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INNOVATIVE METHODOLOGICAL APPROACHES FOR EVALUATING THE MAGNETOCALORIC EFFECT IN FUNCTIONAL MATERIALS

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Dedicated to my wife Chiara

"The test of all knowledge is experiment. Experiment is the sole judge of scientific truth"

> Richard Phillips Feynman (1918 – 1988) The Feynman Lectures on Physics (1964)

ABSTRACT

The experimental characterization of magnetocaloric effect has a fundamental role in the development of an efficient, environmentally friendly and cost-effective room-temperature magnetic refrigeration technology. The proper measure of the magnetocaloric effect as a function of temperature and magnetic field, in terms of adiabatic temperature change and isothermal entropy change, is required to compare the potentiality of different materials and to lead to their development. Moreover, the test of materials performance under operative conditions and the characterization of other physical and chemical features of magnetocaloric materials are essential to optimize the design of refrigeration machines and to prefigure new technological applications.

This Thesis deals with advanced characterization methods of the magnetocaloric effect, which go beyond the standard magnetocaloric measurements and which have the purpose to test the materials response under real and extreme operative conditions and to investigate the relationship between the magnetocaloric effect and other magnetic, thermodynamic and structural properties of materials.

The first part of the Thesis reports an in-depth thermodynamic analysis of the experimental setups for the direct measurement of the adiabatic temperature change. The influence of the temperature sensor, of non-ideal adiabatic conditions and of the sample thermal conductivity are discussed. Two innovative experimental setups for the measurement of the adiabatic temperature change in thin sheets and under pulsed magnetic fields are presented. Both the instruments are based on non-contact measurement techniques: the first employs an IR temperature detector, while the second exploits a thermo-optical effect, which is named "Mirage Effect". The description and evaluation of the experimental setups are reported, together with the characterization of some of the most promising magnetocaloric materials (Gd, Fe₂P-based compounds, Heusler alloys, La-Ca manganites, La-Fe-Co-Si, Mn-based antiperovskites).

The second part of the Thesis analyses some of the materials properties that could be detrimental for application in magnetic refrigeration devices. In particular, the influence of the transition width on the magnetocaloric effect at first- and second-order transitions is discussed. Theoretical predictions, derived from phenomenological models of the transformations, are compared with experimental analysis of several Ni-Mn-based Heusler alloys. The obtained results reveal a strong correlation between the structural and microstructural characteristics of these alloys with their magnetic and magnetocaloric properties, both at the magnetostructural martensitic transformation and at the Curie transition.

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1. MAGNETIC REFRIGERATION: FROM MATERIALS TO APPLICATIONS

"Can we imagine living without refrigeration?"

The answer is as much simple as the question: "No, we can not!"

Refrigeration is everywhere and has a fundamental role in our modern society. Just think about food and health products preservation, air conditioning for buildings, transports and data storage centres, cryogenic for industrial processes and scientific research. Refrigeration contributed and continues to contribute to the evolution and the wellness of humanity [1]. Nevertheless, the refrigeration is one of the major worldwide energy consumer: it represents the 17% of the global electricity consumption [2] and this datum is constantly increasing, especially for the refrigeration diffusion in developing countries [3]. Furthermore, the current refrigeration technology is based on the compression of gases that are harmful for the earth's protective ozone layer (hydrochlorofluorocarbons, HCFCs) or that are strong greenhouse gases (hydrofluorocarbons, HFCs). At the end of 2016, during the United Nations meeting in Kigali (Rwanda), delegates from 197 countries signed a treaty to eliminate by 2030 the HCFCs and to reduce drastically, in the next thirty years, the HFCs [4].

Therefore, a heavy problem opens, involving technological, scientific, industrial, economic and social implications: we have to combine an increasing demand for refrigeration with the attention to the global energy consumption and to the well-known environmental problems. In the short- and medium-term, the vapour-compression systems will remain predominant. The reduction of emissions, with the control of leakages and a better recovery at the end of life, and the refrigerants substitution (with more "natural" refrigerants like ammonia, CO₂, hydrocarbons, water, air) can be possible improvements of the current technology and represent a partial solution to the question. However, they introduce further technological and safety drawbacks (e.g. the increase of working pressures, the reduction of the energy efficiency, the toxicity and the flammability of some new refrigerants) [1].

Meantime, it is necessary to explore, on a long-term perspective, new refrigeration technologies characterized by better efficiency, reduced environmental impact and lower energy consumption. Several interesting technologies are in development all over the world: adsorption-absorption systems, magnetic-refrigeration, thermoelectric cooling, refrigeration based on acoustic waves [1]. Monothematic conferences, prototypes and research publications are steadily rising. These new refrigeration solutions represents realistic perspectives but they still require improvements in terms of cost, efficiency and capacity.

Among them, magnetic-refrigeration, based on a thermomagnetic effect, which is called Magnetocaloric Effect (MCE), represents, to date, one of the most advanced and promising solutions. Together with a low ecological impact, the absence of hazardous fluids, low noises and a reduced electrical energy consumption, several studies predict for magnetic refrigeration an efficiency more than 60 %; considerably higher than the maximum efficiency reached by commercial vapour compressors (about 40%) [5–7]. Since the 1970s, many prototypes have been successfully built and tested [8,9]. In recent years, the first nearly commercial machines were presented. However, it is not easy to predict a forthcoming mass production of cost-effective, energetically efficient, durable and harmless magnetic refrigerators.

The basic idea of a magnetic cooling system is schematized in Figure 1.1. A magnetic refrigerator is mainly based on four elements: 1) a magnetocaloric (MC) material, which represents the refrigerant active element; 2) a source of magnetic field, which is usually based on permanent magnets; 3) a mechanical device to move the MC material inside and outside the magnetic field; 4) a system for heat transfer, consisting of a working fluid and heat exchangers. When the MC material is inserted into the magnetic field, its temperature increases, due to the MCE. When the magnetic field is removed, the material cools down. A heat-transfer fluid moves heat between the MC material and the heat exchangers. The refrigeration cycle is realized by a cyclical repeat of magnetization and demagnetization processes.



Figure 1. 1. Schematic illustration of a magnetic cooling system.

Although the operation principle of a magnetic refrigerator seems simple, its practical realization requires to overcome several problems. All the elements, which compose a magnetic cooling system, still require to be improved by a deep and transversal research activity, involving material science, physics, chemistry, engineering and economy.

In particular, the key point to realize a marketable magnetic refrigerator is to find a magnetic material, characterized by a high MCE induced near room temperature by a low magnetic field. This material should be made of abundant and inexpensive elements, a good thermal conductor, mechanically and chemically stable, easily synthesizable and workable and not subjected to alteration over time.

Besides basic knowledge on magnetic materials, the search for efficient cooling materials has required and still requires the development and a continuous improvement of experimental techniques and methodologies for the characterization of the magnetocaloric effect. In the last decades, measurement protocols and experimental setups were developed and optimized to characterize the magnetocaloric properties of standard samples on the laboratory-scale, by combining magnetometric and calorimetric techniques. However, the realization of new technologies based on magnetocaloric materials, requires the test of their performance under operative and extreme conditions and the study of possible alterations of their properties due to mass production routes or to post-synthesis manufacturing.

In this framework, this Thesis presents innovative solutions for the direct characterization of the magnetocaloric effect and highlights as several features of magnetic transitions drastically affect the exploitable magnetocaloric effect of materials. Two were the main aims that led this work. The first was to extend the magnetocaloric characterization to materials' shapes and to conditions closer to those used in real applications and in possible new technological advancements. The second purpose was to understand the role of some features of materials, as the width of magnetic transitions, in determining their magnetocaloric properties. This study aimed to obtain useful information for the optimization of the magnetocaloric performance of materials and for the development of industrial processes for their manufacturing.

The Thesis is organized in three main sections.

Section A is devoted to a brief summary of the state of the art about the magnetocaloric effect near room temperature (Chapter 2) and to an overview of the main experimental techniques that were used for the experimental work (Chapter 3).

Section B examines the experimental techniques for the direct measurement of the magnetocaloric effect, as adiabatic temperature change, and presents two new experimental setups. The influence of non-ideal adiabatic conditions, of the temperature sensor and of the sample thermal conductivity are discussed in Chapter 4 on the basis of experimental measurements and heat transfer simulations. Chapter 5 and Chapter 6 contain a description of two innovative experimental solutions, based on non-contact techniques, for the direct measurement of the magnetocaloric effect in thin samples and under pulsed magnetic field.

Section C reports on the effect of the broadness of magnetic transition on the magnetocaloric effect of materials. The width of first-order magnetostructural transitions is discussed in Chapter 7 on the basis of a phenomenological model of the transformation and on experimental results obtained for a series of Ni,Mn-based Heusler alloys at their martensitic transformation. Chapter 8 considers the broadening of second-order Curie transitions through a mean-field approach and the analysis of a specific case: the detrimental effect of cold working on the magnetocaloric properties of a NiMnIn Heusler alloy.

Finally, Chapter 9 summarizes the main conclusions of this work and suggests several outlooks for future research activities.

Some years ago, Karl A. Gschneidner Jr., one of the "fathers" of magnetic refrigeration at room temperature, said: "*The limitations of magnetic refrigeration are only in the minds of the individual engineers and scientists*".

I think that he might be right. We can imagine a green-world in which new technologies and environment go hand in hand. We have only to fulfil that, by joining our knowledge with the dreamer imagination. As Einstein said: "The imagination is more important than knowledge. Knowledge is limited; imagination encircles the world."

SECTION A - INTRODUCTION STATE OF THE ART AND EXPERIMENTAL TECHNIQUES

In 1917 Weiss and Picard observed a reversible temperature variation of 0.7 K in a nickel sample near its Curie transition due to the application of a 1.5 T magnetic field. The magnetocaloric effect had been discovered! Exactly 100 year later, many magnetocaloric materials are known, more than 60 prototypes of magnetic refrigerators are in operation and the market release of this technology seems to be incoming.

The chance to develop an efficient, powerful and green refrigeration technology pushed a transversal research activity, which involved physicist, chemists, material scientists and engineers. Two are the main milestones that marked the way until today. The first was the discovery of a giant magnetocaloric effect across a first-order magneto-structural transition. The energy contribution due to the structural transformation significantly increases the intensity of the magnetocaloric effect. The second one was the design of the active magnetic regenerator cooling cycle, which gives the possibility to reach temperature spans much higher than the temperature variations produced by the magnetocaloric effect. Among the comprehension of the physical basis of the magnetocaloric effect and the engineering development of cooling devices, the research on materials took a key role. The search for a magnetic material with a large magnetocaloric effect, a tuneable critical temperature, good thermal, mechanical and chemical properties, low cost and which is free of critical elements, was the goal of the international research community in the last two decades.

In the following Chapter, a brief summary of the actual state of the art about the magnetocaloric effect near room temperature is reported. Great attention is paid to the main features that characterize the magnetocaloric effect at second- and first-order magnetic transitions. The more significant and promising magnetocaloric materials are described in the light of their possible applications in cooling devices. Experimental techniques and methods for the measurements of the magnetocaloric effect are discussed.

The second Chapter of this Section is an introduction at the experimental work and includes an overview of the main techniques that were used during this Thesis. In particular, two home-built experimental setups are described in details. The first is an in-field differential scanning calorimeter, which allows a complete magnetocaloric characterization of materials showing a first-order magnetic transition. The second instrument is a probe for the direct characterization of the magnetocaloric effect under adiabatic conditions and for the study of materials subjected to thermomagnetic cycles in nearly operative conditions.

2. THE MAGNETOCALORIC EFFECT: THEORY, MATERIALS AND APPLICATIONS

2.1 The Magnetocaloric Effect

The Magnetocaloric Effect (MCE), experimentally discovered by Weiss and Picard in 1917 [10–12], is a thermomagnetic phenomenon intrinsic to all magnetic materials. It displays itself like an entropy (ΔS_T) or a temperature (ΔT_{ad}) variation of a magnetic material due to the change of an applied magnetic field $(\Delta H = H_1 - H_0)$, under isothermal or adiabatic (isentropic) conditions, respectively [13].

$$\Delta S_T(T, \Delta H) = S(T, H_1) - S(T, H_0) \tag{2.1}$$

$$\Delta T_{ad}(T, \Delta H) = T(S, H_1) - T(S, H_0)$$
(2.2)

The MCE originates from the coupling between the magnetic spins system of the material and an external magnetic field. In the case of a conventional ferromagnetic or paramagnetic material, the effect of an external magnetic field rise $(\Delta H > 0)$ is to align the material magnetic moments. Considering the total entropy of the material composed by magnetic, lattice and electronic term, the moments arrangement under isothermal conditions generally results in a decrease of the entropy term associated with the magnetic degrees of freedom $(\Delta S_T < 0)$. Instead, if the material is under adiabatic conditions, the magnetic terms, with a resulting increase of the material's temperature $(\Delta T_{ad} > 0)$ [14]. The decrease of the external magnetic field $(\Delta H < 0)$ leads to the opposite effect: an increase of magnetic entropy $(\Delta S_T > 0)$ and, under adiabatic conditions, a cooling of the material $(\Delta T_{ad} < 0)$.

