

Entropy change linked to the magnetic field induced martensitic transformation in a Ni–Mn–In–Co shape memory alloy

V. Recarte,^{1,a)} J. I. Pérez-Landazábal,¹ S. Kustov,² and E. Cesari²

¹*Departamento de Física, Universidad Pública de Navarra, Campus de Arrosadía 31006 Pamplona, Spain*

²*Departament de Física, Universitat de les Illes Balears, Ctra. de Valldemossa, km 7.5, E-07122 Palma de Mallorca, Spain*

(Received 13 October 2009; accepted 18 January 2010; published online 2 March 2010)

Experimental results on the temperature dependence of the entropy change induced by magnetic field in a Ni–Mn–In–Co ferromagnetic shape memory alloy have been analyzed. Different behaviors of the entropy change ΔS versus temperature have been observed, depending on the value of polarizing magnetic field. In addition, the magnetocaloric effect shows over certain temperature range, a limit value corresponding to the transformation entropy ΔS_{tr} . To explain the experimental results, a model, which takes into account the value of the martensitic transformation temperature shift and the transformation temperature range, has been proposed. The model allows to estimate the entropy change as a function of temperature and applied magnetic field from a few experimental data and therefore a first estimation of the refrigerant capacity of the system can be done. © 2010 American Institute of Physics. [doi:10.1063/1.3318491]

I. INTRODUCTION

The magnetocaloric effect (MCE) is characterized by the temperature change produced in a sample when a magnetic field is applied or removed under adiabatic condition or equivalently, as the entropy change in isothermal conditions. Both terms are related through the specific heat of the sample.¹ One of the topics of increasing interest is the search for an alternate technology for refrigeration that would replace the conventional gas compression-expansion technique. In this way, magnetic materials exhibiting MCE are promising candidates.^{1,2} Among these materials ferromagnetic shape memory alloys (FSMA) based on Heusler compounds show large values of MCE at the martensitic transformation (MT) due to the abrupt change in the magnetization through the structural transition. The difference in ferromagnetic exchange interactions in each phase promotes a discontinuous magnetization, and hence, a magnetic entropy change at the MT temperature.³ From the application point of view, large values of the MCE effect over broad temperature ranges are desirable.

In particular, Ni–Mn–Ga alloys close to Heusler Ni_2MnGa are the most studied FSMA due to their magnetostrictive behavior which allows their use as a magnetic actuator.⁴ The maximum direct MCE ($\Delta S < 0$) observed in this alloy system ($\Delta S = -20.4$ J/kg K at 5 T) occurs when both the first order structural and second order magnetic transition (from paramagnetic to ferromagnetic at T_c) temperatures lie close to each other.⁵ Regarding the study in other Heusler alloys, inverse MCE when application of a magnetic field adiabatically causes the sample to cool, was reported in Ni–Mn–Sn alloys with $\Delta S = 18$ J/kg K at 5 T.⁶ The inverse MCE is a direct consequence of the evolution of the magnetization over the temperature range of the first order struc-

tural transition ($\partial M / \partial T > 0$ as the magnetization of the martensite is lower than that of the austenite).¹ Subsequently, the inverse MCE at the MT has been observed in different systems, Ni–Mn–In,^{7–13} Ni–Mn–Sn ribbons,¹⁴ Ni–Mn–Sn–X (X=Co, Fe, Cr),^{15,16} Ni–Mn–Sb,¹⁷ Ni–Mn–Sb–Co,¹⁸ and Ni–Mn–In–Co.¹⁹ The large inverse MCE in these FSMA is due to the strong difference between the magnetization of phases involved in the magnetostructural transition as the martensite is paramagnetic.²⁰ Such MT, which is accompanied by a change in the magnetic ordering is an example of a magnetostructural transition.²¹

