

This is the Author's Pre-print version of the following article published in Functional Materials Letters, 10, 1740007 (2017). Electronic version of an article published as <https://doi.org/10.1142/S1793604717400070>

© World Scientific Publishing Company

<http://www.worldscientific.com/worldscinet/fml>

Large and reversible elastocaloric effect around room temperature in a Ga doped Ni-Mn-In alloy

Juan-Pablo Camarillo¹, Christian-Omar Aguilar-Ortiz¹, Horacio Flores-Zúñiga¹, David Ríos-Jara¹, Daniel-Enrique Soto-Parra², Enric Stern-Taulats³, Antoni Planes³ and Lluís Mañosa³.

¹ Instituto Potosino de Investigación Científica y Tecnológica, Camino a la Presa San José 2005, Col. Lomas 4a, CP.78216 San Luis Potosí, Mexico.

² Centro de Investigaciones en Materiales Avanzados S. C., Miguel de Cervantes 120, Chihuahua 31109, Mexico

³ Departament d'Estructura i Constituents de la Matèria. Facultat de Física, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Catalonia, Spain.

E-mail: horacio.flores@ipicyt.edu.mx

Abstract

We report a giant elastocaloric effect near to room temperature in a polycrystalline Ni-Mn-In-Ga ferromagnetic shape memory alloy. A maximum entropy change value close to $32 \text{ JK}^{-1}\text{kg}^{-1}$ was obtained by applying a 100 MPa compressive stress. Moreover, we report a value of 4.9 K for a reversible adiabatic temperature change. These values are compared with those reported for the magnetocaloric effect within a high magnetic field. The strong sensitivity in the isothermal entropy change and adiabatic temperature change to the uniaxial stress allow the alloy to present remarkable elastocaloric effect strength values of $|\Delta S_{\text{me}}|/|\Delta\sigma|=320 \text{ JK}^{-1}\text{kg}^{-1}\text{GPa}^{-1}$ and $|\Delta T_{\text{ad}}^{\text{me}}|/|\Delta\sigma|=49.0 \text{ KPa}^{-1}$.

Introduction

Nowadays, the energy employed for refrigeration and air conditioning represents 20% of world consumption where the dominant technology for temperature control is the Vapor

Compression-Expansion Cycle [1]. Caloric effects research has increased lately because they represent a new alternative of refrigeration technology which evermore are friendly with the environment. These effects are related with entropy changes or temperature changes produced in a material during either application, or the removal of external forces in isothermal and isoentropic processes, respectively.

Caloric effects due to external forces such as magnetic field (magnetocaloric effect), stress (elastocaloric effect), electric field (electrocaloric effect) and hydrostatic pressure (barocaloric effect) have been reported.

The Magnetocaloric effect is probably the most studied; however, the elastocaloric effect has been highlighted as one of the most promising alternatives for solid state refrigeration [2]. High elastocaloric effects are achieved for structural phase transition such as martensitic transition in ferromagnetic shape memory alloys (FSMA), which are classified as multicaloric materials due to their capacity to exhibit more than one type of caloric effect [3]. Ductile shape memory alloys reported high isothermal entropy changes and large relative cooling power due to the stress-induced martensitic transformation [4][5], furthermore high efficiency and cyclic stability have been studied [6][7].

Giant caloric effects in the Ni-Mn-In system have already been reported due to the external magnetic field [8], [9],[10] and hydrostatic pressure [11][12]. Furthermore, multicaloric character existence could be useful in order to couple caloric effects on the same material [13].

First reports of isothermal entropy change showed moderate values of ΔS_{me} for uniaxial stress up to 10 MPa ($Ni_{52.6}Mn_{21.9}Ga_{24.2}Fe_{1.3}$ [14], $Ni_{50.5}Mn_{21.7}Ga_{24.7}Co_{3.1}$ [15], $Ni_{43}Mn_{40}Sn_{10}Cu_7$ [16]). Recently a ΔS_{me} of $11.1 \text{ JK}^{-1}\text{kg}^{-1}$ for $\Delta\sigma=310$ MPa has been reported in a $Ni_{43.5}Co_{6.5}Mn_{39}Sn_{11}$ [17] alloy. For $Ni_{46}Mn_{38}Sb_{12}Co_4$ alloy a value of $\Delta S_{me}\sim 21 \text{ JK}^{-1}\text{kg}^{-1}$ for $\Delta\sigma=104$ MPa has been reported [18].