The entropy variation under isothermal and isobaric conditions can be correlated, by applying the Maxwell equation, with the bulk magnetization of the material (M(T,H)) [15]:

$$\Delta S_T(T, \Delta H)_p = \int_{H_0}^{H_1} \left(\frac{\partial S}{\partial H}\right)_{T,p} dH = \int_{H_0}^{H_1} \left(\frac{\partial M(T, H)}{\partial T}\right)_{H,p} dH$$
(2.3)

Otherwise, taking into account the 2^{nd} and the 3^{rd} law of thermodynamics, it can be derived from the specific heat $c_p(T,H)$ of the material, as a function of temperature and magnetic field [13]:

$$\Delta S_T(T, \Delta H)_p = \int_0^T \frac{c_p(T', H_1)}{T'} dT' - \int_0^T \frac{c_p(T', H_0)}{T'} dT'$$
(2.4)

Likewise, it is possible to obtain the expression of the adiabatic temperature change by inserting the specific heat under constant pressure in the differential of total entropy [16]:

$$\Delta T_{ad}(T,\Delta H)_p = -\mu_0 \int_{H_0}^{H_1} \left(\frac{T}{c_p(T,H)} \frac{\partial M(T,H)}{\partial T} \right)_{H,p} dH$$
(2.5)

By observing equations 2.3, 2.4 and 2.5, a significant MCE is expected at temperatures where the first order temperature derivative of magnetization is higher and the specific heat is strongly influenced by the magnetic field. This normally occurs near magnetic phase transitions. Otherwise, interesting values of ΔT_{ad} are observed at low temperature where the specific heat tends toward zero (Equation 2.5). This is the case of the adiabatic demagnetization of paramagnetic salts that was proposed by Debye and Giauque and successfully exploited by Giauque and MacDouglass in 1933 to reach temperatures below 1 K [17–19].

Figures 2.1.a and 2.1.b show sketches of the temperature behaviour of magnetization and entropy of a magnetic material near an ideal Curie transition between the ferromagnetic and the paramagnetic state. Magnetization and entropy vary with continuity at the transition. The application of a magnetic field increases the magnetization at the transition and decreases the entropy with a maximum ΔS_T at the Curie transition (T_c) . The temperature behaviour of ΔS_T for different applied magnetic fields is reported in Figure 2.2. All the $\Delta S_T(T)_H$ curves collapse on an universal curve, by following the scaling laws of second-order magnetic transitions [20].

The maximum ΔS_T depends on the saturation magnetization of the material and on the intensity of the applied magnetic field (Equation 2.3). The ΔT_{ad} is related to the ΔS_T , but its values are ruled by the specific heat and by the transition temperature, as it is shown in the following approximated relation [14]:

$$\Delta T_{ad}(T,\Delta H)_p \simeq -\frac{T}{c_p(T_0,H_0+\Delta H)} \quad \Delta S_T(T,\Delta H)_p \tag{2.6}$$



Figure 2. 1 Schematic of the MCE across a second-order transition. (a) Temperature dependence of magnetization with (pink line) and without (green line) an applied magnetic field. (b) Corresponding behaviour of entropy. The MCE, as adiabatic temperature change (ΔT_{ad} , horizontal) and isothermal entropy change (ΔS_T , vertical), is highlighted with black arrows.



Figure 2. 2 Schematic of the temperature dependence of the isothermal entropy change across a second-order magnetic transition induced by different applied magnetic fields.

A relevant MCE can develop also near first-order magnetic transitions. This case is schematically represented in Figures 2.3 and 2.4. Both magnetization and entropy curves show a jump discontinuity, which characterizes the nature of the transition. The application of a magnetic field (H_1) introduces a contribution to the total energy that promotes the phase characterized by the higher magnetization, with a resulting shift of the transition temperature (T_t from T_0 to T_1). This shift has a positive rate with the magnetic field ($dT_t/dH > 0$, Figure 2.3) if the low-temperature phase has a higher magnetization than the hightemperature one; or a negative rate in the opposite case ($dT_t/dH < 0$, Figure 2.4). When the transition is field-induced, in the temperature interval between T_0 and T_1 , an isothermal entropy change or an adiabatic temperature change occurs. The MCE near a first-order transition can be "Direct" ($\Delta S_T < 0$, $\Delta T_{ad} > 0$, Figure 2.3.b) or "Inverse" ($\Delta S_T > 0$, $\Delta T_{ad} < 0$, Figure 2.4.b), depending on the dT_t/dH . In both cases, the ΔS_T is the sum of two contributions: the enthalpy of the phase transformation and the magnetic entropy variation due to the alignment of the magnetic moments with the field [14]. The first term, which can be derived from the latent heat of the transformation (L), is usually dominant and this allows to generally approximate the entropy variation as $\Delta S_T \approx L/T_t$ [21].

By utilizing the magnetic Clausius – Clapeyron equation, the maximum entropy variation, for a complete phase transformation, is correlated to the magnetization difference between the two phases (ΔM) and to the sensitivity of the transition temperature to the magnetic field (dT_t/dH) [16]:

$$\Delta S_{T max} = -\mu_0 \frac{dH}{dT_t} \Delta M \tag{2.7}$$

This is the maximum limit for the ΔS_T , which does not depend on the applied magnetic field value (H_1). By increasing the value of H_1 , the ΔS_T remains constant but the temperature range in which it is maximum gets larger (Figure 2.5), following the transition temperature shift ($T_1 - T_0 \approx (dT_t/dH)\Delta H$). From equation 2.7, by approximating the ΔS_T as L / T_t , we obtain:

$$\frac{dT_t}{\mu_0 dH} = -T_t \frac{\Delta M}{L} \tag{2.8}$$

Regarding the maximum ΔT_{ad} for a complete phase transformation, it can be derived from the ΔS_T by following equation 2.6 [16]:

$$\Delta T_{ad\ max} \approx \mu_0 \frac{T}{c_p} \frac{dH}{dT_t} \Delta M \tag{2.9}$$

If the magnetic field is not enough to complete the transformation, the maximum ΔT_{ad} is ruled by the transition temperature shift $(T_1 - T_0)$ induced by the magnetic field change (ΔH):

$$\Delta T_{ad\ max} = T_1 - T_0 = \frac{dT_t}{dH} \Delta H \tag{2.10}$$



Figure 2. 3 Schematic of the MCE across a conventional first-order transition. (a) Temperature dependence of magnetization with (pink line) and without (green line) an applied magnetic field. The black arrow indicates the positive shift of the transition temperature due to the magnetic field. (b) Corresponding behaviour of entropy. The MCE is highlighted with black arrows.



Figure 2. 4 Schematic of the MCE across an inverse first-order transition. (a) Temperature dependence of magnetization with (pink line) and without (green line) an applied magnetic field. The black arrow indicates the negative shift of the transition temperature due to the magnetic field. (b) Corresponding behaviour of entropy. The inverse MCE is highlighted with black arrows.

The latent heat of the transformation, the shift rate of the transition temperature and the magnetization change between the two phases are the main parameters that control the MCE at first-order transitions. Equation 2.8 shows that they are strongly linked together. Among them, the latent heat has a key role to determine the MCE properties: on the one hand it increases the ΔS_T , but on the other hand it has a negative role on the dT_t/dH that can reduce the ΔT_{ad}

(Equation 2.10). A right balance has to be found between these two opposite effects in order to obtain promising MC materials [22].

Equations 2.7 and 2.9, derived from the magnetic Clausius–Clapeyron equation, are valid for a complete phase transformation. However, for real materials, the typical intensity of the applied magnetic fields (up to 1.2 T) is generally not enough to induce a complete phase transformation. In this case, ΔS_T and ΔT_{ad} values are reduced as a function of the transformed phase fraction (a more detailed discussion is presented in Chapter 7). Nevertheless, a correct estimation of ΔS_T and ΔT_{ad} values from magnetometry and calorimetry data can be obtained also in the case of first-order transitions, on the basis of equations 2.3, 2.4 and 2.5. Indeed, real materials usually show first-order transitions that occur in a finite temperature range, without discontinuities in M(T) and S(T). This has been proven to be true also in the case of pure and homogenous materials [23]. The absence of discontinuities gives the possibility to correctly integrate Equations 2.3, 2.4 and 2.5 [24].



Figure 2. 5 Schematic of the temperature dependences of isothermal entropy change at a first-order (on the bottom) and at an "inverse" first-order (on the top) magnetic transition, induced by different applied magnetic fields.

 ΔS_T and ΔT_{ad} values observed across first-order transitions can be much higher than the ones detected at second-order transitions, thanks to the sharp change in M(T) and to the contribution of the latent heat. However, they are defined only in a small temperature range between T_0 and T_1 . Moreover, the characteristic irreversible nature of first-order transitions affects the reversible MCE induced by subsequent applications of a magnetic field [25]. Figures 2.6.a and 2.6.b schematize the temperature and field dependences of the magnetization near a first-order transition. The back and forth transformations do not occur at the same temperature/field but they are separated by a hysteresis $(\Delta T_{hyst} = T_{0h} - T_{0c})$, where T_{0h} and T_{0c} are the transition temperatures on warming and on cooling the material; $\Delta H_{hyst} = H_2 - H_1$, where H_1 and H_2 are the magnetic field values that induce the back or forth transitions). The thermal hysteresis (ΔT_{hyst}) is usually proportional to the field hysteresis (ΔH_{hyst}) [13].

$$\Delta T_{hyst} = \frac{dT_t}{dH} \Delta H_{hyst} \tag{2.11}$$

Their relation is ruled by the dT_t/dH , which defines the slope of equilibrium lines in the (H - T)-plane (Figure 2.6.c). Two equilibrium lines are shown in Figure 2.6.c: the red one represents the transition from the phase A to the phase B ($A \rightarrow B$) and it is crossed by increasing temperature or decreasing field; the blue one represents the reverse transition $(B \rightarrow A)$ that is crossed on decreasing temperature or increasing field. In the area between the two equilibrium lines, the magnetic phase is not univocally defined, but the state of the system depends on its thermo-magnetic history.



Figure 2. 6 Sketches of the thermal (a) and magnetic (b) hysteresis at a first-order magnetic transition. (c) Magnetic phase diagram of the transition. Red and blue lines are the equilibrium lines of the two phases and correspond to the two opposed transformations. The yellow area highlight the coexistence interval of the two phases for a broad first-order transformation (a detailed description of the figure is reported in main text).

Let us have a look on what happens with the MCE across a hysteretic transition. We consider initially the material completely in phase *B* (at high temperature); then we cool down it to a temperature between T_{0c} and T_{0h} and we apply the magnetic field H_1 (arrow number 1): the equilibrium line is crossed (blue continuous line), the transition $B \rightarrow A$ is induced and a positive ΔT_{ad} develops (arrow number 2). By removing the magnetic field (arrow number 3), the system

can cross or not cross the red equilibrium line, depending on the thermal hysteresis width, on the intensity of the applied magnetic field and on the ΔT_{ad} developed by the material. Figure 2.6.c shows the case in which the system remains in the A phase and a MCE is not observed when the magnetic field is removed (arrow number 3 in the (H - T)-plane). Subsequent magnetization or demagnetization processes do not induce any phase transformation. In this case, the MCE is completely irreversible; it appears only at the first field change.

As said above, real first-order transitions evolve in a finite temperature/field range through out-of-equilibrium mixed states [26]. By considering this fact, the equilibrium lines in the (H - T)-plane should be considered as extended areas, whose contours are schematized with red/blue dashed lines in Figure 2.6.c. When the magnetic field is applied or removed, the material can perform partial transitions between metastable states, though the equilibrium lines are not crossed. This allows the material to follow minor-loops with cyclical processes of magnetization and demagnetization and a resulting reversible MCE [27–33]. The description and the control of these minor-loops together with the understanding and the improvement of mechanisms causing the hysteresis are still under investigation [13,28,33–36]. However, it is now clear that thermal hysteresis is the main obstacle to an efficient use of materials exploiting firstorder transitions in magnetic cooling devices.

2.2 Magnetocaloric cooling devices

In the last quarter of nineteenth century, the Slovenian physicist J. Stefan suggested to exploit the Curie transition of ferromagnetic materials in energy conversion devices (heat pumps, refrigerators and power generation devices) [37,38]. Later, Edison and Tesla proposed different versions of thermo-magnetic generators, based on the Curie temperature of ferromagnetic materials [39–42]. Regarding the MCE, it was exploited, for the first time, in the first half of the twentieth century, to reach temperatures under 1 K, through the cycling adiabatic demagnetization of paramagnetic salts [17–19]. About 50 years later, in 1976, Brown designed the first magnetic refrigerator working at room temperature [43]. His prototype reached a temperature span of 48°C between the hot end (47°C) and the cold end (-1°C), by exploiting gadolinium plates as magnetocaloric active element and a superconductive magnetic field source of 7 T [43]. Since then, more than 60 prototypes were built all over the world by universities, research centres and companies [9].

The operation principle of a magnetic refrigerator is simple. By exploiting the MCE it is possible to implement a thermo-magnetic cycle with four fundamental steps: 1) magnetization of the MC material, 2) heat transfer between the material and a hot reservoir (or cold in the case of an inverse MCE), 3) demagnetization of the material, 4) heat transfer to a cold reservoir (or hot). Four elements are essential: a MC material with a transition temperature in the working temperature range, a source of magnetic field (that is usually realized with permanent magnets), a heat transfer fluid (working fluid) and two heat reservoirs. Different thermodynamic cycles have been proposed. The most used cycles for real applications are the Brayton cycle, that is based on adiabatic processes of magnetization and demagnetization, and the Ericsson cycle, based on isothermal processes of magnetization an demagnetization [44]. These cycles work well but the temperature variations of MC materials (up to 5 K), which can be achieved with magnetic field generated by permanent magnets (up to 1.2 T). are much lower than the required temperature span between the cold and warm heat reservoirs (over 30 K). A way to increase the temperature span is to use thermodynamic cycles that include a heat regenerator. In 1982, Steyert [45] and Barclay [46] introduced and developed the concept of Active Magnetic Regenerator (AMR), in which the MC material is at the same time the active refrigerant element and the regenerator for the working fluid. The thermodynamic cycles with regeneration, mainly exploited in prototypes, are based on Brayton-like cycles. The AMR Brayton-like cycle can be decomposed in four steps (schematized in Figure 2.7):

- 1) a magnetic field is applied to the AMR (a porous structure made of MC materials), increasing its temperature;
- 2) a working fluid flows through the AMR from the cold reservoir to the hot one. The fluid cools the AMR and its temperature increases during the passage. The fluid flow results in a longitudinal temperature gradient of the AMR. Overall, heat is removed from the AMR and it is transferred to the hot reservoir;
- the magnetic field is removed. The AMR results to be cooled by the MCE. A longitudinal temperature gradient remains in the AMR. Each infinitesimal part of the AMR exploits its own MCE;
- 4) the working fluid flows from the hot reservoir to the cold one. The fluid is cooled by the AMR and comes out with a temperature lower than that of the cold reservoir.