When a system undergoes a first order transformation the entropy of the system as a function of the temperature suffers a discontinuity linked to the transformation entropy ΔS_{tr} . On the other hand, application of a magnetic field promotes a shift in the transformation temperature expressed by the Clausius–Clapeyron equation. If the effect of the magnetic field is strong enough to induce the first order transition but its effect on the heat capacities of the two phases is small a limit value of the MCE with $\Delta S \approx \Delta S_{tr}$ should be expected.²²

In fact it is the magnetic measurements from which the MCE is usually estimated probably, because they are more available than the direct measurement of the field-induced adiabatic temperature change ΔT . The isothermal entropy change ΔS induced by the applied magnetic field is obtained from isothermal magnetization curves $M(H)_T$ by numerical integration of the Maxwell relation. In the case of first order magnetostructural transitions this procedure has been a matter of controversy due to the presence of transformation hysteresis.^{23–25} Fictitious high values of ΔS , i.e., a spike peak, can be obtained from isothermal magnetization curves as a mathematical artifact. According to classical thermodynamics, the entropy change $\Delta S(T, H)$ can be indirectly determined from magnetic measurements using the following expression:¹

^{a)}Author to whom correspondence should be addressed. Electronic mail: recarte@unavarra.es.

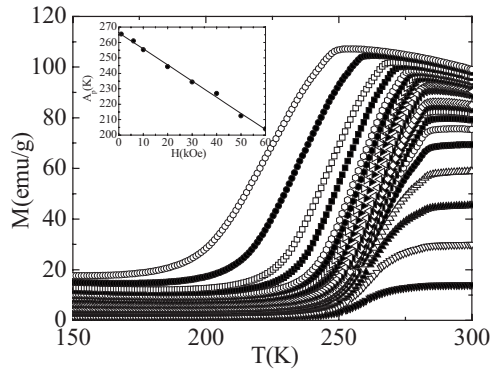


FIG. 1. Temperature dependence of the magnetization, $M(T)$ for different applied fields. From bottom to top: 100 Oe, 200 Oe, 300 Oe, 400 Oe, 500 Oe, 600 Oe, 700 Oe, 800 Oe, 900 Oe, 1 kOe, 1.5 kOe, 2 kOe, 4 kOe, 6 kOe, 8 kOe, 10 kOe, 20 kOe, 30 kOe, and 40 kOe. The inset shows the shift in the MT temperature, A_p , as a function of the applied magnetic field.

$$\Delta S(T, H) = S(T, H) - S(T, 0) = \mu_o \int_0^H \left(\frac{\partial M(T)}{\partial T} \right)_H dH. \quad (1)$$

The numerical integration of $\partial M / \partial T$ from a set of magnetization versus temperature spectra at different constant values of applied field $M(T)_H$, using Eq. (1), is the correct procedure.²⁵

In this paper, the analysis of the MCE in a Ni–Mn–In–Co alloy is reported. The measured MCE under an applied magnetic field up to 60 kOe shows clearly a limit value corresponding to the transformation entropy. A simple model taking into account the temperature shift in the MT under the magnetic field and the temperature interval where the reverse MT spreads has been proposed to explain the observed behavior.

II. MATERIAL AND EXPERIMENTAL TECHNIQUES

An alloy with nominal composition $\text{Ni}_{45}\text{Mn}_{36.7}\text{In}_{13.3}\text{Co}_5$ at. % was produced by arc-melting followed by several consecutive remeltings in order to homogenize the ingot. After 24 h homogeneity at 1170 K under vacuum, samples were annealed at 1070 K for 1800 s and slowly cooled in air. To evaluate the MCE associated to the MT temperature dependences of the magnetization $M(T)_H$ after zero field cooling were determined at different applied magnetic fields during heating between temperatures which include the reverse MT temperature domain by using a Quantum Design MPMS XL-7 SQUID magnetometer.²⁶ Zero field cool heating runs avoid the arrest of the transformation effect which would take place on cooling runs under field.^{27–29} Differential scanning calorimetry (DSC) analysis reveals that in zero field the martensite to austenite transition peak maximum is at $A_p = 258$ K, the transformation entropy, estimated as the latent heat ΔH divided by DSC peak temperature, $\Delta S_{tr} = 10 \pm 1$ J/kg K and the Curie temperature, $T_c = 386$ K in agreement with Ref. 29.

