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On the composition and magnetic field dependence of the transformation entropy in shape memory alloys

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ABSTRACT

It is illustrated that the composition or magnetic field dependence of the transformation entropy, Δs, in shape memory alloys, SMAs, can lead to $\Delta s^{-1} \propto A_f - M_f$ type relation (A_f and M_f are the austenite and martensite finish temperatures, respectively). This relation (taking M_s instead of A_f, where M_s is the martensite start temperature) was originally derived from the Landau theory, but until now it was verified only in ferromagnetic SMAs investigated under external magnetic field. Analysing the validity conditions of the above relation we argue in favour of relation $\Delta s^{-1} \propto A_f - M_f$. Furthermore, it is pointed out that relation between Δs^{-1} and a difference of the transformation temperatures is expected only if both shows monotonic dependence on a third variable (composition, degree of atomic order or magnetic field). Thus, $\Delta s^{-1} \propto A_f - M_f$ plots, based on the dependence on composition or on the degree of atomic order of Δs and $A_f - M_f$, are constructed in different ferromagnetic SMAs and in $Ni_{50+x}Ti_{50-x}$ alloys. The origin of the composition and magnetic field dependence of Δs in non-ferromagnetic and ferromagnetic SMAs is also discussed.

1. Introduction

The magnetic order can influence the transformation entropy, Δs_{tr}, in ferromagnetic shape memory alloys, SMAs, [1–11]. The large difference in magnetization values between austenite, A, and martensite, M, e.g. in metamagnetic shape memory alloys (where A is ferromagnetic and M is weakly magnetic or paramagnetic) leads to promising properties [1]. These are for instance the magnetic field induced shape recovery [12], high values of magnetoresistance [13] and the inverse magnetocaloric effect [14]. Changes in magnetic order result in change of the transformation entropy and understanding of such effects is important for applications too.

The effect of composition can also have an influence on the transformation entropy. While it is independent of composition in non-ferromagnetic SMAs, with the only exception of $Ni_{50+x}Ti_{50-x}$ alloys [15], it showed a well-expressed composition dependence in NiMnGa [16] or in a set of metamagnetic alloys (see e.g. [1]). We will discuss the consequences of the composition and magnetic field dependence of Δs_{tr}, which can result in a relation between Δs_{tr} and a certain difference of the martensitic transformation temperatures.

For non-magnetic SMAs the main contribution to Δs_{tr} is of vibrational origin, Δs_v, and stems from phonon softening of austenite near the transformation temperature [17,18]. For ferromagnetic SMAs, FMSMAs, there is also a magnetic contribution, Δs_m, to Δs_{tr}:

$$\Delta s_{tr} = \Delta s_v + \Delta s_m. \tag{1}$$

For A to M transformations $\Delta s_v = s_M - s_A < 0$, while $\Delta s_m > 0$ for metamagnetic alloys [7].

From ferroelastic description of martensitic transformations, MT, in the framework of the Landau theory, a reciprocal relation between the transformation entropy, Δs_{tr}, and the difference of the martensite a start and finish temperatures, $M_s - M_f$ was derived [4,10,19], in the following form

$$M_s - M_f \approx \frac{1}{\Delta s_{tr}} \frac{3\varepsilon_M^2 C'(M_s)}{2}. \tag{2}$$

Here Δs_{tr} denotes the transformation entropy per unit volume. ε_M and C' are the transformation strain ($\varepsilon_M = \frac{a}{c} - 1$, characterizing the tetragonal distortion of the martensite, a and c are the corresponding lattice parameters) and the shear modulus of the austenite, respectively. Although in its derivation general considerations were used, i.e. it is expected that it should be valid for non-ferromagnetic shape memory

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alloys as well, experimental verification of this relationship exists until now only for transformations in ferromagnetic alloys observed under external magnetic field [10]. It was argued in the literature that such a relation has quite universal character at least in metamagnetic alloys where it was observed [6,11].

In this communication we will discuss the validity conditions of (2) and illustrate that from the Landau theory a reciprocal relation between Δs and the $T_1 - T_2$ temperature difference can be derived (where T_2 and T_1 are the liability temperatures: the austenite is unstable below T_2 and the martensite is unstable above T_1). $T_1 - T_2$ represents the maximal possible width of the hysteresis [20–22] (if the forward and reverse MT would take place at T_2 and T_1, i.e. $T_2 = M_s = M_f$ and $T_1 = A_s = A_f$, A_s and A_f are the austenite start and finish temperatures, respectively). In fact, in the $T_1 - T_2$ interval the two phases can coexist (both are stable) if once have been nucleated [22]. During cooling or heating the foremost temperature at which the phase transition occurs is the equilibrium transformation temperature, T_o (lying between T_2 and T_1), at which the difference of the free energies of the two phases (which is the drivng force) is zero [22]. In real systems, due to the presence of nucleation barrier(s), dissipation processes and creation/annihilation of local internal elastic energies, the experimentally determined transformation temperatures show undercooling/overheating and have terms expressing the contributions from the above energies [23,24]. Thus, the real width of the hysteresis ($\Delta T_h = \frac{A_s+A_f}{2} - \frac{M_s+M_f}{2}$) is usually less than $T_1 - T_2$, and we will argue that instead of $M_s - M_f$ or ΔT_h the choice of $A_f - M_f$ is better for replacing $T_1 - T_2$. The dissipative/nucleation and elastic contributions to the transformation temperatures can be dependent on the metallurgical conditions (grain size, microstructure, martensite variant structure, etc.) of the alloy investigated, while the transformation entropy is less sensitive for them. Indeed, it was demonstrated recently in Ni-Mn-based alloys [25] that while Δs was independent of the microstructure $M_s - M_f$ was influenced by it.

We will argue that functional relationship between Δs_{tr} and $M_s - M_f$ or $A_f - M_f$ (which, although still can be less than $T_1 - T_2$, provides the best experimental approach for it) can exist only if both Δs_{tr} and $M_s - M_f$ or $A_f - M_f$ are monotonic functions of a third variable, which can be the composition, degree of atomic order or external magnetic field. Indeed, it was found in a set of different shape memory alloys that both Δs_{tr} and the transformation temperatures (or some combination of them like $M_s - M_f$, ΔT_h, or $A_f - M_f$) had well defined composition or magnetic field dependence [1–8,10,11,16,26–28]. Thus, it will be shown that a relation Δs_{tr}^{-1} versus $A_f - M_f$ exists not only for Δs_{tr} measured during changing the magnetic field, but in zero external field, even in a non-ferromagnetic ($Ni_{50+x}Ti_{50-x}$) system, if there is a systematic composition dependence of the above quantities.

Understanding the origin of $\Delta s^{-1} \propto A_f - M_f$ type relations is important for all shape memory alloys and especially for metamagnetic shape memory alloys under external magnetic field, where the magnetic contribution dominates the transformation entropy, determining the magnetocaloric behaviour as well. Enlightening that the above relationship can exist if both the entropy change and the $A_f - M_f$ difference depend on a third variable (composition, degree of atomic order or magnetic field) can help process optimization of SMAs for different applications [29–33].

