# Magnetostructural transition and magnetocaloric effect in $Ni_{55}Mn_{20}Ga_{25}$ single crystals

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A first order transition from a paramagnetic-austenite phase to a ferromagnetic-martensite phase occurring in off-stoichiometry single crystals of $Ni_2MnGa$ at 313 K presents unique features due to the multifunctional character of the magnetic shape memory alloy. A remarkable magnetocaloric effect, associated with an entropy change up to $\Delta S \approx -86$ J kg$^{-1}$ K$^{-1}$ and an adiabatic temperature change $\Delta T \approx 2.2$ K, accompanied by mechanical strain $\Delta\varepsilon \geqslant 3\%$ have been observed in samples subjected to changes of the applied magnetic field $\Delta H = 4 \times 10^6$ A/m ($\approx 5$ T). The effects of magnetic field, temperature, and stress on the entropy variation $\Delta S$ are quantified and compared.

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## INTRODUCTION

In recent years there has been a great interest in the possibility of using solid state materials for cooling applications, an interest justified by energy savings and by environmental concerns arising from current gas-based refrigeration technologies. The magnetocaloric effect (MCE) derived from materials with first-order magnetic phase transitions may be employed in the future to operate air conditioners and refrigerators on the macroscale, and for thermal sensing or localized heating/cooling on the microscale or nanoscale in micro/nanoelectromechanical systems.

Magnetostructural transitions leading to a "giant" MCE at room temperature have been directly observed in $Gd_5(Si_{1-x}Ge_x)_4$ (Refs. 1 and 2) with a $\Delta T_{ad}$ of the order of 8 K under a magnetic field variation $\Delta H = 4 \times 10^6$ A/m (5 T), while other ferromagnetic transition-metal alloys like $Ni_2MnGa$,[3,4] $MnFeP_{0.45}As_{0.55}$,[5] and La(FeSi) (Ref. 6) have only been indicated as likely candidates. All these alloys are currently under scrutiny for their potential in magnetocaloric applications.[6–8]

$Ni_2MnGa$ Heusler alloys have two main structural phases, a cubic austenite which is stable at a temperature $T > A_f$ and a tetragonal martensite that is stable for $T < M_f$. Each phase can be ferromagnetic or paramagnetic at room temperature, depending on composition.[3,9] In the specific case of $Ni_{55}Mn_{20}Ga_{25}$, $A_f = 320$ K and $M_f = 294$ K. The transition from an austenite cubic lattice single crystal with {100} faces to a single-variant martensite is associated with a macroscopic contraction up to 6% due to the appearance of a shorter "*c*" axis, also carrying the magnetic anisotropy when the alloy is ferromagnetic.

This work is directed to the study of the magnetic, mechanical, and magnetocaloric response of $Ni_{55}Mn_{20}Ga_{25}$ oriented single crystals (SC) with {100} faces, devoid of internal stresses and important structural inhomogeneities such as grain and variant boundaries. A very large entropy change, up to $|\Delta S| \approx 86$ J kg$^{-1}$ K$^{-1}$, and an adiabatic temperature change $\Delta T_{ad} \approx 2.2$ K are observed for a magnetic field change $\Delta H = 4 \times 10^6$ A/m (5 T) as the SC undergoes the first-order phase transition close to RT in an interval from $T = 309$ to 312 K.

If the entropy change is estimated from the latent heat of transformation measured by differential scanning calorimetry or from the Clausius-Clapeyron equation [Eq. (4)] a much lower value $|\Delta S| \approx 22$–$29$ J kg$^{-1}$ K$^{-1}$ is obtained.[2] The peak $|\Delta S|$ and $\Delta T_{ad}$ values obtained in $Ni_{55}Mn_{20}Ga_{25}$ SCs are comparable with those reported for $Gd_5Si_2Ge_2$,[4] $MnFeP_{0.45}As_{0.55}$,[5] and La(FeSi) (Ref. 6) in similar conditions.