III. RESULTS AND DISCUSSION

Figure 1 shows $M(T)_H$ curves for different applied fields between 100 Oe and 60 kOe in the temperature range of the

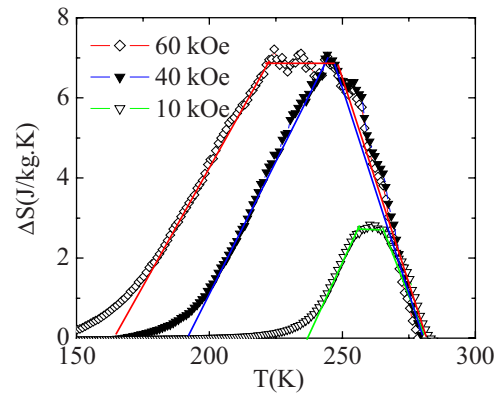


FIG. 2. (Color online) Entropy change ΔS for different maximum applied fields in the temperature range of the reverse MT. Colors lines correspond to the fitting of the experimental data according to the proposed schema.

reverse MT. In the entire range of applied magnetic fields the magnetization increases during heating in the range of the magnetostructural transition due to the higher magnetization of the austenite. The decrease in the MT temperature under applied field can be estimated directly from the position of the maximum of $\partial M(T)_H / \partial T$ derivative, which can be considered as similar to the DSC peak temperature A_p . The sensitivity of the MT to the applied field obtained this way is 1 K kOe^{-1} , see the inset in Fig. 1. This value can be compared with the one obtained from the Clausius–Clapeyron equation and DSC data. Taking, for $H = 60$ kOe, the difference between the magnetizations of austenite and martensite $\Delta M = 95 \pm 5$ emu/g and $\Delta S_{tr} = 10 \pm 1$ J/kg K, one obtains:

$$\frac{dT}{dH} = -\mu_o \frac{\Delta M}{\Delta S_{tr}} \approx (-0.9) \pm 0.1 \text{ K /kOe}, \quad (2)$$

The latter value is in a good agreement with the one obtained from the direct determination of the MT shift.

According to Eq. (1), positive values of the entropy change are expected when the magnetization increases with temperature for the full set of applied fields as in the measurements shown in Fig. 1. Figure 2 shows the evolution of the entropy change ΔS for three different applied magnetic fields, 10, 40, and 60 kOe, in the temperature range of the reverse MT. A maximum entropy change $\Delta S = 7$ J/kg K is achieved for 40 kOe at a temperature of 245 K and for 60 kOe in a temperature range between 225 and 245 K. For the lowest field, 10 kOe, a similar behavior to that of 60 kOe is observed but a lower maximum value of the entropy change, $\Delta S = 3$ J/kg K is reached. The evolution of the MCE as a function of the applied magnetic field can be explained based on the entropy variation during the first order transition, taking into account the thermoelastic nature of the MT. Figure 3(a) shows schematically variations in the entropy S (or austenite fraction x_A) with temperature under different polarizing fields. $S_0(T)$ (black line) represents the entropy at zero field. Due to the presence of an elastic term in the thermoelastic balance the MT spreads over certain temperature range:³⁰ the reverse MT starts at $A_s(0)$ and finishes at $A_f(0)$ and the entropy change is linked to the transformation entropy $\Delta S_{tr} = \Delta E_{tr} / T_0$, where ΔE_{tr} is the transformation enthalpy and T_0 is the equilibrium temperature between both