The maximum temperature span of the working fluid that enters and exits the magnetocaloric material at the cold side is limited by the adiabatic temperature change obtained during the demagnetization and by the heat transfer between

the working fluid and the magnetocaloric material [9]. This temperature span and the operating frequency are the main parameters determining the cooling power of the magnetic refrigerator.



Figure 2. 7 Schematic illustration of the four steps of an Active Magnetic Regenerator Brayton-like cycle.

Several refrigerator prototypes have been realized by varying the MC material, the magnetic field source, the thermodynamic cycle, the operating frequency, the cooling power and the temperature span. For a review of the prototypes built until 2015 see Ref.s [8,9]. Between 2015 and 2016, two commercial prototypes of magnetocaloric refrigerator were presented: the first in Las Vegas (Nevada) by Haier, Astronautics and BASF, the latter at Carrefour's head office by Cooltech. However, it is difficult to predict the time still required to reach a mass production of magnetic refrigerators. The major obstacle for a global diffusion of this technology is the cost of MC materials and of permanent magnets.

2.3 Magnetocaloric materials

The MC material is the core of magnetic refrigeration devices: it represents the active refrigerant element that corresponds to the refrigerant gas in vapourcompression devices. The implementation of a functioning magnetic refrigerator requires materials with a high MCE near room temperature [47]. However, high values of ΔT_{ad} and ΔS_T are not enough to ensure operation, power and efficiency of refrigerators [9]. First of all, the MCE must be as reversible as possible. A hysteretic behaviour, characteristic of first-order transitions, can drastically reduce the MCE exploitable in thermo-magnetic cycles and, consequently, the efficiency and the power of the refrigerators [48,49]. Furthermore, the $\Delta T_{ad}(T)$ and $\Delta S_T(T)$ have to be high in the entire working temperature range of refrigerator, especially if AMR cycles are implemented. This can be achieved by using MC materials with a second-order transition or by assembling layered regenerators, which consist of materials with different transition temperatures [50-54]. Others important properties of MC materials, which have to be considered, are the thermal conductivity and diffusivity. Indeed, to increase the power and the efficiency of magnetic refrigerators, the frequency of thermomagnetic cycles has to increase. This requires a fast heat transfer between the MC material and the heat-transfer fluid, and thus good thermal properties of MC materials [55-57]. Furthermore, for an industrial and commercial production of magnetic refrigerators, some other features of MC materials are fundamental. The abundance and the cost of raw materials together with the cost and time required for the materials preparation have a significant role in determining the final cost of refrigerators. The manufacture of magnetic regenerators with complex forms, characterized by a high surface to volume ratio, requires good mechanical, manufacturing and casting properties [9,58,59]. For last, MC materials have to maintain unaltered their properties during the whole life cycle of the refrigerator. Corrosion effects and mechanical fatigue effects due to the cyclical passage across magnetostructural transitions (microcracks formation, performance fading, pulverisation) have to be avoided in order to ensure a long-time stability of refrigerators efficiency and power [49,60,61].

Let us come now to a brief description of the most promising MC materials for room-temperature refrigeration.

2.3.a Gadolinium

The MCE was discovered and initially studied near second-order transitions of ferromagnetic materials. Among them, gadolinium was the first material utilized in a room-temperature magnetic refrigeration prototype [43], thanks to its Curie transition at about 294 K [62]. Gadolinium shows a relevant MCE $(\Delta T_{ad \ max} = 3.3 \text{ K} \text{ and } \Delta S_{T \ max} = 3.1 \text{ Jkg}^{-1}\text{K}^{-1}$ for a polycrystalline commercial sample in a $\mu_0 \Delta H$ of 1 T [21,63]) in a large temperature range around its Curie transition, which emerges from its high magnetic moment produced by 4f electrons ($M_s = 7.5 \mu_B$ per atom). Though the majority of built prototypes exploit gadolinium and it is considered a benchmark for room temperature MC materials, its high cost and the request, to ensure good MC properties, of a high purity degree make difficult its application in marketable devices [62,63].

2.3.b Gd₅Si₂Ge₂

A revolution in MC materials' research occurred in 1997 when V. K. Pecharsky and K. A. Gschneidner discovered a Giant Magnetocaloric Effect (GMCE) in the ternary intermetallic compound $Gd_5Si_2Ge_2$ [64,65]. The entropy variation observed in this material is at least two times larger than that of Gd. This effect is due to a magneto-structural transition between an orthorhombic ferromagnetic phase and a monoclinic paramagnetic phase, which involves a large lattice discontinuity. The temperature transition can be modified between 20 and 305 K by varying the Si-Ge ratio and by introducing in the compound a small amount of Ga [15]. The wide thermal hysteresis, larger than the transition shift induced by a 2 T magnetic field, and the high cost and the low availability of Gd and Ge make difficult the use of this material in magnetic refrigerators.

However, since this discovery, research on magnetic materials with first-order magnetic transitions near room temperature has been constantly increasing. The most studied and promising materials' families are: the class of Fe₂P-based compounds (Mn,Fe)₂(P,X) with X=As,Si,Ge,B, the intermetallic compounds La(Fe,Si)₁₃ and the NiMn-based Heusler alloys. The first two classes of materials present, for some compositions, a weak first-order transition, in which the energy barrier between the two phases is comparable to the thermal energy near the transition [13]. This allows to have a gradual change of the transition nature from first- to second-order by varying the composition and to reduce the thermal hysteresis down to zero; increasing, in this way, the reversibility of the MCE.

2.3.c La(Fe,Si)13

The cubic LaFe_{13-x}Si_x (x < 2.5) compound is characterized by a magnetic transition that gradually changes from a weak first-order magneto-elastic transition, for a low Si content (Si ≤ 1.6), to a second-order transition [66]. The first-order transition involves a significant volume change ($\Delta V \sim 1\%$), without variation of the structural symmetry [67]. The intrinsic hysteresis of the transformation is small [68]. A large MCE occurs with the field induced transition [69,70]. The addition of interstitial H or the partial substitution of Al, Co or Mn, modify the transition temperature (from 200 to 340 K), the transition order and the intensity of the MCE [66,71,72]. In particular, the insertion of H expands the crystalline lattice and modifies the material electronic structure, with a resulting preservation of the weak character of the first-order transition and the increase of the critical temperature [73]. High MCE values, low hysteresis, abundance and low cost of constituent elements and scalable production routes make this class of materials very interesting for energy conversion applications. On the other hand, the strong volume change and the presence of interstitial hydrogen are drawbacks for long-term stability [74,75]. To overcome this problem, one solution could be the realization of composite materials, in which the MC material is embedded into a metallic [76] or polymer matrix [77]. This improves the stability and the machinability of the sintered materials, but at the expenses of MC and thermal properties [78].

2.3.d (Mn,Fe)₂(P,X)

Other interesting MC materials are the Fe₂P-based (Mn,Fe)₂(P,X) compounds, with X=As,Ge,Si,B [79–82]. These compounds present, for specific compositions, a weak first-order magneto-elastic transition characterized by a variation of lattice parameters together with the preservation of the hexagonal crystal structure, a low volume change and a low thermal hysteresis. At first, a GMCE was observed in the MnFeP_{0.45}As_{0.55} compound [79]. The substitution of As with Si or Ge solves the problem of toxicity but it can increase the transition thermal hysteresis, that is linked to the anisotropic change in lattice parameters, and worsens the mechanical properties of the material [83]. The GMCE observed in these materials originates from the loss of local moments at the 3f sites of the hexagonal cell, which is due to a hybridization of their orbitals with the surroundings Si/P atoms [81]. This makes the transition very sensitive to the change of Si/P rate or to the substitution of the non-magnetic elements. For example, the introduction of B moves the transition towards a second-order type, reduces the thermal hysteresis, increases the transition temperature shift with the magnetic field and the mechanical stability [22,84]. High reversible values of ΔS_T and ΔT_{ad} , the tunability of transition temperature, the absence of critical elements and a good mechanical stability make these compounds very promising for refrigeration applications.

2.3.e Ni-Mn-X Heusler alloys

Heusler alloys form a wide class of multi-functional materials that present many different interesting properties (conductive, superconductive, magnetic, magneto-optical, magneto-caloric, baro-caloric, thermoelectric, topological...) and are studied for several applications (magnetic recording, spintronics, thermoelectric energy conversion, magnetic refrigeration, as topological insulators and shape-memory materials) [85]. The general formula is X_2YZ , where X is a transition metal, Y a transition metal or a rare earth metal and Z an element from the IIIA-VA groups. Their flexible structure allows a large number of elements combinations. Until now, more than 1500 different Heusler alloys are known [85].

Regarding the MCE, a GMCE was discovered, in this class of material, in the Ni₂MnGa alloy near its first-order martensitic transition [86]. This transition is a displacive solid-solid transformation between a cubic phase (austenite) and a low-symmetry phase (martensite). In magnetic Heusler alloys, the strong correlation between magnetic and structural degrees of freedom allows to induce the martensitic transition with an external magnetic field [87]. A GMCE was observed in various off-stoichiometric Mn-rich Heuslers with general formula Ni₂Mn_{1+x}Y_x, where Y=Ga, In, Sn, Sb [88–91]. These alloys display, for some compositions, a low-temperature martensitic phase characterized by a low magnetization, due generally to an AFM state [92]. In this case, an inverse-MCE is observed [90,91,93,94]. The structural transition, characterized by a significant volume discontinuity, can be induced also by applying an external pressure, leading to a barocaloric effect [95].

The transitions temperatures (of both the structural and the Curie transition) and the magnetic ordering of the two phases can be varied by modifying the composition of the alloy or by introducing appropriate substitutional elements (e.g.: Co, Fe, Cu) [96,97]. This gives the possibility to control and to modify the MC properties of the alloy (nature from direct to inverse, intensity, temperature range) [93]. The increase of the magnetization discontinuity (ΔM) between the two phases at the transition promotes high MCE values [90,94,98]. However, the large thermal hysteresis, which characterizes the martensitic transition, prevents the cyclability of the effect by employing low magnetic fields ($\mu_0 H \leq 1$ T). The MCE observed in subsequent field application can be drastically or entirely reduced [90]. The main reason of the large thermal hysteresis is the

lattice mismatch between the two phases, which involves a symmetry change and a high elastic energy cost [99–101]. To reduce this energy contribution at the phase boundaries, the martensite develops an adaptive twinned micro- or nanostructure [102,103]. Changes of composition modify the adaptivity of the martensitic phase to the austenitic phase with a resulting variation of the hysteresis width. Other factors, which affect the thermal hysteresis, are linked to the material microstructure (defects, grain size, local strains, phase coexistence), the magnetic features (magnetic ordering, magnetic anisotropies, magnetic domain structure, spin fluctuations) and the chemical order [28]. Though the thermal hysteresis in these alloys is usually larger than the shift of the transition temperature induced by typical magnetic fields ($\mu_0 H \leq 1$ T), some works demonstrated the possibility to achieve a reversible MCE by following minor loops in the mixed-phase region, thanks to the finite width of the structural transformation [33,35,104]. In minor-loops, the forth and back transformations proceed mainly by phase-boundaries movements, reducing the high energy cost due to nucleation processes.

A special mention also deserves the MCE observed in these alloys near the Curie transition, because, though it has lower intensities compared to the MCE at the structural transition, it is fully reversible. As mentioned in Chapter 2.1, the MCE near a second-order transition depends mainly on the material magnetization and on the intensity of the applied magnetic field. The Heusler alloys with the highest values of magnetization are the Co-rich ones (e.g. the alloy Co₂FeSi has a M_s of 6 µ_B per formula unit). However, their Curie temperatures are so high (~ 10^3 K) that these materials are useless for room-temperature energy conversion machines [105]. The substitution of Co with Ni decreases the Curie temperature quite close to room-temperature (for the alloys Ni₂MnZ, Z=In, Sn, Sb) but reduces the saturation magnetization [106,107]. An excess of Mn atoms, that can occupy the sites of Z atoms, increases the magnetization with a small effect on the Curie temperature. The propensity of the Mn atoms to create an AFM coupling at short distances and the appearance of the martensitic phase at room-temperature for a low content of the Z element limit the achievable increase of magnetization to a value of about 6 μ_B per formula unit for the Ni₂Mn_{1.4}In_{0.6} alloy [108]. The complex configuration of magnetic interactions of the Heusler cubic cell and the possibility to introduce other elements give the chance to further increase the magnetization and to tune the Curie temperature.

The absence of rare-earths, the simple preparation processes and the possibility to exploit several compositions and elements substitutions make these materials extremely attractive for magnetic refrigeration devices and for others applications, although some drawbacks have to still be overcome.