2. On the validity conditions of $\Delta s^{-1} \propto M_s - M_f$ type relations

2.1. Relations from the Landau theory

2.1.1. Basic relations

In [4] and [19], from general considerations for ferroelastic cubic to tetragonal martensitic transformations, the following relations were derived in the framework of Landau theory (in the absence of external fields). The expansion of the difference of the free energy of the strained and unstrained austenite can be given in the following simple form [34,35]

$$\Delta f = f(T,u) - f(T,0) = \frac{1}{2}c_2(T)u^2 + \frac{1}{3}\alpha u^3 + \frac{1}{4}bu^4. \tag{3}$$

Here u is the shear-strain order parameter (the shear strain on one (110) plane in one [110] direction). The $c_2(T)$ elastic modulus shows phonon softening and given by $c_2(T) = c_{2o}(T - T_2)$, with $c_{2o} > 0$, while $\alpha(>0)$ and $b(>0)$ are temperature independent constants. c_2 changes its sign at T_2, below which the austenite is unstable. $c_{2o} = \frac{\partial c_2}{\partial T}$ has entropy per volume dimension. From the minimization of (3), the equilibrium values of the order parameter, u_o, was obtained [4,19]:

$$\mathrm{u_o} = 0 \ \text{ for } \ T > \mathrm{T_1} \tag{4}$$

and

$$\mathrm{u_o(T)} = -\frac{\alpha}{2b}\left[1 \pm \sqrt{1 - \frac{4c_2(\mathrm{T})b}{a^2}}\right] = -\frac{\alpha}{2b}\left[1 + \sqrt{1 - \frac{c_2(\mathrm{T})}{c_t}}\right], \ \text{for } \ T_2 < \mathrm{T} < \mathrm{T_1}. \tag{5}$$

At temperatures below T_2 ($c_2(T_2) = 0$) the austenite is unstable, while above T_1, which is given by $1 = \frac{c_2(T_1)}{c_t}$ condition, i.e.

$$c_2(T_1) = c_t = c_{2o}(T_1 - T_2) = \frac{\alpha^2}{4b}, \tag{6}$$

the martensite is unstable. T_1 and T_2 are the liability temperatures. At these temperatures $u_o(T_1) = -\frac{\alpha}{2b}$, and $u_o(T_2) = -\frac{\alpha}{b}$, respectively. $u_o(T_2)$ is related to $\varepsilon_M = \frac{a}{c} - 1$ [4,19] as $u_o(T_2) = 3\varepsilon_M$. Furthermore, $c_2(T) = \frac{C'(T)}{3}$ fulfils, where C' is the shear modulus.

Using Eq. (6) the expression $c_2(T) = c_{2o}(T - T_2)$ can also be written as [19]

$$c_2(T) = \frac{\alpha^2}{4b}\frac{T - T_2}{T_1 - T_2} = c_t\frac{T - T_2}{T_1 - T_2}, \tag{7}$$

and thus $\frac{c_2(T)}{c_t} = \frac{T - T_2}{T_1 - T_2}$ in (5). It is important noting that according to (6) since, all input parameters, c_{2o}, α and b, are constants and fixed, the $T_1 - T_2$ difference is an inherent property for a given alloy.

It was also shown in [4] that, for ferromagnetic SMAs, due to the inclusion of an energy term related to the change of magnetic order during the MT, the forms of the above expressions ((3)-(6)) can be still kept with modified expansion coefficients: $c_2^*(T)$, $\alpha^*(T)$ and $b^* = const.$ The magnetic energy difference of the strained and unstrained austenite had the form [4,34]

$$\Delta f_m = -\delta_{ex}M^2u_1. \tag{8}$$

Here δ_{ex} and M denote the volume (isotropic) magnetostriction coefficient (the anisotropic part of the magnetostriction was neglected) and the magnetization of austenite. The value of the order parameter, u_1, is related to the relative volume change caused by the MT:

$$u_1 = \frac{1}{3}\frac{\Delta V}{V}. \tag{9}$$

The form of (8) indicates that in [4] it was assumed that the change of magnetic energy has purely magnetoelastic origin. Indeed (8) describes the effect of spontaneous volume magnetostriction during MT. According to [4] the magnetic exchange energy, $\frac{1}{2}J_iM_i(T)^2$ ($i = A,M$), is independent of the strain, u, and only the magnetoelastic energy will change during MT. If the elastic subsystem does not interact with its magnetic subsystem (i.e. $\delta_{ex} = 0$) during MT, there are no changes in the directions of the magnetic moments and thus the magnetic contribution to the entropy change would be zero. The corrected coefficients, $c_2^*(T)$ and $\alpha^*(T)$, contain additive terms proportional to $\delta_{ex}M(T)^2$ (and thus α^* is also temperature dependent):

$$c_2^*(T) = c_2(T) + \frac{\alpha_2}{c_1}\delta_{ex}M^2(T),$$

$$\alpha^*(T) = \alpha + \frac{3b_7}{2c_1}\delta_{ex}M^2(T), \tag{10}$$

$$b^* = b - \frac{\alpha_2^2}{2c_1}.$$

In the above relations the α_2, b_7 and c_1 (constant) coefficients are the corresponding moduli present in the Landau expansion of the free energy density if $u_1 = \frac{1}{3}\frac{\Delta V}{V}$ is not zero ($c_1 = 3B$, where B is the bulk modulus) [4].

2.1.2. Expressions for the entropy

The total transformation entropy, according to the general relation, $\Delta s_{tr} = -\frac{\partial(\Delta f^*)}{\partial T}$, is given as [4]

$$\begin{aligned}\Delta s_{tr} &= -\frac{1}{2}\frac{\partial c_2^*}{\partial T}u_0^2(T) - \frac{1}{3}\frac{\partial \alpha^*}{\partial T}u_0^3 \\ &= -\frac{1}{2}\frac{\partial c_2}{\partial T}u_0^2(T) - \frac{1}{2}\left(\frac{\partial c_2^*}{\partial T} - \frac{\partial c_2}{\partial T}\right)u_0^2(T) - \frac{1}{3}\frac{\partial \alpha^*}{\partial T}u_0^3 \\ &= \Delta s_v + \Delta s_m.\end{aligned} \tag{11}$$

Here

$$\Delta s_v = -\frac{1}{2}\frac{\partial c_2}{\partial T}u_0^2(T), \tag{12}$$

is the non-magnetic (vibrational) entropy change, while the magnetic part, using that u and u_1 are interrelated ($2u_1 \cong -\left(\alpha_2 u^2 + b_7 u^3\right)\frac{1}{c_1}$: see Eq. (9) in [4]), can be further rewritten as [4]

$$\Delta s_m = -\frac{1}{2}\left(\frac{\partial c_2^*}{\partial T} - \frac{\partial c_2}{\partial T}\right)u_0^2(T) - \frac{1}{3}\frac{\partial \alpha^*}{\partial T}u_0^3 = 2\delta_{ex}u_1 M\frac{\partial M}{\partial T}. \tag{13}$$

A relation similar to (2) can be obtained for Δs_v, if (12) is rewritten (using (6) and (7) too) as

$$\Delta s_v = -\frac{1}{2}\frac{\partial c_2}{\partial T}u_0^2(T) = -\frac{9}{2}c_{2o}\varepsilon_M^2 = -\frac{9}{2}\frac{c_2(T_1)}{T_1 - T_2}\varepsilon_M^2 = -\frac{3}{2}\frac{C(T_1)}{T_1 - T_2}\varepsilon_M^2. \tag{14}$$

Since $c_{2o} > 0$, Δs_v is negative for austenite to martensite transformations. Relation (14), if we take into account the plausible assumption that the slope of c_2 is approximately the same at T_1 and T_2 [36], is the same as (26) of [4], but with minus sign since the M to A transition was considered in [4]. Comparing (14) with (2) we can see that they are equivalent (again for $\Delta s_{tr} = \Delta s_v$, i. e. in non-ferromagnetic SMAs) if $C(T_1) = C(M_s)$ and $T_1 - T_2 = M_s - M_f$. In the light of our comments above, the latter assumption can be questionable. This will be discussed in details below. Nevertheless, it is clear from the first glance, that $T_1 - T_2 \cong A_f - M_f$ choice is better, since it gives the largest difference (but which can be still less than $T_1 - T_2$) and the experimental error of it is the smallest one. (The transformation temperatures have typically $\pm 1 - 2K$ error bar.)

