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Theory of giant magnetocaloric effect in the shape memory alloy undergoing magnetostuctural phase transition

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The theory of the giant conventional and inverse magnetocaloric effects (MCEs) is advanced on the basis of the theory of magnetism developed by A.I. Akhiezer, V.G. Bar'yakhtar, and S.V. Peletminsky in the classic monograph "Spin Waves". The MCE in the shape memory alloy undergoing the first-order phase transition from the cubic ferromagnetic (FM) phase to the tetragonal antiferromagnetic (AFM) phase is considered. The agreement between the theoretical results and existing experimental data is demonstrated. It is argued that the alloys undergoing the phase transition to AFM phases with weak exchange interaction between the magnetic sublattices are promising for use in the magnetic refrigeration technique. The possibility of observation of the giant MCE in the layered magnetic structure with weak spin-exchange coupling between the FM layers is discussed.

Keywords: metamagnetic shape memory alloy, martensitic transformation, specific heat, adiabatic temperature change.

1. Introduction

Magnetic and magnetoelastic properties of the Heusler-type shape memory alloys (SMAs) are intensively studied due to their sensitivity to the magnetic field application ([1–3] and references therein). The SMAs exhibiting a magnetostructural phase transition (MSPT) are conventionally referred to as the metamagnetic shape memory alloys (MetaMSMAs). The unusual properties of these alloys are of practical and academic interest.

The practical interest in the MetaMSMAs is caused mainly by the observation of giant magnetocaloric effect (MCE) (both conventional and inverse) induced by the strong magnetic field [4,5]. Due to the giant MCE, the MetaMSMAs are considered promising for the use in the magnetic refrigeration technique [3,5]. The search of the alloys exhibiting the large field-induced temperature change and wide temperature interval of the MCE existence is critically important.

The academic interest to MetaMSMAs is provoked by the difficulties in comprehension of their phase transformational, magnetic and magnetocaloric properties. In particular, the strong doubts about the applicability of the traditional theory of MCE to the alloy undergoing the first-order magnetostructural phase transition are stated (see, e.g., [6]): the traditional theory is based on the magnetic Maxwell relations, which are valid only for the equilibrium ferromagnetic phase, while the giant MCE is observed due to the first-order MSPT, which goes through the two-phase state. In this connection, a new approach to the theoretical description was advanced [7], using as the basis a classic theory of ferromagnetic and antiferromagnetic solids [8].

The MSPT from the cubic ferromagnetic (FM) phase to the tetragonal antiferromagnetic (AFM) phase is inherent to the number of MetaMSMAs [9]. The giant MCE caused by this MSPT was studied in Ref. 7 starting from the Landau expansion for the Gibbs free energy G of MetaMSMA. The fundamental thermodynamic equations for the entropy S and heat capacity C_P,

$$S = -(\partial G / \partial T)_P, \;\; C_P = T(\partial S / \partial T)_P, \tag{1}$$

were used. The field-induced temperature change ΔT was computed then from the well-known formula

$$\Delta T \approx -\frac{T}{C_P}[S(H,T)-S(0,T)], \tag{2}$$

where T is the temperature of MetaMSMA measured before the magnetic field application.

In the present article, we will show that the MetaMSMAs with weak spin-exchange interaction between the magnetic sublattices are good candidates for the use in the magnetic refrigeration technique.

2. Free energy of MetaMSMA

The magnetostructural phase transition in MetaMSMAs can be considered as a combination of magnetic FM→AFM phase transition and first-order martensitic transformation from the high-temperature cubic to the low-temperature tetragonal or orthorhombic crystal phase. The Gibbs free energy of MetaMSMA can be presented as a sum of three terms:

$$G = G_{\text{el}} + G_{\text{mag}} + G_{me}. \tag{3}$$

The term G_{el} depends on the spontaneous strains arising in the course of MSPT, G_{mag} depends on the magnetic state of alloy and G_{me} describes the magnetoelastic coupling. The FM→AFM phase transition in the strong magnetic field **H** can be studied theoretically by minimization of the energy