2.3.f Fe-Rh

Fe-Rh alloys (close to 1:1 stoichiometry) show a relevant inverse MCE, an elastocaloric and a barocaloric effect [109–111] at a very sharp first-order magnetoelastic transformation near room temperature. This transformation occurs from an antiferromagnetic to a ferromagnetic state on heating and it is accompanied by a very large volume change (about 1%) without change in the crystal symmetry (CsCl structure) [112]. Though it was the first system in which a giant MCE and elastocaloric effect were reported, the irreversibility of these effects braked the interest on these alloys [113]. Only recently, it was demonstrated the possibility to obtain a reversible effect upon field (or pressure or mechanical stress) cycles, corresponding to a reversible ΔT_{ad} up to 6 K and a ΔS_T up to 12.5 Jkg⁻¹K⁻¹ with a $\mu_0 \Delta H = 2$ T [30,111,114]. Although the high cost of Rh makes difficult to exploit these alloys for large scale applications, the outstanding values of MCE and barocaloric effect [111,115] make these alloys promising for small scale solid-state cooling devices.

2.3.g La-based Manganites

Ferromagnetic lanthanum-based manganites (general formula La₃MnO₃), with perovskite structure, display a not negligible MCE across their magnetic ordering transition. The transition can be tailored in a wide temperature range (~ 100 – 375 K) by substituting La ions with other ions (Y³⁺ or Bi³⁺, Ca²⁺, Ma²⁺, Sr²⁺, Pb²⁺, Na¹⁺, K¹⁺, Ag¹⁺, Li¹⁺...) or by a partial replacement of Mn with another transition metal or a semimetal or by creating an excess of oxygen. An interesting MCE was observed also in Pr or Nd La-free manganites. A complete review regarding the MCE in manganite materials can be found in Ref. [116]. Although the MCE values of manganites are low compared to that of the most promising materials, the low cost of starting elements and of processing, the possibility to tune the critical temperature and to shape them into fine structures [117] make these compounds interesting for the realization of magnetic cooling systems.

To conclude, we report in Table 2.1 a comparison between the measured MCE, as ΔS_T and ΔT_{ad} , of some of the most studied MC materials. For detailed reports about MC materials and their properties see the reviews [7,13,16,113,118–120]. Until today, it is not clear which is the best material to be used as active element in magnetic refrigerators. Fe₂P-based and La-Fe-Si compounds represent the most promising materials thanks to their high reversible MCE and the possibility to tune the transition temperature in order to realize layered MC regenerators. However, the realization of these smart structures requires an

accurate	e control of the	composi	ition	in order to e	ensure	a precise g	grad	ient in the
critical	temperatures	along t	the	regenerator.	This	represents	an	additional
challenge in the development of industrial routes of materials preparation.								

	Tran.	T_t	$\mu_0 \Delta H$	ΔS_T	ΔT_{ad}	Ref.
Material		(K)	(T)	(Jkg ⁻¹ K ⁻¹)	(K)	
Gd (commercial)	Curie	~ 295	1	-3.1	3.3	[72]
$La_{0.67}Sr_{0.33}MnO_3$	Curie	~370	1	-1.6	1	[121]
La.67(Ca.89Sr.11).33Mn1.1O3	Curie	~ 275	1	-3.7	1.3	[117]
$Ni_{1.97}Mn_{1.4}In_{0.63}$	Curie	~316	2	-2	3.3	[108]
Ni45.2Mn36.7In13Co5.1	M-S	~317	2	19	-6.2	[90]
$\mathrm{Gd}_5\mathrm{Si}_2\mathrm{Ge}_2$	M-S	~ 278	2	-14	7.3	[64]
MnAs	M-S	~318	2	-31	4.7	[122]
${ m FeRh}$	M-E	~316	2	12.5	-6	[111,114]
$MnFeP_{0.45}As_{0.55}$	M-E	~303	1	-13	2.8	[79, 123]
MnFe.95P.595Si.33B.075	M-E	~ 281	1	-9.8	2.7	[22]
${ m LaFe_{11.6}Si_{1.4}}$	M-E	$\sim \! 196$	1	-22	4.2	[66]
$LaFe_{11.14}Co_{0.76}Si_{1.1}$	M-E	~ 267	1	-7.2	1.8	[124]
$La(Fe_{.89}S_{.11})_{13}H_{1.3}$	M-E	~ 291	2	-24	6.9	[73]

Table 2. 1 Some properties of different magnetocaloric materials: transition nature (second-order Curie transition; M-S: magneto-structural first-order transition; M-E: magneto-elastic first-order transition), transformation temperature in zero applied magnetic field (T_l) , maximum entropy change (ΔS_T) and maximum adiabatic temperature change (ΔT_{ad}) for a magnetic field change $\mu_0 \Delta H$.

2.4 Magnetocaloric characterization techniques

The MC properties of materials, in terms of adiabatic temperature change and isothermal entropy change, are collected by following direct and indirect methods. The isothermal entropy change as a function of temperature and of applied magnetic field is derived from M(T,H) or $c_p(T,H)$ data, or can be "directly" measured with purpose-built calorimeters. The adiabatic temperature change is obtained by an elaboration of $c_p(T,H)$ curves or can be directly measured by dedicated experimental setups. It was demonstrated that these techniques give consistent results [22,125] if the right measurement protocols are followed, especially in the case of first-order transitions, and if demagnetizing effects are taken into account [126].

2.4.a Magnetization measurements

In literature, the MCE is often reported in form of isothermal entropy change as a function of temperature and of magnetic field. The $\Delta S_T(T, H)$ is calculated, by using the Maxwell relation (equation 2.3), by a numerical elaboration of magnetometry data [127]. Isothermal $M(H)_T$ or isofield $M(T)_H$ series of magnetization curves can be collected by a standard magnetometric equipment, available in many laboratories. Isothermal measurements are often favourite thanks to a shorter data collection time and to a better control of sample temperature. Anyhow, in the case of second-order transitions the two methods give the same results [128].

Regarding first-order magnetic transitions, the hysteretic character of the transition makes the magnetic phase of the material not univocally defined as function of temperature and magnetic field. The M(T,H) values near the transition depend on the magneto-thermal history of the material. Figure 2.8.a shows the critical (H-T)-diagram for a conventional first-order magnetic transition between phase A and phase B, with $M_A > M_B$. An intrinsic temperature/field hysteresis separates the two opposite transformations: $A \rightarrow$ B (red line) and $B \rightarrow A$ (blue line). This can induce a wrong estimation of the ΔS_T if it is calculated by performing subsequent isothermal M(H) measurements on increasing (or decreasing) temperature [24,129,130]. Furthermore, as discussed in the Chapter 2.1, real first-order transitions occur over a finite temperature range, developing across mixed states that depend on the magnetothermal history of the system. By performing subsequent M(H) measurements at different temperatures the material can remain trapped in non-equilibrium mixed states and this can affect the estimation of ΔS_T . The integration of equation 2.3 has indeed to be done between equilibrium states [13]. To avoid these problems and to obtain a correct estimation of ΔS_T , a specific measurement protocol has to be followed. The protocol consists in the resetting, before each measurement, of the initial state of the material [24,131]. Therefore, when the M(H) measurements are performed only the field-induced transition occurs starting from the same initial state. Green and violet arrows in Figures 2.8.a and 2.8.b schematize the protocols for a conventional ("direct") or an "inverse" firstorder transition to probe the $A \rightarrow B$ and the $B \rightarrow A$ transformations, respectively. In the case of a "direct" transition, before each M(H) measurement, performed increasing the magnetic field (green arrows), the equilibrium starting phase has to be reset by increasing the material temperature, at zero applied field, far above the transition temperature T_{0H} (green dot). The inverse protocol has to be used to probe the $A \rightarrow B$ transition (violet arrows). In the case of an "inverse" first-order transition, the two protocols have to be reversed (Figure 2.8.b).



Figure 2. 8 Schematization of the magnetization measurement protocols to evaluate the MCE at a "direct" (a) or an "inverse" (b) first-order magnetic transition. Red and blue lines are the equilibrium lines of the two phases. The white area indicates the temperature-field coordinates at which the state of the system is not univocally defined. The arrows show the correct protocols to follow to perform M(H) measurements by increasing (green) or decreasing (violet) the magnetic field. The violet and green circles state the reset temperatures for the two protocols.

Isofield M(T) measurements, performed on an adequate temperature range, avoid this problem because the transition is completely crossed during each measurement. However, the necessity to avoid a large thermal-gradient between sample and sample-holder imposes to use very slow temperature sweep rates, with a resulting significant increase of measurement time.

Though the elaboration of magnetization data is the most used, simple, convenient and available method to obtain a MCE characterization of materials,
the required numerical integration and derivation processes of magnetization data cause large errors (10-30%) in the deduced $\Delta S_T(T, \Delta H)$ values [127,125].

Figure 2.9 shows an example of (a) isothermal M(H) and (b) isofield M(T) measurements performed on a Ni-Co-Mn-Ga [125] Heusler alloy across its first-order inverse martensitic transformation. The isothermal measurements were performed by following the green protocol described in Figure 2.8.b. Figure 2.9.c presents the isothermal entropy change, and the corresponding experimental errors, of the material in a field span $\mu_0 \Delta H = 1.8$ T, derived by the numerical elaboration of magnetometry data.



Figure 2. 9 (a) Isothermal M(H) and (b) isofield M(T) magnetization measurements of a Ni-Co-Mn-Ga Heusler alloy near its first-order martensitic transition. (c) $\Delta S_T(T)$ in a $\mu_0 \Delta H = 1.8 T$ derived from the magnetometric measurements by using the Maxwell relation.

2.4.b Direct measurement of the adiabatic temperature change

The adiabatic temperature change represents the most important MC parameter to design magnetic refrigerators [9,99]. The ΔT_{ad} can be directly measured, by means of a thermometer, during the variation of a magnetic field applied to the material under adiabatic conditions. This allows to reduce the experimental error and to observe directly the thermodynamic response of the material to the magnetic stimulus [125]. However, the direct ΔT_{ad} measurement requires the development of custom-built experimental setups and this justifies because often only the $\Delta S_T(T, \Delta H)$ of materials is reported in literature.

A review of the realized experimental setups for this purpose can be find in Ref. [126]. These instruments are based on the principle of measuring the sample temperature while a magnetic field is changed under quasi-adiabatic conditions. The temperature is usually measured with thermocouples [132–134] or high precision thermoresistances, little influenced by the magnetic field [135,136]. Some experimental setups based on non-contact temperature measurements techniques, like thermoacoustic methods [137,138] or on the detection of IR-radiation [139,140] have also been proposed. The realization of nearly-ideal adiabatic conditions is the trickiest aspect of such measurements. It requires the

suppression of heat transfers between the sample and the environment during the application of the magnetic field. Vacuum environments and heat shields are usually adopted, though they make difficult the control of sample temperature before the application of the field. Adiabatic conditions can be also improved by fast magnetic field changes, obtainable by turning on and off an electromagnet [132,135], or by moving with a mechanical device the sample inside a steady field [133,135,136] or by applying pulsed magnetic fields [132,141]. The non-perfect adiabatic conditions and the resolution of temperature sensor rule the measurements error.

In the case of first-order transitions, different ΔT_{ad} values can be obtained depending on the followed measurement protocol, as in the case of the estimation of ΔS_T from magnetometry data. In order to correctly measure the complete ΔT_{ad} , induced by a definite ΔH , a protocol similar to that used in magnetic measurements has to be adopted. Before each measurement, the material has to be reset to the starting equilibrium phase by increasing/decreasing its temperature above/below its transition temperature. The ΔT_{ad} measured following this protocol can be partially or totally irreversible due to the presence of hysteresis. Figure 2.10.a shows an example of a direct ΔT_{ad} measurement performed on the Ni-Co-Mn-Ga sample, whose magnetic behaviour is reported in Figure 2.9.



Figure 2. 10 (a) Direct ΔT_{ad} measurement performed on a Ni-Co-Mn-Ga sample at 338.2 K by applying a magnetic field of 1.8 T. Dashed red line represents the applied magnetic field as a function of time. (b) Complete temperature behaviour of the adiabatic temperature change of the sample.

The measurement was performed with a resistive temperature sensor by turning on and off a low-inductive electromagnet (details about the experimental setup are reported in Chapter 3.5). Before each measurement, the sample was cooled down to a temperature lower than T_{0c} . The figure shows as the measured ΔT_{ad} is completely irreversible: after the first application of the magnetic field that induces a negative ΔT_{ad} (blue arrow), when the magnetic field is removed and it is subsequently applied again no temperature changes are observed. Figure 2.10.b shows the $\Delta T_{ad}(T)$ of the sample made by performing several ΔT_{ad} measurements at different temperatures.



Figure 2. 11 Direct ΔT_{ad} measurements performed on a Gd sample by a cyclical application of a magnetic field ($\mu_0 \Delta H = 1$ T) during a temperature sweep. Inset: ΔT_{ad} as a function of temperature.

On the other hand, a cyclical protocol of measurement can be advantageous to quickly collect the reversible ΔT_{ad} exploitable in thermo-magnetic cycles. This measurement can be performed by a cyclical application of the magnetic field to the material during a slow temperature sweep [22,104,135]. Figure 2.11 shows an example of this kind of measurement performed on a Gd sample with a magnetic field change of 1 T. The inset reports the $\Delta T_{ad}(T)$ obtained by elaborating all the temperature changes measured during the temperature sweep.

A detailed discussion about some experimental equipment for the direct measurement of adiabatic temperature change and a presentation of two innovative setups are reported in Chapter 4.

2.4.c Calorimetry

The measurement of the specific heat as a function of temperature and magnetic field gives a complete, although indirect, magnetocaloric characterization. Following the standard thermodynamics, the total entropy S(T,H) of a system can be calculated by integrating its specific heat $c_p(T,H)$:

$$S(T,H) = \int_0^T \frac{c_p(T',H)}{T'} dT'$$
(2.12)

Two entropy curves, at the magnetic fields H_1 and H_0 , are enough to deduce the $\Delta T_{ad}(T, \Delta H)$ and the $\Delta S_T(T, \Delta H)$. The $\Delta S_T(T, \Delta H)$ is calculated by using Equation 2.4, while the $\Delta T_{ad}(T, \Delta H)$ estimation requires the inversion of $S(T)_H$ curves.