Direct measurements of ΔT_{ad}^{me} in Ni-Mn-In system have been reported: $Ni_{45}Mn_{36.4}In_{13.6}Co_5$ and $Ni_{45.7}Mn_{36.6}In_{13.3}Co_{5.1}$ alloys report values of ΔT_{ad}^{me} of 3–4 K for $\Delta\sigma= 100\text{-}150$ MPa respectively [19], [20]. In $Ni_{45}Mn_{44}Sn_{11}$ a $\Delta T_{ad}^{me}\sim 5.7$ K has been reported for $\Delta\sigma=242$ MPa [21]. A highly textured polycrystalline sample of $Ni_{48}Mn_{35}In_{17}$ presented $\Delta T_{ad}^{me}=4$ K for $\Delta\sigma\sim 300$ MPa [22]. In this work we report the entropy and temperatures changes on isothermal and adiabatic process for elastocaloric effect (ΔS_{me} y ΔT_{ad}^{me}) due to the martensitic transition presented in $Ni_{50}Mn_{34}In_{13}Ga_3$ alloy. We report an entropy change $\Delta S_{me}\sim 32 \text{ JK}^{-1}\text{kg}^{-1}$ and a reversible adiabatic temperature change of $\Delta T_{ad}^{me} \sim 4.9$ K for a 100MPa stress.

Experimental details

A polycrystalline ingot was prepared by arc-melting from pure metals (>99.9%) under argon atmosphere on a water-cooled Cu crucible. The bulk was re-melted several times to insure homogeneity, annealed at 1173 K during 24h and then quenched into a mixture of ice-water.

The alloy undergoes martensitic transformation between 297 K and 280 K (A_F and M_F , respectively). The DSC curve shown in Fig. 1a) was obtained using a commercial TA-instruments TA-Q200 and the transformation enthalpy and entropy were quantified as 11.2 Jg^{-1} and $39.0 \text{ JK}^{-1}\text{kg}^{-1}$, respectively. The chemical analysis determined by EDS shows a composition of $\text{Ni}_{51.4\pm 1.0}\text{Mn}_{33.6\pm 0.7}\text{In}_{12.1\pm 0.2}\text{Ga}_{2.9\pm 0.3}$. The XRD measurement shows a $L2_1$ austenite and modulated martensite mixture at 295 K (Fig.1 b).

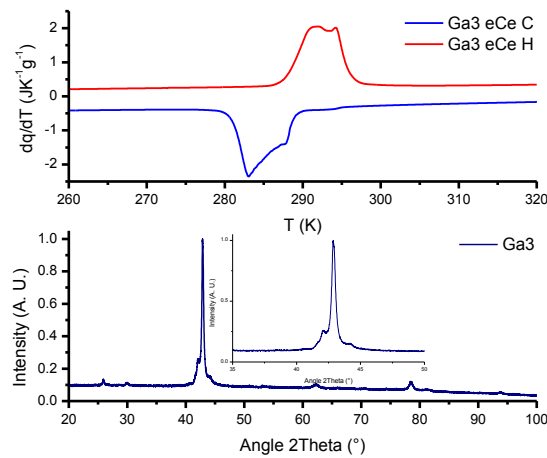


Figure 1. (a) DSC curve of the sample of study. (b) XRD from the powdered alloy.

For the elastocaloric effect determination a specimen with $4.97 \pm 0.05 \text{ mm}^2$ cross-section and $3.31 \pm 0.01 \text{ mm}$ length (mass $\sim 0.1300 \text{ g}$) was employed. The measurements were carried out on the purpose-built equipment described in reference [15]. The set-up allows the measuring of the adiabatic temperature change (ΔT_{ad}) with a thermocouple attached to the sample and by manually releasing or applying stress. For the stress-induced entropy change, the set-up also allows to perform iso-stress measurements of the length while scanning temperature (at a rate of 0.7 Kmin^{-1}).

Results

Figure 2 shows curves of length versus temperature in both senses of the martensitic transformation; inverse and forward martensitic transformations appear at the top and bottom, respectively. The measurements were taken between 0 and 100 MPa of compressive stress. It can be seen that the strain magnitude strongly increases during the martensitic transformation with the applied stress (up to 2.5% for 40 MPa) and reaches a maximum of 2.8% for 100 MPa. This saturation in the strain as a function of the stress reflects a high density of martensitic variants oriented in the direction of the applied stress. The temperature at half strain as a function of applied stress during the martensitic transformations ($T^*_{0.5}$) follows the effect of the applied stress on the martensitic transformation temperature (Inset Fig. 2). The shifting of the martensitic transformation to higher temperatures due to the increase of external stress shows a conventional elastocaloric effect. Taking the relation between $T^*_{0.5}$ and applied stress as a linear slope of ~ 0.13 , KMPa^{-1} can be measured. This value is similar to those reported in other ferromagnetic shape memory alloys ([17], [18] and [23]).