$$G_{\text{mag}} + G_{me} = J_0(T)(\mathbf{M}_1^2+\mathbf{M}_2^2)/2 + J_{12}(T)\mathbf{M}_1\mathbf{M}_2 - \delta_1(\mathbf{M}_1^2+\mathbf{M}_2^2) - 2\delta_{12}\mathbf{M}_1\mathbf{M}_2 - (\mathbf{M}_1+\mathbf{M}_2)\mathbf{H}, \tag{4}$$

where $\mathbf{M}_1$, $\mathbf{M}_2$ are the magnetization vectors of the sublattices, $J_0(T)$ and $J_{12}(T)$ are the spin-exchange parameters, which depend on the temperature due to the entropy term $-TS$ in the defining thermodynamic relationship for Gibbs free energy, δ_1 and δ_{12} are magnetoelastic constants describing the volume magnetostriction, v is the relative volume change caused by both volume magnetostriction and MSPT. The expressions similar to Eq. (4) are widely used in the theory of magnetism [8]. The condition $|\mathbf{M}_1| = |\mathbf{M}_2|$ is valid for the solid with equivalent magnetic sublattices.

Simple algebraic calculations show that the Gibbs free energy densities of ferromagnetic and antiferromagnetic phases in the strong magnetic field can be expressed in terms of the saturation magnetization, $M_S(T)$, and magnetization of antiferromagnetic phase, $M(H,T)$, as

$$G_{FM}(T,H) = \frac{1}{2}J_{FM}(T)M_S^2(T) - M_S(T)H, \tag{5}$$

$$G_{AFM}(T,H) = \frac{1}{2}J_{AFM}(T)M_S^2(T) - \frac{1}{2}J_{12}(T)M^2(T,H), \tag{6}$$

where

$$J_{FM}(T) = \frac{1}{2}[J_0(T)+J_{12}(T)] - (\delta_1+\delta_{12})v,$$
$$J_{AFM}(T) = J_{FM}(T) - J_{12}(T) - (\delta_1-\delta_{12})v \tag{7}$$

are the spin-exchange parameters renormalized by magnetoelastic constants. According to the Landau theory of phase transitions the spin-exchange parameters J_{FM} and J_{AFM} linearly depend on the temperature in the vicinity of the Curie temperature, T_C, and FM–AFM phase transition temperature, T_0, respectively:

$$J_{FM}(T) = j_{FM}(T-T_C)/T_C,$$
$$J_{AFM}(T) = j_{AFM}(T-T_0)/T_0,$$

where j_{FM} and j_{AFM} are the dimensionless constants. In the magnetic field exceeding the characteristic field of spin-flip phase transition

$$M(T) = \begin{cases} HM_S(T)/H_S(T), & \text{if } H < H_S(T), \\ M_S(T), & \text{otherwise,} \end{cases} \tag{8}$$

where $M_S(T)$ is expressed by the standard equation of the theory of ferromagnetism, $H_S(T)$ is a magnetic saturation field, which corresponds to the field-induced phase transition from the magnetic state with nonparallel magnetization vectors to the ferromagnetic state with $\mathbf{M}_1 \parallel \mathbf{M}_2$ ("spin-flip" phase transition, for more details see [10]). The Eq. (6) is valid at $H < H_S(T)$, the value $H_S(T)$ vanishes at $T \to T_0$, because at $T > T_0$ the FM state is stable even in the absence of external magnetic field. The temperature of FM → AFM phase transition in the magnetic field is the solution of equation $H = H_S(T)$.

The magnetic part of Gibbs free energy of the MetaMSMA undergoing the first-order MSPT from cubic ferromagnetic to low-symmetry antiferromagnetic phase is expressed as

$$G = \alpha G_{FM} + (1-\alpha)(G_{AFM} + G_{\text{el}}), \tag{9}$$

where $0 < \alpha < 1$ is a temperature- and field-dependent volume fraction of AFM phase. For the computations, we have used the G_{el} function presented in Ref. 11.

