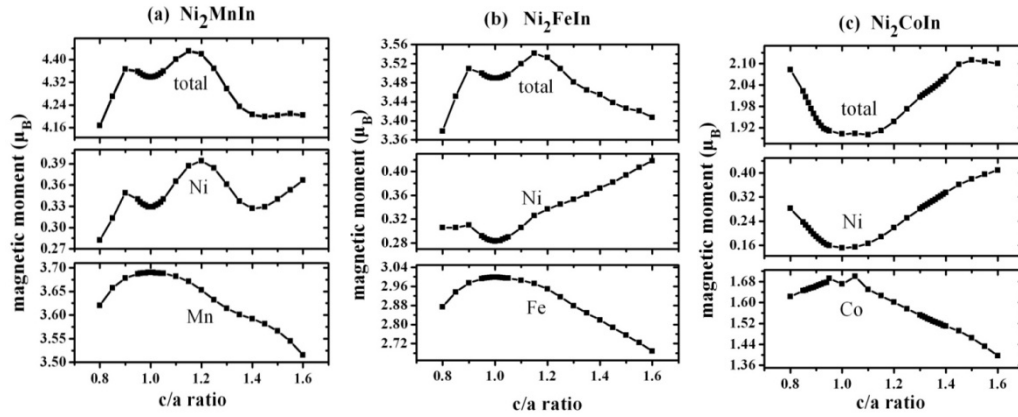


Fig.6 Evolution du moment magnétique total et partiel avec le rapport c/a dans les composés

Ni_2XIn : (a) $\text{X} = \text{Mn}$, (b) $\text{X} = \text{Fe}$; (c) $\text{X} = \text{Co}$.

3.1.4 Densité d'états et de distribution de charge

Pour continuer à étudier la nature des propriétés magnétiques, les densités d'états résolues en spin (DOS) sont calculées par la méthode des tétraèdres de Thompson en utilisant les corrections de Blöchl.

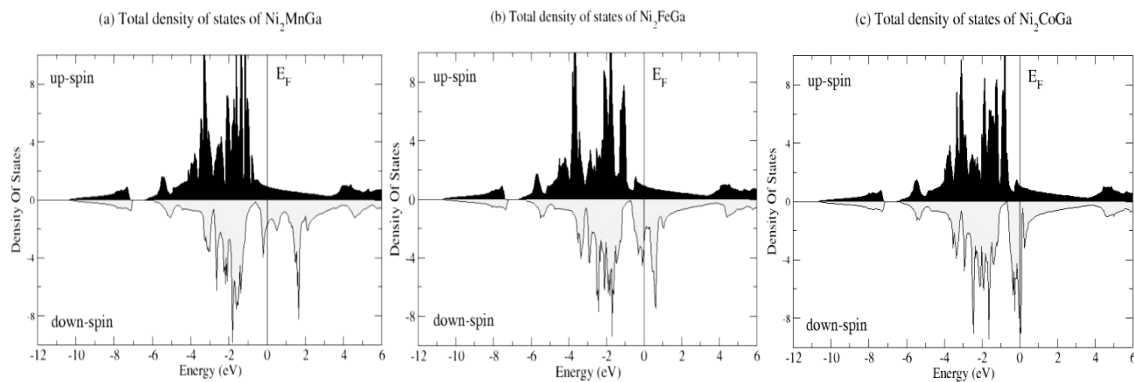


Fig. 7 DOS résolues en spin totales des composés suivants: (a) Ni_2MnGa , (b) Ni_2FeGa , et (c) Ni_2CoGa .

En comparant les densités d'états totales résolues en spin des Fig.7, nous constatons que les différences entre les moments magnétiques de ces matériaux sont déterminées par la

différence du nombre d'électron de spin up et de spin down au niveau de Fermi pour chaque composé. Du composé Ni_2MnGa au composé Ni_2CoGa , la DOS des électrons de spin down, au niveau de Fermi, augmente progressivement, tandis que la DOS des électrons de spin up au niveau de Fermi est restée quasiment inchangée (bandes entièrement occupées). Par conséquent, le moment magnétique total du composé Ni_2MnGa au composé Ni_2CoGa diminue. La densité d'états partielle a également été calculée, et elle indique que la diminution du moment magnétique provient de la contribution des états 3d de l'élément X ($X = \text{Mn, Fe, Co}$). Ceci est l'origine principale des variations des moments magnétiques total dans ces alliages. La DOS partielle est dominée par les états 3d de l'atome de Ni et de l'atome X dans la région de valence (au dessous du niveau de Fermi). Les états 3d down de l'élément X domine la région antiliante au dessus du niveau de Fermi.