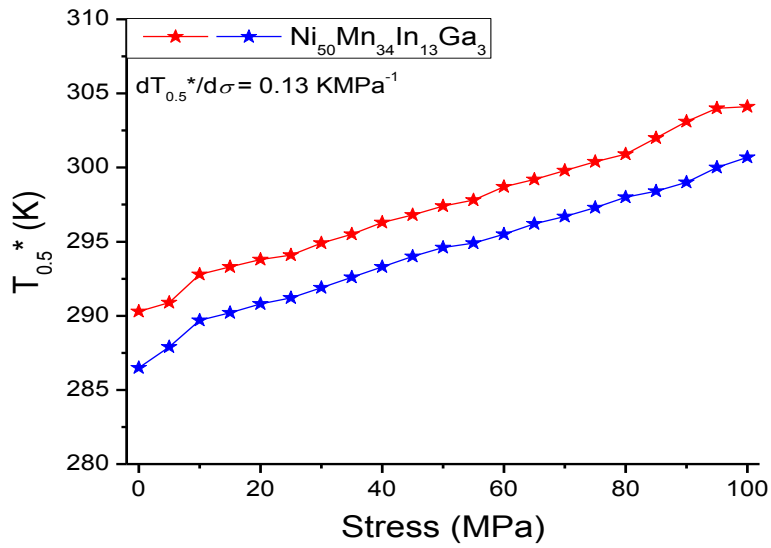
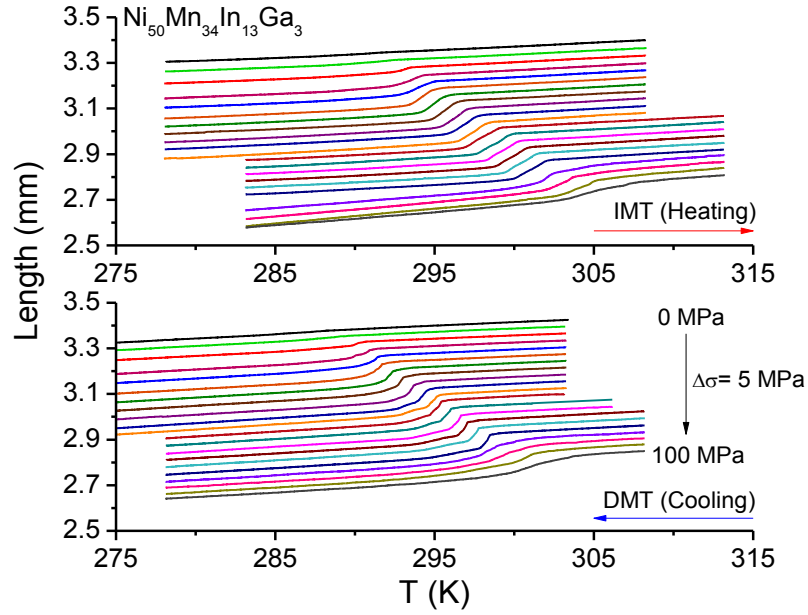


Figure 2. (a) Length curves measured during the inverse martensitic transformation and (b) direct martensitic transformation for different compressive stresses. Curves in (c) show the effect in $T_{0.5}^*$ for heating and cooling due to the increasing compressive stress.

From data in Fig. 2, the stress-induced entropy change (ΔS_{me}) was calculated by Maxwell relations $(\partial S / \partial \sigma)_T = V(\partial \varepsilon / \partial T)_\sigma = \phi(\partial L / \partial T)_F$, where, the stress σ is defined by the force (F) and the cross-section (ϕ) of the sample. By applying the definitions of volume (V)

$V = \phi l$ and deformation (ϵ) $\epsilon = \frac{L}{l}$ it is possible to use expression (1) by measuring the sample length (L) and temperature (T) for computing ΔS_{me} .

$$\Delta S_{me}(T, \sigma) = \int^{\Delta\sigma} \left(\frac{\partial S}{\partial \sigma} \right)_T d\sigma = \int^{\Delta F = \Delta\sigma\phi} \left(\frac{dL}{dT} \right)_F dF$$

Isothermal entropy change $\Delta S_{me}(T, \sigma)$ is shown in Fig. 3 where a value close to the transformation entropy change of $32 \text{ JK}^{-1}\text{kg}^{-1}$ was obtained at 100 MPa. This suggests that stresses around 100 MPa could induce a partial reversible transition close to room temperatures, analogous to the case of the magnetocaloric effect, where a reversible contribution has been shown for the reverse transition under an applied magnetic field. [10].