3. Magnetization and heat capacity of MetaMSMA

The isofield temperature dependences of magnetization of the spatially homogeneous solid, undergoing the FM→AFM phase transition, can be computed from Eq. (8). This equation was modified for the spatially inhomogeneous MetaMSMA undergoing the first-order MSPT [7,12]. The $M(T)$ functions computed for the spatially inhomogeneous MetaMSMA with strong (a) and weak (b) antiferromagnetic coupling between the magnetic sublattices are shown in Fig. 1. The theoretical curves reproduce the features of experimental temperature dependences of magnetization obtained for Ni–Mn–Sn (Fig. 1a), Ni–Mn–In (Fig. 1b),

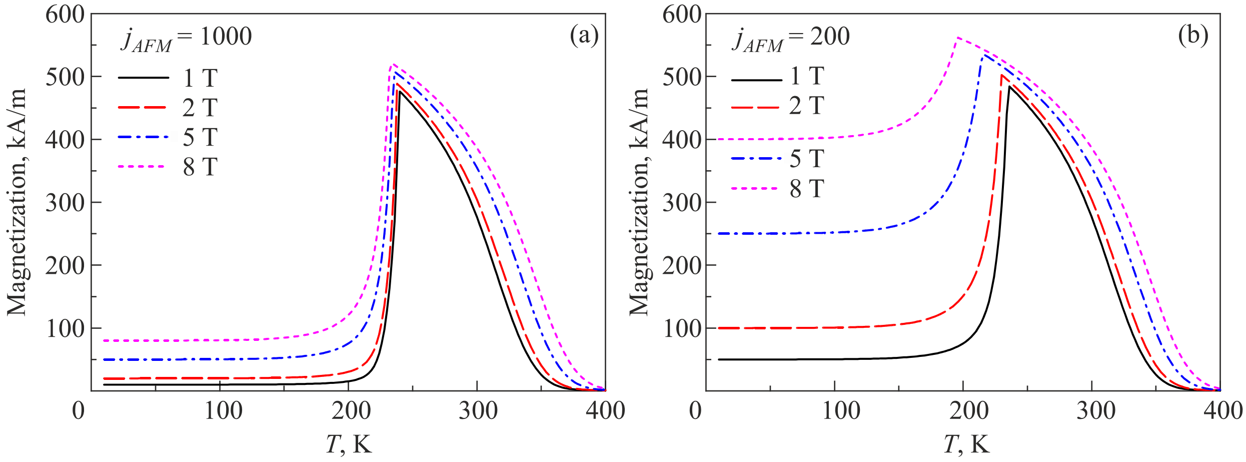

Fig. 1. The isofield magnetization curves computed for the alloy with strong (a) and weak (b) exchange interaction between the magnetic sublattices (j_{AFM} is a dimensionless constant). The values of Curie temperature, MSPT temperature and $M_S(0)$ of 320 K, 240 K and 600 kA/m, respectively, were used for computations.

and Ni–Mn–In–Co (Figs. 1a, 1b) (see, e.g., [4,13]). The abrupt decrease of magnetization value on the cooling of MetaMSMA corresponds to the temperature interval of the first-order MSPT, the "tail" of magnetization, which is visible at $T > T_C$, is peculiar to the SMAs. It should be stressed, that the pronounced decrease of phase transition temperature under the magnetic field (Fig. 1b) was mentioned by many scientists as unexplained feature of the martensitic transformation. However, it was shown recently that this effect of the magnetic field cannot be caused by magnetoelastic coupling [14], but follows from the equation $H = H_S(T)$ [15]. This fact supports the conception of magnetically driven MSPT [15].

Using the Eqs. (1)–(7) and theoretical $M(T)$ functions shown in Fig. 1, one can compute the heat capacity of MetaMSMA (Fig. 2) and the adiabatic temperature change (Fig. 3), caused by the magnetic field application to the alloy specimen.

The curves presented in Fig. 2a have a sharp peak of heat capacity at the temperature of MSPT and a smoothed local maximum at the Curie temperature. The drastic increase of the heat capacity in the temperature range of MSPT is practically important, because it diminishes the adiabatic temperature change (Eq. (2)). However, our theory shows that this disadvantageous feature of heat capacity is reduced in the case of weak antiferromagnetic coupling between the magnetic sublattices. Figure 2b shows the influence of strong magnetic field on the heat capacity of MetaMSMA. The inset illustrates the agreement between theoretical results and experimental data obtained for Ni–Mn–Sn alloy [16].