## EXPERIMENTAL PROCEDURES AND ANALYTICAL METHODS

$Ni_{55}Mn_{20}Ga_{25}$ SCs were prepared using the Bridgman method with a process described in detail in Ref. 10. The sample density $\rho = 8285$ kg/m$^3$ was determined with an helium pycnometer. Differential scanning calorimetry (DSC) curves, $dQ/dt$, were measured with heating rates $dT/dt = 5$–$10$ K/min in flowing argon to define the start, peak, and finish temperatures of the austenite-to-martensite (*A*-*M*) (start $M_s$, peak $M_p$, finish $M_f$) and martensite-to-austenite (*M*-*A*) phase transitions (start $A_s$, peak $A_p$, finish $A_f$). The $\Delta S$ and latent heat $\Delta L$ connected to the transformation were calculated using

$$\Delta L = \int_{A_s}^{A_f} \frac{dQ}{dT} dT; \quad \Delta S = \int_{A_s}^{A_f} \frac{dQ}{T\,dT} dT. \tag{1}$$

The DSC measurements show that the *A*-*M* and *M*-*A* temperatures are $A_s = 306$ K, $A_p = 314$ K, $A_f = 320$; $M_s = 305$ K, $M_p = 300$ K, $M_f = 294$ K. $\Delta L = -7.4$ kJ/kg corresponds to a $\Delta S = -24$ J kg$^{-1}$ K$^{-1}$, a value three times lower than the $\Delta S$ obtained with a field-induced phase transformation and the Maxwell relation [Eq. (2)].

The temperature dependence of $M(T)_H$ under a magnetic field $H$ with no applied stress, is shown in Fig. 1. At temperatures $T \leqslant A_f$ (heating) a first-order structural phase transitions occurs around $A_f = 313$ K. Comparing the $M(T)_H$ magnetization curves measured with an applied field $H_a = 8$

 

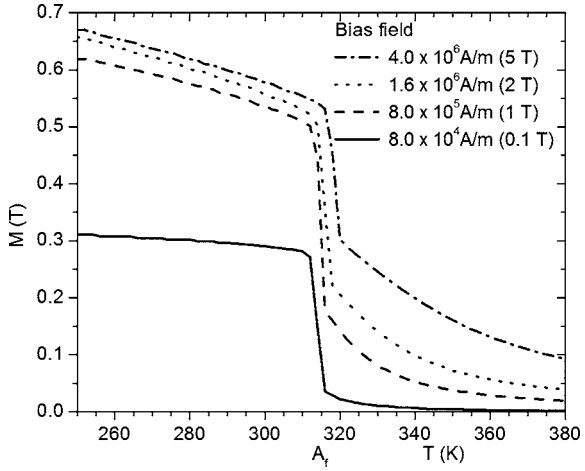


FIG. 1. Temperature dependence of the magnetization $M(T)_H$ for $Ni_{55}Mn_{20}Ga_{25}$ for different values of applied field bias $H$. Curves measured during heating, with $H=8\times10^4$ A/m, $8\times10^5$ A/m, $1.6\times10^6$ A/m, $4\times10^6$ A/m (0.1, 1, 2, 5 T).

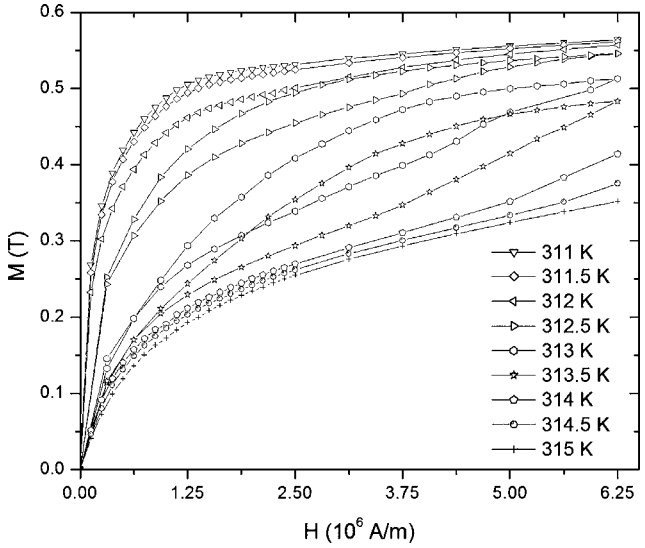


FIG. 2. Isothermal $M(H)_T$ curves showing a field induced austenite to martensite phase transition in the temperature interval between 312 and 314 K.