Regarding second-order transitions, the entropy variation due to the magnetic field starts rigorously from the absolute zero. This requires to measure the $c_p(T,H)$ from the lowest possible temperature, in order to reduce the error due to the entropy variation at the starting measurement temperature T_0 [21].

In the case of ideal first-order transitions, the integration of the specific heat across the transition temperature is not allowed because it presents a singularity at the transition point [142]. However, real materials usually show first-order transitions that occur in a finite temperature range. The heat flux measured, through a Differential Scanning Calorimeter (DSC), during a temperature sweep across the transformation, displays a peak at the first-order transition. Figure 2.12.a, shows, as an example, the DSC measurements performed on a Ni-Co-Mn-Ga sample across its martensitic transformation [125]. At the critical temperature, a peak in the heat flux is evident. The peak is shifted to a lower temperature by the application of the magnetic field ($\mu_0 H_1 = 1.8$ T, red dashed line) and by performing the measurements cooling down the sample (blue lines), due to the thermal hysteresis. By integrating the measured heat flux (dQ/dT, Equation 2.13), the relative entropy curves of the material are calculated (Figure 2.12.b).

$$S(T,H) - S(T_0,H) = \int_{T_0}^T \frac{dQ/dT'(T',H)}{mT'} dT'$$
(2.13)

From these, both $\Delta T_{ad}(T, \Delta H)$ and the $\Delta S_T(T, \Delta H)$ can be derived (Figure 2.12.c). It was demonstrated that these results are consistent with the $\Delta S_T(T, \Delta H)$ calculated from magnetometry data and by direct measurement of $\Delta T_{ad}(T, \Delta H)$ [125].



Figure 2. 12 (a) DSC measurements of a Ni-Co-Mn-Ga sample performed without (continuos line) and with a 1.8 T applied magnetic field (dashed lines), through temperature sweeps on heating (red lines) and on cooling (blue lines). (b) Material's entopy as a function of temperature calculated from DSC data. (c) $\Delta T_{ad}(T)$ and $\Delta S_T(T)$ derived from entropy curves.

Commercial calorimeters are not usually suitable for working under a magnetic field. Several custom-built calorimeters have been realized to obtain the magnetocaloric characterization of materials. Until a few years ago, the most used in-field calorimeters were the relaxation calorimeters, in which the sample temperature change, due to the addition of a small amount of heat, is measured. An example is the fully automated in-field calorimeter presented by Pecharsky and Gschneidner [143]. These calorimeters have very long measurement times and entail large intrinsic errors when determining the specific heat across first-order transitions [144,145].

Differential Scanning Calorimeters (DSC) have lower measurement times and are particularly suitable for the measurement of latent heat near first-order transitions. In these calorimeters, the heat flux between the sample and a thermal bath is measured during a sweep in temperature with a constant rate. Several in-field DSC have been proposed. They are usually based on Peltier elements as heat flow sensors [125,146-149]. This inexpensive solution allows to obtain high reproducible values of specific heat and latent heat of transformations with a high sensitivity. These calorimeters can be introduced in electromagnets, permanent magnets or superconductive magnets to characterized the thermodynamic properties of materials under an applied magnetic field. A detailed description of an example of homemade Peltier-based DSC is reported in Chapter 3.4.

A third type of calorimeter, the temperature modulated micro calorimeter, is used to measure very small samples (down to some micrograms) or to discriminate the contribution of latent heat from a peak in heat flux heat capacity, in order to define the transition order [150,151].

As in the case of the elaboration of magnetization data, the numerical integration of the temperature dependence of heat flux introduces significant errors in the estimation of the $\Delta T_{ad}(T, \Delta H)$ and the $\Delta S_T(T, \Delta H)$. A detailed analysis of the errors has been reported in Ref.s [127,144].

Through a Peltier-based DSC, it is also possible to directly measure the isothermal ΔS_T [22,149,152]. The measurement is performed through the application of a magnetic field at the material under isothermal conditions. The ΔS_T is proportional to the heat flux that flows between the sample and the thermal bath.

3. EXPERIMENTAL TECHNIQUES

3.1 Samples preparation

3.1.a Arc Melting

Bulk Heusler samples, studied in this thesis, were prepared by using the arcmelting technique. In this type of furnace, the starting materials, in form of fragments, are melted inside a water-cooled copper crucible through an electric arc. To prevent oxidation, the melting is done in a protective Ar atmosphere. Several melting of the samples are repeated on each side to improve homogeneity. The alloys discussed in Chapter 7 were prepared by using an homemade arc-melting system built at the IMEM-CNR Institute (Parma, Magnetic Materials Group). Whereas, the NiMnIn sample, studied in Chapter 8, was made at FAME (TU Delft) in a home-made arc-melting furnace, which was constructed with the aim to ensure high quality samples by minimizing the oxidation (details can be found in the PhD thesis of M. Boeije [153]).

3.1.b Melt Spinning

Ribbons of Ni-Mn-In-Sn, presented in Chapter 6, were prepared at FAME (TU Delft) with the melt-spinning, a technique that promotes a rapid cooling of the melted alloy and the formation of nanocristalline and amorphous materials. The melt spinner that was used in this Thesis is a commercial instrument by Edmund Bühler GmbH. The working principle of the instrument is schematized in Figure 3.1. The starting materials are melted by radio-frequency induction heating inside a quartz ampoule in Ar gas atmosphere (about 700 mbar). Convection currents facilitate the mixing of the melted metal. An Ar gas pressure (about 900 mbar) is used to eject the molten from a small nozzle in the bottom of the ampoule over a spinning copper wheel. The velocity of the wheel is tuneable and determines the thickness and the crystallinity of the obtained ribbons. The surface velocity of the wheel used for this work was of 46 ms⁻¹. The cooling of the melted metal, ejected on the wheel, is very rapid and reaches cooling rates between 10^4 and 10^7 Ks⁻¹ [154]).



Figure 3. 1: Schematic illustration and photography of the melt-spinning technique.

3.2 Structural and microscopy analysis

3.2.a Diffraction analysis

Room temperature powder X-ray diffraction (XRD) experiments, reported in Chapters 6 and 8, were performed at FAME (TU Delft) with a PANalytical Xpert Pro powder diffractometer equipped with a Cu Ka radiation.

Temperature-dependent X-ray diffraction patterns of samples discussed in Chapter 7 were collected by Dr. S. Fabbrici (IMEM-CNR Institute, Parma) with a Thermo ARL X'tra diffractometer equipped with a solid-state Si(Li) Peltier detector and an environmental chamber.

Neutron diffraction data (Chapter 8) were collected with the PEARL diffractometer at the TU Delft Reactor Institute (RID) [155]. This new diffractometer operates with monochromatic neutrons and has a detectors bank (⁶LiF-ZnS:Ag scintillators) which covers a range of scattering angles $10.4^{\circ} < 2\theta < 158^{\circ}$. For the reported measurements it was selected the 533 reflection of the Ge monochromator ($\lambda = 1.67$ Å).

Rietveld refinements of the collected patterns were carried out using the JANA2006 software [156].

3.2.b Microscopy analysis

Electron microscopy and energy dispersive spectroscopy (EDS) were carried out with a SEM-FEG Zeiss SUPRA 60 scanning electron microscope (SEM) at the SMFI Department, University of Parma (Soft Matter Group, Prof. L. Cristofolini) The EDS microanalysis was performed through an X-Act Silicon Drift Detector LN2-free and the Aztec analysis software (Oxford Instruments). The EDS microanalysis of samples discussed in Chapter 7 was carried out with a PHILIPS 515 SEM at the IMEM-CNR Institute (Parma).

Optical microscopy images (Chapter 8) were collected with a Zeiss Axiotech optical microscope at SMFI Department, University of Parma (Soft Matter Group, Prof. L. Cristofolini). The reflected light differential interference contrast (DIC) technique was used in order to put in evidence small height variations on the samples surface. A dedicated sample-holder was designed, in order to perform microscopy characterizations of the samples surface as a function of temperature. The realized sample-holder is composed of a thermally isolated ceramic plate, which temperature is controlled by an ITC503 temperature controller (Oxford Instruments) through a Pt100 temperature sensor and a resistive heater. The ceramic was selected in order to reduce the shift of the sample surface due to the thermal expansion of the plate. A ceramic conductive paste is used to ensure a good thermal contact between the sample and the ceramic plate. A dedicated software, developed in Matlab, manages the temperature control and the acquisition of microscopy images through a highresolution camera.

The preparation of Heusler samples surface, to perform microscopy analysis, required the development of an ad-hoc system to lapping the materials at high temperatures (up to 400 K). A handle copper sample holder was designed to maintain constant the sample temperature during the procedure of manual lapping, performed with different sand-papers and micro-particles oil suspensions. A Pt100 temperature sensor and a resistive heater (Omega Kapton Insulate Flexible Heaters, 40 W) are used to control and modify the temperature of the sample holder.

3.3 Magnetization measurements

3.3.a SQUID Magnetometry

Magnetization measurements, reported in this Thesis, were performed in a superconducting quantum interference devices (SQUID) MPMS-XL magnetometer (Quantum Design) at SMFI Department (University of Parma) and at FAME (TU Delft). This magnetometer is able to perform DC and AC magnetic measurements with a high sensitivity (10^{-5} Am²) over a temperature range between 2 K and 400 K and in an applied magnetic field up to 5 T. M(T) measurements were performed in the sweeping mode by utilizing different sweep rates (from 5 Kmin⁻¹ to 1 Kmin⁻¹), depending on the accuracy required in the temperature determination. This procedure was preferred to the settled

temperature mode in order to avoid thermal overshoots/undershoots that can alter the reliability of measurements in materials whose magnetic properties depend on their thermo-magnetic history. Series of M(T) measurements at different magnetic field were carried out in order to calculate the ΔS_T near firstorder transformations. The isofield protocol was preferred in order to avoid errors correlated with the hysteretic behaviour of first-order transformations (see the discussion of Paragraph 2.4.a). The calculation of the error propagation due to the numerical elaboration of magnetization data was performed as described in Ref. [127].

3.3.b Thermo-magnetic analysis

Thermomagnetic analysis of Heusler samples (Chapter 7) were performed at IMEM-CNR Institute (Parma, Magnetic Materials Group) with a purpose-built susceptometer, which works with an AC magnetic field of 0.5 mT at 500 Hz in the temperature range 80-1000K.

3.3.c Pulsed field magnetic measurements

Magnetization measurements under pulsed magnetic fields, reported in Chapter 6, were carried out at IMEM-CNR Institute (Parma, Magnetic Materials Group) with an experimental setup developed for the Singular Point Detection technique [157]. A pulsed magnetic field (rising time of 0.5 ms and tuneable amplitude up to 25 T) is applied to the sample, which is placed inside one of two identical pickup coils, series-connected. The measured voltage signal is proportional to the first derivative of the material magnetization as a function of time. The second coil compensates the signal induced by the external field. The sample temperature is controlled by a liquid nitrogen cryostat, which has a temperature working range of 80 K - 300 K.

3.4 In-field differential scanning calorimetry

A homemade in-field differential scanning calorimeter (DSC) was used to carry out measurements of specific heat and of latent heat as a function of temperature and magnetic field. A sketch of the calorimeter is presented in Figure 3.2. The measurements are performed by recording the heat flux between the sample and the controlled thermal bath during a continuous and constant temperature variation. Two miniaturized thermoelectric modules (6x6 mm²), differentially connected, act as heat-flux sensors (based on the Seebeck effect). Two cylindrical aluminium crucibles (internal diameter: 5 mm) are fixed on the top of the modules in order to reduce the error due to radiative heat dissipation. The sample is placed inside one crucible, while the other is left empty. The differential connection of the modules allows to remove the contribution to the heat flux due to the crucibles and to the upper plates of the modules. In this way, the total voltage output of the modules (V) results proportional only to the heat flux between the sample and the thermal bath (\dot{Q}).

$$V = S\dot{Q} \tag{3.1}$$

The proportionality coefficient *S* depends on the characteristic of the thermoelectric modules (Seebeck coefficient and thermal conductance).

The two modules are fixed with a thermoconductive epoxy on the base of a copper case, which acts as thermal bath. A high-power Peltier cell (40 W, 4 A), placed below the copper case, is used to control the case temperature (between 250 K and 420 K). A Pt100 temperature sensor, positioned between the two modules, measures the temperature of the case. The temperature control and stabilization are realized through an ITC503 temperature controller (Oxford Instruments), which has a temperature resolution of ± 0.01 K. The ITC voltage output manages the current output of a KEPCO 50 bipolar power supply.



Figure 3. 2: Schematic illustration and photography of the homemade in-field differential scanning calorimeter, described in details in the text.

The copper case and the Peltier cell are inserted in a vacuum chamber (external diameter 5 cm). The base of the chamber is made of copper to enhance the thermal exchange with a waterblock (at the base), which keeps constant the temperature of the lower plate of the power Peltier element. The vacuum environment (10^{-5} mbar) and the metallized surfaces of the chamber reduce the heat-dissipation from the copper case and prevent the instauration of thermal gradients. The chamber was designed in order to be placed inside the polar expansions of an electromagnet, with the aim to perform measurements with an applied magnetic field up to 1.85 T. The field is applied parallel to the top plates of the thermoelectric modules.