4. Magnetocaloric effect

Figure 3a shows the field-induced temperature change computed for MetaMSMAs with the strong and weak antiferromagnetic coupling between the magnetic sublattices. It is seen that the reduction of AFM coupling by factor 0.2

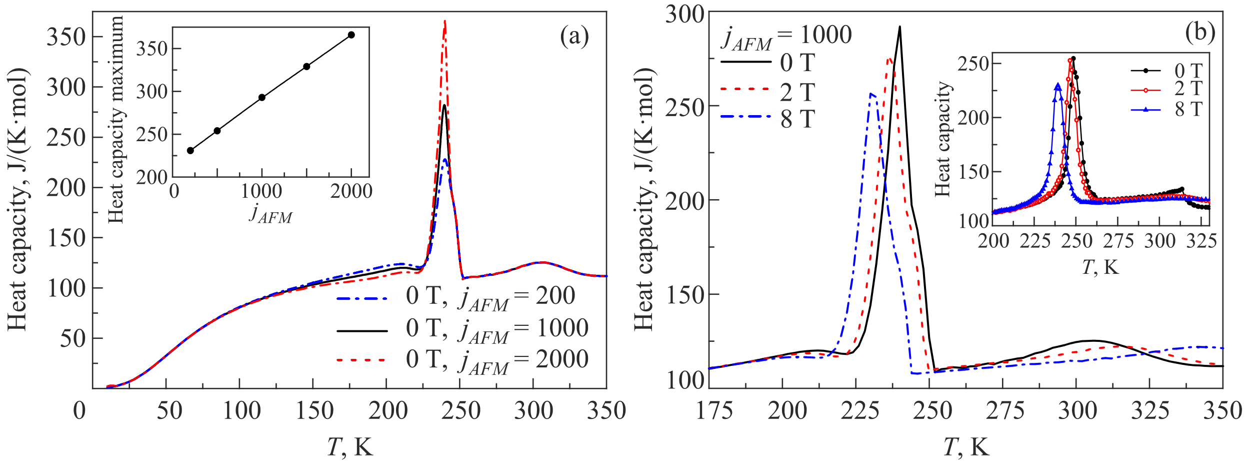

Fig. 2. (a) Theoretical temperature dependences of heat capacity of MetaMSMA computed for j_{AFM} = 200, 1000, 2000. Inset shows the linear dependence of heat capacity maximum on the exchange constant j_{AFM}. (b) The influence of the magnetic field on the heat capacity of MetaMSMA. The experimental field dependences of heat capacity obtained for Ni–Mn–Sn alloy [16] is shown in the inset.

