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The phase diagrams of Ni–Mn–Ga alloys in the magnetic field

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Abstract

With the help of the Ginzburg–Landau theory the temperature–magnetic field phase diagrams of Heusler alloys Ni–Mn–Ga are theoretically investigated. The influence of the parameters of the magnetoelastic constants and elastic moduli on the phase diagrams are discussed. It is shown that with the determined combination of the phenomenological parameters, the critical magnetic field for the phase transition appears. The theoretically predicted value of the critical magnetic field is possible to be achieved in the experiment with the help of modern magnetic field sources.

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1. Introduction

Ni–Mn–Ga Heusler alloys are well-known ones from the family of "intelligent" substances. The outstanding properties of these intermetallic compounds such as the giant magnetoinduced strains [1,2], the reversible shape memory effect [3,4] (depending on composition it appears both in ferromagnetic and in paramagnetic states), large magnetocaloric effect [5] in the room temperature range allow us to say about great perspectives of industrial application of these alloys. These unusual properties are due to the thermoelastic martensitic transformation from the high-temperature cubic (or austenite) phase to the low-temperature tetragonal (or martensite) phase. Recently, it has been shown that several other intermetallic Heusler alloys combining 3d transition elements and III group metals ($3s^23p^1$) exhibit the same effects, e.g. CoNiGa, NiFeGa, CoNiAl and other compounds.

The aim of the present work is the theoretical investigation of the phase diagrams of structural and magnetic phase transitions in $Ni_{2+x}Mn_{1-x}Ga$ alloys under the influence of a strong magnetic field and in particular, the possibility to observe the martensitic phase transition critical point.

The considered correlation between magnetic and elastic effects is also observed in other rare-earth and transition metal alloys, e.g. MnAs [6], $Gd_5Ge_2Si_2$ [7].

2. Theory

According to the Ginzburg–Landau theory we can write the free energy of a cubic ferromagnet in the following form [8–10]:

$$F = -Ae_1 + \frac{A_0 e_1^2}{2} + \frac{a_1(e_2^2+e_3^2)}{2} + De_1(e_2^2+e_3^2) + \tfrac{1}{3}be_3(e_3^2-3e_2^2) + \tfrac{1}{4}c_1(e_2^2+e_3^2)^2 + \frac{Be_1 m^2}{\sqrt{3}} - M_0\mathbf{Hm} + \tilde{B}_1\left[\frac{e_2(m_x^2-m_y^2)}{\sqrt{2}}\frac{e_3(3m_z^2-\mathbf{m}^2)}{\sqrt{6}}\right]$$

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$$+ K(m_x^2 m_y^2 + m_y^2 m_z^2 + m_z^2 m_x^2) + \tfrac{1}{2}\alpha_1 \mathbf{m}^2 + \tfrac{1}{4}\delta_1 \mathbf{m}^4 + Pe_1. \tag{1}$$

Here e_i are the linear combinations of the deformation tensor components, $e_1 = (e_{xx} + e_{yy} + e_{zz})/\sqrt{3}$, $e_2 = (e_{xx} – e_{yy})/\sqrt{2}$, $e_3 = (2e_{zz} – e_{yy} – e_{xx})/\sqrt{6}$; A is a coefficient proportional to the thermal expansion coefficient; $A_0 = (c_{11} + 2c_{12})/\sqrt{3}$ is the bulk modulus; a_1, b, D and c_1 are the linear combinations of the second-, third- and fourth-order elastic moduli, respectively, $a_1 = c_{11} – c_{12}$, $b = (c_{111} – 3c_{112} + 2c_{123})/6\sqrt{6}$, $D = (c_{111} – c_{123})/2\sqrt{3}$, $c_1 = (c_{1111} + 6c_{1112} – 3c_{1122} – 8c_{1123})/48$; $\mathbf{m} = \mathbf{M}/M_0$ is the normalized magnetization vector (M_0 is the magnetization saturation); B and $\tilde{B}_1$ are the volume (exchange) and anisotropic magnetoelastic constants; K is the first cubic anisotropy constant; α_1 and δ_1 are the exchange constants and P is the hydrostatic pressure.

Minimization of Eq. (1) with respect to e_1 leads to the following:

$$e_1 = [A - D(e_2^2 + e_3^2) - \frac{B\mathbf{m}^2}{\sqrt{3}} - P]/A_0. \tag{2}$$