$\times10^4$ A/m, $8\times10^5$ A/m, $1.6\times10^6$ A/m, $4\times10^6$ A/m (0.1–1–2–5 T) it can be noted that the phase transition shifts to higher $T$ with increasing $H_a$, at a rate $\Delta T/\Delta H_a\approx1$ K/T, a shift attributed to the additional Zeeman energy term $M\cdot H$ which stabilizes the martensite phase with respect to heating, a phenomenon also occurring under a compressive mechanical stress along [100], see Fig. 4 and Ref. 11.

Magnetization isotherms $M(H)_T$ were measured with a vibrating sample magnetometer (VSM) and a superconducting quantum interference device (SQUID) magnetometer. The samples were characterized after a zero-field cooling (ZFC) from the temperature of 380 K$\gg A_f$ down to 250 K $\ll M_f$. For a given composition, the martensite and austenite phases possess different saturation magnetization, initial susceptibility and magnetization curves.[7,13] First quadrant $M(H)_T$ branches measured in the $(M,H)$ plane at temperatures $T$ close to the $A$-$M$ transition show a nonmonotonic behavior connected to the magnetic-field-induced transition, see Fig. 2. The analysis of Arrott plots[12] indicates that in $Ni_{55}Mn_{20}Ga_{25}$ the Curie temperature $T_c=312.6$ K falls within the $M$-$A$ transition region between $A_s=306$ K and $A_f=320$ K.

Under the assumption that equilibrium thermodynamics can be applied, the entropy change $\Delta S$ can be estimated from the $M(H)_T$ isothermal curves using the Maxwell relation[1,14]

$$\left[\frac{\partial S(T,H)}{\partial H}\right]_T=\left[\frac{\partial M(T,H)}{\partial T}\right]_H. \tag{2}$$

Integration of the right hand term with respect to field, in the field interval $\Delta H$ allows the estimation of $\Delta S$, and for $\Delta H=H_2-H_1$ if $H_1=0$ we have

$$\Delta S\left(\frac{T_1+T_2}{2}\right)=\frac{1}{T_2-T_1}\left[\int_0^H M(T_2,H)dH-\int_0^H M(T_1,H)dH\right], \tag{3}$$

where $T_1$ and $T_2$ are the respective temperatures of two adjacent magnetization curves (see Fig. 2). A summary of the $\Delta S$ values obtained from Eq. (3) is presented in Fig. 3.[15] The Clausius-Clapeyon equation can also be used to determine the entropy variation

$$\frac{\Delta H}{\Delta T}=-\frac{Q}{T_M\Delta M},\quad \Delta S=-\frac{Q}{T_M}, \tag{4}$$

where $Q$ is the evolved heat of transformation, and $T_M$ is the $A$-$M$ temperature. The calculation requires estimates of the magnetization change $\Delta M$ associated to the first order phase transition (Figs. 1 and 2) and of the average temperature shift $\Delta T/\Delta H$ of the transition point with increasing field $[M(T)_H$

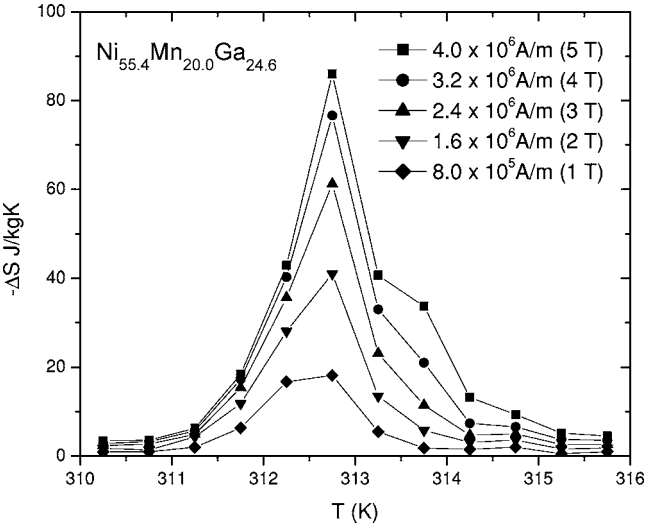


FIG. 3. Temperature dependence of the entropy variation produced by a magnetic field variation of $8\times10^5$ A/m to $4\times10^6$ A/m (1–5 T). The curves are obtained using the Maxwell relation [Eqs. (2) and (3)] and isothermal magnetization curves data (Fig. 2).

curves, see Fig. 1] or the average field shift $\Delta H/\Delta T$ of the transition point with increasing temperature [$M(H)_T$ curves, see Fig. 2].

