Revision of Clausius–Clapeyron Relation for the First-Order Phase Transition in Ni–Mn–In Heusler Alloys

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The derivation is presented of the Clausius–Clapeyron relation (CCR) in the second order of expansion of free energy potential on the change of temperature and magnetic field on the example of Ni–Mn–In Heusler alloys with the first-order metamagnetostructural phase transition (FOMMSPT), which can be treated as thermoelastic structural transition: austenite—martensite merging with metamagnetic transition: ferromagnet–antiferromagnet. It is shown that the second-order CCR describes satisfactory the nonlinear shift in the characteristic temperatures of the FOMMSPT in magnetic fields up to 25 T. It qualitatively and quantitatively explains the observed nonlinear dependence of the characteristic temperatures and the hysteresis of FOMMSPT including its elimination in some compositions of the Ni–Mn–In Heusler alloys under sufficiently high magnetic field.

***Index Terms*— Ni–Mn–In Heusler alloy, Clausius–Clapeyron relation (CCR), magnetic materials, magnetic properties, the first-order phase transition (FOPT).**

I. Introduction

At PRESENT, the Clausius–Clapeyron relation (CCR) is widely used to describe the linear shift in the characteristic temperatures of the first-order phase transitions (FOPTs) in solids under action of external fields [1]–[5]. The CCR is applied for thermodynamical treatment of not only the magnetostructural the FOPTs under magnetic field, but also for the martensitic transformation induced by external mechanical stress [6]–[8]. The derivation of the CCR in the literature is rarely discussed [9], [10], usually only the final expression is indicated

$$\frac{dT}{dH} = -\frac{\Delta M}{\Delta S_M} \tag{1}$$

where dT is the shift of the characteristic temperatures of FOPT at the magnetic field change dH, ΔM is the change of the magnetization of the sample, and ΔS_M is the change of the sample's entropy due the FOPT in zero field. The physical meaning of the CCR is the linear dependence of the change of the FOPT characteristic temperatures on the external field and the inverse dependence on the change of entropy at the FOPT in zero field. The linear character of this dependence is a consequence of the fact that this relation was obtained in the linear approximation of the free energy potential expansion into a series of the members, connected with the temperature and the field changes. Obviously, if the general approach is correct, then the CCR is to be valid only for the not very high fields [1], [2], [8].

Recently, the first-order metamagnetostructural phase transition (FOMMSPT) in some nonstoichiometric compositions of Ni–Mn–In, Ni–Mn–Sn Heusler alloys has attracted large attention due to high sensitivity of this transition to the magnetic field and accompanying phenomena such as the magnetic-field-induced shape memory effect, the strong inverse magnetocaloric effect, and the elastocaloric effect, promising from the point of view of applications [11]. The nature of the FOMMSPT is usually treated as a transition from the high temperature ferromagnetic cubic structural (austenitic) phase to the low-temperature, weak-magnetic, low-symmetry (martensitic) structural phase [12]. The CCR successfully describes the shift of characteristic temperatures of the FOMMSPT in Ni–Mn–In alloys for those compositions, in which the characteristic temperatures of the FOMMSPT are below approximately 250 K, under not too high magnetic fields (as a rule 0–5 T) [1].

The anomalous (nonlinear) behavior of the characteristic temperatures of the FOMMSPT in Ni–Mn–In Heusler alloy at an external high magnetic field was found in [13]. In addition, the critical behavior, e.g., elimination of the FOPT, not described by the CCR, was revealed by measuring the magnetic moment and the electrical resistivity of $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ sample in magnetic fields up to 18 T. The similar critical behavior of the characteristic temperatures was observed in the $Ni_{37}Co_{11}Mn_{42.5}Sn_{9.5}$ Heusler alloy also. The critical behavior was associated with the kinetic phenomena at the FOMMSPT in magnetic field at low temperatures [14]. At present, there is no theoretical description of the anomalous behavior of the characteristic temperatures of the FOMMSPT in these alloys.

The purpose of this paper is to derive the variant of the CCR capable to describe anomalous behavior of the characteristic temperatures of the FOMMSPT in the high magnetic fields and to check experimentally the results of calculations on the example of the Ni–Mn–In Heusler alloys.