Fig. 3, displays a narrow hysteresis between cooling and heating entropy curves related to the reversibility in the fraction of material that undergoes the forward and reverse transitions. This is important in order to favor reversibility close to transition temperatures with the applied stress. In order to increase transition temperatures, shift to improve reversibility, large stresses will be required.

Fig. 4 depicts the reversibility expected within the transition temperature range for the studied range of applied stresses. We report a maximum reversible entropy change of $26 \text{ JK}^{-1}\text{kg}^{-1}$ for a stress close to 100 MPa. It is worth mentioning that these results were obtained during the early stages of thermal cycling under an applied stress.

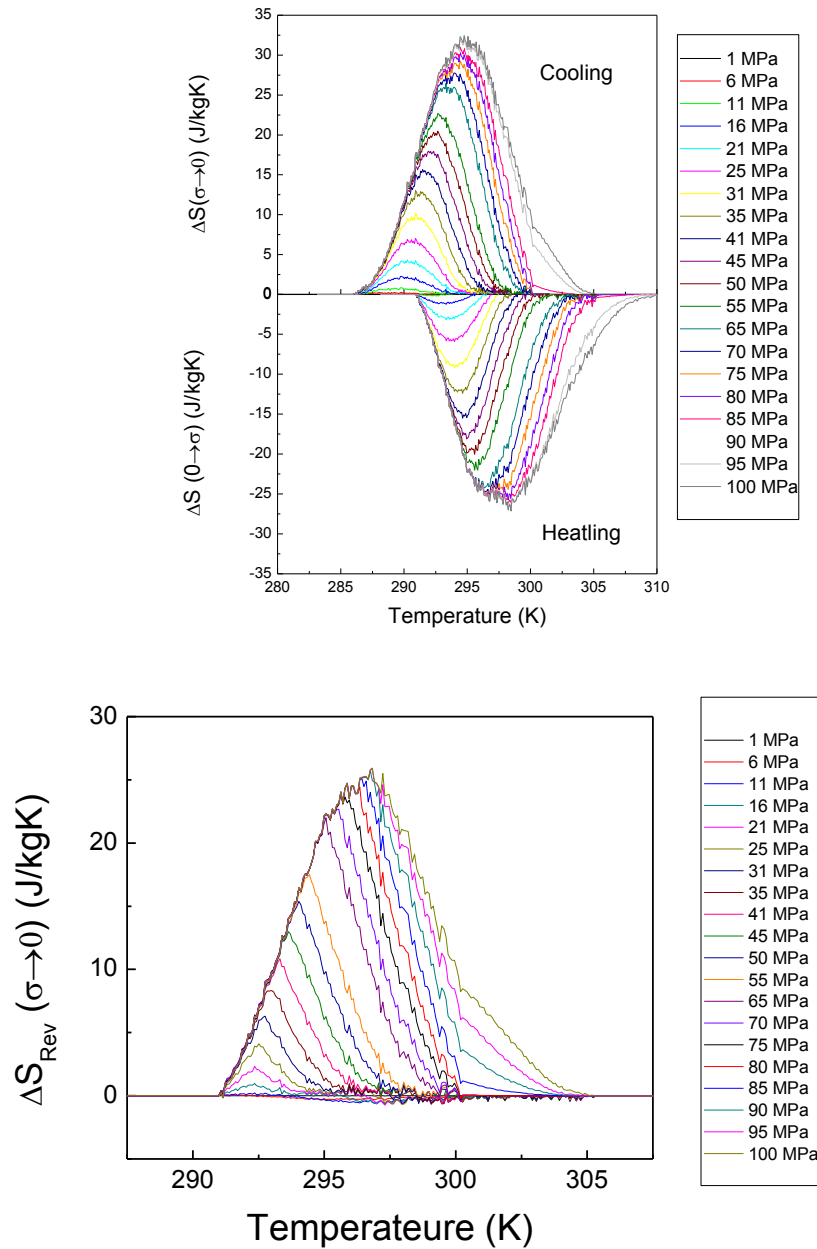


Fig. 3. Stress-induced entropy change as a function of the temperature and applied stress between 5 and 100 MPa in the alloy. The inset shows the maximum value of ΔS_{me} as a function of applied stress (solid lines are to guide the eye).

