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Magnetocaloric Effect in Metamagnetic Shape Memory Alloy

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In the present article, the results of quantitative theoretical analysis of the normal and inverse magnetocaloric effects (MCEs) in metamagnetic shape memory alloy (MMSMA) are reported. Taking into account that the direct experimental evidences of antiferromagnetic ordering were obtained recently, the theoretical analysis was carried out starting from the expression for the magnetic energy of antiferromagnet with two magnetic sublattices. The adiabatic temperature change caused by the inverse and normal MCEs in MMSMA was evaluated and compared with experimental data obtained for $Ni_2Mn_{1.4}Sn_{0.6}$ alloy. The adiabatic temperature change depends on the magnetic-field-induced entropy change and heat capacity of the alloy. To obtain the quantitative agreement between the experimental and theoretical data the magnetic and non-magnetic contributions to the heat capacity of MMSMA were taken into account and evaluated. Due to this, the contribution of spontaneous deformation, which accompanies the magnetostructural phase transition, to the total value of MCE was discovered. The increase of heat capacity caused by the change of magnetic state of the alloy during the phase transition was computed as well. It was shown that the temperature peak of heat capacity, observed in the temperature range of magnetostructural phase transformation of Ni-Mn-Sn alloy, is caused by both spontaneous deformation of the crystal lattice and magnetic ordering of the alloy. It was shown that the presence of the peak of heat capacity diminishes the expected from the Debye equation value of adiabatic temperature change by factor 2.5. To the best of our knowledge, the role of spontaneous deformation of the crystal lattice in the temperature dependence of heat capacity and inverse MCE was not considered until now.

Keywords: Magnetostructural transition, Specific heat, Adiabatic temperature change, Debye equation.

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1. INTRODUCTION

The global demand for the development of new materials for refrigeration technologies stipulates the interest to the materials exhibiting the giant magnetocaloric effect (MCE) in the temperature range of the first-order phase transition [1-5]. The cooling of metamagnetic shape memory alloys (MMSMAs) causes the first-order magnetostructural phase transition from the cubic ferromagnetic phase (austenite) to the tetragonal phase with low magnetization value (martensite) [6-9]. The abrupt change of the magnetic state of MMSMA results in an inverse MCE that is the cooling of alloy [4, 6]. Normal MCE (heating of alloy due to the magnetic field application) is observed near the Curie temperature [1, 2]. The direct measurement of inverse MCE meets certain experimental difficulties [8], and so, the evaluation of magnetic-field-induced entropy change from the calorimetric measurements is widely used for characterization of magnetocaloric materials and is known as the indirect measurement of MCE [10].

Theoretical evaluation of the magnetic-field-induced entropy change is a complicated theoretical problem because of the difficulties arising in the course of theoretical description of magnetostructural phase transition. An effective and rather simple way of the problem solution was proposed recently [11]. In this article, we accomplish the results reported in Ref. [11] by the calculation of adiabatic temperature changes caused by the inverse and normal MCEs in MMSMAs, compare the obtained theoretical value with the experimental one and discover the contribution of the spontaneous deformation, characterizing the cubic-tetragonal phase transition, to the total value of MCE.

2. THEORETICAL BASIS AND RESULTS

The adiabatic temperature change induced by the application of a magnetic field is expressed by the well-known equation

$$\Delta T_{ad} \approx -\frac{T\Delta S}{C(T)}, \qquad (1)$$

which involves the heat capacity of shape memory alloy. The temperature dependence of heat capacity exhibits the pronounced increase in the temperature range of magnetostructural phase transformation (see Fig. 1). The stepwise change of heat capacity is observed at the Curie temperature $T_C \approx 320$ K.

The orthodox equation for the heat capacity can be presented in the form

$$C = \kappa\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 dx}{4\,sinh^2(x/2)}, \qquad (2)$$

where κ value is prescribed by the chemical composition and volume (weight) of the experimental specimen, $\theta_D = s(\hbar/k_B)(6\pi^2 N_A \rho n/M)^{1/3}$, is the Debye temperature, k_B and N_A are the Boltzmann and Avogadro constants, respectively, n is the number of atoms in the unit cell of the crystal lattice, M is the molar mass, ρ is

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the mass density, and s is an average velocity of the sound waves (see e.g. [12]). Experimental temperature dependence of heat capacity is in agreement with the Debye equation well below and well above the magnetostructural transformation temperature if $\theta_D = 310$ K and $\kappa = 110$ J/K·mol.