A much more accurate and direct evaluation of the MCE potential can also be obtained either from DSC measurements under an applied field $H$ or from the adiabatic temperature change $\Delta T_{\mathrm{ad}}$ associated with a field variation $H$, a case which will be discussed in the final section.[16,17]

The isothermal $M(H)_T$ curves (Fig. 2) measured at temperatures ranging from 311 to 315 K exhibit the following behavior: at low temperature (i.e., 311 K) $M(H)$ curves with a higher peak magnetization $M_p$ are found, as expected from a ferromagnetic martensite phase. Lower $M_p$ values are observed at $T>315$ K when the sample is in the paramagnetic austenite phase. For intermediate values $312.5\ \mathrm{K}\leqslant T\leqslant 314\ \mathrm{K}$, associated with the $A$-$M$ transition, highly nonmonotonic $M(H)$ curves are measured, with an inflection point marking the magnetostructural phase transition.[1,13,18] The magnetic field $H_T$ triggering the onset of the field induced $A$-$M$ transition shifts with temperature from about $H_{T\alpha}=1.6\times10^6$ A/m (2 T) at $T_\alpha=312.0$ K to about $H_{T\beta}=3.6\times10^6$ A/m (4.5 T) at $T_\beta=314.5$ K. The maximum entropy change estimated using the isothermal $M(H)_T$ data and the Maxwell relation Eqs. (2) and (3) is $|\Delta S|\approx 86\ \mathrm{J\,kg^{-1}\,K^{-1}}$ at 312.75 K for a field change $\Delta H=4\times10^6$ A/m (5 T), with an estimated 10% total error.[19] This peak value becomes $\approx 41\ \mathrm{J\,kg^{-1}\,K^{-1}}$ at $\Delta H=1.56\times10^6$ A/m (2 T) and $\approx 18\ \mathrm{J\,kg^{-1}\,K^{-1}}$ at $\Delta H=8\times10^5$ A/m (1 T) (see Fig. 3).

Using the Clausius-Clapeyron equation [Eq. (4)] a much smaller value $|\Delta S|\approx 24$–$29\ \mathrm{J\,kg^{-1}\,K^{-1}}$, comparable to the DSC results, can be derived from magnetization curves (Figs. 1 and 2), when a value $\Delta M=0.25$–$0.3$ T, associated with the abrupt magnetization change at the transition, is assumed. The $\Delta T/\Delta H$ values are obtained from $\Delta T=4$ K with a $\Delta H_a=4$ T from the $M(T)$ curves in Fig. 1, and $\Delta H=H_{T\beta}-H_{T\alpha}$ and $\Delta T=T_\beta-T_\alpha$ in the case of $M(H)$ curves in Fig. 2. In the case of Eq. (4) the estimated error on $\Delta H/\Delta T$ may be much larger than 10% due to the limited number of available $M(T)$ and $M(H)$ curves and uncertainties in the $\Delta M$ value.

Among other possible sources of error the effect of magnetic hysteresis was also calculated from the comparison of $M(H)_T$ "forward and return" magnetization branches. The results show that hysteresis losses only contribute with $\sim 2$ kJ/kg, a value at least one order of magnitude lower than the total heat exchanged during the transformation (of the order of 20 kJ/kg).[20]

The entropy change $\Delta S$ can also be derived from the stress-strain $\sigma(\epsilon)$ behavior of the $Ni_{55}Mn_{20}Ga_{25}$ SCs. Mechanical testing was performed with a double column test machine fitted with an optical extensometer, a Peltier cell heater/cooler, and a Cu-Constantan thermocouple to measure $T$. Before each mechanical compression along [100] the SC conditions were reset by heating above $A_f$. No magnetic field was applied.

