ELECTRONIC STRUCTURE AND MARTENSITIC TRANSFORMATION IN Ni_2MnGa HEUSLER ALLOY

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The electronic structure of the Ni_2MnGa Heusler alloy has been investigated for martensitic transformation $\beta_1 \rightarrow \beta_1' \rightarrow \beta_1'' \rightarrow \beta_1'''$ by the self-consistent TB-LMTO method. The distortion influences the shape of the densities of states. The β_1 is the most stable phase. We present the values of total and local magnetic moments for all phases of Ni_2MnGa alloy.

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1. Introduction

The ferromagnetic Ni_2MnGa Heusler alloy is known to exhibit a martensitic transformation from cubic to tetragonal phase. The neutron studies [1, 2] established the existence of a weakly first-order structural phase transition at about 265 K. A number of studies have been concentrated on premartensitic transition. The results of elastic, thermal, and electron microscopy measurements clearly show the formation of premartensitic phase existing in the temperature range of 30–60 K above the martensitic transformation temperature [3]. The fact of the existence of premartensitic state is confirmed by the behaviour of the elastic constants [4, 5]. The elastic constant C' associated with the transverse acoustic (TA_2) branch plays an important role in the structural transformation. The basic feature of this kind of transition is the unstability of the phonon system, which leads to the crystal lattice rearrangement. The nearly complete softening in the $(q,\ q,\ 0)$ TA_2 branch results in a premartensitic first-order transition which involves a commensurate periodic distortion of the parent structure Ni_2MnGa with the periodicity equal to that of the soft mode [2]. The specific heat, elastic constants, and magnetic susceptibility in a ferromagnetic Ni_2MnGa alloy exhibit anomalous behaviour [6, 7] at the temperature of condensation of the [110] TA_2 phonon at the $q = 0.33$. But the phonon anomaly is not related to the magnetic ordering.

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The magnetoelastic, structural, and magnetic properties of the Ni_2MnGa Heusler alloy have been studied in Refs. [8–11]. In Refs. [8, 9] the phenomenological description of martensitic transition based on the Landau expansion has been proposed which includes magnetoelastic interaction. Ac susceptibility and ultrasonic measurements under an applied magnetic field [8] have experimentally evidenced the magnetoelastic coupling. The obtained temperature dependences of the magnetisation [9] are compared with experimental data.

The large magnetic fields (8 kOe at 265 K) induce strains in Ni_2MnGa crystal [10]. The model of the magnetic-field-induced strain was presented in Ref. [12] for magnetic shape-memory alloys. The linear field dependences of magnetisation and strain in Ni_2MnGa at low fields are reasonably well described by the model, which includes the effects of magnetic anisotropy within the martensitic twins and also accounts for phase-boundary motion.

The structural and magnetic properties of the Heusler alloys are mainly determined by their lattice parameters and chemical composition. It has been shown that the dependence of the martensitic transition on the Ni excess ($Ni_{2(1+\delta)}Mn_{1-2\delta}Ga$) demonstrates a step-like behaviour: for the sample 52% Ni the transition temperature T_M is not changed compared to the sample 50% Ni, whereas for the sample 55% Ni the transition is completely suppressed [11]. From measurements of the susceptibility no indication of a martensitic phase transition could be found in the substituted samples $(Ni_{1-3\varepsilon}Fe_{2\varepsilon}Cu_{\varepsilon})_2MnGa$.

The studies of the deformation behaviour of Ni_2MnGa β_1 phase under uniaxially compression and tension along the $\langle 100\rangle$ and $\langle 110\rangle$ axes show that the crystalline structure of stress-induced and thermal martensite was identified [13, 14].

In this paper we show the band structure calculations of $\beta_1 \rightarrow \beta_1'''$ transition in Ni_2MnGa system at zero temperature, provided the studies are performed under constraint which keeps track of experimental [14] volume change during the transition.

2. Details of calculation

The electronic structures of Ni_2MnGa alloys for different phases (parent β_1 martensitic — β_1', β_1'', β_1''') have been studied by self-consistent tight-binding linear muffin-tin orbital (TB-LMTO) method [15] including the spin–orbit interaction in the atomic sphere approximation (ASA). The exchange-correlation potential was assumed in the form proposed by von Barth and Hedin [16]. In the atomic sphere approximation the Wigner-Seitz (W–S) cell is replaced by the sphere with the average radius S, which is determined by the following condition:

$$S_{av} = a\left(\frac{3}{4\pi N}\right)^{1/3}, \tag{1}$$

where a denotes the lattice parameter and N is the number of atoms in the cell. The values of the W–S radii for the components were estimated from the following relation:

$$\sum_n \left(\frac{S_n}{S_{av}}\right)^3 = N, \tag{2}$$

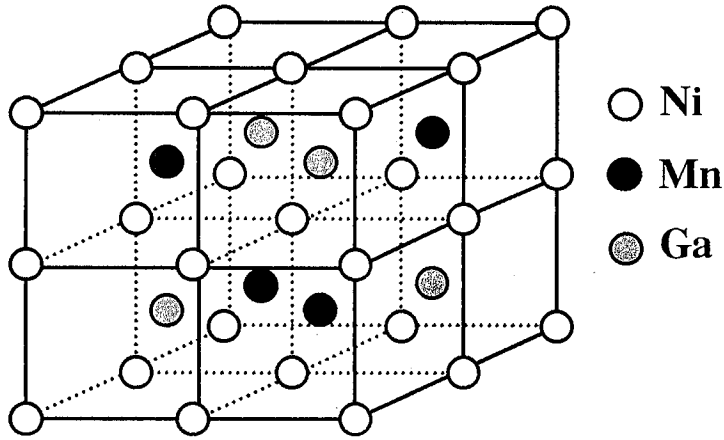

Fig. 1. The $L2_1$ Heusler structure.

where the summation is over all types of atoms in the cell and S_n is the atomic radius. The sum of the sphere volumes for all types of atoms (with the radius S_n) has the same value as the basic cell volume. The atomic potentials on boundaries of spheres must be of equal value. At present the calculations have been carried out for the experimental values of the lattice parameters [14].

The band structure was calculated for 256 k-points in the irreducible wedge of the Brillouin zone. The calculations were performed for $L2_1$ undistorted and distorted crystallographic structures. The $L2_1$-type structure consists of four interpenetrating fcc sublattices at the origin base in (0,0,0), (1/4,1/4,1/4), (1/2,1/2,1/2), and (3/4,3/4,3/4) (the Mn and Ga components forming one sublattice and Ni atoms forming another sublattice, Fig. 1).

3. Results

The changes of the electronic structure for transitions $\beta_1 \rightarrow \beta_1' \rightarrow \beta_1'' \rightarrow \beta_1'''$ are demonstrated in Figs. 2, 3, 4, and 5. The calculations have been made for experimental lattice parameters [14]. The β_1 phase is the undistorted cubic $L2_1$ structure, β_1', and β_1''' have tetragonal symmetry and β_1'' is orthorhombic (Table).

For all densities of states (DOS) the lower part (below –0.5 Ry) is dominated by s states of the Ga atom. This branch is separated from the upper part by a gap of the order of 0.1 Ry. The p and d electrons of the Ni and Mn atoms give contribution to the main part of the total DOS. The total and partial densities of states for β_1 phase (parent) of Ni_2MnGa system for the two spin polarisations are presented in Fig. 2. The Fermi level is located in a valley between the two peaks, in the right hand side of the peak formed by d-electrons of Ni atom. Figures 3 and 4 show the densities of states for β_1' and β_1'' phases of Ni_2MnGa. The minority upper Ni peak splits near the Fermi level. The above distortions ($c/a \neq 1$ for β_1' and $c/a \neq 1$, $b/a \neq 1$ for β_1'' — Table) affect the shape of partial minority Ni subband. The Ni peak splits on two or three peaks (for β_1' and β_1'', respectively), while the peak corresponding to d-states of Mn atom near Fermi level does not shift and remains undistorted. In β_1''' phase of Ni_2MnGa compound the split of Ni

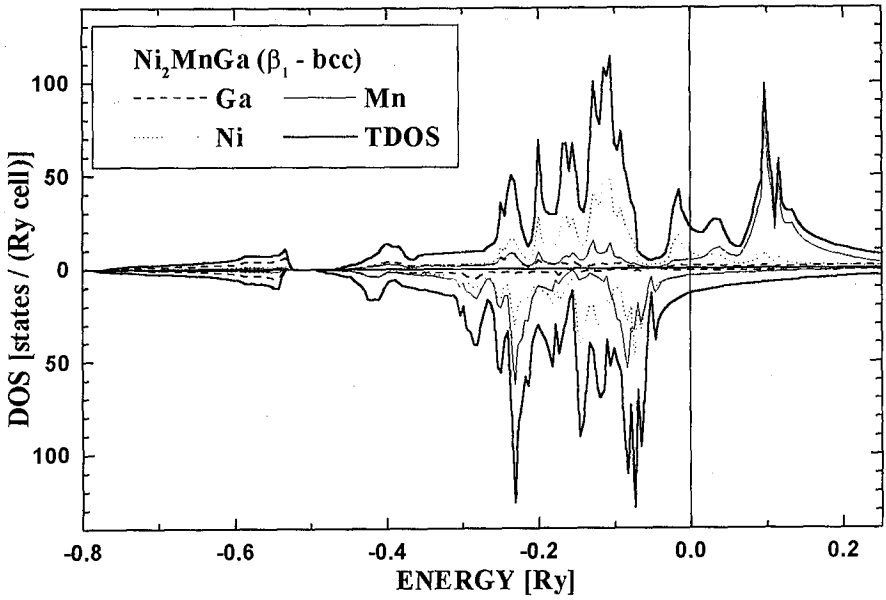

Fig. 2. The total and partial electronic densities of states of β_1 phase ($L2_1$) Ni_2MnGa. The vertical line represents the Fermi level.