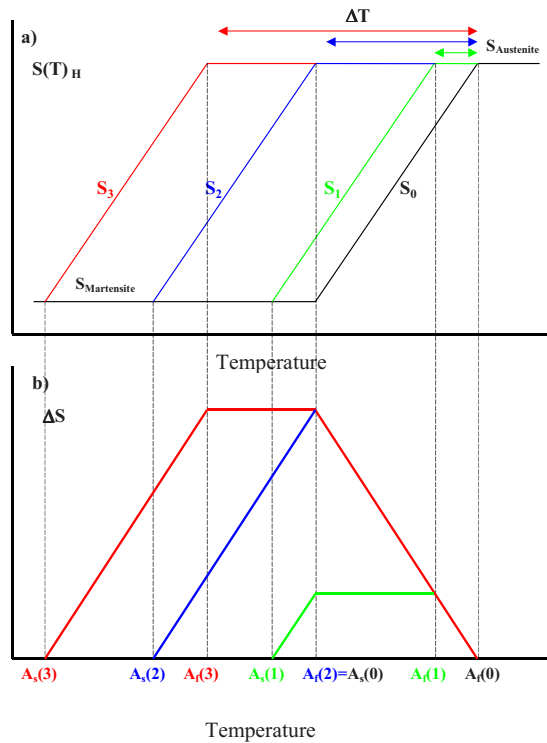


FIG. 3. (Color online) (a) Schematic T-S diagram of a magnetic system in the vicinity of a first order phase transition. The magnetic field shifts the transition to lower temperature. The effect of the field on the heat capacity has been neglected. (b) Schematic representation of the entropy change induced by the magnetic field for the system proposed in Fig. 3(a).

phases. As it has been pointed out, in the present Ni–Mn–In–Co alloy the magnetic field stabilizes the austenite with respect to the martensite lowering the equilibrium temperature with the temperature shift, $\Delta T = T_0(H) - T_0(0) < 0$, given by the Clausius–Clapeyron relation. Thus, S_1 , S_2 , and S_3 (green, blue, and red lines, respectively), describe the entropy versus temperature for increasing applied fields, $H_1 < H_2 < H_3$. The small effect of the magnetic field on the heat capacity both below and above the transition has been neglected in this scheme as well as the temperature and field dependence of $\Delta S_{tr} = \Delta E_{tr}/T_0$ as it is commonly accepted.²² It is worth to notice that the above assumptions on ΔS_{tr} together with dT/dH being independent of the field, lead to ΔM being independent of the field (or equivalently $(\partial M/\partial T)_H = \text{constant}$, which sounds a bit more surprising than the more usual $\Delta S_{tr} \approx \text{constant}$).³¹ Hence, from temperatures where the low temperature phase is stable, the maximum entropy change due to the application of a magnetic field must be the transformation entropy $\Delta S = \Delta S_{tr} = \Delta E_{tr}/T_0$ provided the applied field induces the complete reverse transformation.²² In the case of the highest magnetic field H_3 , there is a temperature range, $A_f(3) < T < A_s(0)$, where the complete reverse MT is induced by the magnetic field and the maximum ΔS is achieved, as is shown by the red line in Fig. 3(b). For higher temperatures, $A_s(0) < T < A_f(0)$, both phases coexist at zero field and only a fraction of the austenite x_A , decreasing with increasing temperature, can be induced by the magnetic field. Therefore the variation in the field-induced x_A determines correspondingly the decrease in ΔS in this temperature range. On the other hand, at lower

temperatures, $A_s(3) < T < A_f(3)$, only a partial reverse transformation can be induced by applied field, with the field-induced x_A increasing from 0 to 1 between $A_s(3)$ and $A_f(3)$, resulting in the corresponding increase in ΔS with temperature, Fig. 3(b). When the magnetic field has a value H_2 , such that the reverse MT start temperature at zero field coincides with the reverse MT finish temperature at nonzero field, $A_s(0) = A_f(2)$, the whole reverse MT can be induced only at this temperature (by the application of H_2) and consequently $\Delta S \approx \Delta S_{tr}$ is achievable only at this point. In this case the MCE effect versus temperature is schematized by a triangular shape, Fig. 3(b), blue line. For lower applied magnetic fields, as H_1 the maximum value of the MCE effect ($\Delta S = \Delta S_{tr}$) is not achieved, and the obtained ΔS in the temperature range $A_s(0) < T < A_f(1)$ is constant and determined by the austenite fraction induced by the corresponding field H_1 Fig. 3(b), green line.