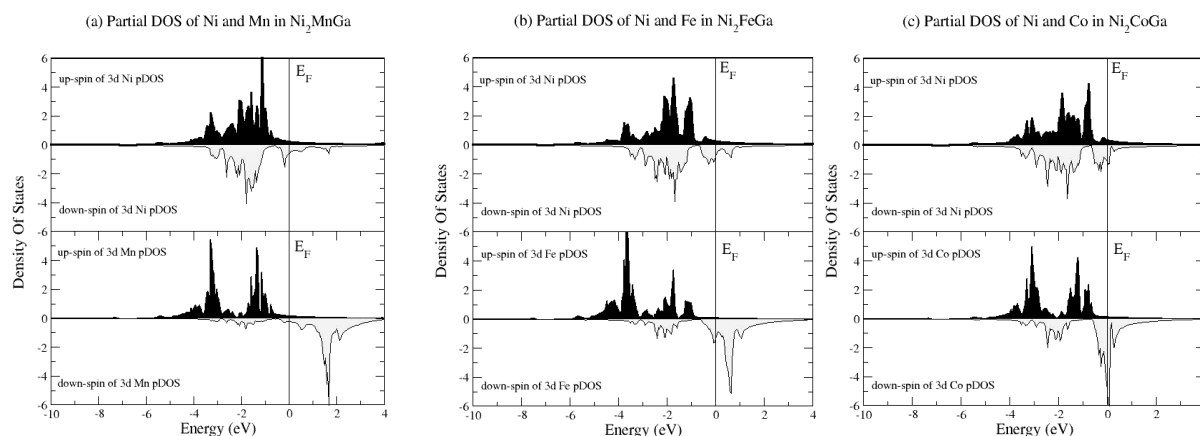


Fig. 8 DOS résolues en spin partielles des électrons 3d de l'atome de Ni et de X pour les phases cubiques de (a) Ni_2MnGa , (b) Ni_2FeGa , et (c) Ni_2CoGa .

Afin d'étudier la nature de la liaison électronique Ni_2XGa , la différence de densité de charge a été calculée, comme le montre les Fig. 9 et Fig. 10. Les isosurfaces de couleur or représentent un excès d'électrons par rapport à la densité de charge des atomes isolés, et la perte d'électrons correspond aux isosurfaces bleues. Nous pouvons voir qu'il ya deux types de liaison différente: à la Fig. 9 (a), il y a un lien fort (liaison covalente) entre les atomes de Ni dans le composé Ni_2MnGa , alors que pour les autres composés, le lien existe entre les atomes de Ni et de X, mais la force de la liaison interatomique est différente. La variation de la force des liaisons interatomique contribue aussi en partie à la variation du paramètre de maille et de la stabilité de ces alliages. Plus le lien est fort, et plus le paramètre de maille (à rayons

atomiques identiques) est sera petit et plus l'énergie de formation du composé sera faible (donc plus stable).