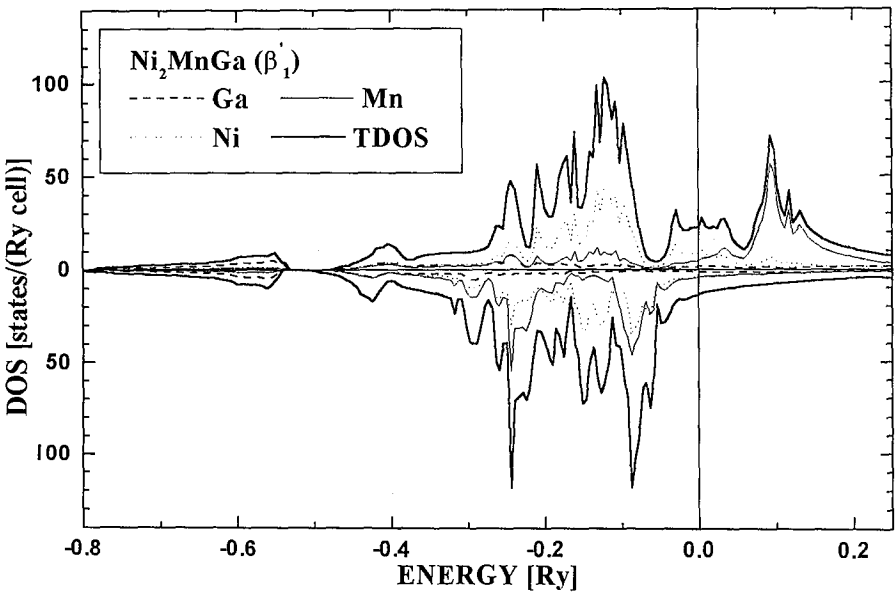

Fig. 3. The total and partial electronic densities of states of β_1' phase Ni_2MnGa.

peak is very small (Fig. 5). The modification of the shape of the peaks near the Fermi level with transitions $\beta_1 \rightarrow \beta_1' \rightarrow \beta_1'' \rightarrow \beta_1'''$ in Ni_2MnGa is a result of the changes of the structure.

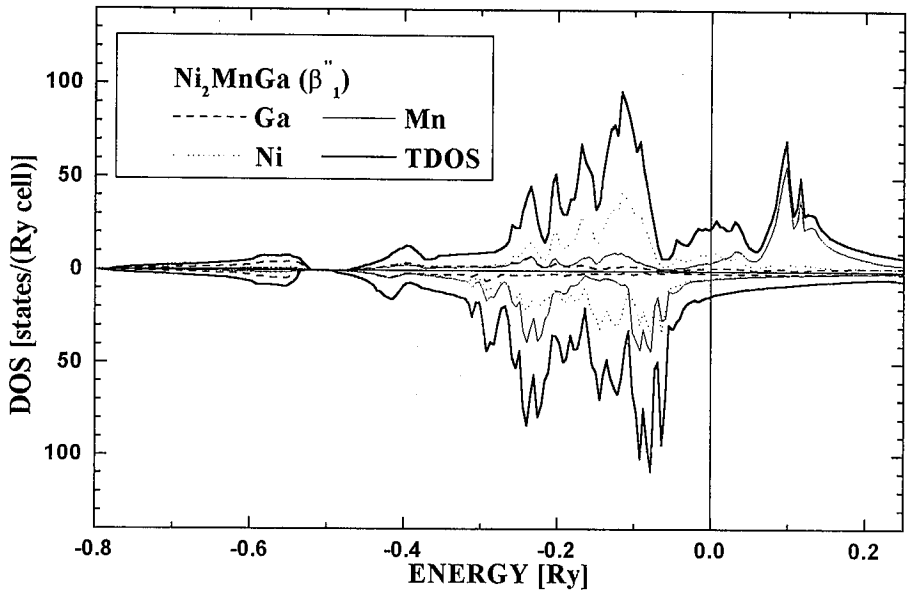

Fig. 4. The total and partial electronic density of states of β_1'' phase Ni_2MnGa.