For the assessment whether a relation of type (2) or (14) can be valid for the total transformation entropy, Δs_{tr}, or not, let us take its form as given by (11),

$$\Delta s_{tr} = -\frac{1}{2}\frac{\partial c_2^*}{\partial T}u_0^2(T) - \frac{1}{3}\frac{\partial \alpha^*}{\partial T}u_0^3, \tag{15}$$

and use the corrected version of relation (7) (see also the Appendix A)

$$c_2^*(T) = c_t^*\frac{T - T_2^*}{T_1^* - T_2^*}. \tag{16}$$

Here, since the presence of magnetoelastic coupling causes a change of the liability temperatures [4], their modified values appear. Furthermore, we can show that c_{20}^* can be expressed as (see Eq. (A4) in Appendix A):

$$c_{2o}^* = \left[c_{2o} + M_o^2\frac{\alpha_2}{c_1}2\delta_{ex}m\frac{dm}{dT}\right] = \frac{c_t^*}{T_1^* - T_2^*} = \frac{c_2^*(T_1^*)}{T_1^* - T_2^*}, \tag{17}$$

where M_o is the saturation magnetization at $0K$ ($M = M_o m$) the T-dependence of m can be calculated e.g. from the Kuzmin relation [37] ($m\frac{dm}{dT}$ in (17) should be taken at T_2^*). The second term in the bracket originates from $c_2^*(T) = c_2(T) + \frac{\alpha_2}{c_1}\delta_{ex}M^2(T)$ relation as it is shown by (10).

Then, for $\frac{\partial c_2^*}{\partial T}$ we have,

$$\frac{\partial c_2^*}{\partial T} = c_{20}^* = \frac{c_2^*(T_1^*)}{T_1^* - T_2^*} \tag{18}$$

where (17) and $c_2^*(T) = c_{20}^*\left(T - T_2^*\right)$ were also used, and thus (15) can be rewritten as

$$\Delta s_{tr} = -\frac{1}{2}\frac{c_2^*(T_1^*)}{T_1^* - T_2^*}u_o^2(T_{tr}) - \frac{b_7}{c_1}\left(\delta_{ex}M_o^2 m\frac{dm}{dT}\right)u_o^3(T_{tr}). \tag{19}$$

In (19) $m\frac{dm}{dT}$ should be taken at $T = T_{tr}$. It can be seen that Δs_{tr} contains two parts. The first one has a dependence on $T_1^* - T_2^*$ which is similar to Eq. (2), and it is the only expression with non-modified values of the liability temperatures for non-ferromagnetic SMAs. In FMSMAs both terms have additions from the magnetoelastic corrections (c_2^*, according to (10), also contains a term proportional to M^2). Thus, the general relation can be expressed in the form

$$\Delta s_{tr} = -\frac{A}{T_1^* - T_2^*} - B_m, \tag{20}$$

For non-ferromagnetic SMAs $B_m = 0$ and $A = A_{nf}$, i.e.

$$\Delta s_{tr} = \Delta s_v = -\frac{A_{nf}}{T_1 - T_2}, \quad \text{with } A_{nf} = \frac{1}{2}c_2(T_1)u_o^2(T_{tr})(>0). \tag{21}$$

For FMSMAs $A = A_{nf} + B_o$ and

$$\begin{aligned}A &= \frac{1}{2}c_2^*(T_1^*)u_o^2(T_{tr}) = A_{nf} + B_o \quad , B_o \\ &= \frac{1}{2}c_{2o}u_o^2(T_{tr})\frac{\alpha_2}{c_1}\left(\delta_{ex}M_o^2 m\frac{dm}{dT}\right)(<O),\end{aligned}$$

and

$$B_m(\delta_A, T_{tr}) = \frac{b_7}{c_1}\left(\delta_{ex}M_o^2 m\frac{dm}{dT}\right)u_o^3(T_{tr})(>0), \tag{22}$$

and the δ_A-dependence of $B_m(\delta_A, T_{tr})$ and $B_0(\delta_A, T_{tr})$ ($\delta_A = 1 - \frac{T_{tr}}{T_c}$, where T_c is the Curie temperature, see also the Appendix B) can be calculated e. g. from the well-known Kuzmin relation [3,37]. It has to be noted, that for the description of the well-known δ_A-dependence of Δs_m in the Landau theory one has to use relation (13), as it was also done in [4].

It has to be noted that relation (2) was originally derived in [4,19] from (12) and from a relation between $\frac{dc_2}{dT}$ and $\frac{d\sigma_{Ms}}{dT}$, as given by the Clausius-Clapeyron relation. In addition, the validity of (2) was demonstrated by calculation of the $M_s - M_f$ difference (in fact the values of $T_1 - T_2$ were calculated, since it was assumed that $M_s - M_f = T_1 - T_2$) for Ni_2MnGa alloys. First, calculations by neglecting the magnetoelastic coupling (Fig. 1) (see the continuous curve in Fig. 1, which is adopted from [4,10]) were performed, and it was concluded that the calculated values substantially exceeded the experimental $M_s - M_f$ values. This is not surprising in the light of our comments above. Furthermore, it was mentioned in [4] that the presence of magnetoelastic coupling should violate the relationship (2), because the temperature interval of the MT is substantially reduced by it (see the dashed curve in Fig. 1). At the same time, after adding the magnetic correction, the inverse relation between the calculated relation between the

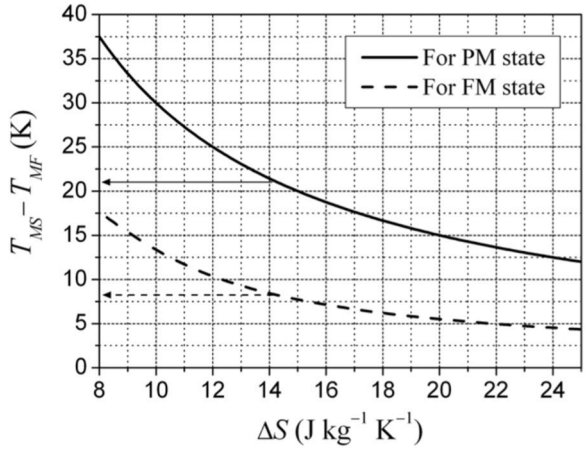

Fig. 1. Relation between $T_1 - T_2$ and the entropy change for zero (continuous line) and non-zero magnetoelastic contribution (dashed line). (The figure is adopted from [10], where the vertical axis in fact corresponds to $T_1 - T_2$ as well as to $T_1^* - T_2^*$, respectively and not to $M_s - M_s$, as shown in [10]; see also the text.).

temperature difference and the total entropy change remained valid since the correction led mainly to a down shift of the curve, and only to a moderate change in the slope of the $\frac{1}{\Delta s_{tr}} \cong \frac{1}{\Delta s_m} \propto (T_1 - T_2)$ relation. Thus, it was concluded that the careful analysis of the effect of magnetoelastic coupling on the characteristic MT temperatures is of interest. This can be further supported by the fact that after the publication of relation (2) in [4] its validity was confirmed for Δs_{tr} values measured under magnetic field only [10]. Since the magnetic entropy is much larger than the non-magnetic (vibrational) contributions [28], the above observation can be considered as experimental evidence of the validity of (2) for Δs_m. At the same time, the results presented in Fig. 1 rather suggest that Δs_v should follow (2) and the magnetic contribution causes a shift of the intercept and only a moderate change in the slope of the $\frac{1}{\Delta s_{tr}} \cong \frac{1}{\Delta s_m} \propto (T_1 - T_2)$ relation. In addition, there is no direct evidence published until now for the validity of (2) (or (15)) in non-ferromagnetic SMAs.