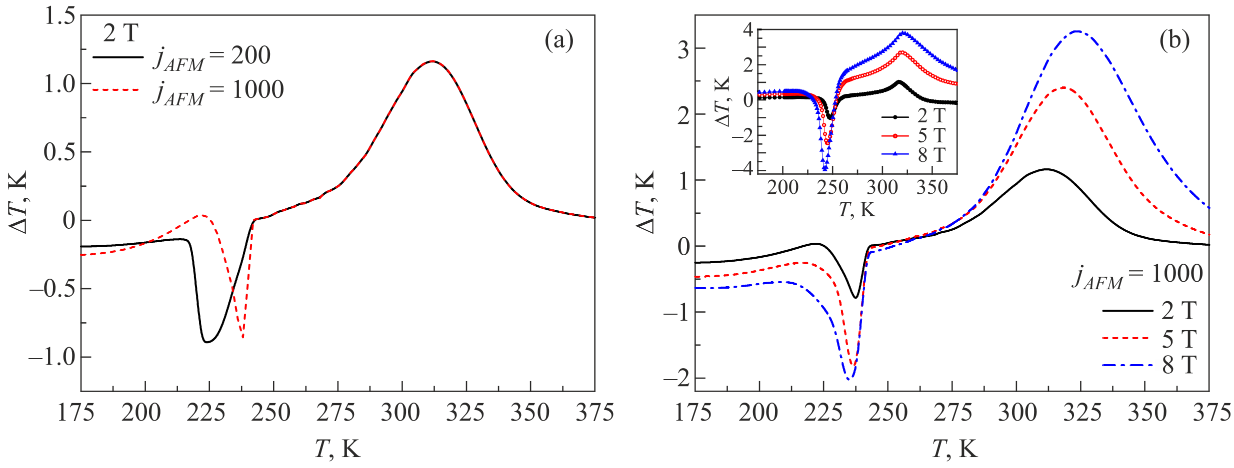

Fig. 3. Magnetic field-induced adiabatic temperature change computed for the different values of j_{AFM} (a) and the magnetic field (b). Inset in the panel (b) shows the experimental data obtained for Ni–Mn–Sn alloy [16].

widens the temperature range of the inverse MCE by factor 2 without noticeable change of the peak value of ΔT. The weak dependence of $\Delta T_{\max}$ on the value of spin-exchange parameter J_{AFM} follows from Eq. (2): the decrease of J_{AFM} reduces both the numerator and denominator of the $\Delta S(H)/C_p$ ratio.

Figure 3b shows that the elevation of the magnetic field value results in the enhancement of both the conventional and inverse MCEs and the influence of this factor on the conventional MCE is very strong. The inset shows that the theory adequately describes the experimental results. The drastic enhancement of conventional MCE by the increase of the magnetic field is caused by the abnormally strong influence of the field on the magnetization of the ferromagnetic phase. This fact is illustrated by Fig. 1 and it is observed in the numerous experiments.

5. Discussion: from MetaMSMAs towards artificial antiferromagnets

It is important that the maximal temperature decrease $\Delta T_{\max} \approx 1$ K is induced by the field $\mu_0 H = 2$ T (Fig. 3a). This value $\Delta T_{\max}$ was calculated using magnetization $M(0) = 600$ kA/m, which is typical for the Ni–Mn–Sn MetaMSMAs. For the Ni–Mn–In MetaMSMAs the experimental low-temperature value of magnetization slightly exceeds 1000 kA/m. The Gibbs free energy is proportional to $M^2(T)$, and so, a rough estimation shows that for the Ni–Mn–In alloy the maximal temperature decrease about of 2.5 K may be induced by the field value of 2 T. Therefore, the inverse MCE in metamagnets may be close in value to that observed, e.g., in the Fe–Rh alloy, which is a prototype material exhibiting this effect.

It is especially important to mention, that the weak antiferromagnetic coupling between the ferromagnetic layers and FM–AFM phase transitions are typical for the artificial antiferromagnets [17,18]. To use artificial AFM in the micro-sized coolers the layered material with weak AFM coupling between ferromagnetic layers, large magnetization value and FM–AFM phase transition temperature, being rather close to the Curie temperature, should be synthesized. This structure will provide the large entropy change under the moderate magnetic field.

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Теорія гігантського магнітокалоричного ефекту у сплаві з ефектом пам'яті форми, в якому відбувається магнітоструктурний фазовий перехід

Віктор А. Львов, Анна Косогор, Володимир А. Черненко

На основі теорії магнетизму, викладеної О.І. Ахієзером, В.Г. Бар'яхтаром та С.В. Пелетмінським в класичній монографії «Спінові хвилі», розвинено теорію прямого та оберненого гігантського магнітокалоричного ефекту (МКЕ). Розглянуто МКЕ у сплаві з ефектом пам'яті форми, в якому відбувається фазовий перехід першого роду з кубічної феромагнітної (ФМ) фази у тетрагональну антиферомагнітну (АФМ) фазу. Продемонстровано узгодження між теоретичними результатами та наявними експериментальними даними. Наведено міркування, які доводять, що сплави, у яких відбувається фазовий перехід в АФМ фазу зі слабкою обмінною взаємодією між магнітними підгратками, є перспективними для застосувань у технології магнітного охолодження. Обговорено можливість спостереження гігантського МКЕ у шаруватій магнітній структурі зі слабким спін-обмінним зв'язком між ФМ шарами.

Ключові слова: метамагнітний сплав з ефектом пам'яті форми, мартенситне перетворення, питома теплота, адіабатична зміна температури.