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Simulation of Thermomagnetic Properties of MnCoGe Alloy

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In this paper, phenomenological modeling and experimental studies were conducted to predict the magnetocaloric properties of the MnCoGe alloy. The temperature dependence of magnetization was measured and calculated using a simple phenomenological model. A good correlation between simulated and experimentally determined data was observed. The phenomenological model allowed us to reveal theoretical values of the magnetic entropy change, full width at half maximum of ΔS_M vs T curve, and relative cooling power.

topics: magnetocaloric materials, magnetic entropy change, relative cooling power

1. Introduction

Since the early nineties of the twentieth century, the issues of nature protection, in particular the problems related to ozone layer depletion, have been treated seriously. High pollution caused by freon compounds destroyed a significant part of this protective part of Earth's atmosphere. The Montreal Protocol, established in 1993, forbade the use of the aforementioned compounds in sprays and domestic cooling devices. Freon was also used as an active element in refrigerators. The efficiency of the cooling process based on the compression/decompression of freon gas is about 45%.

A more efficient cooling technique is magnetic refrigeration based on the magnetocaloric effect [1]. The temperature change in magnetic material at adiabatic conditions is realized by the variations of the external magnetic field. An example of the magnetocaloric material with a Curie temperature close to room temperature is pure Gd [2, 3]. Its disadvantage is that it is relatively expensive.

A significant increase in the number of papers on the topic has been observed after the discovery of a giant magnetocaloric effect in the $Gd_5Ge_2Si_2$ alloy by Pecharsky and Gschneider [4]. For many years, a lot of different materials have been studied, such as the manganites [5], the La(Fe,Si)$_{13}$-type alloys [6–8], or Heusler alloys [9].

Another interesting group of magnetocaloric materials are equiatomic alloys of MM'X-type (where M, M' are transition metals and X — metaloid) [10–13]. The good magnetocaloric properties of these alloys are due to the formation of low-temperature orthorhombic TiNiSi-type (space group *Pnma*) and high-temperature hexagonal Ni_2Ti (space group $P6_3/mmc$). Modifications of chemical composition of the MnCoGe alloy induce changes in structural and magnetocaloric properties. Hamad in [14] proposed a phenomenological model to predict the thermomagnetic properties. The experimental studies of the MnCoGe alloy were carried out by one of the authors of the present paper in [15].

The aim of the present work is to verify the usefulness of the Hamad model applied to experimental data of MnCoGe alloy.

2. Experimental techniques

The MnCoGe alloy sample was prepared by arc-melting of the high purity (min. 3 N) constituent elements under low pressure of protective gas Ar. In order to ensure the homogeneity of the sample, the ingot was remelted several times. Phase constitution was studied by Bruker D8 Advance diffractometer with Cu K_α radiation, and the analysis results were shown previously in [15]. Thermomagnetic properties were studied using Quantum Design PPMS (VSM option) in a magnetic field of up to 5 T and a wide range of temperatures and magnetic fields. The accuracy of measurements was 0.001 emu. The Maxwell relation was used to calculate the magnetic entropy change [4]

$$\Delta S_M(T, \Delta H) = \mu_0 \int_0^H \mathrm{d}H \left(\frac{\partial M(T,H)}{\partial T}\right)_H, \tag{1}$$

where μ_0, H, M, and T are the magnetic permeability of vacuum, strength of the magnetic field, magnetization, and temperature, respectively.

The RCP values were calculated taking into account temperature dependences of magnetic entropy change using the following equation [16]

$$RCP = -\Delta S_{\max M}\ \delta T_{\mathrm{FWHM}}, \tag{2}$$

where RCP is relative cooling power, δT_{FWHM} is the full width at half maximum of magnetic entropy change peak.

3. Phenomenological model by Hamad

The phenomenological model proposed by Hamad in [15] allows one to predict magnetization variations upon temperature in accordance with the following equation

$$M = \frac{(M_i + M_f)}{2} \tanh\Big(A\,(T_{\mathrm{C}} - T)\Big) + B\,T + C, \tag{3}$$

where T_{C}, M_i, and M_f are the Curie temperature, and the initial and final value of magnetization at ferromagnetic–paramagnetic transition, respectively. The values of parameters required by the model were obtained from an experimental M vs T curve, which is shown in Fig. 1 together with marked selected points. These points were used for modeling the coefficients A, B, and C given with the following formulas

$$A = \frac{2\,(B - S_{\mathrm{C}})}{M_i - M_f}, \tag{4}$$

$$B = \frac{\mathrm{d}M}{\mathrm{d}T}, \tag{5}$$

$$C = \frac{M_i - M_f}{2} - B\,T_{\mathrm{C}}, \tag{6}$$

$$S_{\mathrm{C}} = \frac{\mathrm{d}M}{\mathrm{d}T} \quad \text{at} \quad T = T_{\mathrm{C}}. \tag{7}$$

The theoretical formula that describes the variation of magnetic entropy upon temperature is based on relationships (1) and (3) and is rewritten in the following form

$$\Delta S_M = \left[-A\frac{(M_i - M_f)}{2}\,\mathrm{sech}^2\big(A(T_{\mathrm{C}} - T)\big) + B\right] H_{\max}. \tag{8}$$