It can be seen, taking into account again that in [4] the negative value of Δs_{tr} (belonging to M to A transformation) was calculated, that the form of (20) is in accordance with the calculated $(T_1^* - T_2^*)$ versus Δs curve in Fig. 1 (with $A_1 > A_2 > 0$ as well as $B_o < 1$ and $B_m > 0$, in which $u_o^3 < 0$ and $\frac{dm}{dT} < 0$). Thus, relation $\frac{1}{\Delta s_{tr}} \cong \frac{1}{\Delta s_m} \propto (T_1^* - T_2^*)$ (see Eq. (20)) holds for the difference of the liability temperatures in the Landau theory. Nevertheless, the questions how $M_s - M_f$ and $T_1^* - T_2^*$ are interrelated and/or why $M_s - M_f$ (or $A_f - M_f$) can be linearly related to $\frac{1}{\Delta s_{tr}}$ are still open and will be addressed in the following chapter.

2.1.3. *Effect of external magnetic field on the transformation entropy*

The effect of external magnetic field was not considered in [4] and [10]. In [36] for the calculations of the entropy change two theoretical models were used. In the first (so-called simplified model, based on the Landau theory) the magnetic energy of the system was calculated using the experimentally measured magnetization, $M_{\exp}(T)$. $M_{\exp}(T)$ corresponds to M_A and M_M in the pure phases and thus these values appear in their magnetic exchange energies $(f_i(T) = \frac{1}{2} J_i(T) M_{io}^2 m_i^2, i = A, M)$ [34] with temperature dependent magnetic order parameters $m_i(T) = \frac{M_i(T)}{M_{io}}$, $(i = M, A)$ as well as in the Zeeman energies $(-M_i H)$. In the two phase region the average value of the exchange parameter, J_{av}, was used. Thus, in the two phase region the magnetic free energy had the form [36]

$$f = \frac{1}{2} J_{av} M_{\exp}(T)^2 - M_{\exp}(T) H = \frac{1}{2} \{(1-\xi) J_A + \xi J_M\} M_{\exp}(T)^2 - M_{\exp}(T) H$$

$$= \frac{1}{2} \xi (J_M - J_A) M_{\exp}(T)^2 - M_{\exp}(T) H = -\xi \delta_{ex} u_1 M_{\exp}(T)^2 - M_{\exp}(T) H, \quad (23)$$

where in accordance with [4], the introduction of the magnetoelastic energy into the free energy difference (8) led to renormalization of the exchange coefficient J_A

$$J_M - J_A = 2\delta_{ex} u_1. \quad (24)$$

In (23) and (24) ξ and J_i denote the martensite volume fraction as well as the magnetic exchange parameters, respectively. Furthermore, for the temperature dependence of the spin exchange parameter

$$J_i = J_{io} \frac{T - T_{ci}}{T_{ci}} \quad (25)$$

holds. (23) and (24) means that in the Landau theory (in accordance with to (13) too) the effect of the external magnetic field is manifested in the magnetic field dependence of $M(T)^2$ in the first term of (23) and in the $-H\Delta M(T) = -H(M_{\exp} - M_A)$ term, since in the free energy change $\Delta f = f - f_A$ (needed for the calculation of the entropy change) only these change during MT. Consequently, the external magnetic field should have an effect via both the field dependence of the magnetization present in the magnetoelastic term and via the $-H\Delta M(T)$ term. On the other hand, in the so-called detailed model, the same expressions, which will be shown below (see Eq. (28b)), were used. It was concluded that the agreement between the results of the two models was good.

2.2. *Transformation temperatures contain contributions from the derivatives of the elastic and dissipation/nucleation energies of transformation. Relations from local equilibrium model*

For the assessment whether a replacement of $T_1 - T_2$ by $M_s - M_f$ of by $\Delta T = A_f - M_f$ is a good choice or not, we have first to take into account that the difference of the liability temperatures is an inherent property of the phase transforming system and as such does not contain contributions from the microscopic details (local nucleation, dissipation and elastic energy contributions) of the transformation. On the other hand, the transformation temperatures naturally contain them. Indeed in the framework a local equilibrium description [23,24] the change of the free energy per unit volume during A to M MT can be given in the following form:

$$\Delta f(\xi) = \Delta f_{ch}(\xi) + D(\xi) + E(\xi) + \Delta f_m(\xi) + \Delta f_H(\xi), \quad (26)$$

where $E(\xi)$ and $D(\xi)$ denote the changes in the elastic, dissipative (frictional) + nucleation energies [23,24], respectively, during MT. $\Delta f_{ch}(\xi)$, $\Delta f_m(\xi)$ and $\Delta f_H(\xi)$ denote the differences in chemical as well as magnetic free energies in the absence and the in the presence of external magnetic field, $\mu_o H$, respectively. These terms are proportional to ξ, and their sum can be given as

$$\xi \Delta f_o = \Delta f_{ch}(\xi) + \Delta f_m(\xi) + \Delta f_H(\xi)$$
$$= \xi \left[(s_M - s_A)(T_o - T) + \Delta f_m^1(m_M, m_A) - \mu_o H \Delta M(T) \right] \quad (27)$$

where

$$\Delta f_{ch}(\xi) = \xi (f_M - f_A) = \xi [(u_M - u_A) - T(s_M - s_A)] = \xi (\Delta u - T\Delta s)$$
$$= \xi (s_M - s_A)(T_o - T), \quad (28a)$$

$$\Delta f_m(\xi) = \xi \Delta f_m^1(m_M, m_A) = \xi [f_{mM}(T, m_M) - f_{mA}(T, m_A)], \quad (28b)$$

$$\Delta f_H(\xi) = -\xi \mu_o H \Delta M(T). \quad (28c)$$

Here $T_o = \frac{\Delta u}{\Delta s}$ is the equilibrium transformation temperature (Δu and Δs is the difference of the internal energy and entropy, respectively) and $\Delta M(T) = M_M(T) - M_A(T)$.

Then, the local equilibrium condition [23,24], in the absence of external stress field, has the form

$$\frac{\partial \Delta f(\xi)}{\partial \xi} = (T_o - T)\Delta s_v + e(\xi) + d(\xi) + \Delta f_m^1(m_M, m_A) - \mu_o H \Delta M(T) = 0. \tag{29}$$

The inverse of the $T(\xi)$ function, which is given by Eq. (29), is the down (cooling) branch of the hysteresis loop [23,24]. It contains terms of the change of the elastic ($e(\xi) = \frac{\partial E}{\partial \xi}$), dissipative and nucleation ($d(\xi) = \frac{\partial D}{\partial \xi}$) as well as magnetic energy during MT. (The nucleation and dissipative terms have the same, positive, sign for both A to M and M to A transformations and they can be compiled into one term [23,24]).