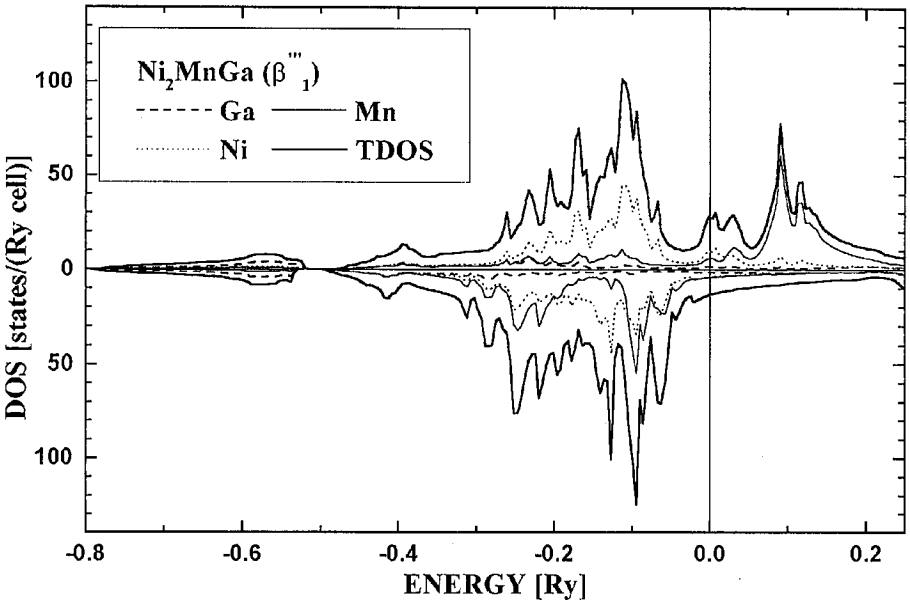

Fig. 5. The total and partial electronic density of states of β_1''' phase Ni_2MnGa.

At the structural phase transition the magnetic moment does not change significantly. In β_1 phase ($L2_1$) the total magnetic moment is $4.079\mu_B$. The Mn atom gives the largest contribution to the total magnetic moment ($3.504\mu_B$). The

TABLE

The total and local magnetic moments, density of states at the Fermi level for Ni_2MnGa alloy.

	β_1	β_1'	β_1''	β_1'''
a [nm]	0.5824	0.590	0.612	0.644
c/a	1	0.9394	0.9052	0.8571
b/a	1	1	0.9444	0.8571
m_{tot} [μ_B]	4.079	4.0534	4.117	4.156
m_{Mn} [μ_B]	3.504	3.447	3.484	3.468
m_{Ni} [μ_B]	0.328	0.343	0.356	0.383
m_{Ga} [μ_B]	−0.081	−0.079	−0.079	−0.078
$N(E_F)$	35.26	35.70	36.20	37.67

shift of the major Mn majority and minority peaks is clearly visible. The Ga atom gives the lowest contribution to the total magnetic moment ($-0.081\mu_B$). For the Ni atom the local magnetic moment is $0.328\mu_B$. The main contribution to Ni partial densities of states for both spin direction lies below E_F (the Fermi energy).

For β_1' phase of Ni_2MnGa alloys the total magnetic moment is $4.053\mu_B$. The magnetic moments are $0.343\mu_B$, $3.447\mu_B$, and -0.079 μ_B for Ni, Mn, and Ga atoms, respectively. A small increase in the total and local magnetic moments is observed for β_1'' phase. The total magnetic moment amounts to $4.117\mu_B$. The contributions to the magnetic moment are $3.484\mu_B$, $0.356\mu_B$, and $-0.079\mu_B$ for Mn, Ni, and Ga atoms, respectively.

In the β_1''' phase of Ni_2MnGa system we obtained the larger values of the moments than the ones reported for the previous phases. The values of local magnetic moment of the Ni atom rises to $0.383\mu_B$, which is a consequence of the shift of a part of the states from the minority Ni peak located slightly below the Fermi level to the energies slightly above E_F. The Mn magnetic moment is $3.468\mu_B$

The difference of energies between β_1 and β_1' is about 191 K. The energy of the premartensitic (β_1'', β_1''') phases is much higher than the energy of the parent (β_1) phase (by $\sim$ 1100 K).

The insignificant increase in densities of states at the Fermi level (from 35.26 to 37.67 [states/(Ry cell)]) was observed for all studied phases of Ni_2MnGa. The present results have confirmed that the magnetic moment was mainly localised on the manganese atom and its value did not change with the small difference of distance between the manganese atoms (two-lattice parameter). This fact is again a consequence of the earlier mentioned large value of separation of the main majority and minority Mn DOS peaks. For Ni atom the value of magnetic moment increases at the transition: $\beta_1 \rightarrow \beta_1' \rightarrow \beta_1'' \rightarrow \beta_1'''$. The small negative contribution from Ga atom to the total magnetic moment was observed for all phases of Ni_2MnGa compound.

Acknowledgments

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