The values of $|\Delta S_{me}(T, \sigma)|$ presented in the alloy $Ni_{50}Mn_{34}In_{13}Ga_3$ are larger than the those previously reported in ferromagnetic shape memory alloys [14] [15] [18]. A comparison-purposed quantity is the relative strength of elastocaloric effect ($\Delta S_{me}/\Delta\sigma$). Near to room

temperature ductile alloys show values between 50 and 160 JK⁻¹kg⁻¹GPa⁻¹ [3]. The alloy Ni₅₀Mn₃₄In₁₃Ga₃ shows a value of 320 JK⁻¹kg⁻¹GPa⁻¹ which is larger than those exhibited in similar alloys [17] [18].

Another figure of merit commonly used in the evaluation of caloric materials is the relative cooling power. The RCP can be estimated according to the expression

$$RCP = \int_{T_{cold}}^{T_{hot}} \Delta S_{me} dT$$

The alloy exhibits an RCP of 205 Jkg⁻¹ applying $\Delta\sigma=100$ MPa. T_{cold} and T_{hot} have been defined using the FWHM criteria (full width half maximum) as 293K and 303K during heating and 290K and 299K for cooling; from which ~80% (166 Jkg⁻¹) are reversible.

In order to measure the reversible adiabatic temperature change in the alloy, a K-type thermocouple was attached to the middle part of the sample. At each measured temperature (T₀) the sample was loaded under a compressive stress until the desired stress, and then released in one-step to promote the adiabaticity of the experiment. The resulting curves of ΔT_{ad}^{me} vs T₀ are shown in Fig. 4. It can be noted that the values of adiabatic temperature change are cyclic, as can be seen in Fig. 5. Furthermore, a reversible $|\Delta T_{ad}^{me}|$ of 1 K can be induced with the application of only 30 MPa.

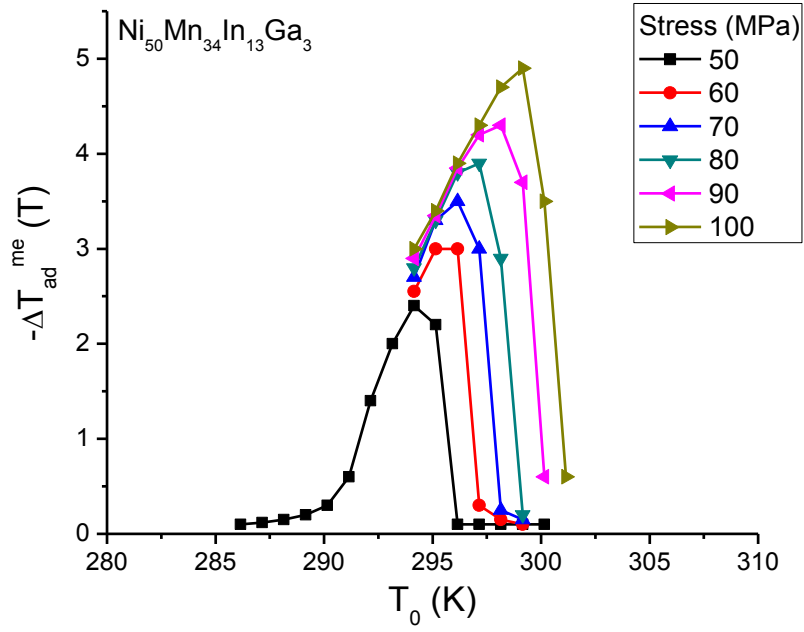


Fig. 4. Dependence of the reversible adiabatic temperature change with the measured temperature and the released stress.