Using the general relation for the entropy change, at a fixed value of ξ

$$\Delta s(\xi) = -\frac{\partial \Delta f(\xi)}{\partial T} = -\frac{d\Delta f}{dT} - \frac{\partial \Delta f}{\partial \xi}\frac{\partial \xi}{\partial T}$$
$$= \xi(s_M - s_A) - \xi \frac{\partial\left(\Delta f_m^1(m_M, m_A) - \mu_o H \Delta M\right)}{\partial T}, \tag{30}$$

where the local equilibrium condition (29) was used ($\frac{\partial \Delta f}{\partial \xi} = 0$). Thus, from (30) at $\xi = 1$ (i.e. for the full down transformation) we get

$$\Delta s_{tr} = (s_M - s_A) - \frac{\partial \Delta f_m^1(m_M, m_A)}{\partial T} + \mu_o H \frac{\partial \Delta M}{\partial T} = \Delta s_v + \Delta s_m + \Delta s_H, \tag{31}$$

which shows that the magnetic contribution naturally contains two terms Δs_m and Δs_H (in accordance with (26) too).

Furthermore, from (29) one can write for the transformation temperature

$$T(\xi) = T_o - \frac{e(\xi) + d(\xi)}{-\Delta s_v} - \frac{1}{\Delta s_v}\left(\Delta f_m^1(m_M, m_A) - \mu_o H \Delta M\right), \tag{32}$$

and thus

$$M_s - M_f = -\frac{e_o + d_o - e_1 - d_1}{-\Delta s_v} = \frac{e_1 - e_o}{-\Delta s_v}. \tag{33}$$

(the last terms of (32) cancel from (33) since these are independent of ξ). In (33) $e_i = \frac{\partial E}{\partial \xi}\Big|_{\xi=i}, i = -0, 1$ and $d_i = \frac{\partial D}{\partial \xi}\Big|_{\xi=i}, i = 0, 1$) and using that $D > 0$ has a linear ξ-dependence [24] $d_o = d_1$ and $D = \int_0^1 d_o d\xi = d_o$. From (33) and using that in a good approximation E has quadratic ξ-dependence ($-E_{up} = E_{down} = E > 0$; $-e_{up} = e_{down} \equiv e = (e_1 - e_o)\xi + e_o > 0$, $E = \frac{e_1 + e_o}{2}$, as well as $d_{down} = d_{up} = d_o$ [24]), one gets for the $A_f - M_f$

$$A_f - M_f = \frac{2d_o + e_1 - e_o}{-\Delta s_v}. \tag{34}$$

It can be seen that this difference is determined by the dissipative energy of a full cycle ($2d_o = 2D$) and the magnitude of the width of the transition ($\frac{e_1 - e_o}{\Delta s_v} = A_f - A_s = -(M_s - M_f)$ for symmetric hysteresis loops [38] and $\Delta s_v < 0$ for down and $\Delta s_v > 0$ for up process).

The Clausius-Clapeyron type relation can be obtained from $\frac{d\Delta f_o}{dT} + \frac{\partial \Delta f_o}{\partial H}\frac{dH}{dT} = 0$ (see (27) and (28)). Thus

$$\frac{d\Delta f_o}{dT} = -\Delta s_{tr} = -\frac{\partial \Delta f_o}{\partial H}\frac{dH}{dT} = -\frac{dH}{dT}\left[\frac{\partial \Delta f_m^1}{\partial H} - \mu_o \frac{\partial (H\Delta M)}{\partial H}\right], \tag{35}$$

which gives

$$\frac{dT_o}{dH} = \frac{\frac{\partial \Delta f_m^1}{\partial H} - \mu_o \frac{\partial (H\Delta M)}{\partial H}}{\Delta s_{tr}}. \tag{36}$$

If Δf_m^1 and ΔM is independent of H, (36) has the usual form of the well-known Clausius-Clapeyron relation

$$\frac{dT_o}{dH} = -\mu_o \frac{\Delta M}{\Delta s_{tr}}. \tag{37}$$

It can be added that the general form of the equilibrium transformation temperature can be obtained from the integral of (37) as

$$T_o(m_i, H) = T_o(0, 0) - \frac{1}{\Delta s_{tr}}\{\Delta f_m^1(m_M, m_A) - \mu_o H \Delta M\}. \tag{38}$$

If we adopt the approach used in [4] then in the above expressions $\Delta f_m^1(m_M, m_A)$ has to be replaced by (8).

It can be seen from the above expressions that while in the transformation temperature (Eq. (32)) the nominator depends on magnetic contributions, in expressions for the $M_s - M_f$ or $A_f - M_f$ differences the nominator depends only on the proper combinations of the derivatives of the elastic and dissipative energies. It means that in non-ferromagnetic SMAs a functional relation for instance between $A_f - M_f$ and $\frac{1}{\Delta s_v}$ is expected only if Δs_v is not constant and both $A_f - M_f$ and $\frac{1}{\Delta s_v}$ has a systematic dependence on a new variable (e.g. on composition or on the degree of atomic order: see the case of $Ni_{50+x}Ti_{50-x}$. discussed below where x is the composition.) On the other hand, in ferromagnetic SMAs, when the full entropy change is determined form experiments, one searches for a functional relation for instance between $A_f - M_f$ and $\frac{1}{\Delta s_{tr}}$. This can exist if both of them has a systematic dependence e.g. on the external magnetic field. Indeed, according to (30), such a dependence of $\frac{1}{\Delta s_{tr}}$ on the magnetic field is expected and if the $A_f - M_f$ difference depends on H too, $\frac{1}{\Delta s_{tr}} \propto A_f - M_f$ can be obtained. In general, one has always to search for the dependence of $A_f - M_f$, given by (34), and $\frac{1}{\Delta s_{tr}}$, given by (31), on the same variable (for non-ferromagnetic SMAs $\Delta s_{tr} \cong \Delta s_v$).

3. Discussion

3.1. Relations of type $M_s - M_f \propto \frac{1}{\Delta s}$ can exist only if both quantities show monotonic dependence either on a third variable (the composition, degree of atomic order or magnetic field)

In the light of the results of the previous chapters it is clear that the relation between $\frac{1}{T_1 - T_2}$ and Δs_v, or between $\frac{1}{T_1^* - T_2^*}$ and Δs_{tr} (see Eqs. (20)-(22)) is an inherent property of the Landau theory. In fact, $\frac{1}{T_1^* - T_2^*}$ is related to the derivative of the c_2^* (or C') modulus: $\frac{dc_2^*}{dT} = c_{20}^* = const = \frac{c_2^*}{T_1^* - T_2^*}$ (see Eq. (17) and Appendix A), which means that for a given alloy this relation is determined by the input parameters of the theory. This also means that in the Landau theory $T_1 - T_2$ is independent of the details of the nucleation, dissipation and local elastic energy changes during the nucleation and growth of martensite in the A to M MT. In contrast, these effects are described by expressions obtained from the local equilibrium description presented in the previous chapter (see Eqs. (33) and (34)), providing relations between the difference of certain transformation temperatures and the vibrational transformation entropy. This can be investigated directly in non-ferromagnetic SMAs. In searching for $\frac{1}{A_f - M_f} \propto \Delta s_{tr}$ type relations in ferromagnetic SMAs, the entropy change, Δs_{tr}, determined form the experimental data, contains magnetic contributions (which can be composition or magnetic field dependent as well as can depend on the degree of atomic order) and thus the dependence of $A_f - M_f$ (or $M_s - M_f$) on one of the above parameters is desired. In figures, will be shown below, the Δs versus $A_f - M_f$ function will be presented (since we argued in favour of this) if data were available for M_f as well as for A_f. If only data for M_f and M_s were given in the corresponding references, then the Δs versus $M_s - M_f$ function is given for comparison (or alone if no complete set of transformation temperatures were given).