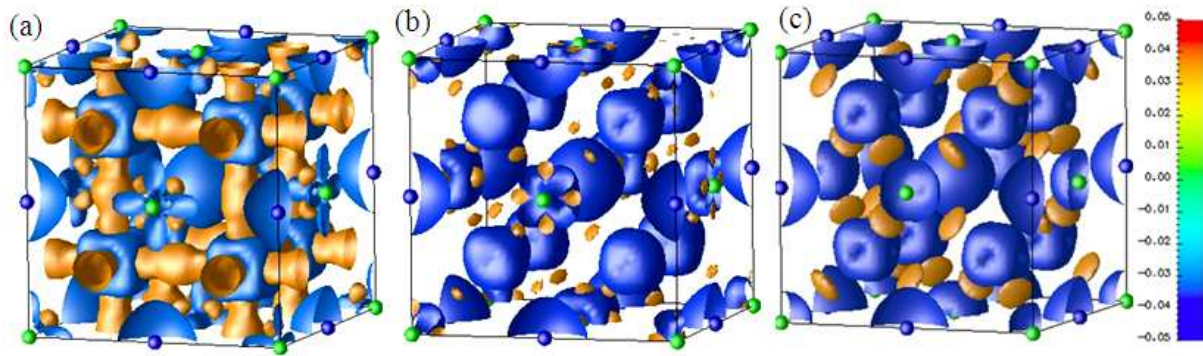


Fig. 9 Isosurfaces de la différence de densité de charge à $\pm 0,035 \text{ e}/\text{\AA}^3$: (a) Ni_2MnGa ;
(b) Ni_2FeGa et (c) Ni_2CoGa .

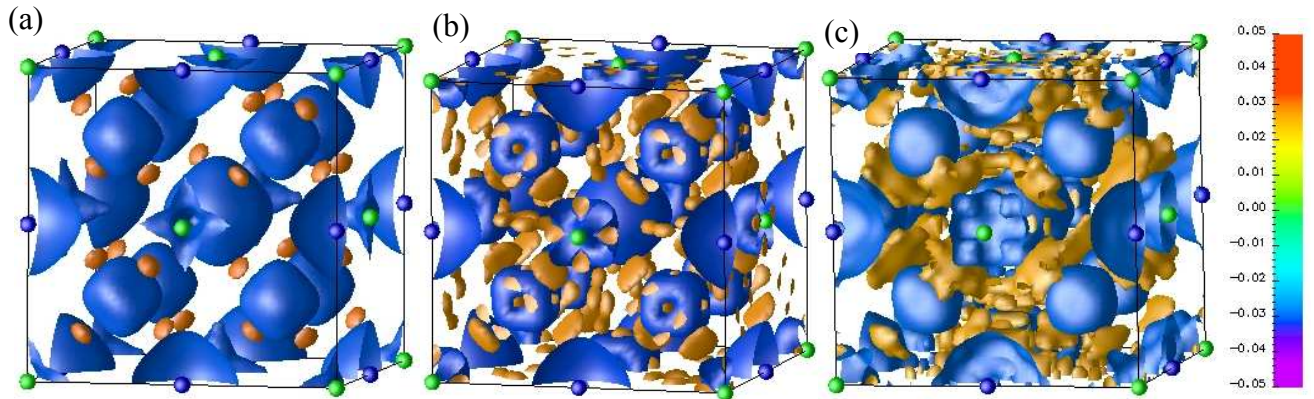


Fig. 10 Isosurfaces de la différence de densité de charge à $\pm 0,03 \text{ e}/\text{\AA}^3$: (a) Ni_2MnIn ;
(b) Ni_2FeIn et (c) Ni_2CoIn .

3.2 Ni_2XY hors-stœchiométrique

3.2.1 Energie de formation des défauts

Pour les composés Ni_2XY hors-stœchiométriques ($\text{X}=\text{Mn}, \text{Fe}, \text{Co}$, $\text{Y}=\text{Ga}, \text{In}$), des énergies de formation des plusieurs types de défauts (échange d'atome, antisite, lacune) ont été calculés, les résultats sont présentés dans les tableaux 3. Les antisites Y et Ni sur les sites du sous-réseau composé des éléments X ont des énergies de formation comparables et faibles. Les antisites des atomes de Ni et de X sur les sites sous-réseau Ga ont énergies de formation les plus élevées. Les valeurs des énergies de formation des défauts est d'une grande importance pour trouver la meilleur composition et ainsi influencer sur le processus de

fabrication de ces alliages. Dans la plupart des cas de l'occupation du site, les atomes en excès occupent directement les sites des atomes en sous stœchiométrie plus, sauf pour la composition pauvre en Ni et riche en Y. Dans ce dernier cas, la paire de défaut ($Y_X + X_{Ni}$) est énergétiquement plus favorable.

Tableau 3 Energies de formation (en eV) des défauts ponctuels dans les composés Ni_2XGa ($X = Mn, Fe, Co$).