The suggested interpretation allows us to explain all basic experimental regularities reported in Fig. 2. Figure 2 indicates that the value of the magnetic field for which the scenario H_2 from Fig. 3 is realized with $A_f(0) = A_s(H)$, is $H_2 \approx 40$ kOe. This implies that the temperature shift ΔT for this field must be similar to the MT temperature range $A_f - A_s$. For the present alloy both figures are in good agreement, $\Delta T \approx A_f - A_s \approx 40$ K, confirming thus, the suggested interpretation. In the case of the maximum applied magnetic field $H_3 = 60$ kOe, a maximum value of $\Delta S \approx \Delta S_{tr}$ is achieved over a temperature range of ≈ 20 K (resulting from ≈ 60 K shift produced by the field minus the extension $\Delta T \approx A_f - A_s$), again as it should be expected from the experimentally determined sensitivity of the MT to the magnetic field of around -1 K kOe⁻¹ and the extension of the transformation. The difference between the maximum ΔS value of about 7 J/kg/K and $\Delta S_{tr} = 10 \pm 1$ J/kg K will be discussed below. Finally, for lower fields the obtained MCE effect is lower and also demonstrates a kind of a plateau as is shown in Fig. 2 for $H_1 = 10$ kOe, again in agreement with the suggested explanation. Thus, qualitatively different behaviors of ΔS revealed by present experiments depend on the applied magnetic field, the field-induced MT temperature shift and the MT range, and can be consistently explained by the proposed model. This simple model/scheme allows estimating $\Delta S(T, H)$ -including the temperature range of its maximum value-under the application of a field H , from a few experimental data, namely, the temperature range of the transformation, the change in the MT temperature due to the magnetic field, and the transformation entropy $\Delta S_{tr} = \Delta E_{tr}/T_0$. Thus a first estimation of the MCE and of the refrigerant capacity can be obtained through this model, without performing the numerical derivatives and integration required by the application of Eq. (1).

Figure 4 shows ΔS plotted as a function of the applied magnetic field for different temperatures. As it has been discussed previously $\Delta S(T) \propto x_A(T)$. At low temperatures, $T < 220$ K, only a partial reverse MT is induced by the magnetic field up to 60 kOe, and the field-induced fraction of austenite x_A increases with temperature, resulting in a similar increase in ΔS . In an intermediate temperature range (225–245 K) the complete reverse MT is induced by the field, even

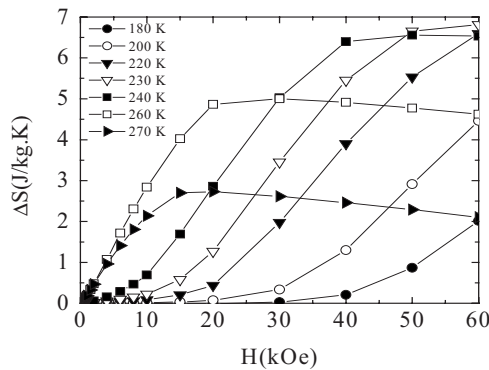


FIG. 4. Entropy change ΔS as a function of the applied magnetic field at different temperature in the MT range.

for lower values than 60 kOe, and ΔS reaches its maximum value. At higher temperatures, where both phases coexist at zero field, the induced austenite fraction x_A and ΔS diminish as the temperature increases.