II. Experimental Details

The polycrystalline samples with the nominal compositions $Ni_{46}Mn_{41}In_{13}$ were synthesized by the arc melting technique in argon atmosphere. Then, the samples were annealed in vacuum for 48 h under 1173 K for homogenization. The elemental

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TABLE I
PHYSICAL SPECIFICATIONS OF THE SAMPLE $Ni_{45.4}Mn_{40.9}In_{13.7}$

Designation	Value in SI	Data source
M_s	214 K	experimental data M=f(T,H)
M_f	205 K	experimental data M=f(T,H)
A_s	219 K	experimental data M=f(T,H)
A_f	231 K	experimental data M=f(T,H)
T_0	222,5 K	experimental data M=f(T,H)
λ_0	2960 J/kg	experimental DSC data
μ_0	$1{,}25\cdot10^{-6}$ H/A^2	-
M_A	75 A·m^2/kg	experimental data M=f(T,H)
M_M	0 A·m^2/kg	formulation of the problem
ΔH	$0..\approx16\cdot10^6$ A/m	formulation of the problem
τ_A	1,90 J/(kg·K^2)	experimental data C_p=f(T) [16]
τ_M	1,84 J/(kg·K^2)	experimental data C_p=f(T) [16]
σ_A	$3\cdot10^{-6}$ m^3/kg	experimental data M=f(T,H)
σ_M	0 m^3/kg	formulation of the problem
γ_A	−0,2 A·m^2/(kg·K)	experimental data M=f(T,H)
γ_M	0	formulation of the problem
$\Delta\varepsilon$	0,011	[17]
E_A	≈10 GPa	[18]
E_M	≈10 GPa	[18]
ρ	6138 kg/m^3	[18]

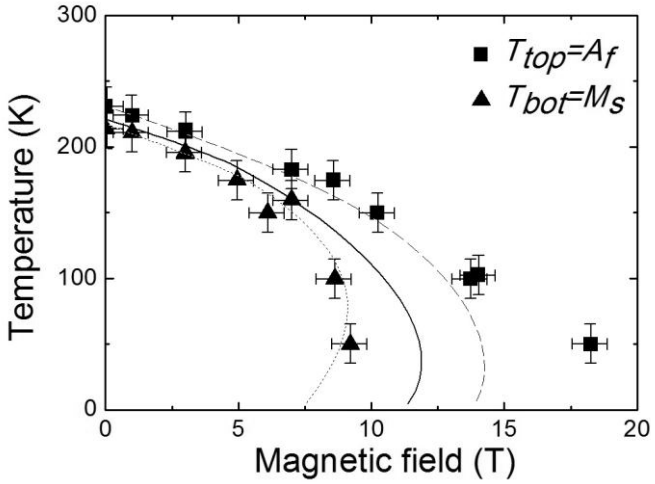

Fig. 1. Comparison of the experimental data with the calculations according to (18), (23), as shown at the top of the next page, and (24), as shown at the top of the next page. The temperatures T_{bot} and T_{top} are experimental data—triangular and square points, respectively; T_{bot} is calculated—dotted line, and T_{top} is calculated—dashed line; and ΔT is calculated—solid line, depending on the magnetic field for the $Ni_{45.4}Mn_{40.9}In_{13.7}$ sample.

chemical composition of the samples and their homogeneity was determined by the Energy-dispersive X-ray spectroscopy (EDX) analysis, and the sample with the $Ni_{45.4}Mn_{40.9}In_{13.7}$ composition was selected for further research. The magnetization of the sample versus temperature $M = f\ (T, H)$ was measured in magnetic fields up to 14 T using the ≪ Quantum Design ≫ Physical Property Measurement System (PPMS) system. The magnetization was studied in the pulsed magnetic fields up to 25 T as well. The latent heat of the FOPT λ_0 was determined by the Differential scanning calorimetry (DSC).

III. RESULTS AND DISCUSSION

The measured data by the DSC and the magnetization versus temperatures and magnetic fields up to 25 T were used to determine the characteristic temperatures of the FOMMSPT and their dependence on the magnetic field. The data for the sample $Ni_{46}Mn_{41}In_{13}$ are presented in Table I and Fig. 1. The temperatures of the FOMMSPT are sensitive to the magnetic field, and they decrease as field increases. The temperature hysteresis of the FOMMSPT widening is observed, because the left and the right edges of the hysteretic loop have the different rates of the shift with increasing field (Fig. 1).