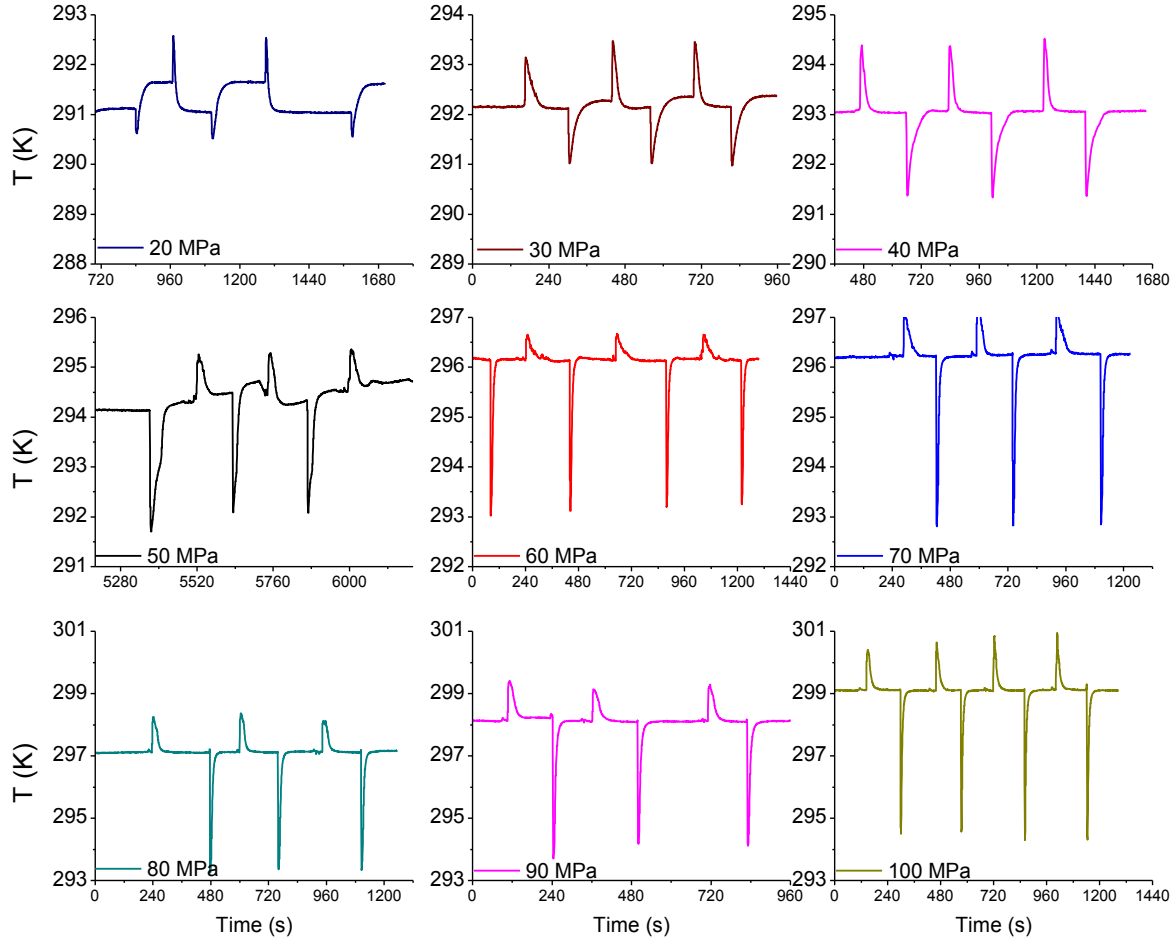


Fig. 5. Maximum values of adiabatic temperature change as a function of the applied stress.

The maximum cyclic $|\Delta T_{ad}^{me}|$ shown by the alloy is ~ 4.9 K for $\Delta\sigma = 100$ MPa measured at 299 K. It is worth remarking that the ΔT_{ad}^{me} exhibited is reversible. This value is also larger than those measured in similar alloys measured around room temperature [19][20][22]. The strength of the elastocaloric effect expressed in terms of the adiabatic temperature change ($|\Delta T_{ad}^{me}|/|\Delta\sigma|$) for this alloy shows a value of 49 KPa^{-1} , which is comparable with those presented in $\text{Ni}_{54}\text{Fe}_{19}\text{Ga}_{27}$ [24].

The high values of $|\Delta S_{me}(T, \sigma)|$ and $|\Delta T_{ad}^{me}|$ are mainly due to the contribution of 2 factors: (i) The high value of transformation entropy change in the alloy, related to the proximity to the ferro- to paramagnetic transition and (ii) The small temperature range where the martensitic transformation occurs (~ 7 K), which is practically independent from the applied stress. This behavior is due to a high compatibility between an important group of favored martensitic variants on the direction of the applied stress, which allows the induction of a practically full martensitic transformation.