The measurement of the heat flux between the sample and the thermal bath during a temperature sweep at a fixed rate permits to extract some thermodynamic properties of the probed material. The specific heat $(c_p(T))$ is calculated from the measured heat flux $(\dot{Q}(T))$, by knowing the sample mass (m), the temperature sweep rate (dT/dt) and the calibration coefficient of the calorimeter (S(T)), which is obtained by a calibration procedure utilizing a sample with a known specific heat (a single-crystal of sapphire):

$$c_p(T) = \frac{\dot{Q}(T)}{m \left(dT/dt\right)} = \frac{V(T)}{S(T)\left(dT/dt\right)m}$$
(3.2)

Absolute values of specific heat, derived in this way, are affected by an error of about 4%. This estimation was done by performing several measurements on sapphire, Cu and Mo references samples. The error on the specific heat is mainly due to the contribution of the thermal grease, used to fix the sample, to variations on vacuum conditions inside the main chamber and to oscillations in the rate of the temperature sweep.

In the case of first-order transformations, the specific heat cannot be defined by following Equation 3.2. Indeed, the heat flux, measured by a DSC in a material across a first-order transformation, includes the contribution of the latent heat, characteristic of the transformation. Ideal first-order transformations occur at a fixed temperature and are characterized by the absorption or the release of a heat amount defined by the latent heat. During a DSC measurement this heat amount appears as a peak in the heat flux, broadened over a finite temperature range, due to the finite thermal conductance of heat flux sensors. This peak is superimposed to the baseline of heat flux, due to the specific heat of the material. In the case of real first-order transformation, the peak related to the latent heat can be further enlarged due to the spread of the transformation over a finite temperature range (as discussed in Chapter 2.1). Anyhow, the total latent heat

of the transformation (*L*) can be calculated by DSC data by integrating the measured heat flux $(\dot{Q}(T))$, after subtraction of the baseline $(c_{p_b}(T))$, between the start (T_s) and finish (T_f) temperature of the transformation:

$$L = \int_{T_s}^{T_f} \left(\frac{\dot{Q}(T')}{m \, dT'/dt} - c_{p_b}(T') \right) dT'$$
(3.3)

A complete MC characterization, in terms of $\Delta S_T(T)$ and $\Delta T_{ad}(T)$, is derived by performing DSC measurements at different magnetic fields. Indeed, the integration of the heat flux, by following Equation 2.13, results in the relative entropy-temperature curve of the material. If entropy-temperature curve are calculated at different magnetic fields, both the $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ can be obtained (as described in Chapter 2.4).

In the case of first-order transitions, the heat flux corresponds to an "effective" specific heat that takes into account both the contribution of the specific heat of the material outside the transition and the contribution of the latent heat that is spread over the temperature span in which the transition occurs (a detailed discussion about this point is reported in Chapter 7). Several works demonstrated that, even in the case of first-order transformations, this procedure is allowed and results in MC values that are comparable with those obtained from other experimental techniques (see for example Ref.s [22,33,125,158]).

The numerical elaboration of specific heat data implies a substantial propagation of the experimental errors. Its calculation is performed by following Ref. [127]. A 0.5% relative error on the measured heat flux is considered in the propagation. This estimation was obtained by repeating several times heat flux measurements on reference samples. This error is lower than that considered for absolute values of the specific heat. Indeed, the numerical elaboration of heat flux data removes the effect of systematic errors, due for example to the conductive grease used to position the sample, which instead affect the estimation of absolute values of specific heat. Instead, an additional error, in the calculated $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ values, is introduced by the entropy variation of the material due to the magnetic field at the starting temperature of the DSC measurement $(S(T_0)_{H_2} - S(T_0)_{H_1})$. This error, which is relevant in particular for second-order transitions, can be corrected by considering the value of ΔS_T at T_0 derived from magnetization measurements.

3.5 Direct adiabatic temperature change probe

Direct adiabatic temperature change measurements were performed with a purpose-built probe (a modified version of the probe described in details in Ref. [135]). The probe, schematized in Figure 3.3, is based on a Cernox® bare chip resistive temperature sensor (Lake Shore Cryotronics), which is made of a small sapphire plate (about $1x0.7x0.2 \text{ mm}^3$, less than 3 mg) and of a thin film resistance (grown on a face of the plate). Its magnetoresistance is negligible in the temperature and magnetic field range in which the probe is used [159]. The Cernox is glued using epoxy resin in a hole of a fiberglass board, equipped with gold contacts, in order to preserve it from mechanical stresses (Figure 3.3.e). Two very thin gold wires connect the Cernox with the board. The board is fixed in a PEEK housing with the side of the contact wires turned to the housing (Figures 3.3.b and 3.3.d). A cavity in the PEEK housing prevents any contact between the Cernox surface and the probe.



Figure 3. 3: Schematic illustrations and photographs of the adiabatic temperature change probe. (a) Overall sketch of the probe. (b,c) Photographs of the two terminal parts of the probe. (d) Sketch of the PEEK sensor-sample housing. (e) Enlarged photography of the Cernox temperature sensor glued on the fiberglass board.

The PEEK housing is glued at the end of a steel tube (external diameter 6mm) with a brass terminal part, designed to minimize the interactions with the magnetic field. The other end of the tube is equipped with a slide seal assembly and a 10 pins electrical connector (Figure 3.3.a and 3.3.c). This configuration was

designed to have the possibility to easily fit the probe to different cryostats and ovens, incorporated in different magnetic field sources (electromagnets and superconductive magnets).

To perform the measurements, the sample is positioned in contact with the back side of the Cernox (the sapphire plate) through a thermoconductive paste (Artic Ceramique, thermal conductivity about 7 Wm⁻¹K⁻¹). The sample is then fixed to the PEEK housing with a thin PTFE tape or it is glued to the fiberglass in two points, depending on its size. The measurements of the Cernox resistance is performed by the four-points technique. The sensor is powered by an AC current of a few μ A at 1 kHz and its voltage signal is acquired and filtered by a lock-in amplifier (7265 DSP Lock-in Amplifier Signal Recovery), whose time constant is set to 10 ms. The temperature measurement is affected by an experimental error of ± 0.04 K, which is mainly due to the electrical noise. The declared time response of the sensor is 0.135 s (a detailed discussion about the time constant of adiabatic temperature change measurements is reported in Chapter 4).

Adiabatic temperature change measurements are carried out by changing the magnetic field in one of two possible ways:

- a) by turning on and off a low inductive electromagnet with the probe fixed in the middle of the poles of the magnet (maximum magnetic field: $\mu_0 H_{max} = 1.9$ T, characteristic time of the field variation: about 1 s);
- b) by moving the probe, through a linear pneumatic actuator (running time about 0.15 s), inside a static magnetic field that is generated by an electromagnet ($\mu_0 H_{max} = 1.9$ T) or by a superconductive magnet ($\mu_0 H_{max} = 7$ T).

The average magnetic field sweep rate is about 1.8 Ts⁻¹ for the first case, while it can reach values of 300 Ts⁻¹ for the second one.

The measurements are performed in vacuum or in a low pressure of He or N gas. A dedicated software (developed in Matlab®) allows to automatically perform adiabatic temperature change measurements by following the protocols described in Chapter 2.4.

The above-described experimental setup can be used also to simulate thermomagnetic Brayton cycles, consisting of two adiabatic and two isofield branches (Figure 3.4.a). The cycles are performed by moving the probe between two regions with controlled values of temperature and magnetic field (Figure 3.4.c). In order to control the temperature of the two regions, an insert was designed for a standard cryostat (Oxford Instruments CF1200). It is a tube made of two copper regions thermally isolated one from the other using TUFNOL® sections. The temperature of the two regions (T_{HOT} and T_{COLD}) is independently controlled through two Pt100 sensors and two resistive heaters (Omega Kapton Insulated Flexible Heaters, 20 W). The insert was designed so that the lower region is situated in the centre of the poles of an electromagnet ($\mu_0 H_{1 max} = 1.85$ T), while the other is outside the poles, where only a small fraction of the magnetic field is present ($\mu_0 H_{0 max} = 0.1$ T).

A dedicated software (developed in Labiew®) controls the movement of the probe between the two regions, characterized by $(T_{HOT} \text{ and } H_0)$ and $(T_{COLD} \text{ and } H_1)$, simulating thermomagnetic cycles by fixing the frequency or the temperatures at which the actuator is powered $(T_{IN} \text{ and } T_{OUT})$. The sample temperature is constantly recorded during the cycles. The heat exchange with the sample during the isofield branches can be varied by changing the pressure of the gas inside the cryostat or by changing the temperatures T_{HOT} and T_{COLD} . An example of a measurement of a Gd sample is reported in Figure 3.4.b.



Figure 3. 4: (a) Schematic of a thermomagnetic Brayton cycle in the entropy-temperature diagram. Two entropy curves are drawn for two different values of applied magnetic field. Arrows highlight the adiabatic (blue and red) and isofield (cyan and orange) branches. (b) Measurement of the temperature variation of a Gd sample during thermomagnetic cycles, performed with the experimental setup schematized in (c) and described in details in main text.

SECTION B - EXPERIMENTAL WORK

INNOVATIVE TECHNIQUES FOR THE DIRECT MEASUREMENT OF THE MCE

The design and the optimization of magnetic refrigerators require the direct characterization of the adiabatic temperature change of materials used as active cooling elements. Indeed, the temperature change of magnetic materials, caused by the magnetocaloric effect, is the driving force that leads the heat transfer in magnetic cooling devices and defines their performances. Nevertheless, although the measurement of the adiabatic temperature change is conceptually simple and clear, it is not frequently reported in literature due to the lack of available commercial instruments. The measurement of the adiabatic temperature change requires the development of a purpose-built experimental setup that is able to record the temperature of a magnetic material placed in adiabatic conditions while an external magnetic field is varied. This section reports an overview on the principle of the adiabatic temperature change measurement and on the main experimental issues that have to be considered to design the instruments and to obtain a correct characterization of the MCE. The effect of non-ideal adiabatic conditions, the role of the temperature sensor and the influence of the sample thermal properties are discussed in Chapter 4 on the basis of experimental measurements and heat transfer simulations.

Afterwards, in Chapters 5 and 6, two innovative experimental solutions are proposed to directly measure the adiabatic temperature change in thin samples and with fast magnetic field changes. The first experimental setup, based on a non-contact temperature sensor, allowed the direct measurement of the adiabatic temperature change of gadolinium sheets with a thickness down to 20 μ m. The measurement of the effective MCE in materials processed in forms with a large surface-to-volume ratio is essential to design performing AMRs characterized by a fast heat exchange with the working fluid. The second experimental setup, which is described in Chapter 6, exploits a thermo-optical effect, the Mirage Effect, to directly measure the adiabatic temperature change induced by fast magnetic field pulses. The short response time of this technique avoids misrepresented results due to the effect of the temperature sensor. The measurement of the MCE, induced by fast field changes, is not only fundamental to test materials' response to thermomagnetic cycles at high frequencies but can also give important information about the kinetics of magnetic transitions.

4. ON THE EXPERIMENTAL MEASUREMENT OF THE ADIABATIC TEMPERATURE CHANGE

4.1 Adiabatic conditions and temperature sensor

The direct measurement of the MCE, as an adiabatic temperature change, is conceptually simple. The sample temperature is recorded while an external magnetic field, applied to the material, is varied under adiabatic conditions. The temperature is usually measured with standard temperature sensors (thermocouples [132–134,141] or small resistive sensors [135,136], see Paragraph 2.4.b for a review of the main realized experimental setups). Whereas, the change of the magnetic field is achieved by turning on and off an electromagnet [132,135] or by moving the sample inside (or outside) a region with a static magnetic field [133,135,136] or by exploiting pulsed magnetic fields [132,141,160]. This apparently simple procedure hides some not negligible issues, which have to be carefully considered to perform accurate measurements.



Figure 4. 1 (a) Schematization of an experimental system to directly measure the adiabatic temperature change in a MC material. (b) Equivalent electric circuit. The grey rectangle highlights the sample-sensor system.

The first problem deals with the practical realization of adiabatic conditions, obtained by reducing as much as possible the heat dissipated from the sample during the measurement. Figure 4.1 shows a schematic illustration of the system to directly measure the adiabatic temperature change and the equivalent electric circuit. The sample is characterized by a heat capacity C_s and a temperature T_s . In the electric circuit, the MCE is represented as a current source, in parallel with the capacitance that corresponds to the sample. The sample is in contact with the temperature sensor, characterized by a heat capacity C_t and a

temperature T_t . The thermal contact between the sample and the sensor, which depends on various factors and which is normally improved through the use of thermoconductive pastes, is taken into account through the total thermal conductance K_{s-t} . The sample-sensor system exchanges heat with the surrounding, which is considered at temperature T_e . In order to achieve good nearly-adiabatic conditions during the variation of the magnetic field, the heat exchanged by the sample should be reduced as much as possible. The heat exchange with the surroundings can be avoided by reducing the thermal contact between the sample and the sample-holder and by using a vacuum environment and radiation shields $(K_{s-e} \rightarrow 0)$. However, this is in contrast with the necessity to change, to control and to stabilize the temperature of the sample before performing the ΔT_{ad} measurement. A compromise has to be found between these two opposite requests. Otherwise, another way to decrease the heat dissipated during the measurement is to perform quick measurements by using fast magnetic field changes. However, this case introduces other drawbacks in the measurement (see in the following).