Let us consider a simple thermodynamic model for explaining these features. The necessary condition for the realization of any the FOPT is the equality of the thermodynamic potentials of the phases at a certain temperature [15]. For the isothermal conditions, the thermodynamic potential of the free energy F must be chosen to calculate the phase equilibrium

$$F = U - TS - MH. \tag{2}$$

Here, U is an internal energy of a magnet. The change of a free energy is

$$dF = -SdT - MdH. \tag{3}$$

Let the equality of the free energies of the phases of austenite—F_A and martensite—F_M of a magnet with the FOPT be observed in zero field at temperature T_0: $F_A(0) = F_M(0) = F_0$. Then, under magnetic field H, the equilibrium point of the phases will shift from T_0 to a certain temperature $T_t = T_t(H)$, which can be calculated in first approximation, passing to finite differences in (3)

$$F_A - F_0 = -S_A(T_t - T_0) - M_A H \tag{4}$$

$$F_M - F_0 = -S_M(T_t - T_0) - M_M H \tag{5}$$

where M_A and M_M are the magnetizations of the austenitic and martensitic phases, respectively. Subtracting (4) from (5), we obtain

$$(T_t - T_0) = -(M_A - M_M)H/(S_A - S_M). \tag{6}$$

This equation is just commonly referred as the CCR. For the Ni–Mn–In alloys with an excess of Ni magnetization of martensite M_M can be neglected in comparison with the magnetization of austenite M_A, which implies

$$\Delta T(H)/T_0 = (T_t - T_0)/T_0 = -M_A H/\lambda_0 \tag{7}$$

where $\lambda_0 = T_0(S_A - S_M)$—the latent heat of the transition in zero field. The sign of change of the FOMMSPT temperature under magnetic field turns out to be negative, as observed in the experiment. The sign of the field effect corresponds to the more general principle of thermodynamics—the Le Chatelier's principle.

We decompose F at temperature T_0 in the Taylor series to terms of the second order in ΔT and ΔH

$$F = F_0 + \frac{\partial F}{\partial T}\Delta T + \frac{\partial F}{\partial H}\Delta H + \frac{1}{2}\frac{\partial^2 F}{\partial T^2}\Delta T^2 + \frac{1}{2}\frac{\partial^2 F}{\partial H^2}\Delta H^2 + \frac{\partial^2 F}{\partial T \partial H}\Delta T \Delta H. \tag{8}$$

Let us take into account that $(\partial F/\partial T)_H = -S$, $(\partial F/\partial H)_T = -M$, $(\partial^2 F/(\partial T \partial H)) = (\partial^2 F/(\partial H \partial T))$, therefore

$$\frac{\partial S}{\partial H} = \frac{\partial M}{\partial T}. \tag{9}$$

$$\Delta T = T_t - T_0 = \frac{-\lambda_0 - T_0(\gamma_A - \gamma_M)\Delta H \pm \sqrt{(\lambda_0 + T_0(\gamma_A - \gamma_M)\Delta H)^2 - 2T_0(\tau_A - \tau_M)\left[T_0(M_A - M_M)\Delta H + \frac{1}{2}T_0(\sigma_A - \sigma_M)\Delta H^2\right]}}{T_0(\tau_A - \tau_M)} \tag{17}$$

$$T_{\text{bot}} - T_0 = \frac{-\lambda_0 - \gamma_A T_0 \Delta H \pm \sqrt{[\lambda_0 + \gamma_A T_0 \Delta H]^2 - 2(\tau_A - \tau_M)T_0\left[M_A T_0 \Delta H + \frac{1}{2}E_M T_0(\varepsilon_{A0} - \varepsilon_{M0})^2\right]}}{(\tau_A - \tau_M)T_0} \tag{23}$$

$$T_{\text{top}} - T_0 = \frac{-\lambda_0 - \gamma_A T_0 \Delta H \pm \sqrt{[\lambda_0 + \gamma_A T_0 \Delta H]^2 - 2(\tau_A - \tau_M)T_0\left[M_A T_0 \Delta H - \frac{1}{2}E_A T_0(\varepsilon_{M0} - \varepsilon_{A0})^2\right]}}{(\tau_A - \tau_M)T_0} \tag{24}$$