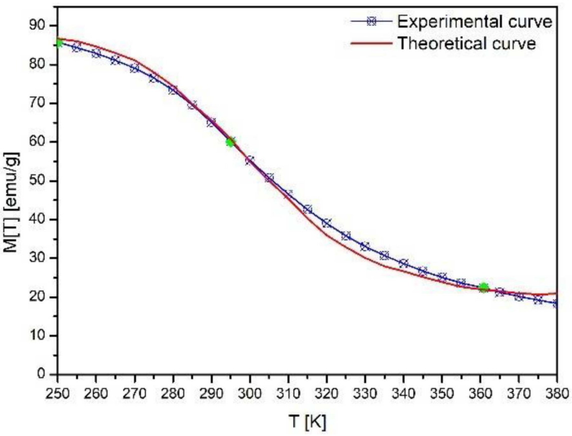

Fig. 1. Experimental and theoretical M vs T curves revealed for the MnCoGe alloy (under the change in magnetic field ~ 5 T).

A careful analysis of equation (8) revealed that the value of magnetic entropy change is strongly related to magnetization sensitivity $\mathrm{d}M/\mathrm{d}T$ at Curie temperature. High magnetic entropy change is dependent on high magnetic moment and the value of the first derivative of magnetization with respect to temperature at Curie point. The maximum value of magnetic entropy change may be written as

$$\Delta S_M = \left(-A\,\frac{(M_i - M_f)}{2} + B\right) H_{\max}. \tag{9}$$

Prediction of the magnetic entropy change and its maximum value is extremely important and determines the usefulness of a given magnetocaloric material. Apart from maximum magnetic entropy change, the working temperature range is a significant parameter for magnetocaloric materials. In practice, the full width at half maximum (FWHM) of the $\Delta S_M(T)$ curve is the figure of merit. The full width at half maximum of magnetic entropy change is determined from the following equation

$$\delta T_{\mathrm{FWHM}} = \frac{2}{A}\cosh^{-1}\left(\sqrt{\frac{2A\,(M_i - M_f)}{A\,(M_i - M_f) + 2B}}\right). \tag{10}$$

Taking into account relationships (2), (9), and (10), the relative cooling power can be written in the following form:

$$RCP = \left(M_i - M_f - 2\frac{B}{A}\right) H_{\max} \times \cosh^{-1}\left(\sqrt{\frac{2A\,(M_i - M_f)}{A\,(M_i - M_f) + 2B}}\right). \tag{11}$$

Relationships (9), (10), and (11) allowed us to calculate magnetocaloric properties and compare them with experimental values. All of them are collected in Table I.

As it is shown in Fig. 1, the modeled temperature dependence of magnetization corresponds very well to the measured curve. The temperature

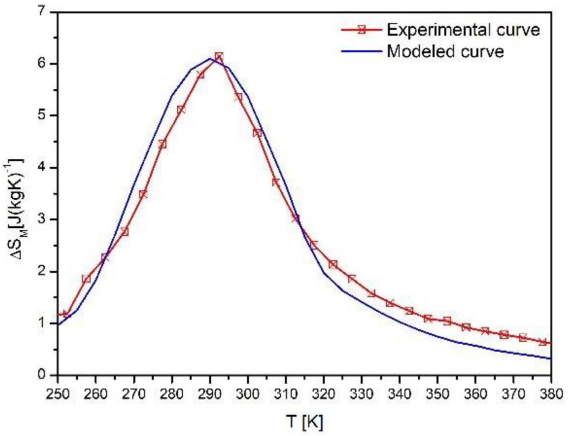

Fig. 2. Experimental and modeled magnetic entropy change for the as-cast MnCoGe alloy.

TABLE I

Experimental and theoretically modeled magnetocaloric properties of the MnCoGe alloy under the change in external magnetic field ~ 5 T.

	ΔS_M [J/(kg K)]	δT_{FWHM} [K]	RCP [J/kg]
Exp. value	6.17	36	222
Theor. value	6.09	43	262

dependence of magnetic entropy change obtained from experimental data and simulated using the phenomenological model were plotted in Fig. 2. Practically, both dependences overlap. The measured and the modeled values are comparable over the whole studied range. The phenomenological model delivered significantly higher values of δT_{FWHM} and, hence, relative cooling power. Modeled maximum entropy change decreased by 1%, while RCP and δT_{FWHM} increased by 18 and 19%, respectively.

Hamad's phenomenological model is a simple technique for the prediction of temperature dependences of magnetization or magnetic entropy change. The modeled values are reliable and comparable with measured results.

4. Conclusions

The evolution of magnetization due to the temperature changes for the MnCoGe alloy under the change in external magnetic field ~ 5 T was modeled. The phenomenological model allowed us to predict the magnetocaloric properties of the MnCoGe alloy, such as magnetic entropy change, relative cooling power, and full width at half maximum. The magnetocaloric effect (MCE) was experimentally predicted indirectly by a calculation of magnetic entropy change based on magnetic isotherms. The produced alloy revealed relatively acceptable magnetocaloric properties and could be applied as an active element in magnetic cooling devices. Values of magnetic entropy change and relative cooling power delivered during modeling are reliable and reasonable. Moreover, they correspond well to their counterparts from experimental investigation.

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