After substitution of Eq. (2) into Eq. (1) the expression for the free energy of ferromagnet is the following:

$$\begin{aligned} F = {} & \frac{-(A-P)^2}{2A_0} + \frac{a(e_2^2 + e_3^2)}{2} + \frac{be_3(e_3^2 - 3e_2^2)}{3} \\ & + \frac{c(e_2^2 + e_3^2)^2}{4} - \frac{B_0 \mathbf{m}^2 (e_2^2 + e_3^2)}{2} - M_0 \mathbf{Hm} \\ & + \tilde{B}_1 \left[\frac{e_2(m_x^2 - m_y^2)}{\sqrt{2}} + \frac{e_3(3m_z^2 - \mathbf{m}^2)}{\sqrt{6}} \right] \\ & + K(m_x^2 m_y^2 + m_y^2 m_z^2 + m_z^2 m_x^2) + \tfrac{1}{2}\alpha \mathbf{m}^2 + \tfrac{1}{4}\delta \mathbf{m}^4, \end{aligned} \tag{3}$$

where

$$\begin{aligned} a &= a_1 + \frac{2(A-P)D}{A_0}, \\ c &= c_1 - \frac{2D^2}{A_0}, \\ B_0 &= \frac{2DB}{\sqrt{3}A_0}, \\ \alpha &= \alpha_1 + \frac{2(A-P)B}{\sqrt{3}A_0}, \\ \delta &= \delta_1 - \frac{2B^2}{3A_0}. \end{aligned} \tag{4}$$

As it can be seen from Eq. (4), the coefficient B_0 is proportional to the volume magnetoelastic constant B.

Let us consider the case then the magnetic field is parallel to the z-axis: $\mathbf{H} \| z$. We will take the values of the magnetic field at which the magnetization is also parallel to the axis z, i.e. $m_x = m_y = 0$, $m_z = m$. Minimization of Eq. (3) with respect to e_2 leads to the equation for determination of this deformation. One of the solutions of this equation is $e_2 = 0$. Let us introduce the notations $B_1 = 2\tilde{B}_1/\sqrt{6}$, $e = e_3$. The part of the energy (Eq. (3)) which depends on e and m will take the form:

$$\begin{aligned} F = {} & \frac{ae^2}{2} + \frac{be^3}{3} + \frac{ce^4}{4} + \frac{\alpha m^2}{2} \\ & + \frac{\delta m^4}{4} + \frac{B_0 e^2 m^2}{2} + \frac{B_1 e m^2}{2} - M_0 Hm. \end{aligned} \tag{5}$$

In further discussion, we assume that the generalized fourth-order elastic modulus $c > 0$ and the exchange constant $\delta > 0$. The signs of α, b, B_0 and B_1 can be both positive and negative [8–10].

According to the Ginzburg–Landau theory in the vicinity of structural (martensitic) phase transition the elastic modulus a tends to zero, and as a consequence, near the transition point ($T \to T_M$) it can be written as $a = a_0(T - T_M(x))/T_{M0}$, where T_{M0} is the temperature of a structural phase transition for a stoichiometric alloy. The same approximation is valid to the exchange constant. Near the Curie temperature ($T \to T_C$) it can be written as $\alpha = \alpha_0(T - T_C)$, where $\alpha_0 = \delta/T_{C0}$, T_{C0} is the Curie temperature for a stoichiometric alloy. As it follows from the experiment [11] the martensitic transition and the Curie temperatures linearly depend on the composition: $T_M = T_{M0} + \gamma x$ and $T_C = T_{C0} – \sigma x$.

By numerical minimization of the free energy (Eq. (5)) with parameters e and m, we can obtain two structural states: the quasicubic phase (QC) with a weak tetragonal distortion and the tetragonal phase with a strong tetragonal distortion (T). However, the phases with the "strong" and "weak" tetragonal distortions can be treated as the martensitic and austenitic phases, respectively. These structural states can be both ferromagnetic and paramagnetic and depend on the values of temperature and an external magnetic field. The analysis shows that there are only four possible types of T–H phase diagrams within these structural and magnetic states.

Let us consider the case when in $Ni_{2+x}Mn_{1-x}Ga$ alloys with the absence of an external magnetic field we have the coupled magnetostructural transition from the paramagnetic austenite phase to the ferromagnetic martensite one. This occurs in the composition interval $0.18 < x < 0.27$ [10]. To be more definite, we choose the alloys with the middle composition from this interval: $x = 0.24$.

For the numerical calculations of the phase diagrams, we used the following values of free energy parameters: $T_{C0} = 375\,K$, $T_{M0} = 200\,K$, $\sigma = 860\,K$, $\gamma = 180\,K$, $M_0 = 210\,emu/cm^3$, $|B_1| = 4.9 \times 10^7\,erg/cm^3$, $|B_0| = 2.4 \times 10^9\,erg/cm^3$, $a_0 = |b|/(50c)$, $\delta = 1.5 \times 10^8\,erg/cm^3$, $c/|b| = 11.1$, $|b| = 3.8 \times 10^{10}\,erg/cm^3$ [11–13].

The phase diagram for the case when $b > 0$, $B_1 > 0$ and $B_0 < 0$ is presented in Fig. 1. For all diagrams below the dashed lines correspond to the lines of phase stability and the solid lines are the lines of phase transitions. The QC phase exists above CB line and the T phase is placed below AB line. It is seen that the phase transition of the first-order from the QC phase to the T phase occurs on DB line and this phase transition has the ending point B (the critical point). To the right of this point the phase