The second problem, that needs to be tackled, concerns the temperature sensor and the thermal contact between it and the sample. Standard temperature sensors (thermocouples and resistive sensors) are electric transducers that require the achievement of the thermal equilibrium between them and the sample through a heat exchange. This heat exchange, essential to perform the temperature measurement, breaks the ideal adiabatic conditions of the sample. The amount of heat that flows from the sample to the sensor is ruled by the sensor heat capacity and can significantly affect the measured ΔT_{ad} . By considering zero the heat losses to the surrounding (K_{s-e} and $K_{t-e} = 0$), the equilibrium temperature between the sensor and the sample (T_{eq}) results from the balancing of their thermal capacities (this statement results from the calculation of the charge distribution between the two capacitances C_s and C_t of the equivalent electric circuit, Figure 4.1.b):

$$T_{eq} = \frac{C_s T_s + C_t T_t}{C_s + C_t} \tag{4.1}$$

If we consider the same initial temperature for sample and sensor (T_0) and that the temperature change of the sample, due to the application of a magnetic field, is ΔT_{ad} , the value of temperature change measured by the sensor (ΔT_{ad}^*) is:

$$\Delta T_{ad}^{*} = \Delta T_{ad} \frac{C_s}{C_s + C_t} \tag{4.2}$$

Equation 4.2 was experimentally verified in Ref. [135]. To get a correct measurement of ΔT_{ad} the ratio between the heat capacity of the sensor and that of the sample has to tend to zero. Otherwise, it is important to make a post-measurement correction of the measured ΔT_{ad} values.

Another important parameter of the temperature sensor is its response time. By considering the sample as an infinite thermal source $(C_s \gg C_t)$ at the temperature T_s , the characteristic measurement time (or measurement time constant, τ_m) required for the sensor to reach 63% of sample temperature depends on the sensor heat capacity, on the thermal conductance of the sensor-sample interface (K_{s-t}) and on the contact surface area (A) [161]:

$$\tau_m = \frac{C_t}{A K_{s-t}} \tag{4.3}$$

If we consider a temperature difference of ΔT between sample and sensor at time 0, the time profile of temperature measured by the sensor follows the function:

$$T_t(t) = T_0 + \Delta T_{ad} (1 - e^{-\frac{t}{\tau_m}})$$
(4.4)

Equations 4.3 and 4.4 are obtained by solving the heat equation of the samplesensor system or the equivalent electric circuit with $C_s \gg C_t$ and $R_{s-t} = K_{s-t}^{-1}$. The asymptotic growth function of the sensor temperature reveals that an infinite time is required to reach the thermal equilibrium between sample and sensor. However, in real measurements, the temperature is considered stable when a quasi-equilibrium state is reached. This state is defined by the finite accuracy requested in the measurement of temperature.

This behaviour is more complex in the case of direct ΔT_{ad} measurements, because the sample temperature is not constant but it changes due to the magnetic field variation. Generally, the time dependence of the recorded temperature during a ΔT_{ad} measurement is a convolution of:

- the time profile of the external magnetic field (H(t))
- the magnetic field dependence of the MCE $(\Delta T_{ad}(H))$
- \circ the response function of the temperature sensor.

The green circles in Figure 4.2 are an example of a ΔT_{ad} measurement performed on a gadolinium sample, near its Curie transition, with the experimental setup based on a Cernox resistive temperature sensor, described in Chapter 3.5. The measurement was performed by inserting the sample inside a region with a static magnetic field, through a linear pneumatic actuator. The normalized temperature change of the sample, as a function of time, is compared to the time profile of the field change on the sample (blue line, measured with a pickup coil placed near the sample). The magnetic field takes about 70 ms to sweep through the 90% of its full change. A time delay between the field profile and the measured temperature change is evident and cannot be explained with the magnetic field dependence of the MCE across a second-order transition ($\Delta T_{ad} \propto$ $H^{2/3}$ [162]). Instead, this delay results from the convolution of the magnetic field time profile with the time response of the temperature sensor. The outcome of a finite-differences heat transfer simulation of the thermodynamic system and the output of the equivalent electric circuit are reported in Figure 4.2 with the red and brown lines. These results match well with the experimental data. The electric simulation also includes the integration time of 10 ms of the lock-in amplifier that is used to perform the acquisition of the sensor signal and that causes the difference with the outcome of the thermal simulation. From these simulations, we obtain a minimum characteristic time for our experimental setup of 110 ms, which derives from the convolution of the magnetic field evolution in time (rising time of 70 ms) and of the temperature response function (characterized by a time constant of about 70 ms).



Figure 4. 2 ΔT_{ad} direct measurement of a Gd sample (green circles) normalized and compared with the corresponding magnetic field variation (blue line). The outcome of a heat transfer simulation of the thermodynamic system (red line) and the output of the equivalent electric circuit (brown line) are superimposed.

Besides the thermal features of temperature sensor, also the thermal contact between it and the sample plays an important role to define the characteristic time of ΔT_{ad} measurement and to establish its accuracy (Equation 4.3). As opposed to the response time characteristic of the field change and of the temperature sensor, which are defined by the experimental setup, the quality of thermal contact between sample and sensor can undergo significant changes. Indeed, the quality of thermal contact depends on the characteristics of the sample surface, on the extension of contact area, on the features and thickness of the conductive paste laid between sample and sensor. A poor thermal-contact between sample and sensor increases the time required to complete the temperature measurement and, thus, the dissipated heat from the sample. Achieving a good thermal contact can be difficult especially with small temperature sensors and with porous or rough samples. The use of conductive pastes or greases improves the thermal contact but it introduces a further source of heat loss, because the paste acts as a thermal mass that absorbs heat from the sample.

4.2 The sample thermal conductivity

In the discussions of previous paragraph, the sample is considered as a single body in which the MCE develops and that exchanges heat with the temperature sensor and with the surroundings. However, this is a simplified picture of real measurements. Indeed, also the thermal conductivity of the sample plays a significant role to determine the time profile of the measured temperature change. In a simplified sketch, the magnetocaloric sample can be considered as composed of several (infinite) sections in which the MCE develops and that exchange heat with the adjacent sections (Figure 4.3). Only the section in contact with the sensor directly exchanges heat with it. The heat transferred from the others sections have to cross the material in order to reach the temperature sensor. This requires a finite time interval.



Figure 4. 3 Schematic illustration and equivalent electric circuit of the experimental system to directly measure the adiabatic temperature change, by considering the effect of the MC material thermal conductivity. The grey rectangle highlights the model of the sample.

In the electric equivalent circuit the sample is approximated as a series of capacitances and current sources, connected in parallel (Figure 4.3.b). The heat transfer among the sections is ruled by the material thermal conductivity (K_s). This results in a relationship between the material thermal conductivity and the

characteristic time constant τ_m of a ΔT_{ad} measurement. Therefore, overall, the τ_m is related to the sensor thermal capacitance (C_t) , to the thermal contact $(A K_{s-t})$ and to the thermal conductivity of the sample (K_s) :

$$\tau_m \approx C_t \ \left(\frac{1}{A K_{s-t}} + \frac{1}{gK_s}\right) \tag{4.5}$$

The above result was obtained by solving the electric circuit, neglecting the heat dissipations to the environment and considering an overall effect of material's thermal conductivity K_s , corrected by a factor g, which takes into account the geometrical features of the sample that contribute to its thermal transport properties. By considering the sample as a single body with an infinite thermal conductivity, Equation 4.5 reduces to Equation 4.3.

In order to probe this expected behaviour of the time constant, adiabatic temperature change measurements were performed on two series of MC samples with different thermal conductivities. The shape and size of the samples were taken similar for all the components of the two series in order to obtain the same geometrical factor g, allowing to rescale the real thermal conductance of the samples on their thermal conductivity.

The measurements were performed with the experimental setup described in details in Chapter 3.5. A pneumatic linear actuator was used to cyclically move the probe with the sample and the thermometer between two regions with controlled temperature (T_{HOT} and T_{COLD}) and magnetic field (H_1 and H_0). In this way, Brayton cycles were reproduced, simulating operative conditions of a magnetocaloric cooling device (for details see Chapter 3.5). Each sample was cycled around the temperature corresponding to its maximum ΔT_{ad} . T_{COLD} and T_{HOT} were set about 10 K below and above the mean temperature of the cycles. The magnetic field in the two regions was $\mu_0 H_0 = 0.1$ T and $\mu_0 H_1 = 1.0$ T for the first series of samples and $\mu_0 H_0 = 0.1$ T and $\mu_0 H_1 = 1.1$ T for the second one. The first measured series of samples includes:

- 1. a gadolinium sample (Goodfellow, 99.9% pure)
- 2. a La0.67Ca0.33MnO3 sample (labelled: LCMO)
- 3. a composite made of LCMO (78 vol%) and silver (7 vol%, labelled: LCMO+Ag)
- 4. a Mn_{1.27}Fe_{0.68}P_{0.48}Si_{0.52} compound (labelled: MnFePSi)
- 5. a composite made of Mn_{1.27}Fe_{0.68}P_{0.48}Si_{0.52} and epoxy (20 wt %) (labelled: MnFePSi+epoxy)

The La-based manganite was prepared by J.A. Turcaud and K. Morrison (Imperial College London) from poly-crystalline powders synthesized by the glycine nitrate process, as presented in Ref. [163]. This manganite, crystallized in a perovskite structure, shows a reversible MCE at its Curie transition and

good mechanical properties, which permitted to reach promising results when it was tested in a refrigeration test-device [117]. A second sample was prepared by impregnating the parent LCMO with Ag, in order to increase its thermal conductivity, as described in Ref. [163].

The MnFePSi sample was prepared by F. Guillou (TU Delft) by ball-milling of elemental starting materials and solid state reaction by following the heat treatments described in Ref.s [22,164]. MnFePSi compounds are among the most promising materials for applications thanks to their considerable MCE, tuneable with the composition, which develops across their magneto-elastic transition. The Mn_{1.27}Fe_{0.68}P_{0.48}Si_{0.52} composition was selected in order to obtain a T_c similar to that of LCMO and a small hysteresis ensuring the cyclability of the MCE [81]. A composite material, characterized by a lower thermal conductivity, was prepared by mixing the MnFePSi compound with 20 wt% of a standard epoxy.

The thermal conductivities of the samples, reported in Table 4.1, were measured through the thermal transport option of the Physical Property Measurement System (PPMS) in the continuous measurement mode, at the Imperial College of London. The samples were cut, for the ΔT_{ad} measurements, with a parallelepiped shape with dimensions of about 1.5x3x5.5 mm³.

Sample	$\boldsymbol{K} (W m^{-1} K^{-1})$	$ au_m$ (s)	$ au_{msim}\left(\mathrm{s} ight)$
LCMO	1.35	0.40 ± 0.05	0.16
LCMO+Ag	2.2	0.15 ± 0.03	0.135
Gd	10	0.11 ± 0.03	0.10
MnFePSi	3.5	0.12 ± 0.03	0.10
MnFePSi+epoxy	1.25	0.20 ± 0.05	0.17

Table 4. 1 Thermal conductivity (K), experimental time constants (τ_m) and simulated time constant $(\tau_{m \ sim})$ of the first series of measured MC materials.

The second series of samples includes a La-Fe-Co-Si sintered sample and four different composites made of La-Fe-Co-Si particles and an epoxy binder matrix:

- 1. La(Fe,Co,Si)13 sintered plate (Vacuumschmelze)
- 2. Composite A (epoxy + 45 vol% of 130 µm La-Fe-Co-Si powder)
- 3. Composite B (epoxy + 45 vol% of 130 μ m La-Fe-Co-Si powder + 19 vol% of 12 μ m, 21 μ m and 57 μ m La-Fe-Co-Si powder in the ratio 1:1:1)
- 4. Composite C (epoxy + 45 vol% of 130 μ m La-Fe-Co-Si powder + 19 vol% of 12 μ m powder milled into smaller particles < 10 μ m)
- Composite D (epoxy + 45 vol% of 130 μm La-Fe-Co-Si powder + 19 vol% of milled graphite powder < 10 μm)

These samples were prepared with the cold plate pressing method, in the form of thin plates (dimensions: about $0.5x3x5 \text{ mm}^3$). The composites are a mixture of La-Fe-Co-Si powders (130 µm particles, produced by Vacuumschmelze) and, as a binder, an epoxy Amerlock Sealer (produced by Ameron). In composites B, C and D additional elements were added to the epoxy in order to increase the final thermal conductivity of the material. All the composites show a Curie transition at about 288 K. Details on sample preparation and on their properties are reported in Ref. [77]. To perform the direct MC measurements, two plates for each sample were overlapped in order to increase the thermal mass of the sample.

Sample	K (W m ⁻¹ K ⁻¹)	$ au_m$ (s)
Sintered	8.93	0.12 ± 0.01
Composite A	1.29	0.21 ± 0.02
Composite B	2.4	0.15 ± 0.03
Composite C	2.68	0.14 ± 0.02
Composite D	1.09	0.2 ± 0.04

Table 4. 2 Thermal conductivity (K) and experimental time constants (τ_m) of the La-Fe-Co-Si series of measured MC materials.



Figure 4. 4 (a) Thermomagnetic cycles performed on the samples LCMO (green diamonds) and LCMO+Ag (pink circles), with a magnetic field change of 0.9 T. (b) Enlargement of a half-cycle of the two samples normalized to the maximum ΔT_{ad} .

Figure 4.4.a shows, as an example, the beginning of a cyclical measurement performed on the LCMO and on the LCMO+Ag samples near their Curie temperature. The ΔT_{ad} of the composite sample is lower than that of the parent compound because of the presence of Ag, which acts as a passive heat capacity

during the magnetic field change. Moreover, the cycle period of LCMO+Ag is lower (9 s) than that of the parent compound (12 s). Considering that the temperature relaxation branches take about the same time, it can be concluded that the time delay for LCMO is mainly due to the adiabatic branches. This is clearer in Figure 4.4.b, which shows a half cycle for each sample normalized to its maximum ΔT_{ad} . The characteristic time of the temperature change (τ_m) of the two materials is different: LCMO reaches 63% of its maximum temperature change in 0.4 s, whereas LCMO+Ag needs only 0.15 s. The difference of time constant between the two samples can be ascribed to their thermal conductivity, which is 1.35 Wm⁻¹K⁻¹ for LCMO and 2.2 Wm⁻¹K⁻¹ for LCMO+Ag.