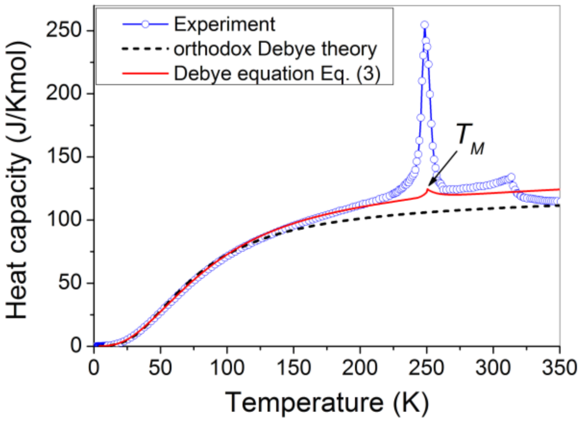

Fig. 1 – Experimental temperature dependence of heat capacity measured for $Ni_2Mn_{1.4}Sn_{0.6}$ alloy (circles) [13] compared with the dependence computed from the orthodox Debye theory (dashed line). Solid line results from Debye equation with temperature-dependent soft elastic modulus [12]

To reproduce the temperature dependence of heat capacity in the vicinity of the magnetostructural phase transformation, the softening of elastic modulus, spontaneous deformation of the crystal lattice, ε_0, and magnetic ordering of the alloy should be taken into account.

The softening of elastic modulus was considered in Ref. [12] and the equation

$$C = \kappa\left[\left(\frac{T}{\theta_l}\right)^3 \int_0^{\theta_l/T} \frac{x^4 dx}{4\sinh^2(x/2)} + 2\left(\frac{T}{\theta_t}\right)^3 \int_0^{\theta_t/T} \frac{x^4 dx}{4\sinh^2(x/2)}\right], \quad (3)$$

$$\theta_l = s_l(\hbar/k_B)(6\pi^2 N_A \rho n/M)^{1/3},$$

$$\theta_t = s_t(\hbar/k_B)(6\pi^2 N_A \rho n/M)^{1/3},$$

was derived.

This equation involves two characteristic temperatures θ_l and θ_t, which are proportional to the velocities of longitudinal, s_l, and transversal, s_t, sound waves, respectively. The softening of elastic modulus results in the pronounced decrease of s_t value in the temperature range of magnetostructural transformation. The theoretical heat capacity computed for a realistic value $s_t(0)/s_t(T_M) = 4$ shows a negligibly small peak at magnetostructural transition temperature (solid line in Fig. 1).

The influence of magnetic ordering and spontaneous deformation on the heat capacity was taken into account starting from the Gibbs free energy of the alloy, which is a sum of magnetic and elastic terms

$$G = G_m + G_{el}. \quad (4)$$

Different MMSMAs demonstrate different magnetic properties in their martensitic phases. Therefore, the different types of magnetic ordering may be inherent to these martensites, depending on the chemical composition and mode of preliminary treatment of alloy specimen. As it was shown recently the main transformational, magnetic and magnetocaloric properties of Ni-Mn-In and Ni-Mn-Sn alloys are satisfactorily described starting from the expression for the magnetic energy of antiferromagnet with two magnetic sublattices (see Ref. [14] and references therein). The direct experimental evidences of antiferromagnetic ordering are presented in Ref. [9]. This magnetic energy can be expressed as [14]

$$G_m = J_0(\mathbf{M}_1^2 + \mathbf{M}_2^2)/2 + J\mathbf{M}_1\mathbf{M}_2 - \mathbf{HM}, \quad (5)$$