Isothermal $\sigma(\epsilon)_T$ curves exhibit different Young's moduli $Y=\Delta\sigma/\Delta\epsilon$, which are connected with the martensite and austenite phases, see Fig. 4 and Ref. 21. The martensite phase

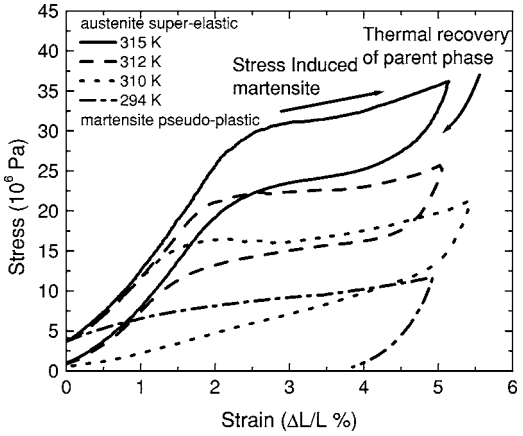


FIG. 4. [100] compressive stress-strain curves measured on the oriented single crystals at different temperatures. Below 311 K the sample in the martensite phase shows a pseudoplastic behavior with a yielding stress $\sim 5$ MPa. In the austenite phase, at temperatures above 312 K the sample becomes superelastic.

easily accommodates stress through the process of detwinning and twin boundary motion, with values of $Y<500$ MPa, while the austenite phase results mechanically stiffer with $Y\approx 1$ GPa. In Fig. 4 we observe that: (a) at $T=294$ K a large strain variation $\Delta\epsilon\sim 5\%$ can be achieved with a small stress increase $\Delta\sigma<10$ MPa, with an almost constant modulus $Y\approx 200$ MPa. Upon stress removal only a limited strain recovery occurs, indicating a pseudoplastic behavior; (b) At $T=310$ K close to the $M$-$A$ transition, $Y$ increases to $\approx 700$ MPa but the behavior is still pseudoplastic, with a well defined yielding point at $\epsilon=2\%$, where $Y$ decreases to $\approx 150$ MPa. Again, a very limited strain recovery is found upon unloading; (c)–(d) at $T=315$ K and above, the material is in the austenite phase, the $\sigma(\epsilon)_T$ curve has a much steeper initial slope $Y\approx 1.2$ GPa up to $\epsilon=2.5\%$. Beyond this threshold a lower slope $Y\approx 150$ MPa is found up to 5% strain, indicating that the sample has undergone a complete stress-induced $A$-$M$ transformation. An almost complete strain recovery is achieved upon stress removal through a reverse $M$-$A$ transformation (superelastic behavior).

In the case of a stress-induced phase transition, under the assumption of a small volume change $\Delta V<1\%$,[22] it is possible to estimate $\Delta S$ using again the anisotropic expression for the Clausius-Clapeyon equation $d\sigma/dT=-Q/T_M\epsilon_X$ where $\sigma$ is the magnitude of the stress, and $\epsilon_X$ is the lattice contraction along the applied stress $\sigma$ direction.[20,23] Using the yielding points obtained from Fig. 4 we can estimate that $d\sigma/dT\approx 2.9$ MPa/K and $\epsilon_X\approx 6\%$ corresponds to a complete $A$-$M$ transformation. In this case we obtain a $|\Delta S|\approx 22\ \mathrm{J\,kg^{-1}\,K^{-1}}$, in agreement with the $|\Delta S|\approx 24\ \mathrm{J\,kg^{-1}\,K^{-1}}$ value obtained for a temperature-induced phase transformation.

In order to better characterize the magnetocaloric potential of $Ni_{55}Mn_{20}Ga_{25}$ SCs, the extremely large $\Delta S$ values obtained using the Maxwell relation [Eqs. (2) and (3)], which make this alloy a promising MCE material, were compared with the direct measurement of the adiabatic temperature rise $\Delta T_{\mathrm{ad}}(T_s)_{\Delta H}$ associated with a magnetic field variation $\Delta H$. $\Delta T_{\mathrm{ad}}$ values were measured using an adiabatic cell inserted