Types of defects	exchange			antisite						vacancy		
	X-Ga	Ni-X	Ni-Ga	Ni _X	X _{Ni}	Ni _{Ga}	Ga _{Ni}	X _{Ga}	Ga _X	V _{Ni}	V _X	V _{Ga}
Ni ₂ MnGa	0.59	1.15	1.48	0.27	0.63	1.23	0.80	1.05	-0.24	0.93	1.17	2.55
Ni ₂ FeGa	0.54	-0.10	1.32	-0.18	-0.01	0.99	0.76	1.35	-0.67	0.81	0.72	2.23
Ni ₂ CoGa	0.22	-0.35	1.03	-0.48	0.06	1.16	0.25	1.37	-1.06	0.75	0.33	2.24

3.2.2 Structure magnétique du composé Ni-X-Y non stœchiométrique

Tableau 4 moments magnétiques atomiques et taux de variation correspondant dans différents types de défauts ponctuels dans les alliages Ni-Mn-Ga.

	Ni atomic moment		Change rate of Ni		Mn atomic moment		Change rate of Mn	
	(μ_B)		moment (%)		(μ_B)		moment (%)	
Pure Ni ₂ MnGa	0.36				3.52			
Ni _{Ga}	Ni _{Ni} 0.40~0.43	Ni _{Ga} 0.11	Ni _{Ni} +11~+19	Ni _{Ga} -69	3.46 ~ 3.54		-2 ~ +1	
Ga _{Ni}	0.29 ~ 0.34		-19 ~ -5		3.49 ~ 3.52		-1 ~ 0	
Ni _{Mn}	Ni _{Ni} 0.31~0.34	Ni _{Mn} 0.22	Ni _{Ni} -14~ -6	Ni _{Mn} -39	3.54 ~ 3.58		+1 ~ +2	
Mn _{Ni}	0.24 ~ 0.35		-33 ~ -3		Mn _{Mn} 3.43~3.44	Mn _{Ni} -3.05	Mn _{Mn} -3 ~ -2	Mn _{Ni} +1
Mn _{Ga}	0.46 ~ 0.49		+28 ~ +36		Mn _{Mn} 3.52~3.58	Mn _{Ga} 3.67	Mn _{Mn} 0 ~ +2	Mn _{Ga} +4
Ga _{Mn}	0.26		-28		3.53 ~ 3.58		0 ~ +2	

Dans cette partie, nous avons principalement d'analyser les moments magnétiques des défauts les plus énergétiquement favorables de type antisites. Les moments magnétiques

atomiques et les taux de variation correspondants de différents types de défauts dans les alliages Ni-XY sont énumérés dans les tableaux 4 et aux Fig. 11 à 12. Le taux de changement des moments atomiques de Ni/X ont été établies en utilisant l'équation (3).

$$\text{Change rate} = \frac{M_{\text{Ni/X}}(\text{defective}) - M_{\text{Ni/X}}(\text{ideal})}{M_{\text{Ni/X}}(\text{ideal})} \times 100\% \quad (3)$$