It has been argued that the maximum value of the entropy change induced by the applied magnetic field is the transformation entropy, $\Delta S \approx \Delta S_{tr}$. However, in our case $\Delta S = 7$ J/kg K and ΔS_{tr} as obtained from calorimetric measurements $\Delta S_{tr} = 10 \pm 1$ J/kg K. To understand the discrepancy between both values a pure magnetic contribution to the entropy change, which represents the conventional direct MCE and have the sign opposite to the entropy change due to the MT, must be taken into account. In fact, a negative MCE with $\Delta S = -2$ J/kg K is obtained at 300 K. This temperature is above $A_f(0)$ and the pure magnetic term is the only remaining contribution outside of the transformation range. This negative contribution to the total MCE explains the larger part of the discrepancy between ΔS and ΔS_{tr} . Besides this correction, the negative slope of $\Delta S(T)$ which can be clearly seen in Fig. 4 for high magnetic fields at 260 and 270 K, is also due to the contribution of this conventional direct MCE: concomitant with the induction of the austenite phase by the magnetic field, the increase in the field promotes the decrease in the magnetic entropy of the system. This effect can also be seen in the negative slope of the curves $M(T)_H$ of Fig. 1 for temperatures above ~ 250 K and higher fields.

In view of technical applications, large values of the MCE effect in broad temperature ranges near room temperature are desirable. A higher shift in the MT temperature, ΔT , under the magnetic field implies a broader range of giant MCE. According to the Clausius–Clapeyron relation to increase ΔT , high and low values of ΔM and ΔS_{tr} , respectively, are required. In contrast, ΔS_{tr} limits the MCE effect and consequently the refrigerant power. Therefore, a compromise between maximum value and the width of the temperature range of the MT-related MCE has to be achieved.

In summary, the inverse MCE at the MT has been measured in a Ni–Mn–In–Co FSMA. The maximum ΔS obtained is limited by the transformation entropy ΔS_{tr} . Thus a $\Delta S = 7$ J/kg K was achieved in a temperature range of 20 K. To explain the experimental results a model, which takes into account the value of the MT temperature shift and the transformation temperature range, has been proposed.

ACKNOWLEDGMENTS

This work has been carried out with the financial support of the Spanish “Ministerio de Ciencia y Tecnología” (Project nos. MAT2006-12838, MAT2008-01587, and MAT-2009-07928) and the Government of Navarra (project entitled “Efecto Magnetocalórico en Aleaciones con Memoria de Forma Ferromagnéticas”).

