Phenomenological theory of structural and magnetic phase transitions in shape memory Ni-Mn-Ga alloys

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Abstract. In the framework of Landau theory the phase diagram of structural and magnetic phase transitions of cubic ferromagnetic Ni-Mn-Ga alloys is constructed by taking into account the strain, the crystal lattice modulation and the magnetic order parameters.

1. Introduction

Structural phase transitions are objects of intensive research because of their key role in the effects of superelasticity and shape-memory. Of special interest are the martensitic transformations, that is structural phase transitions of the first order from the parent highly symmetric phase to low symmetry phases at low temperatures. The main order parameters used for the description of martensitic transformation in the framework of Landau theory are the components of the elastic strain tensor \cite{1}. At high temperatures Ni-Mn-Ga alloys possess the cubic structure, but at low temperature they have the tetragonal ones. For a wide range of composition the martensitic transformations occur for the compounds being in ferromagnetic states. The structural transitions in Ni-Mn-Ga alloys are accompanied by changes in the magnetic subsystem through the magnetoelastic interaction.

It is now well established that the martensitic transitions in Ni-Mn-Ga alloys are accompanied by the appearance of premartensite modulated phases \cite{2,3}. Experimentally the premartensitic phase was detected through the partial softening of the $(1/3,1/3,0)$ phonon mode \cite{2}. It was shown also that the transition from the parent phase into the premartensitic modulated phase is of the first order. Thus, the description of phase transitions in this alloy system requires a generalization of Landau theory for the case of three interacting order parameters responsible for the magnetization, the strain and the crystal lattice modulation.

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2. Energy of a cubic ferromagnet

To describe the phase transitions in Ni-Mn-Ga alloys we will use the expression for the free energy of a cubic ferromagnet

\[ F = F_m(m) + F_e(e_i) + F_{\psi} (|\Psi|^2) + F_{e\psi}(e_i|\Psi|^2) + F_{me}(m_i, e_j) + F_{m\psi}(m_i, |\Psi|^2). \]  

(1)

The first three terms represent the magnetic, strain and crystal lattice modulation energies of the cubic ferromagnet, and the next three terms represent the energy of interaction between these subsystems. \( m = M/M_0 \) is the unit vector of macroscopic magnetization, \( e_i \) are the components of the strain tensor, and \( \Psi \) is the order parameter responsible for the crystal lattice modulation.

The magnetic energy of the cubic ferromagnet can be written as [4,5]

\[ F_m = F_{ex} + F_a. \]  

(2)

Here \( F_{ex} \) is the exchange energy

\[ F_{ex}(m) = \frac{1}{2} \alpha \left( m_x^2 + m_y^2 + m_z^2 \right) + \frac{1}{4} \delta \left( m_x^2 + m_y^2 + m_z^2 \right), \]  

(3)

where \( \alpha \) and \( \delta \) are the exchange constants. In the vicinity of the Curie point \( T_C \) \( \alpha = \alpha_0(T - T_C)/T_C \). \( F_a \) is the energy of the magnetic anisotropy

\[ F_a(m) = K (m_x^2 m_y^2 + m_y^2 m_z^2 + m_z^2 m_x^2). \]  

(4)

Here \( K \) is the constant of cubic anisotropy.

The energy of the strain subsystem can be written as [1]

\[ F_e(e_j) = \frac{1}{2} (C_{11} + 2C_{12})e_1^2 + \frac{1}{2} \alpha (e_2^2 + e_3^2) + \frac{1}{4} C_{44} \left( e_1^2 + e_2^2 + e_3^2 \right) \]

\[ + \frac{1}{3} b e_3 \left( e_3^2 - 3e_2^2 \right) + \frac{1}{4} c \left( e_2^2 + e_3^2 \right)^2, \]  

(5)

where

\[ e_1 = \frac{1}{3}(e_{xx} + e_{xy} + e_{xz}), \quad e_2 = \frac{1}{\sqrt{2}}(e_{xx} - e_{yy}), \quad e_3 = \frac{1}{\sqrt{6}}(2e_{zz} - e_{xx} - e_{yy}), \]

\[ e_4 = e_{xy}, \quad e_5 = e_{yz}, \quad e_6 = e_{xz}, \]

\[ a = C_{11} - C_{12}, \quad b = \frac{1}{2\sqrt{6}}(C_{111} - 3C_{112} + 2C_{121}), \]

\[ c = \frac{1}{48}(6C_{111} + 6C_{112} - 3C_{112} - 8C_{121}), \]  

(6)

where \( C_i \) are the elastic moduli of the second, third and fourth orders. In the vicinity of the martensitic transformation temperature \( T_m \), \( a = C_{11} - C_{12} = \alpha_0(T - T_m)/T_m \).