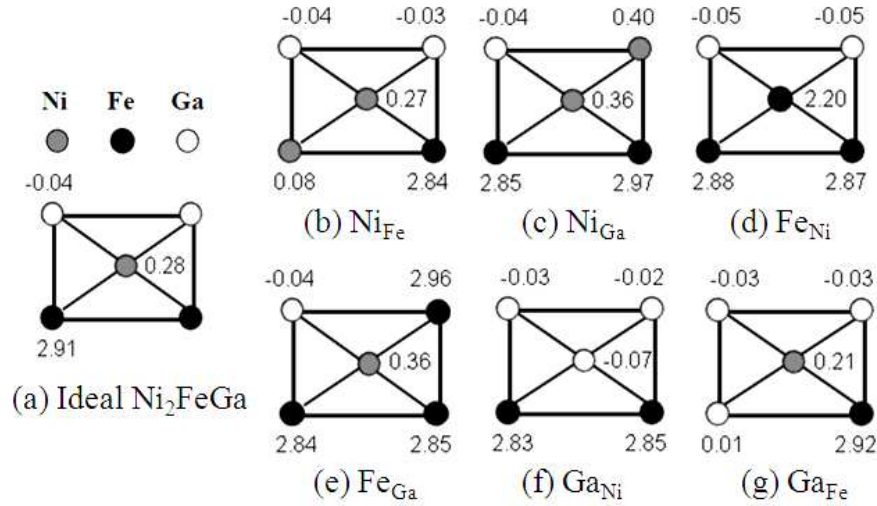


Fig. 11 Moment magnétique atomique dans le plan (110) en présence de différents défauts de type antisites dans l'alliage Ni-Fe-Ga (a) idéal Ni_2FeGa ; (b) Ni_{Fe} ; (c) Ni_{Ga} ; (d) Fe_{Ni} ; (e) Fe_{Ga} ; (f) Ga_{Ni} ; (g) Ga_{Fe} .

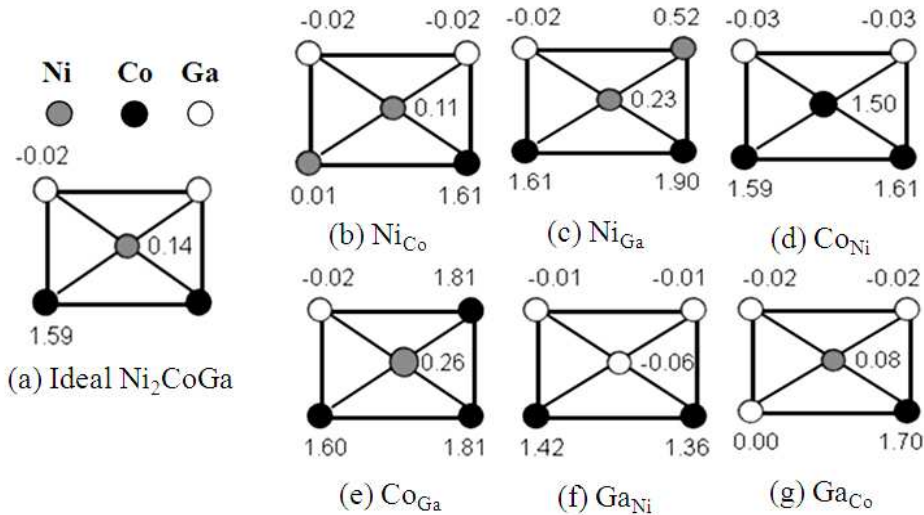


Fig. 12 Moment magnétique atomique dans le plan (110) en présence de différents défauts de type antisites dans l'alliage Ni-Co-Ga (a) Idéal Ni_2CoGa ; (b) Ni_{Co} ; (c) Ni_{Ga} ; (d) Co_{Ni} ; (e) Co_{Ga} ; (f) Ga_{Ni} ; (g) Ga_{Co} .

La principale conclusion de cette section est que l'ampleur de la variation dans les moments de l'atome de Ni est beaucoup plus grande que celle de X dans le composé Ni_2XY avec défaut. La valeur du moment magnétique dépend Ni très sensiblement de la distance entre Ni et X. Plus la distance est petites et plus le moment de Ni grand.

3.3 Effets de l'élément Co sur les propriétés de Ni-Mn-Ga alliage

3.3.1 Site préférentiel de l'atome de Co et influence sur les paramètres de maille d'équilibre

Pour les différents sites possibles de l'atome de Co, les énergies de formation sont différentes. A partir de nos résultats de calcul, si l'atome de Co occupe le site Ni, Mn et Ga, les énergies de formation sont -0,36 eV, -0,32 eV et -0,25 eV par atome, respectivement. Par conséquent, les résultats indiquent que l'énergie de formation des atomes de Co préfèrent occuper les sites Ni dans le composé Ni_2MnGa .

Pour les deux phases austénite et martensite, les paramètres du réseau calculés et les moments magnétiques totaux sont indiqués dans le tableau 5. En général, avec l'augmentation de la teneur en Co, les paramètres du réseau optimisé diminue régulièrement dans la phase parent (austénitique), tandis que pour la martensite, le paramètre de maille a augmente et le paramètre de maille c diminue, ce qui conduit à une diminution du rapport c/a. Le moment magnétique total augmente avec la teneur en Co dans les deux phases, principalement parce que le ferromagnétisme de l'atome de Co est plus fort que celui de l'atome de Ni.