Furthermore, it is expected that Δs_v in non-ferromagnetic SMAs is

constant [15] and independent of the derivatives of E and D and thus no functional relation between $M_s - M_f$ (or $A_f - M_f$) and Δs_v exists. Indeed it was shown in non-ferromagnetic SMAs, in the framework of the law of corresponding states for metals (based on the similarity of the interatomic potentials) [15,39], that $\frac{\Delta s_v}{k}$ (k is the Boltzmann-constant) can depend only on one, so-called phonon softening, parameter, $t_o(x) = \frac{T_o(x)}{T_m(x)}$, where $T_m(x)$ is the composition, x, dependent melting point. In addition, the reduced (dimensionless) values, $\frac{\Delta s_v}{k}$, had the same constant values at $t_o(0)$ within sub-classes of host SMAs, having the same type of crystal symmetry change during MT (e.g. B2/B19′(monclinic), in $Ni_{50+x}Ti_{50-x}$, $Ti_{45-x}Ni_{45+x}Cu_5$; B2/18 R (rhombohedral), in CuAlBe, CuZn, CuZnAl; and B2/B19 (orthorhombic) in $Ti_{50-x}Ni_{40+x}Cu_{10}$). This constant value showed only a moderate change between sub-classes: it changed from 0.16 (B2/18 R) to 0.56 (B2/B19′). Furthermore, it was observed that $\frac{\Delta s_v}{k}$ was independent of $t_o(x)$ and thus on x too, with only one exception: in $Ni_{50+x}Ti_{50-x}$ $\frac{\Delta s_v}{k}$ had approximately linear dependence on t_o, which means a composition dependence via the x-dependence of t_o. Thus, we can conclude that in non-ferromagnetic shape memory alloys, except the $Ni_{50+x}Ti_{50-x}$ system, the $\Delta s_{tr} = \Delta s_v$ entropy change is constant, independent of composition [15] (and see also [35] where the same conclusion is obtained for Cu-based SMAs).

3.1.1. Correlation based on composition dependence

The results, presented in Chapter 2.2, suggest that functional relation between $M_s - M_f$ (or $A_f - M_f$) and Δs_{tr} exist only if both quantities have a systematic dependence on a third variable. In the case of $Ni_{50+x}Ti_{50-x}$ (where $\Delta s_{tr} \cong \Delta s_v$) both have composition dependence [26,27]. Thus, Fig. 2 shows $\frac{1}{\Delta s}$ versus $M_s - M_f$ as well as versus $A_f - M_f$ plots in $Ni_{50+x}Ti_{50-x}$, on the basis of data published in [26,27]. In ferromagnetic SMAs, where the magnetic entropy is much larger than the non-magnetic (vibrational) contributions [40], both $\Delta s_m \cong \Delta s_{tr}$ and $M_s - M_f$ (or $A_f - M_f$) can also have a composition dependence too. Indeed, it was obtained that in $Ni_{2-x}Mn_{1-x}Ga$ [16] alloys as well as in NiMnIn and NiCoMnIn [1] alloys both have composition dependence. Thus, Figs. 3a and 3b show the $\frac{1}{\Delta s}$ versus $M_s - M_f$ as well as versus $A_f - M_f$ plots for $Ni_{2-x}Mn_{1-x}Ga$ system as well as for NiMnIn and NiCoMnIn systems.

3.1.2. Correlation based on change in degree of atomic order

In [3] the effect of degree of atomic order on the values of Δs_{tr} and $M_s - M_f$ was investigated in NiMnIn alloys (see Table 2 and Fig. 1 in [3]).

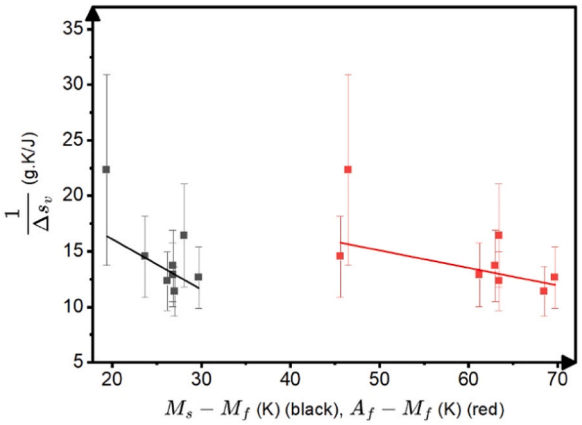

Fig. 2. Relation between Δs_v and $M_s - M_f$ as well as $A_f - M_f$ in $Ni_{50+x}Ti_{50-x}$ alloys on the basis of experimental data published on composition dependence in [26,27]. The error bars for Δs_v are the same as given in [26,27]. The maximum error bar for the $A_f - M_f$ difference is about $\pm 5K$ [26]. The slope of the $\frac{1}{\Delta s_v}$ versus $A_f - M_f$ plot, obtained from a linear fit, is $-0.16 \pm 0.08 \left(\frac{J}{g}\right)^{-1}$.

Thus, Fig. 4 shows the relation between Δs_{tr} and $M_s - M_f$ in NiMnIn alloys, when the degree of atomic order was changed by varying the annealing temperatures and the cooling rate, both of which had an influence on the long-range chemical order and on the magnetic order (i.e. on the values of T_c and T_{tr}: see also below).

3.1.3. Correlation based on magnetic field dependence

In metamagnetic SMAs the $\frac{1}{\Delta s_{tr}}$ versus $M_s - M_f$ plot is shown in Fig. 5, reproduced from Fig. 4 of [10]. It was mentioned in [10] that they were determined from transformations under magnetic field. The only exception is that three points from [3] are not shown here, since these were measured in zero magnetic field (see also our comments below) and thus represent a set of data in which the dependence on the degree of atomic order is the reason of the relation (see Fig. 4 above).

3.2. On the origin of the composition or magnetic field dependence

We have seen that in general functional relationship between $M_s - M_f$ (or $A_f - M_f$) and Δs_v, or $\Delta s_{tr} = \Delta s_v + \Delta s_m + \Delta s_H$, exist only if both quantities have a systematic dependence on a third variable (the composition, magnetic field or, as we will point below, the degree of atomic order). Thus, it is worth summarizing the possible origins of such dependences. Before a detailed discussion it is worth recalling the results of [15]; the reduced entropy change $\frac{\Delta s_{tr}}{k}$, and thus Δs_{tr}, can depend only on the phonon softening parameter $t_o(x) = \frac{T_o(x)}{T_m(x)}$. According to expression (38) the composition dependence of Δs_{tr} can originate from its first term in non-ferromagnetic SMAs. The next two term can be responsible for the dependence on the degree of atomic order (via the change in the magnetic order in the second term), while the magnetic field dependence is related to the possible field dependence of the second and third terms.