There are six different but crystallographically equivalent directions of the wave vector of the experimentally observed soft acoustic phonons \((1/3, 1/3, 0)\). These can be written as \( k_1 = \zeta(1, 1, 0), \quad k_2 = \zeta(0, 1, 1), \quad k_3 = \zeta(1, 0, 1), \quad k_4 = \zeta(1, 1, 0), \quad k_5 = \zeta(0, 1, 1), \quad k_6 = \zeta(1, 1, 0) \). Accordingly, the order parameter of the crystal lattice modulation contains twelve components, namely the
six amplitudes $|\Psi_1| \ldots |\Psi_6|$, and the six phases $\varphi_1 \ldots \varphi_6$, where $\Psi_j = |\Psi_j| \exp(i\varphi_j)$. The displacements of atoms corresponding to these lattice modulations can be written as $u_j(r) = |\Psi_j| p_j \sin(k_j r + \varphi_j)$, where $p_1, \ldots, p_6$ are the unit polarization vectors parallel to the $[1,1,0]$, $[0,1,1]$, $[1,0,1]$, $[1,1,1]$, $[1,0,1]$, $[1,1,1]$ axes.

Let us take into account only one phonon mode $(1/3, 1/3, 0)$, $\Psi = |\Psi| \exp(i\varphi)$. In this case the energy of the lattice modulation can be written as [6–8]

$$F_{\psi}(\Psi) = \frac{1}{2} A |\Psi|^2 + \frac{1}{4} B |\Psi|^4 + \frac{1}{6} C_0 |\Psi|^6 + \frac{1}{6} C_1 \left[ |\Psi|^6 + (\Psi^*)^6 \right],$$

where $A$, $B$, $C_0$ and $C_1$ are the crystal lattice modulation constants. In the vicinity of the premartensitic transformation temperature $T_{pr}$, $A = A_0(T - T_{pr})/T_{pr}$. The last term in this expression could be minimized with respect to the phase of $|\Psi|^6(\exp(-i6\varphi) + \exp(i6\varphi)) = 2|\Psi|^2 \cos(6\varphi)$. The minima of this energy term will be obtained at $\varphi = \pm \pi/6$, $\pm \pi/2$, $\pm 5\pi/6$, if $C_1 > 0$, and $\varphi = 0$, $\pm \pi/3$, $\pm 2\pi/3$, $\pi$, if $C_1 < 0$. We will assume below that $\varphi = 0$, $C = C_0 - |C_1|$ and $C > 0$.

The energy of the interaction between the strain and the crystal lattice modulation can be written as [6–8]

$$F_{\epsilon\psi}(\Psi, \epsilon_i) = \left( \frac{1}{\sqrt{3}} D_1 \epsilon_1 + \frac{2}{\sqrt{6}} D_2 \epsilon_3 + D_3 \epsilon_4 \right) |\Psi|^2,$$

where $D_i$ are the coupling constants.

The energy of the interaction between the magnetization and the strain can be written as [5]

$$F_{\text{me}}(m_i, \epsilon_j) = \frac{1}{\sqrt{3}} B_1 \epsilon_1 m^2 + B_2 \left[ \frac{1}{\sqrt{2}} \epsilon_2 \left( m_x^2 - m_y^2 \right) + \frac{1}{\sqrt{6}} \epsilon_3 \left( 3m_z^2 - m^2 \right) \right]$$

$$+ B_3 \left( \epsilon_4 m_x m_y + \epsilon_5 m_y m_z + \epsilon_6 m_z m_x \right).$$

This expression represents the elementary form of the magnetoelastic energy with the magnetoelastic constants $B_i$.