Tableau 5 présente les paramètres de maille à l'équilibre ($T=0K$) et les moments magnétiques de l'austénite et de martensite tétragonale ferromagnétiques pour les alliages $Ni_{8-x}Mn_4Ga_4Co_x$ ($x = 0, 0,5, 1, 1,5$ et 2). Les abréviations cubique (Cub.) et quadratique (Tet.) se réfèrent à la phase parente et à la phase martensite, respectivement.

x		a (Å)	c (Å)	c/a	Magnetic moment (μ_B)
0	Cub.	5.805			4.224
	Tet.	3.853	6.633	1.724	4.280
0.5	Cub.	5.803			4.331
	Tet.	3.851	6.579	1.702	4.309
1	Cub.	5.799			4.436
	Tet.	3.863	6.512	1.685	4.343
1.5	Cub.	5.796			4.534
	Tet.	3.927	6.300	1.604	4.538
2	Cub.	5.793			4.637

Tet.	4.072	5.855	1.515	4.620
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3.3.2 Effet de l'addition de Co sur la stabilité des phases et sur la transition de Curie

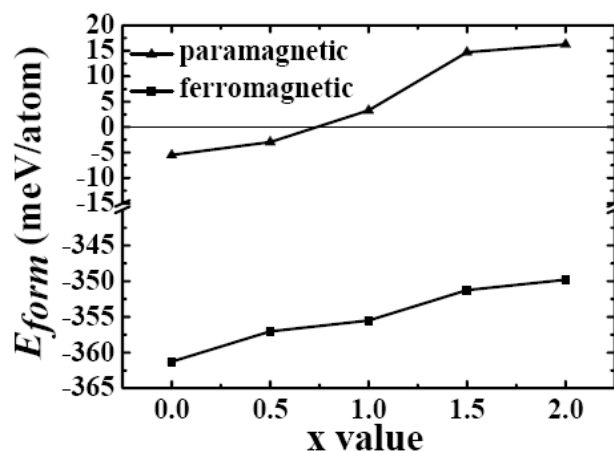


Fig. 13 Energies de formation de l'austénite paramagnétique et ferromagnétique des composés $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ ($x = 0, 0,5, 1, 1,5$ et 2).

Les énergies de formation calculées dans la structure l'austénite paramagnétique et ferromagnétique des composés $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ ($x = 0, 0,5, 1, 1,5$ et 2) sont données dans la Fig. 13. On voit que l'énergie de formation de l'austénite paramagnétique est beaucoup plus élevée que celle de la phase ferromagnétique à toutes les compositions étudiées, ce qui est cohérent avec le fait que l'austénite est la phase paramagnétique à haute température. L'austénite ferromagnétique est plus stable que l'austénite paramagnétique. Les phases deviennent instable dans les deux états paramagnétique et ferromagnétique lorsque les atomes de Ni sont substitués par des atomes de Co parce que l'énergie de formation augmente progressivement avec la teneur en atome de Co. La différence des énergies totales entre les phases paramagnétiques et ferromagnétiques austénitiques, qui se traduit par l'augmentation de la température de Curie T_c quand les atomes de Ni sont substitués par des atomes de Co.

3.3.3 Effet de l'addition de Co sur la densité d'états électroniques

Pour continuer à étudier l'effet de l'addition de Co sur la structure électronique et les propriétés magnétiques, la densité d'états résolue en spin (DOS) pour les alliages $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ où $X=0$ (X0), $X=1$ (X1) et $X=2$ (X2), sont présentés sur la Fig. 14.