Summary and conclusions

We have studied the giant elastocaloric effect in a Ga doped Ni-Mn-In alloy by means of an indirect method employing length (σ, T) curves, and a direct method via adiabatic temperature change during the release of the uniaxial stress. Our sample exhibits a large entropy change of $\sim 32 \text{ JK}^{-1}\text{kg}^{-1}$ due the application of a low uniaxial stress of 100 MPa across the martensitic transformation from this $26 \text{ JK}^{-1}\text{kg}^{-1}$ are reversible. The alloy presents a reversible ΔT_{ad}^{me} of 4.9 K around room temperature due to the release of 100 MPa. These values are comparable to those obtained for the magnetocaloric effect with high external magnetic field application. The narrow range in temperature where the martensitic transformation occurs and the shifting of the transformation temperatures allows to induce martensite via stress almost completely; this produces a stress-induced entropy change and adiabatic temperature change larger than those shown in similar

alloys. The alloy shows relative strengths of elastocaloric effect $|\Delta S_{me}|/|\Delta\sigma|$ and $|\Delta T_{ad}^{me}|/|\Delta\sigma|$ of $320 \text{ JK}^{-1}\text{kg}^{-1}\text{GPa}^{-1}$ and 49.0 K GPa^{-1} , respectively.

Acknowledgements

The authors would like to acknowledge financial support from the Mexican Council of Science and Technology (CONACYT CB-2010-01-157541) and from the Spanish Ministry of Science (MAT2016- 75823-R) and to thank Beatriz Adriana Rivera Escoto and Laboratorio Nacional de Investigaciones en Nanociencia y Nanotecnología (LINAN), IPICYT, for the availability of their laboratory facilities. EST acknowledges support from AGAUR (Catalonia).

References.

- [1] A. Kitanovski, U. Plaznik, U. Tomc, and A. Poredoš, "Present and future caloric refrigeration and heat-pump technologies," *Int. J. Refrig.*, vol. 57, pp. 288–298, Sep. 2015.
- [2] B. Y. W. Goetzler, M. Ashrae, R. Zogg, M. Ashrae, J. I. M. Young, A. M. Ashrae, C. Johnson, and A. M. Ashrae, "Alternatives to HVAC Technology," *ASHRAE J.*, no. October, pp. 12–23, 2014.
- [3] X. Moya, S. Kar-Narayan, and N. D. Mathur, "Caloric materials near ferroic phase transitions," *Nat. Mater.*, vol. 13, no. 5, pp. 439–50, Apr. 2014.
- [4] E. Bonnot, R. Romero, L. Mañosa, E. Vives, and A. Planes, "Elastocaloric Effect Associated with the Martensitic Transition in Shape-Memory Alloys," *Phys. Rev. Lett.*, vol. 100, no. 12, pp. 1–4, Mar. 2008.
- [5] L. Mañosa, S. Jarque-Farnos, E. Vives, and A. Planes, "Large temperature span and giant refrigerant capacity in elastocaloric Cu-Zn-Al shape memory alloys," *Appl. Phys. Lett.*, vol. 103, no. 21, p. 211904, 2013.
- [6] J. Cui, Y. Wu, J. Muehlbauer, Y. Hwang, R. Radermacher, S. Fackler, and M. Wuttig, "Demonstration of high efficiency elastocaloric cooling with large T using NiTi wires Demonstration of high efficiency elastocaloric cooling with large D T using NiTi wires," vol. 073904, pp. 2–6, 2012.
- [7] C. Bechtold, C. Chluba, R. L. De Miranda, and E. Quandt, "High cyclic stability of the elastocaloric effect in sputtered TiNiCu shape memory films," vol. 091903, pp. 2–6, 2012.