where $\mathbf{M}_1$ and $\mathbf{M}_2$ are the magnetization vectors of the two magnetic sublattices, J_0 and J are the temperature dependent parameters, which describe the magnetic exchange inside and between the sublattices, respectively, $\mathbf{H}$ is a magnetic field. The elastic energy of the alloy, which undergoes a cubic-tetragonal transformation, is expressed as

$$G_{el} = \frac{1}{2}c_2(T)u^2 + \frac{1}{3}a_4u^3 + \frac{1}{4}b_4u^4, \quad (6)$$

where the coefficients $c_2(T)$, a_4, b_4 are denoted as in Ref. [15] and the variable $u = 2(c/a - 1)$ is related to the lattice parameters a and c of tetragonal lattice. This variable is equal to zero in cubic phase and is related to spontaneous deformation of the crystal lattice in tetragonal phase: $u = 3\varepsilon_0$.

The heat capacity of alloy can be computed from the standard thermodynamic relationships

$$S = -(dG/dT)_p,\ C_p = T(dS/dT)_p. \quad (7)$$

The Eqs. (4)-(7) were used for the quantitative analysis of the temperature dependence of heat capacity of $Ni_2Mn_{1.4}Sn_{0.6}$ alloy. The obtained results are presented graphically in Fig. 2 for the explanation of the role of different parts of Gibbs energy in MCE. The numerical values of parameters involved into Eqs. (4)-(7) are presented in Ref. [11].

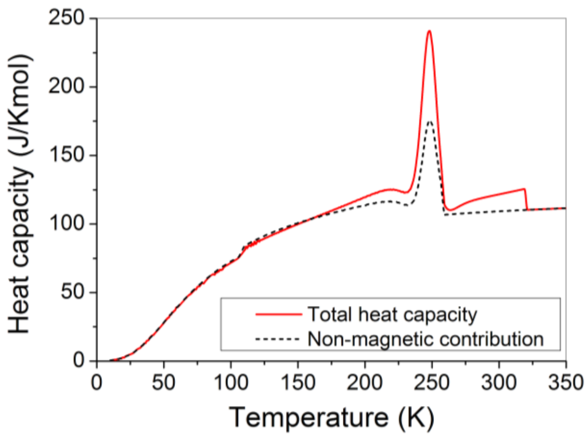

Fig. 2 – Theoretical temperature dependence of heat capacity computed for $Ni_2Mn_{1.4}Sn_{0.6}$ alloy taking into account spontaneous deformation of the crystal lattice (dashed line). Total heat capacity, which includes both non-magnetic and magnetic parts, is shown by the solid line

The "non-magnetic" heat capacity computed taking into account the Debye term and the contribution caused by spontaneous deformation of the crystal lattice is presented in Fig. 2 by the dashed line. The solid line shows the total heat capacity, which includes the magnetic term as well. It is seen that the deformational and magnetic parts of heat capacity are comparable in value.

The theoretical maximum of heat capacity 241 J/Kmol is close in value to the experimental one 254 J/Kmol (see Fig. 1, Fig. 2).

The practically important value characterizing the MCE is adiabatic magnetic-field-induced temperature change (Eq. (1)). The interrelation between the total and non-magnetic heat capacity depicted in Fig. 2 for the evaluation of temperature change is illustrated by Fig. 3. The temperature change was computed for $\mu_0 H = 2T$. The minimum of ΔT_{ad} shows the inverse MCE, while its maximum corresponds to the normal MCE. It is seen, first, that the temperature change computed using the Debye equation for the heat capacity is larger than the temperature change resulting from the total heat capacity value by factor 2.5. Second, the comparison of total and non-magnetic lines demonstrates the substantial influence of spontaneous deformation on inverse MCE.