The energy of the interaction between the magnetization and the crystal lattice modulation can be written as

$$F_{\text{m}\psi}(m_i, \Psi) = \left[ \frac{1}{3} N_1 m^2 + N_2 \left( \frac{m_x^2}{3} - \frac{m_y^2}{3} \right) + N_2 m_x m_y \right] |\Psi|^2.$$

Here $N_i$ are the coupling constants.

The expression (1) given above for the energy of cubic ferromagnet allows to obtain the complete phase diagram of structural and magnetic phase transitions, which includes the appearance of static modulations of the crystal lattice.

3. Phase diagram

The results of the numerical calculations are shown in Fig. 1. It is the T-x diagram, where $x$ is the deviation from the stoichiometry in Ni$_{2+\delta}$Mn$_{1-\delta}$Ga alloys. The diagram was obtained for the following values of the parameters: $a_0 = 10^{11}$ erg/cm$^3$, $b = 5 \times 10^{11}$ erg/cm$^3$, $c = 10^{13}$ erg/cm$^3$, $B_2 = 10^7$ erg/cm$^3$, $K = -10^6$ erg/cm$^3$, $\delta = 5 \times 10^9$ erg/cm$^3$, $a_0 = 5 \times 10^9$ erg/cm$^3$, $M_0 = 500$ Oe,
Fig. 1. The calculated T-x phase diagram of the Ni-Mn-Ga alloys. The solid lines show the phase transitions, and the dashed lines show the loss of equilibrium.

The (T, x)-plane phase diagram for Ni$_{2x}$Mn$_{1-x}$Ga

$D_2 = 10^3$ erg/cm$^3$, $N_1 = 10^3$ erg/cm$^3$, $N_2 = 10^2$ erg/cm$^3$, $N_3 = -10^2$ erg/cm$^3$, $T_c = T_{c0} - \gamma x$, $T_m = T_{m0} + \sigma x$, $T_{pr} = T_{pr0} + \beta x$, $T_{r0} = 300$ K, $T_{m0} = 200$ K, $T_{pr0} = 260$ K, $\gamma = 230$ K, $\sigma = 700$ K, $\beta = 200$ K, $A_0 = 10^{23}$ erg/cm$^3$, $B = 10^{28}$ erg/cm$^3$, $C = 10^{33}$ erg/cm$^3$. It can be seen from Fig. 1 that there are seven different phases. The phase 1 is the paramagnetic cubic phase. The phase 2 is the paramagnetic tetragonal phase. The phase 3 is the ferromagnetic cubic phase with the magnetization oriented along [111] axis. The phase 4 is the angular ferromagnetic cubic phase with the crystal lattice modulation. In this phase the direction of the magnetization is in the (110) plane. The phase 5 is the paramagnetic tetragonal phase with the crystal lattice modulation. The phase 6 is the ferromagnetic tetragonal phase. In this phase the magnetization is oriented along the [100] axis. Finally, the phase 7 is the ferromagnetic tetragonal phase with the crystal lattice modulation. In this phase the magnetization is also oriented along the [100] axis. The solid lines in Fig. 1 are the lines of the phase transitions, while the dotted lines are the lines of the loss of phase stability. The CE and AD lines are the lines of the second order phase transitions from the paramagnetic into ferromagnetic phases. Other lines are the lines of the first order transitions. The B'/E and AB lines are the lines of the martensitic transformation. The EA line is the line of the coupled ferromagnetic and structural first order transition. The TT' line is the line of the premartensitic and intermartensitic transitions. The phase diagram obtained is in a good agreement with experimental data [5].
4. Conclusions

In the framework of Landau theory the phase diagram of structural and magnetic phase transitions of cubic ferromagnetic Ni-Mn-Ga alloys is constructed taking into account the strain, the crystal lattice modulation and the magnetic order parameters. It is shown that the martensitic phase transition can be accompanied by the premartensitic or intermartensitic transformations, resulting in a static modulations of a crystal lattice. The martensitic transitions as well as premartensitic and intermartensitic transformations can be accompanied by the orientational magnetic phase transitions and by order – disorder magnetic phase transitions. These transitions can be either of the first or of the second order.

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References