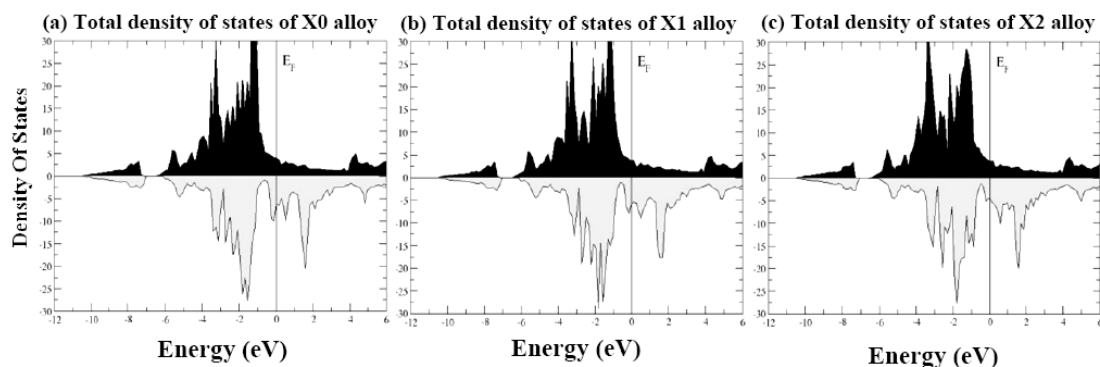


Fig. 14 DOS totale résolue en spin pour les alliages (a) X0, (b) X1 et (c) X2.

Comme on le voit sur les Fig. 14(a) à 14(c), avec l'augmentation de la teneur en Co, la DOS des électrons de spin down autour du niveau de Fermi (principalement au -0.2 eV) diminue progressivement, tandis que la DOS de spin up demeure presque inchangée. Cela donne lieu à une augmentation du moment magnétique total dans ces alliages en fonction de la teneur en Co. Les moments magnétiques totaux sont 4,224, 4,436 et 4,637 μ_B pour les alliages X0, X1 et X2, respectivement.

À la Fig. 15, les DOS partielles sont dominées par l'effet de liaison des états 3d de spin up du Ni, du Mn et du Co. Les états 3d spin up des atomes de Ni et Co sont semblables (les sommets sont dans la même position). Cet effet est une conséquence de l'hybridation des niveaux électroniques entre les atomes de Ni et Co. Dans la deuxième section de la Fig. 15, les états 3d spin down du Mn dominent la région antiliante au-dessus du niveau de Fermi avec un pic à 1,8 eV.

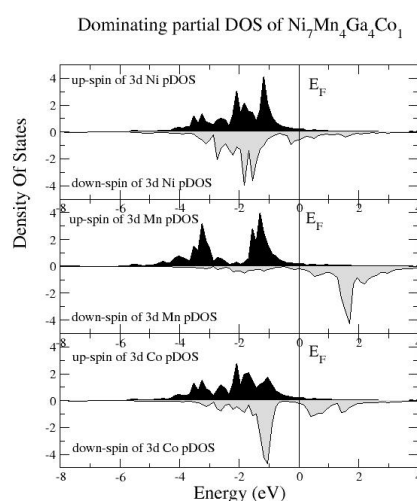


Fig. 15 Calculé spin-resolved densité partielle de l'état pour l'alliage X1.

4 Conclusion

Les paramètres de maille, les moments magnétiques total et partiel, l'énergie de formation, la densité d'états et la distribution de charge de la phase cubique du stœchiométrique Ni_2XY ($\text{X} = \text{Mn}, \text{Fe}$ et Co , $\text{Y} = \text{Ga}, \text{In}$), et l'effet du rapport c/a sur l'énergie totale et les propriétés magnétiques dans Ni_2XY ont été systématiquement calculés. Les résultats montrent que les paramètres de maille, des distances inter atomiques, les moments magnétiques total ou partiel diminuent graduellement avec l'augmentation du numéro atomique de X et que le module de compressibilité affiche une tendance inverse. Les énergies de formation calculée des systèmes montrent une déstabilisation de la structure cubique si l'atome de Mn est substitué par Fe ou Co. La valeur de E_f pour Ni_2FeIn est juste en dessous de zéro, alors que E_f est au-dessus de zéro pour le composé Ni_2CoIn . Au cours de la déformation tétragonale, un seul minimum d'énergie apparaît au rapport $c/a = 1$ pour les composé stœchiométriques Ni_2MnIn et Ni_2FeIn , alors que deux minima d'énergie apparaissent au rapport $c/a = 0,88$ et $c/a = 1,36$ et un maximum local en $c/a = 1$ pour le composé Ni_2CoIn . Le structure martensitique de Ni_2CoIn est la phase la plus énergétiquement stable. L'étude de la variation du moment magnétique total avec le rapport c/a peut efficacement prédire la variation du moment magnétique au cours de la transition tétragonale martensitique. De Ni_2MnIn à Ni_2CoIn , la DOS total de spin down au niveau de Fermi augmente progressivement, tandis que la DOS de spin up reste quasiment inchangé, ce qui explique la variation du moment magnétique dans ces alliages. La DOS partielle est dominée par les états 3d de Ni et de X au dessous du niveau de Fermi. Les états 3d down de l'élément X dominant la région antiliante. Avec la substitution de Mn par Fe ou Co, il y a deux différences principales dans les DOS partielles, l'une est l'intensité du pic centré sur -2eV est augmentée, l'autre est un déplacement de énergie de Fermi. Il y a des liaisons dans les alliages Ni_2XIn , qui sont situés entre les atomes de Ni et de X atomes ($\text{X} = \text{Mn}, \text{Fe}$ et Co), mais l'intensité de liaison est différent.