Then, we introduce three important parameters

$$\frac{\partial^2 F}{\partial T^2} = -\left(\frac{\partial S}{\partial T}\right)_H = \frac{-C_H}{T} = -\tau \tag{10}$$

$$\frac{\partial^2 F}{\partial H^2} = -\left(\frac{\partial M}{\partial H}\right)_T = -\sigma \tag{11}$$

$$\frac{\partial^2 F}{\partial T \partial H} = -\frac{\partial S}{\partial H} = -\gamma. \tag{12}$$

We obtain the expansion of free energy of the austenitic and martensitic phases $F_A(T, H)$ and $F_M(T, H)$ near point of their equality T_0

$$F_A - F_0 = -S_A \Delta T - M_A \Delta H - \frac{1}{2}\tau_A \Delta T^2 - \frac{1}{2}\sigma_A \Delta H^2 - \gamma_A \Delta T \Delta H \tag{13}$$

$$F_M - F_0 = -S_M \Delta T - M_M \Delta H - \frac{1}{2}\tau_M \Delta T^2 - \frac{1}{2}\sigma_M \Delta H^2 - \gamma_M \Delta T \Delta H. \tag{14}$$

Subtracting (13) from (14), we obtain

$$(S_A - S_M)\Delta T + (M_A - M_M)\Delta H + \frac{1}{2}(\tau_A - \tau_M)\Delta T^2 + \frac{1}{2}(\sigma_A - \sigma_M)\Delta H^2 + (\gamma_A - \gamma_M)\Delta T \Delta H = 0. \tag{15}$$

We take into account that $(S_A - S_M) = \lambda_0 / T_0$ and obtain

$$\lambda_0 \Delta T + T_0(M_A - M_M)\Delta H + \frac{1}{2}T_0(\tau_A - \tau_M)\Delta T^2 + \frac{1}{2}T_0(\sigma_A - \sigma_M)\Delta H^2 + T_0(\gamma_A - \gamma_M)\Delta T \Delta H = 0. \tag{16}$$

Equation (16) can be called the CCR in the second order of the expansion (the second-order CCR). The roots of (16) will be the value of the displacement of the equilibrium point of the phases, which will be equal to (17), as shown at the top of this page.

We take into account that $M_M = 0$, $\sigma_M = 0$, $\gamma_M = 0$, we also assume that the austenite magnetization does not depend on the magnetic field (we neglect the paraprocess), and suppose that $\sigma_A = 0$ then

$$\Delta T = T_t - T_0 = \frac{-\lambda_0 - T_0\gamma_A H \pm \sqrt{(\lambda_0 + T_0\gamma_A H)^2 - 2T_0^2(\tau_A - \tau_M)M_A H}}{T_0(\tau_A - \tau_M)}. \tag{18}$$

The free energy of the alloy in the intermediate region of the FOPT is equal to $F = \min(F_A, F_M)$

$$F_A - F_0 = -S_A \Delta T - M_A \Delta H - \frac{1}{2}\tau_A \Delta T^2 - \frac{1}{2}\sigma_A \Delta H^2 - \gamma_A \Delta T \Delta H + \frac{1}{2}E_A(\varepsilon_A - \varepsilon_{A0})^2 \tag{19}$$

$$F_M - F_0 = -S_M \Delta T - M_M \Delta H - \frac{1}{2}\tau_M \Delta T^2 - \frac{1}{2}\sigma_M \Delta H^2 - \gamma_M \Delta T \Delta H + \frac{1}{2}E_M(\varepsilon_M - \varepsilon_{M0})^2. \tag{20}$$

To find the temperature $T_{\text{bot}} = M_s$ and $T_{\text{top}} = A_f$ of the absolute loss of phase stability (the upper and lower boundaries of the hysteresis loop of the FOPT) in a magnetic field H, we obtain the following expressions, respectively:

$$F_A(T_{\text{bot}}, H, \varepsilon_{A0}) = F_M(T_{\text{bot}}, H, \varepsilon_{A0}) \tag{21}$$

$$F_A(T_{\text{top}}, H, \varepsilon_{M0}) = F_M(T_{\text{top}}, H, \varepsilon_{M0}). \tag{22}$$