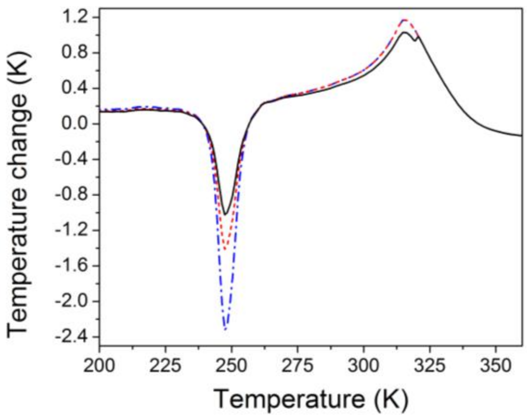

Fig. 3 – Theoretical values of magnetic-field-induced temperature change computed taking into account only non-magnetic part of heat capacity (dashed line) and total heat capacity value (solid line). The temperature change computed using Debye equation is shown by dashed-dotted line for comparison

Fig. 4 shows the excellent agreement between the theoretical and experimental [13] values of MCE obtained for $Ni_2Mn_{1.4}Sn_{0.6}$ alloy.

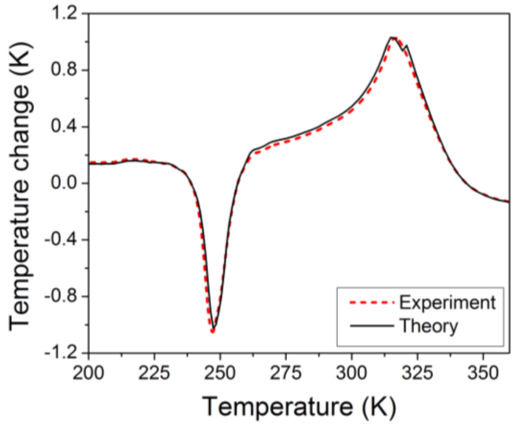

Fig. 4 – Theoretical value of MCE compared with experimental data obtained for $Ni_2Mn_{1.4}Sn_{0.6}$ alloy [13]

3. CONCLUSIONS

The consistent theoretical analysis of heat capacity showed that:

1) The temperature peak of heat capacity observed in the temperature range of magnetostructural phase transformation of $Ni_2Mn_{1.4}Sn_{0.6}$ alloy diminishes the expected value of adiabatic temperature change by factor 2.5.

2) The reduction of the maximum value of inverse MCE is caused by

i) spontaneous deformation of the crystal lattice;

ii) magnetic ordering of the alloy.

To the best of our knowledge, the role of spontaneous deformation of the crystal lattice in the temperature dependence of heat capacity and inverse MCE was not considered until now.

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Магнітокалоричний ефект у метамагнітному сплаві з ефектом пам'яті форми

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У даній статті представлені результати кількісного теоретичного аналізу прямого та оберненого магнітокалоричного ефекту (МКЕ) у метамагнітному сплаві з ефектом пам'яті форми (ММСЕПФ). Враховуючи нещодавно отримані експериментальні дані, що свідчать про антиферомагнітне упорядкування, був проведений теоретичний аналіз, який стартує з виразу для магнітної енергії антиферомагнетика з двома магнітними підгратками. Адіабатична зміна температури, зумовлена прямим та оберненим МКЕ в ММСЕПФ, була оцінена та порівняна з експериментальними даними, отриманими для сплаву $Ni_2Mn_{1.4}Sn_{0.6}$. Адіабатична зміна температури залежить від зміни ентропії, спричиненої магнітним полем, і теплоємності сплаву. Для отримання кількісного узгодження між експериментальними та теоретичними даними були враховані та оцінені магнітний і немагнітний внески до теплоємності ММСЕПФ. Завдяки цьому був виявлений внесок спонтанної деформації, що супроводжує магнітоструктурний фазовий перехід, до загальної величини МКЕ. Також обчислено збільшення теплоємності, зумовлене зміною магнітного стану сплаву під час фазового переходу. Показано, що температурний пік теплоємності, спостережений в температурному інтервалі магнітоструктурного фазового перетворення сплаву Ni-Mn-Sn, є зумовленим як спонтанною деформацією кристалічної гратки, так і магнітним впорядкуванням сплаву. Показано, що наявність піку теплоємності зменшує очікувану з рівняння Дебая величину адіабатичної зміни температури у 2,5. Наскільки нам відомо, роль спонтанної деформації кристалічної гратки в температурній залежності теплоємності та оберненого МКЕ досі не розглядалася.

Ключові слова: Магнітоструктурне перетворення, Теплоємність, Адіабатична зміна температури, Рівняння Дебая.