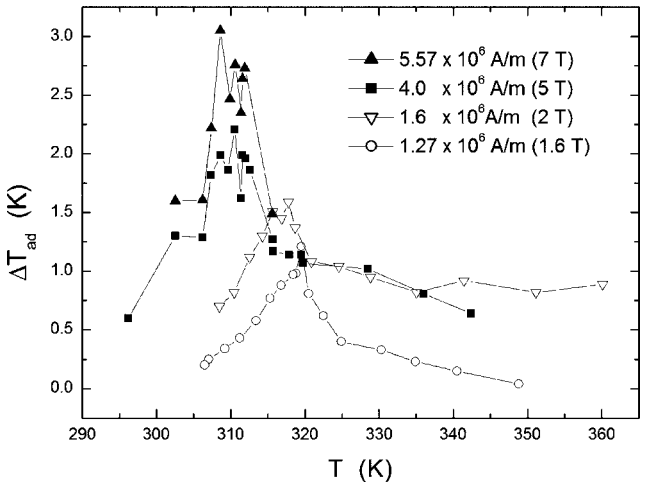


FIG. 5. Summary of the adiabatic temperature changes $\Delta T_{ad}(T)_{\Delta H}$ induced by a variable magnetic field change $\Delta H$. The temperature of the sample is first stabilized at $T$ ($\Delta T/\Delta t \approx 0.05$ K/min) and then an increasing/decreasing field ramp $\Delta H$ is applied, with peak values up to 4–$5.57\times10^6$ A/m (5–7 T).

in a 7 T cryomagnet. After stabilizing the sample temperature at a reference point $T_s$ with a $\Delta T/\Delta t$ drift less than $\pm$ 0.05 K/min, in the vicinity of the phase transition, an increasing (then decreasing) magnetic field $\Delta H$ was applied in a [100] sample direction at a constant rate of $\Delta H/\Delta T = 1$ T/min from 0 up to $H_{max} = 1.27, 1.56, 4, 5.56 \times 10^6$ A/m (1.6, 2, 5, 7 T) and then back to 0. The field increase (decrease) is associated with an almost linear $T$ increase (decrease) up to a peak value $T \approx T_s + \Delta T_{ad}$ and then back to $T_s \pm 0.1$–0.2 K. In the case of an adiabatic transformation, the temperature of the lattice must change as the total entropy of the body during an $A$-$M$ transformation is conserved. The experimental uncertainties of the order of $\pm$0.1-0.2 K, measured in direct contact with the sample, are connected to the nonideal adiabatic conditions, magnetic hysteresis and eddy currents. Figure 5 shows a plot of the $\Delta T_{ad}$ values measured at different temperatures and for different field variations $\Delta H$ during cooling from $T > 345$ K $> A_f$. The $\Delta T_{ad}$ peak is centered on the $A$-$M$ transition and its amplitude increases with $\Delta H$ increasing from $1.27 \times 10^6$ A/m to $5.57\times10^6$ A/m (1.6–7 T). For a $\Delta H = 4 \times 10^6$ A/m (5 T), $\Delta T_{ad} \approx 2.2$ K, while for $\Delta H = 5.56 \times 10^6$ A/m (7 T), $\Delta T_{ad} \approx 3$ K. For $\Delta H > 1.56\times10^6$ A/m (2 T) the $\Delta T_{ad}$ curves show a plateau up to 360 K, a behavior connected to the field (or stress)-stabilization of the martensite phase at high temperature, and which is also found in the $M(T)_H$ curves for $H > 8\times10^5$ A/m (1 T) (Fig. 1), where long tails of $M(T)_H$ are observed up to 360 K, due to an additional Zeeman energy term $M \cdot H$ which tends to stabilize the martensite phase well above $A_f$. The $\Delta T_{ad}$ peak shift from 317 to 310 K observed when $\Delta H$ increases, is partly reflected in the $\Delta S$ curves (Fig. 3). The $\Delta S$ curves also exhibit secondary features between $T = 313$ and 315 K, but their lower resolution and indirect derivation does not allow for a close comparison with the $\Delta T_{ad}$ curves.

## CONCLUSIONS

Different isothermal and adiabatic experimental procedures were used in order to characterize the magnetostructural transition of $Ni_{55}Mn_{20}Ga_{25}$ oriented single crystals and also to evaluate its MCE potential. A good agreement was found between $|\Delta S|$ values connected to the first order phase transition, obtained with temperature-induced (24 J kg$^{-1}$ K$^{-1}$), stress-induced (22 J kg$^{-1}$ K$^{-1}$) and field-induced transformations (24–29 J kg$^{-1}$ K$^{-1}$ using the Clausius-Clapeyron equation and a proper $\Delta M$ value). The Maxwell approach [Eqs. (2) and (3)] was used to evaluate the entropy change in the whole 0–5 T applied field range, yielding a much larger value $|\Delta S| = 86$ J kg$^{-1}$ K$^{-1}$, connected to the temperature dependence of the magnetization $M(T)$ within the two structural phases and at the transition point as depicted in Fig. 1.[2]