- [8] V. K. Sharma, M. K. Chattopadhyay, and S. B. Roy, "Large inverse magnetocaloric effect in Ni₅₀Mn₃₄In₁₆," vol. 1869, 2007.
- [9] a Planes, L. Manosa, X. Moya, T. Krenke, M. Acet, and E. Wassermann, "Magnetocaloric effect in Heusler shape-memory alloys," *J. Magn. Magn. Mater.*, vol. 310, no. 2, pp. 2767–2769, Mar. 2007.
- [10] E. Stern-Taulats, P. O. Castillo-Villa, L. Mañosa, C. Frontera, S. Pramanick, S. Majumdar, and A. Planes, "Magnetocaloric effect in the low hysteresis Ni-Mn-In metamagnetic shape-memory Heusler alloy," *J. Appl. Phys.*, vol. 115, no. 17, p. 173907, May 2014.
- [11] L. Mañosa, D. González-Alonso, A. Planes, E. Bonnot, M. Barrio, J.-L. Tamarit, S. Aksoy, and M. Acet, "Giant solid-state barocaloric effect in the Ni-Mn-In magnetic shape-memory alloy," *Nat. Mater.*, vol. 9, no. 6, pp. 478–81, Jun. 2010.
- [12] E. Stern-Taulats, A. Planes, P. Lloveras, M. Barrio, J. Tamarit, S. Pramanick, S. Majumdar, S. Yüce, B. Emre, C. Frontera, and L. Mañosa, "Tailoring barocaloric and magnetocaloric properties in low-hysteresis magnetic shape memory alloys," *Acta Mater.*, vol. 96, pp. 324–332, Sep. 2015.
- [13] A. Chauhan, S. Patel, R. Vaish, and C. R. Bowen, "A review and analysis of the elasto-caloric effect for solid-state refrigeration devices: Challenges and opportunities," *MRS Energy Sustain.*, vol. 2, no. ii, p. E16, 2015.
- [14] D. E. Soto-Parra, E. Vives, D. González-Alonso, L. Mañosa, A. Planes, R. Romero, J. a. Matutes-Aquino, R. a. Ochoa-Gamboa, and H. Flores-Zúñiga, "Stress- and magnetic field-induced entropy changes in Fe-doped Ni-Mn-Ga shape-memory alloys," *Appl. Phys. Lett.*, vol. 96, no. 7, p. 071912, 2010.
- [15] P. O. Castillo-Villa, D. E. Soto-Parra, J. A. Matutes-Aquino, R. A. Ochoa-Gamboa, A. Planes, L. Mañosa, D. González-Alonso, M. Stipich, R. Romero, D. Ríos-Jara, and H. Flores-Zúñiga, "Caloric effects induced by magnetic and mechanical fields in a Ni₅₀Mn₂₅-xGa₂₅Cox magnetic shapememory alloy," *Phys. Rev. B*, vol. 83, no. 17, p. 174109, May 2011.
- [16] P. O. Castillo-Villa, L. Mañosa, A. Planes, D. E. Soto-Parra, J. L. Sánchez-Llamazares, H. Flores-Zúñiga, and C. Frontera, "Elastocaloric and magnetocaloric effects in Ni-Mn-Sn(Cu) shape-memory alloy," *J. Appl. Phys.*, vol. 113, no. 5, p. 053506, 2013.
- [17] Z. Yang, D. Y. Cong, L. Huang, Z. H. Nie, X. M. Sun, Q. H. Zhang, and Y. D. Wang, "Large elastocaloric effect in a Ni-Co-Mn-Sn magnetic shape memory alloy," *Mater. Des.*, vol. 92, no. 3, pp. 932–936, Feb. 2016.
- [18] R. Millán-Solsona, E. Stern-Taulats, E. Vives, A. Planes, J. Sharma, A. K. Nayak, K. G. Suresh, and L. Mañosa, "Large entropy change associated with the elastocaloric effect in polycrystalline Ni-Mn-Sb-Co magnetic shape memory alloys," *Appl. Phys. Lett.*, vol. 105, no. 24, p. 241901, Dec. 2014.
- [19] B. Lu, F. Xiao, A. Yan, and J. Liu, "Elastocaloric effect in a textured polycrystalline Ni-Mn-In-Co metamagnetic shape memory alloy," *Appl. Phys. Lett.*, vol. 105, no. 16, p. 161905, Oct. 2014.

- [20] B. Lu, P. Zhang, Y. Xu, W. Sun, and J. Liu, "Elastocaloric effect in Ni₄₅Mn_{36.4}In_{13.6}Co₅ metamagnetic shape memory alloys under mechanical cycling," *Mater. Lett.*, vol. 148, pp. 110–113, Jun. 2015.
- [21] W. Sun, J. Liu, B. Lu, Y. Li, and A. Yan, "Large elastocaloric effect at small transformation strain in Ni₄₅Mn₄₄Sn₁₁ metamagnetic shape memory alloys," *Scr. Mater.*, vol. 114, pp. 1–4, 2016.
- [22] Y. J. Huang, Q. D. Hu, N. M. Bruno, J. Chen, I. Karaman, J. H. Ross, and J. G. Li, "Giant elastocaloric effect in directionally solidified Ni–Mn–In magnetic shape memory alloy," *Scr. Mater.*, vol. 105, pp. 42–45, Aug. 2015.
- [23] W. Ito, B. Basaran, R. Y. Umetsu, I. Karaman, R. Kainuma, and K. Ishida, "Shape Memory Response in Ni₄₀Co₁₀Mn₃₃Al₁₇ Polycrystalline Alloy," *Mater. Trans.*, vol. 51, no. 3, pp. 525–528, 2010.
- [24] Y. Xu, B. Lu, W. Sun, A. Yan, and J. Liu, "Large and reversible elastocaloric effect in dual-phase Ni₅₄Fe₁₉Ga₂₇ superelastic alloys," *Appl. Phys. Lett.*, vol. 106, no. 20, 2015.