3.2.1. Composition dependence

3.2.1.1. Non-ferromagnetic alloys. The following, possible interpretation for the composition dependence of Δs_v was offered in [15]. In some systems not only the phonon mode related to the elastic constant $c_2 = \frac{c'}{3}$ (the so called basal plane shear) softens, but softening of the c_{44} modulus (belonging to non-basal plane shear) occurs as well [15, 38–41]. Thus, if the weight of softening of the above two phonon modes changes with composition, then a composition dependence of the reduced transformation entropy can be expected.

3.2.1.2. Ferromagnetic alloys. Since in ferromagnetic SMAs (in zero magnetic field) the magnetic contribution depends on the $\delta_A = 1 - \frac{T_{tr}}{T_c}$ parameter [1–4,6,10] (and see also Appendix B), the composition dependence of Δs_m should stem from the x-dependence of both T_c and T_{tr}. Indeed, as it can be seen from [1,3] and [16], both the $M_s - M_f$ (or $A_f - M_f$) difference and $\Delta s_{tr} \cong \Delta s_m$ depends on the composition. Furthermore, in both [1] and [16] the effect of phase change of the martensite with x (either change from paramagnetic to ferromagnetic state [1] or change from five-layered to seven-layered modulated martensite in the composition range investigated), was also mentioned as a possible contribution to the x-dependence of the transformation entropy.

Comparing the slopes of the $\frac{1}{\Delta s}$ versus $A_f - M_f$ linear relations, based on composition dependence of the parameters (see the figure captions of Fig. 2 and Fig. 3) we can conclude that they are quite different (even the sign is different for $Ni_{50+x}Ti_{50-x}$ alloys). This is not surprising but rather expected since the possible reasons of the composition dependence can be different in the above alloys.

3.2.2. Magnetic field dependence

In [6,11], the results of which are shown in Fig. 4, the magnetic field

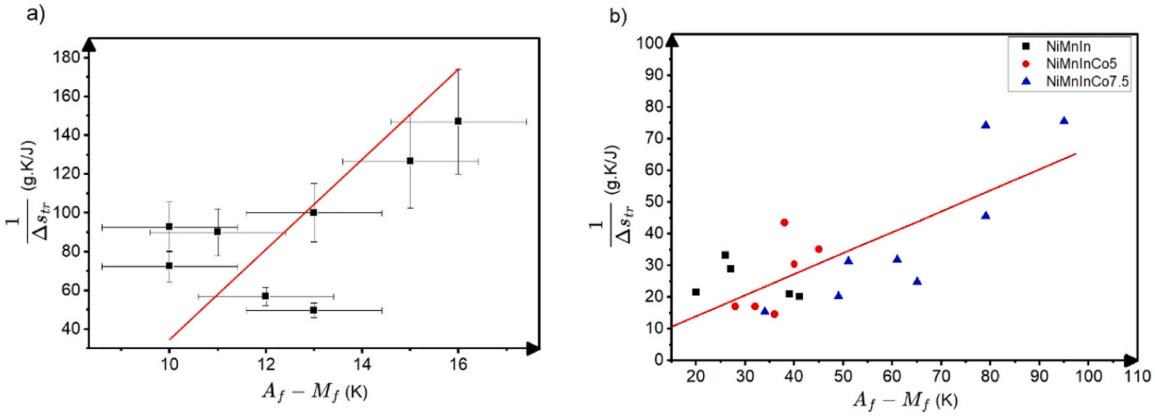

Fig. 3. Relation between composition dependent Δs_{tr} and $A_f - M_f$ in a) $Ni_{2-x}Mn_{1-x}Ga$ alloys (data from [16]) as well as in b) NiMnInCo alloys (data from [1]). The slopes of the $\frac{1}{\Delta s_{tr}}$ versus $A_f - M_f$ plots, obtained from linear fits, are $23 \pm 11 (J/g)^{-1}$ as well as $0.67 \pm 0.14 (J/g)^{-1}$, respectively. The error bars in a) were estimated from [16].

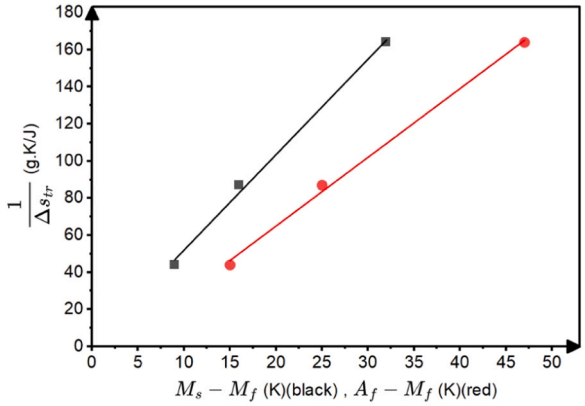

Fig. 4. Relation between Δs_{tr} and $M_s - M_f$ and $A_f - M_f$ in NiMnIn alloys, when the degree of atomic order was changed by varying the annealing temperatures [3] and the cooling rate.

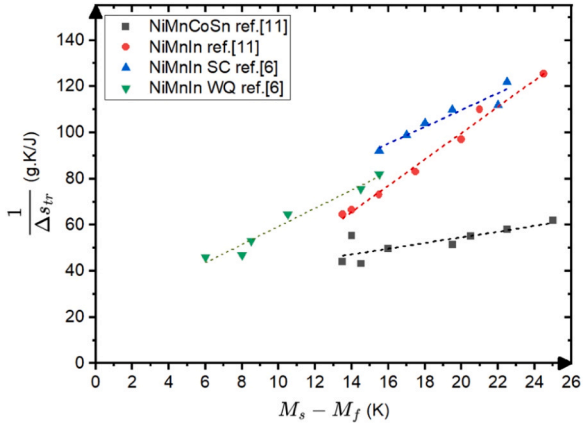

Fig. 5. Relation between $\frac{1}{\Delta s_{tr}}$ versus $M_s - M_f$ in alloys (data from [6,11]) in which Δs_{tr}belongs to magnetic field induced transformation entropy. (Redrawing data from Fig. 4 of [10] points from [3] are not shown because for those not the magnetic field dependence but the dependence on the degree of atomic order is responsible for the correlation (see Fig. 4 above)). The theoretically calculated straight line for Ni_2MnGa in [4] (because it belongs to H=0) is also omitted. The lines connecting points obtained for the same system are only to guide the eyes.

induced transformation entropy was calculated from the Clausius-Clapeyron relation (see Eq. (38)), such a way that $\frac{dT_{tr}}{dH}$ and ΔM were calculated at each different values of the magnetic field, H. Thus, the observed H-dependence of Δs should stem from the different H-dependence of $\frac{dT_{tr}}{dH}$ and ΔM. Indeed in [6,11] a non-linear dependence of $T_M = \frac{M_s + M_f}{2}$, and $T_A = \frac{A_s + A_f}{2}$ as well as ΔM on H was obtained (see Fig. 4 in [6]). It is clear that the H-dependence of ΔM is the consequence of the change of the magnetization as it approaches to saturation with increasing field. In fact, the field dependence of the magnetization in FMSMAs is a delicate question [28] due to the possible interplay of mesoscopic twin structure and the magnetic domain structure. It was demonstrated in [28] that the negative value of ΔM first decreased, and after a minimum (at H, which was necessary to induce a single variant martensite) increased and reached a saturation with increasing field in NiMnGa alloys. Since the minimum situated at relatively low field (at about (0.2 T), and since in [6] and [11] this low-field region was not investigated, we consider here the course of the $\Delta M(\mu_o H)$ function after the above minimum, where indeed ΔM is an increasing function approaching to a saturation in metamagnetic systems. It is worth mentioning that in [28] the thermally induced entropy change was also determined in DSC under different fixed values of H and no field dependence was obtained. Thus, it was concluded that the presence of constant magnetic field did not influence the temperature induced transformation entropy, while application of changing magnetic field resulted in a field-dependence of both the magnetic field induced entropy change and jump of magnetization, as well as of the dissipated energy.