The great disparity between the very large isothermal $|\Delta S|$ values and the adiabatic temperature change $\Delta T \sim 2.2$ K is connected to the large heat capacity $C_p$ and its variation within the transition interval,[24] and future investigations should help clarify the temperature dependence of $C_p$ under intense applied fields. These results indicate that direct $\Delta T_{ad}$ measurements are the most reliable method for the evaluation of the MCE potential of a material, and this is particularly true in the case of transition metal alloys where, due to the rather high $C_p$ with respect to rare earth systems,[24,25] important differences can be found between the values of isothermal entropy and adiabatic temperature changes.

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[1] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).

[2] F. Casanova, X. Batlle, A. Labarta, J. Marcos, L. Manosa, and A. Planes, Phys. Rev. B **66**, 100401(R) (2002).

[3] V. V. Khovailo, V. Novosad, T. Takagi, D. A. Filippov, R. Z. Levitin, and A. N. Vasilev, Phys. Rev. B **70**, 174413 (2004).

[4] H. Tang, A. O. Pecharsky, D. L. Schlagel, T. A. Lograsso, V. K. Pecharsky, and K. A. Gschneidner, J. Appl. Phys. **93**, 8298 (2003).

[5] O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, Nature (London) **415**, 150 (2002).

[6] S. Fujieda, A. Fujita, and K. Fukamichi, Appl. Phys. Lett. **81**,

1276 (2002).
[7] L. Pareti, M. Solzi, F. Albertini, and A. Paoluzi, Eur. Phys. J. B **32**, 303 (2003).
[8] J. Marcos, L. Manosa, A. Planes, F. Casanova, X. Batlle, and A. Labarta, Phys. Rev. B **68**, 094401 (2003).
[9] V. A. Chernenko, E. Cesari, V. V. Kokorin, and I. N. Vitenko, Scr. Metall. Mater. **33**, 1239 (1995).
[10] M. Pasquale, C. P. Sasso, S. Besseghini, E. Villa, T. A. Lograsso, and D. L. Schlagel, IEEE Trans. Magn. **38**, 2847 (2002).
[11] M. Pasquale, C. P. Sasso, G. Bertotti, V. L'vov, V. Cherneneko, and A. De Simone, J. Appl. Phys. **93**, 8641 (2003).
[12] A. Arrott, Phys. Rev. **108**, 1394 (1957).
[13] X. Zhou, W. Li, H. P. Kunkel, and G. Williams, J. Phys.: Condens. Matter **16**, L39 (2004).
[14] A. H. Morrish, *The Physical Principles of Magnetism* (Wiley, New York, 1965), Chap. 3.
[15] V. K. Pecharsky and K. A. Geschneider, Jr., J. Appl. Phys. **90**, 4614 (2001).
[16] J. Marcos, F. Casanova, X. Batlle, A. Labarta, A. Planes, and L. Manosa, Rev. Sci. Instrum. **74**, 4768 (2003).
[17] V. K. Pecharsky and K. A. Geschneider, Jr., J. Appl. Phys. **86**, 565 (1999).
[18] M. Pasquale, C. P. Sasso, and L. H. Lewis, J. Appl. Phys. **95**, 6918 (2004).
[19] V. K. Pecharsky, J. O. Moorman, and K. A. Geschneider, Jr., Rev. Sci. Instrum. **68**, 4196 (1997).
[20] V. Provenzano, A. J. Shapiro, and R. D. Shull, Nature (London) **429**, 853 (2004).
[21] F. Bonfanti, Ph.D. thesis, Univ. Milan, 2003.
[22] V. V. Godlevsky and K. M. Rabe, Phys. Rev. B **63**, 134407 (2001).
[23] V. A. L'vov, V. A. Chernenko, E. Cesari, and J. Pons, in *Recent Research Developments in Materials Science and Engineering* (Transworld Research Network, 2002), Vol. 1, pp. 673–733.
[24] L. Mañosa, A. Gonzalez-Comas, E. Obradó, A. Planes, V. A. Chernenko, V. V. Kokorin, and E. Cesari, Phys. Rev. B **55**, 11068 (1997).
[25] O. Tegus, Ph.D. thesis, Univ. Amsterdam, 2003.