- ¹A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Applications* Series in Condensed Matter Physics, (Institute of Physics, Bristol, UK, 2003).
- ²V. K. Pecharsky, and K. A. Gschneidner, *Phys. Rev. Lett.* **78**, 4494 (1997).
- ³J. Marcos, A. Planes, L. Mañosa, F. Casanova, X. Batlle, and A. Labarta, *Phys. Rev. B* **66**, 224413 (2002).
- ⁴K. Ullakko, J. K. Huang, C. Kantner, R. C. O’Handley, and V. V. Kokorin, *Appl. Phys. Lett.* **69**, 1133 (1996).
- ⁵X. Zhou, W. Li, H. P. Kunkel, and G. Williams, *J. Phys.: Condens. Matter* **16**, L39 (2004).
- ⁶T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, and A. Planes, *Nature Mater.* **4**, 450 (2005).
- ⁷Z. D. Han, D. H. Wang, C. L. Zhang, S. L. Tang, B. X. Gu, and Y. W. Du, *Appl. Phys. Lett.* **89**, 182507 (2006).
- ⁸X. Moya, L. Mañosa, A. Planes, S. Aksoy, M. Acet, E. F. Wassermann, and T. Krenke, *Phys. Rev. B* **75**, 184412 (2007).
- ⁹T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, A. Planes, E. Suard, and B. Ouladdiaf, *Phys. Rev. B* **75**, 104414 (2007).
- ¹⁰X. Zhang, B. Zhang, S. Yu, Z. Liu, W. Xu, G. Liu, J. Chen, Z. Cao, and G. Wu, *Phys. Rev. B* **76**, 132403 (2007).
- ¹¹A. K. Pathak, M. Khan, I. Dubenko, S. Stadler, and N. Ali, *Appl. Phys. Lett.* **90**, 262504 (2007).
- ¹²P. A. Bhohe, K. R. Priolkar, and A. K. Nigam, *Appl. Phys. Lett.* **91**, 242503 (2007).
- ¹³V. K. Sharma, M. K. Chattopadhyay, R. Kumar, T. Ganguli, P. Tiwari, and S. B. Roy, *J. Phys.: Condens. Matter* **19**, 496207 (2007).
- ¹⁴B. Hernando, J. L. Sánchez-Llamazares, J. D. Santos, V. M. Prida, D. Baldomir, D. Serantes, R. Varga, and J. González, *Appl. Phys. Lett.* **92**, 132507 (2008).
- ¹⁵T. Krenke, E. Duman, M. Acet, X. Moya, L. Mañosa, and A. Planes, *J. Appl. Phys.* **102**, 033903 (2007).
- ¹⁶D. H. Wang, C. L. Zhang, Z. D. Han, H. C. Xuan, B. X. Gu, and Y. W. Du, *J. Appl. Phys.* **103**, 033901 (2008).
- ¹⁷J. Du, Q. Zheng, W. J. Ren, W. J. Feng, X. G. Liu, and Z. D. Zhang, *J. Phys. D* **40**, 5523 (2007).
- ¹⁸Z. D. Han, D. H. Wang, C. L. Zhang, H. C. Xuan, J. R. Zhang, B. X. Gu, and Y. W. Du, *J. Appl. Phys.* **104**, 053906 (2008).
- ¹⁹J. Liu, N. Scheerbaum, J. Lyubina, and O. Gutfleisch, *Appl. Phys. Lett.* **93**, 102512 (2008).
- ²⁰R. Y. Umetsu, R. Kainuma, Y. Amako, Y. Taniguchi, T. Kanomata, K. Fukushima, A. Fujita, K. Oikawa, and K. Ishida, *Appl. Phys. Lett.* **93**, 042509 (2008).
- ²¹S. B. Roy, P. Chaddah, V. K. Pecharsky, and K. A. Gschneider, Jr., *Acta Mater.* **56**, 5895 (2008).
- ²²V. K. Pecharsky, K. A. Gschneider, A. O. Pecharsky, and A. M. Tishin, *Phys. Rev. B* **64**, 144406 (2001).
- ²³G. J. Liu, J. R. Sun, J. Shen, B. Gao, H. W. Zhang, F. X. Hu, and B. G. Shen, *Appl. Phys. Lett.* **90**, 032507 (2007).
- ²⁴C. P. Sasso, M. Kuepferling, L. Giudici, V. Basso, and M. Pasquale, *J. Appl. Phys.* **103**, 07B306 (2008).
- ²⁵L. Tocado, E. Palacios, and R. Burriel, *J. Appl. Phys.* **105**, 093918 (2009).
- ²⁶UNPN-E007 Feder project 2003.
- ²⁷V. K. Sharma, M. K. Chattopadhyay, and S. B. Roy, *Phys. Rev. B* **76**, 140401(R) (2007).
- ²⁸W. Ito, K. Ito, R. Y. Umetsu, R. Kainuma, K. Koyama, K. Watanabe, A. Fujita, K. Oikawa, K. Ishida, and T. Kanomata, *Appl. Phys. Lett.* **92**, 021908 (2008).
- ²⁹S. Kustov, M. L. Corró, J. Pons, and E. Cesari, *Appl. Phys. Lett.* **94**, 191901 (2009).
- ³⁰P. Wollants, J. R. Roos, and L. Delaey, *Prog. Mater. Sci.* **37**, 227 (1993).
- ³¹A. Tishin, K. A. Gschneider, Jr., and V. K. Pecharsky, *Phys. Rev. B* **59**, 503 (1999).