We substitute (19) and (20) into expressions (21) and (22) and solve the latter with respect to T_{bot} and T_{top}. We take into account that $M_M = 0$, $\sigma_M = 0$, and $\gamma_M = 0$, and also assume that the austenite magnetization does not depend on H (neglecting a paraprocess), and set $\sigma_A = 0$, then we get

We take the values of the physical characteristics from Table I for the numerical calculations. We plot the graphs for the expressions of ΔT, T_{bot}, and T_{top} in the dependence on the magnetic field and compare the theoretical and experimental data (see Fig. 1). The experimental data were obtained by measurements of $M = f(T, H)$ at magnetic fields up to 14 T for the sample $Ni_{45.4}Mn_{40.9}In_{13.7}$ as well as measurements in the pulsed magnetic fields up to 25 T.

As can be seen from Fig. 1, the values of T_{bot}, calculated theoretically and obtained experimentally, are in good agreement. However, the experimental values of T_{top} behave anomalously after reaching a magnetic field of 10 T. The value of H at which the characteristic temperatures are at the vertex of the parabolic curve is the critical magnetic field of the FOMMSPT.

The behavior of the characteristic temperatures of the FOMMSPT in a magnetic field from the parabolic dependence for $Ni_{45.4}Mn_{40.9}In_{13.7}$ does not manifest a pronounced extremum. For the sample of $Ni_{43}Mn_{37.65}In_{12.35}Co_7$ Heusler alloy with a large coefficient of field sensitivity $k = -14.4$ K/T, higher characteristic temperatures (M_s increases from 214 to 247 K), and a larger difference ($T_C - M_s$) (the difference ($T_C - M_s$) increases from 120 to 180 K), it is possible to observe an explicit extremum [19], [20].

The parabolic behavior of the characteristic temperatures of the FOMMSPT in the $Ni_{46}Mn_{41}In_{13}$ alloy in a magnetic field according the second-order CCR was previously experimentally observed in [7]. It was found by measuring the sample's magnetization in pulsed magnetic fields and SQUID magnetometer, which characteristic temperatures M_s and A_f of $Ni_{45}Co_5Mn_{36.1}In_{13.9}$ single-crystal behaved according to the parabolic law, and the A_f showed anomalous behavior after passing through the extremum.

Thus, it is possible to predict the characteristic temperatures M_s and A_f behavior under high magnetic fields more accurately by using the developed theoretical model. Should be noted that this model has significant discrepancies with the experimental data at calculation A_f temperature under magnetic fields more than 10 T for the $Ni_{46}Mn_{41}In_{13}$ Heusler alloy. It can be explain by the influence of kinetic phenomena, which our model does not take into account. However, the model works very well under fields less than 10 T, and we think that it requires verification on other famous systems with the FOMMSPT such as Ni–Mn–Sn [21], Fe–Rh [22], [23].

IV. Conclusion

The derivation is presented of the CCR in the second order of expansion of free energy potential on the change of temperature and magnetic field on the example of the $Ni_{46}Mn_{41}In_{13}$ Heusler alloys with the FOMMSPT. It is shown that the second-order CCR describes satisfactory the nonlinear shift in the characteristic temperatures of the FOMMSPT in magnetic fields up to 25 T. It qualitatively and quantitatively explains the observed nonlinear dependence of the characteristic temperatures and the hysteresis of FOMMSPT including its elimination in some compositions of the $Ni_{46}Mn_{41}In_{13}$ Heusler alloys under sufficiently high magnetic field. The general conclusions are made at considering of our theoretical model.

1) The thermodynamic model describing the FOMMSPT on the basis of the second-order CCR was proposed. The model explains qualitatively the following properties of the FOMMSPT in the Ni–Mn–In Heusler alloys: a) the nonlinear decrease of the phase transition temperature with increasing of the magnetic field; b) the broadening of the hysteresis loop with increasing of the magnetic field; c) the faster shift of the left edge of the hysteresis loop compared to the right edge; and d) the possibility of the existence of a critical point on the $T-H$ diagram.
2) The calculations based on the proposed thermodynamical model of the FOMMSPT characteristic temperatures for the Heusler alloy $Ni_{46}Mn_{41}In_{13}$ are in good agreement with the experimental data under magnetic fields less than 10 T.

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