Finally, it has to be noted that the calculations of the magnetic field induced entropy changes, based on the application of the Maxwell relation and/or the Clausius-Clapeyron relations, should be made with care [32,36] (see also Eqs. (36)-(37)). For instance, the Maxwell relation was obtained in equilibrium phases and thus is not applicable to mixed two-phase region present in first order MTs [36], while for application of the Clausius-Clapeyron relation see Eqs. (36) and (37) and [28,32].

4. Conclusions

- It is illustrated that the composition or magnetic field dependence of the transformation entropy, Δs, in shape memory alloys, SMAs leads to $\Delta s^{-1} \propto A_f - M_f$ type relation
- It is argued that the Landau theory leads to an inherent relation (determined solely by the input parameters of the theory) between the transformation entropy and the reciprocal value of the difference of the liability temperatures. Approximating this by a difference of the transformation temperatures is questionable since these should

be always smaller and should contain contributions from the local changes in the dissipation and elastic energies.

- The local equilibrium description of MTs provides (see Eqs. (32) and (33)) that $M_s - M_f$ as well as $A_f - M_f$ are inversely proportional to $-\Delta s_v$ and the proportionality factors are $e_1 - e_o$ as well as $2d_o + e_1 - e_o$, respectively ($e_i = \frac{\partial E}{\partial \xi}\Big|_{\xi=i}$, $d_i = \frac{\partial D}{\partial \xi}\Big|_{\xi=i}$ $i = 0, 1$, where E (> 0 for the down process) and D(> 0 in both directions of transformation) are the elastic and dissipative energies and ξ is the martensite volume fraction).
- It is expected that the vibrational entropy change is constant and independent of the derivatives of E and D. Thus, functional relation between $M_s - M_f$ (or $A_f - M_f$) and $\frac{1}{\Delta s_v}$ exists only if both shows monotonic dependence on a third variable (the composition or degree of atomic order). In non-ferromagnetic SMAs Δs_v is constant and there is a composition dependence only in $Ni_{50+x}Ti_{50-x}$ alloys, leading to $\frac{1}{\Delta s_v} \propto A_f - M_f$ (or $M_s - M_f$) type relation.
- In FMSMAs (where $\Delta s_m \cong \Delta s_{tr}$) $\frac{1}{\Delta s_{tr}} \propto A_f - M_f$ (or $M_s - M_f$) type relation exist if both Δs_m and $A_f - M_f$ (or $M_s - M_f$) depend
  i) on the composition or on the degree of atomic order in zero magnetic field (because both T_{tr} and T_c can depend on them) as well as
  ii) on the external magnetic field (causing change in the jump of magnetization and in the transformation temperatures).

CRediT authorship contribution statement

Beke Dezso L.: Writing – review & editing, Validation, Conceptualization. **A.A. Azim:** Visualization, Methodology, Formal analysis, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A

According to [4], the definition of the modified liability temperatures are

$$c_2^*(T_2^*) = 0,$$

and

$$c_2^*(T_1^*) = c_t^* = \frac{\alpha^{*2}}{4b^*}. \tag{A1}$$

Using (10) the above conditions can be rewritten as

$$c_2^*(T_2^*) = 0 = c_{2o}(T_2^* - T_2) + \frac{\alpha_2}{c_1}\delta_{ex}M^2(T_2^*) \tag{A2}$$

and

$$c_2^*(T_1^*) = c_t^* = c_{2o}(T_1^* - T_2) + \frac{\alpha_2}{c_1}\delta_{ex}M^2(T_1^*). \tag{A3}$$

Taking their difference

$$c_2^*(T_1^*) = c_t^* = c_{2o}(T_1^* - T_2^*) + \frac{\alpha_2}{c_1}\delta_{ex}\left[M^2(T_1^*) - M^2(T_2^*)\right]$$

$$= (T_1^* - T_2^*)\left(c_{2o} + M_o^2\frac{\alpha_2}{c_1}2\delta_{ex}m\frac{dm}{dT}\right) = (T_1^* - T_2^*)c_{2o}^*. \tag{A4}$$

where M_o is the saturation magnetization at $0K$ and $m = \frac{M(T)}{M_o}$ and the T-dependence of m can be calculated from the Kuzmin relation [A1]. In obtaining (A4) it was used that $\Delta M^2 = M^2(T_1^*) - M^2(T_2^*) \cong M_o^2\frac{dm^2}{dT}(T_1^* - T_2^*) = 2M_o^2 m\frac{dm}{dT}(T_1^* - T_2^*)$ where $m\frac{dm}{dT}$ should be taken at T_2^*.

Finally, using (A4) and that c_2^* also linearly depends on T;

$$c_2^*(T) = c_{20}^*(T - T_2^*) = c_t^*\frac{T - T_2^*}{T_1^* - T_2^*} \tag{A5}$$

holds too.

[A1] Kuz'min, M. D., Richter, M., & Yaresko, A. N. (2006). Factors determining the shape of the temperature dependence of the spontaneous magnetization of a ferromagnet. *Physical Review B*, *73*(10), 100401. https://doi.org/10.1103/PhysRevB.73.100401

Appendix B

We can start from the expression for $\Delta f_m^1(m_M, m_A)$ (see Eqs. (23), (25) and (28b))

$$\Delta f_m^1(m_M, m_A) = \frac{1}{2}J_M(T)M_M^2(T) - \frac{1}{2}J_A(T)M_A^2$$

$$= \frac{J_{Mo}}{2}\ \frac{T - T_{cM}}{T_{cM}}M_{Mo}^2 m_M^2(T) - \frac{J_{Ao}}{2}\ \frac{T - T_{cA}}{T_{cA}}M_{Ao}^2 m_A^2(T). \quad \text{(B1)}$$

Introducing $\delta_i = 1 - \frac{T}{T_{ci}}$ relations ($i = A,M$), as well as the relation between δ_A and $\delta_M(\delta_M = \frac{\delta_A - \delta}{1-\delta})$ where $\delta = \frac{T_{cA} - T_{cM}}{T_{cA}}$, and taking into account that the temperature dependence of the reduced magnetizations, m_i, can be expressed via δ_A only [B1], the temperature dependence of $\Delta f_m^1(m_M, m_A)$ is determined by the T-dependence of δ_A. Thus,

$$\Delta s_m(T_{tr}) = -\frac{\partial \Delta f_m^1}{\partial T} = -\frac{\partial \Delta f_m^1}{\partial \delta_A}\frac{d\delta_A}{dT} = \frac{1}{T_{cA}}\frac{\partial \Delta f_m^1}{\partial \delta_A}, \quad \text{(B2)}$$

and the $\frac{\partial \Delta f_m^1}{\partial \delta_A}$ derivative should be taken at T_r. This means that $\frac{\partial \Delta f_m^1}{\partial \delta_A}$ depends on $\delta_A(T_{tr}) = 1 - \frac{T_{tr}}{T_{cA}}$ only.

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Data Availability

Data will be made available on request.

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