Les énergies de formation des différents types de défauts (échange d'atomes, antisites et lacunes) et la variation des moments magnétiques atomiques dans les composés non-stœchiométriques Ni_2XIn alliages à mémoire de forme ferromagnétiques ont été systématiquement calculés pour la première fois. Les antisites In et Ni sur les sites de

sous-réseau de l'atome X ont des énergies de formation comparables et faibles. Cette information est d'une grande importance pour optimiser la composition au cours du processus de fabrication de ces alliages. Pour les alliages non-stoechiométriques Ni_2XIn , dans la plupart des cas, les atomes de l'élément en excès occupent directement les sites pauvres en un élément, sauf dans le cas riche en In et pauvre en Ni. L'excès des atome d'In occupent les sites X et les atomes X doivent se déplacer vers les sites libres de Ni. L'amplitude de la variation des moments de l'atome Ni est beaucoup plus grande que celle des atomes de Mn dans les composés Ni_2XIn avec défauts. La valeur du moment magnétique de Ni dépend très sensibles à la distance entre Ni et X. Plus la distance est petite et plus le Moment de Ni sera grand.

La structure cristalline, la stabilité thermique et les propriétés magnétiques de la $\text{Ni}_{8-x}\text{Mn}_4\text{Ga}_4\text{Co}_x$ ($x=0, 0,5, 1, 1,5$ et 2) alliages à mémoire de forme ferromagnétiques ont été systématiquement calculés pour la première fois. Les atomes de Co préfèrent occuper les sites Ni. Avec l'augmentation de la teneur en Co, les paramètres de maille optimisée diminue dans la phase austénitique régulièrement, alors que pour la phase martensite, le paramètre de maille a augmente et le paramètre de maille c diminue, entraînant ainsi une diminution du rapport c/a. Les énergies de formation calculées montrent l'instabilité structurelle avec l'augmentation de la teneur en Co pour l'austénite paramagnétique et ferromagnétique. La différence d'énergie totale entre les austénitiques paramagnétique et ferromagnétiques augmente avec la teneur en Co, qui se traduit par l'augmentation de la température de Curie T_c (quand Ni est remplacé par Co). Avec l'augmentation de la teneur en Co, la densité d'états de spin down au niveau de Fermi diminue progressivement, tandis que la densité d'états de spin up reste quasiment inchangée. Cela donne lieu à une modification du moment magnétique total de ces alliages. La densité d'états partielle est dominée par les états 3d du Ni, de Mn et de Co dans la région de liaison au dessous du niveau de Fermi et les états 3d de spin up du Mn dominant la région antiliante au-dessus du niveau de Fermi.

L'objectif de ce travail était de combler l'écart entre les observations expérimentales et des calculs théoriques, de fournir des preuves directes de l'explication des résultats expérimentaux des alliages de Ni-Mn-Ga et Ni-Mn-In; d'étudier la nature physique des certaines propriétés; jeter des bases solides pour l'amélioration des performances des alliages

présents et d'aider à la conception de nouveaux alliages à mémoire de forme ferromagnétiques prometteurs.

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