Figure 4. 5 Experimental time constants (blue triangles) of the temperature change as a function of the reverse of the thermal conductivity for the two series of measured samples. Yellow circles show the time constants for the first samples series calculated through heat transfer simulations. The grey lines are the linear interpolations of the data.

Cyclical measurements were performed for all the samples of the two series. The adiabatic branches of the cycles were interpolated with the exponential function 4.4 in order to obtain, for each sample, the characteristic time of temperature change. The values of τ_m , reported in Tables 4.1 and 4.2, are an average of values obtained for hundreds of subsequent cycles for each material. Figures 4.5.a and 4.5.b show the measured time constants as a function of the inverse of thermal conductivity of the materials for the two series. The reported error bars correspond to the statistical variations of the measured data. Figure 4.5.a also includes simulated time constants of the first series of samples, which were calculated by heat transfer simulations carried out by Dr. Giacomo Porcari (University of Parma) using a finite-difference explicit method (details can be found in Ref. [78]).

Both simulations and experimental results, for the two series of samples, show a linear behaviour of the time constant with the inverse of the sample thermal conductivity $\tau_m = a + bK_s^{-1}$, as expected from Equation 4.5. Indeed, the sample geometry and the experimental configuration (temperature sensor and thermoconductive paste) are the same for all the measurements. Thus the sensor thermal mass, the contribution of thermal contact and the geometrical factor can be considered constant in each series. The time constants of Gd, of MnFePSi and of the sintered sample, which are the samples with the highest values of thermal conductivity, are close to the limit defined by the response time of the experimental setup (about 0.11 s, Chapter 4.1). The increase of the time constant for the other samples is due to their lower thermal conductivity. The different slope of the linear behaviours of the two series is related to the geometrical factor.

The only sample that shows a time constant that is not in agreement with the linear behaviour and with the thermal simulations is the parent LCMO. The reason of this discrepancy is not clear and will be the subject of a future research activity. Nevertheless, it is probably related to a parasite thermal resistance of grain boundaries, which can vary among different samples and that is reduced with the addition of silver.

Instead, an opposite effect is observed in the case of the La-Fe-Co-Si composites. In this case, the interfacial thermal resistance between the epoxy matrix and the active magnetocaloric material decreases the thermal conductivity of the material and so the time constant of the temperature change. Indeed, finiteelements simulations based on a tomography image of sample A, performed by K. Sellschopp (IFW Dresden), demonstrated that the low thermal conductivity of the epoxy could not explain the large time constant observed in the composite, compared with the sintered parent sample [165]. The time constant increases due to the heat transfer between the active element and the passive matrix.

These outcomes demonstrate the not negligible role of the materials thermal transport properties, related to their intrinsic thermal conductivity and to extrinsic factors such as the presence of inter-grains thermal resistances, determining the characteristic time constant of ΔT_{ad} measurements. The increase of the time constant can affect the absolute measured values of ΔT_{ad} by raising the heat dissipated during the measurements. Moreover, this additional time delay between the magnetic field change and the measured temperature change can bring to a wrong estimation of the field-behaviour of temperature change ($\Delta T_{ad}(H)$), which is often derived from time dependent direct measurements.

On the other hand, the procedure of characterization, described in this chapter, is useful to obtain important information regarding the performance of MC materials exploitable in thermomagnetic devices. Indeed, the response time of magnetocaloric materials derived by simulating thermomagnetic cycles, is a key

parameter to predict the achievable frequency of magnetic refrigerators, which is mainly ruled by the time needed to the heat transfer between the MC active element and the transfer-fluid. From the presented results, it is clear as a low thermal conductance drastically reduces the maximum achievable operation frequencies of energy conversion devices, and thus their useful power, efficiency and cost.

4.3 Conclusions

In conclusion, this chapter presented an overview of the main issues that can significantly affect the experimental measurement of the adiabatic temperature change or bring to an ambiguous interpretation of its results. The quality of nearly-adiabatic conditions, the thermodynamic role of the temperature sensor and the thermal transport features of the sample have to be considered to design a proper experimental setup and to analyse the obtained experimental results. In particular, these features assume a primary role when the measurements are performed on samples with a small thermal mass or by using fast magnetic field changes. Moreover, these factors become relevant when the kinetic of the MCE is studied or when the field dependence of the ΔT_{ad} is derived from measurement as a function of time.

In the following chapters, these remarks are applied in order to lead to the development of two new experimental setups for the direct measurement of adiabatic temperature change in thin samples (Chapter 5) and by using pulsed magnetic fields (Chapter 6).

5. NON-CONTACT DIRECT MEASUREMENT OF THE MCE

5.1 The measurement of thin samples

One of the main limits of the magnetic cooling systems, designed and realized until now, is the slow heat exchange between the active magnetocaloric material and the working fluid. The time required to complete the heat exchange defines the maximum working frequency of cooling devices and, consequently, their power, efficiency and unit cost [9]. To optimize the heat transfer, active regenerators with a high surface-to-volume ratio have been proposed and realized. In literature are reported prototypes and projects that exploit the MC material in form of thin sheets, small balls, complex structures micromanufactured or made of composite materials, with the MC material incorporated in a high-conductive matrix [8,9,59,77,117,166,167].

In order to lead to the design of prototypes and to predict their performances, the characterization of the MCE has to be performed on materials in the real form exploited in applications. Indeed, different preparation processes and subsequent processing of the materials can change their properties (see e.g. [168,169]). Moreover, the characterization of the MCE in thin samples can be useful to design new innovative applications, such as micro or miniaturized solid-state cooling devices (e.g. [170,171]).

This request opens a challenge in the characterization of MC materials, because if on one hand the ΔS_T can be easily derived, for all samples, from standard magnetometry measurements, on the other the direct measurement of the ΔT_{ad} can be very difficult in the case of samples with a small thermal mass. Indeed, as reported in Chapter 4, the sensor thermal mass and non-perfect adiabatic conditions can significantly affect the ΔT_{ad} measurement. The complexity of performing direct MC measurements on thin samples is demonstrated by their lack in literature. Indeed, in recent literature many works can be found treating growth, structural and magnetic characterization of low-dimensional materials as thin sheets, ribbons and thin films (e.g. [172–176]). However, till today, only a few attempts to directly measure the MCE in these systems have been explored [139,140,177–179]. One proposed solution is to use non-contact measurement techniques. By removing the thermal contact between sample and sensor, the heat dissipated during the measurement decreases and better adiabatic conditions are achieved. In literature are reported some experimental setups based on thermoacoustic method [137,138] or on the optical detection of the emitted thermal radiation with thermography [139] or with an IR sensor [140]. These techniques have proved suitable for the characterization of thin samples, although some drawbacks still limit their use. Thermoacustic methods estimate the magnetic field induced temperature change by superimposing to a magnetic ac field a static or slowly sweeping dc field. The ΔT values obtained by using these techniques are demonstrated to be accurate; nevertheless, they are far from probing the material's response in adiabatic conditions and in operating-like conditions (i.e. under fast sweeping fields with the field intensity usually exploited in applications). The only presented IR-sensor-based setup directly measured for the first time the MCE of a thick film. However, this measurement was performed by using a small AC magnetic field (tens of mT). Also with this experimental setup, the response of the magnetic material to a magnetic stimulus comparable with that used in real prototypes is not directly detected. Thermocameras characterized by a good temperature resolution ($dT_{min} < 0.1$ K) are appropriate for a spatially resolved study of the material's surface temperature. However, they are very expensive, not handy to simulate thermomagnetic cycles, due to the presence of moving mechanical parts, and they cannot tolerate the presence of the magnetic field. A handy instrument, which does not need of a complex post-measurement elaboration, has not yet been proposed.

In this Chapter, a new experimental setup is presented. This new instrument, based on a non-contact temperature sensor, a thermopile, was realized with the aim of performing direct measurements of the adiabatic temperature change of thin samples. The short sensor response time and the very good quasi-adiabatic conditions, achieved thanks to the absence of contact between sample and sensor and to a specially designed sample-holder, allowed to correctly measure the adiabatic temperature change of gadolinium sheets with thickness down to $20 \,\mu\text{m}$.

5.2 A new thermopile-based setup

Thermopile temperature sensors are made of a thin photoabsorbent membrane. characterized by a small thermal mass and a low reflection coefficient, that is suspended on an array of serially-interconnected miniaturized thermocouples. The membrane exchanges heat, as thermal radiation, with the surroundings until the achievement of the thermal equilibrium. The thermocouples have one junction in contact with the membrane and the other in contact with a heat sink at the base of the sensor. A variation of the membrane temperature, respect to the sensor case, causes a voltage signal (by Seebeck effect), which is amplified by the serial connection of the junctions. The output signal of the sensor is proportional to the incident heat-flux and consequently to the temperature of the emitting body. The calibration of the sensor is usually performed through a black-body emitting simulator. The response times of these sensors, typically of the order of milliseconds, depends mainly on the thermal mass of the membrane. The membrane and the array of thermocouples are usually locked in a hermetically-sealed package, with a silicon window, which allows the transmission of the IR thermal radiation. The electronic noise, mainly of Johnson type, is generally low. This permits to reach a very good sensitivity, if an accurate calibration procedure is performed and the temperature of the sensor case is kept constant. However, the emissivity coefficient of the emitting bodies and the geometrical configuration of the measurement can introduce relevant errors in the temperature measurement. Indeed, emissivity coefficient values lower than 0.6 leads to a different thermal equilibrium state, due to the balance of the absorbed and emitted thermal radiation from the sensor, which can be approximated by a black body. Moreover, the geometrical configuration of the measurement has to be carefully considered to obtain a correct estimation of the temperature. Radiation emitted from the background or from other bodies can be absorbed by the membrane if the angle of view of the sensor is not completely covered by the studied material or if the sample is semitrasparent or very reflective [161]. Nevertheless, the small dimensions, the mechanical stability, the good sensitivity and the very low cost (of the order of tens of euro) make these temperature sensors very useful.

Our new experimental setup is based on a commercial thermopile (ZTP-135SR of General Electric Company), which is composed of a $0.7 \times 0.7 \text{ mm}^2$ photoabsorbing membrane placed on the top of an array of 60 junctions. A silicon window (diameter 2.4 mm) allows the transmission of the thermal radiation with a wavelength between 6 µm and 16 µm and defines a view angle of 90°. The time constant of the sensor has been experimentally estimated by placing an optical chopper between the sensor window and a copper plate kept at a constant temperature, which acts as a source of constant IR radiation (Figure 5.1.a). In this way, the sensor receives an IR square-wave. The time constant is considered as the time needed for the sensor signal, at every half-period, to reach 63% of its maximum value (Figure 4.1.b). The obtained time constant is 27 ms. It has to be noticed that the minimum time required for achieving the maximum signal value is about 85 ms and hence the operative frequency limit, in case of simulation of thermomagnetic cycles, should be about 6 Hz.



Figure 5. 1 (a) Sketch of the experimental setup used to measure the response time of the thermopile. An optical chopper is inserted between the thermopile and a copper plate (on the left), kept at a constant temperature. (b) Response curve of the thermopile exposed to a square wave, obtained chopping the IR radiation emitted from the copper plate.

The experimental setup, designed for adiabatic temperature change measurements, is schematically showed in Figure 5.2. The structural part of the instrument is composed of a long plate of copper, water-cooled, which acts as a multipurpose optical bench, on which one can align the temperature sensor and the sample holder. The plate is inserted in a cylindrical vacuum chamber (diameter: 22 mm, maximum vacuum: 10-5 mbar), which can be placed in between the poles of a low-inductive electromagnet that is able to generate a maximum magnetic field of 2.4 T. The sensor and the sample are placed in a copper box $(8x9x7 \text{ mm}^3 - \text{see Figures 5.2.b and 5.2.c})$, closed on the top with a brass plate thermally connected to the box by a thermoconductive paste (Arctic Silver Ceramique, k = 7 Wm⁻¹K⁻¹). The sensor is inserted in a face of the box and thermally connected with it in order to keep both at the same temperature. The sample is suspended at the centre of the box with a frame of nylon wires. This solution allows to reduce the thermal contact between the sample and the environment and, so, to minimize the heat lost because of conductive dissipation. The sample is placed 1 mm away from the sensor so that a minimum surface of $4.5x4.5 \text{ mm}^2$ is enough to fully cover the view angle of the sensor. This helps to reduce the error due to background radiation. The longer axis of the sample is positioned parallel to the magnetic field to minimize the effects of shape anisotropy.



Figure 5. 2 Sketch of the experimental setup. (a) Vacuum chamber with the optical copper bench. (b) Copper box with the sensor (on the right side), the sample and the copper finger (on the left side). (c) Top view of the sketch b). (d) Diagram of the electronic control system.

A thermoelectric module, located under the box and in contact with the watercooled plate, and a Pt100 sensor allow to control and stabilize the box temperature (T_b) between 260 K and 350 K (see Figure 5.2). The temperature stabilization is made through an ITC503 Temperature Controller (Oxford Instruments). A thermoconductive paste ensures a good thermal contact between the box and the module.

The magnetic field change is obtained by switching on and off the electromagnet, which takes about 1 s to reach its maximum field (H_{max}) . The time constant of the exponential rise (63% of H_{max}) is lower than 0.3 s. The field change is controlled through a DAQ board (National Instruments BNC-2120) and synchronized with the signal acquisition by a dedicated control program developed in Matlab.

The output signal of the sensor is amplified and filtered with a notch filter ($f_0 = 50 \text{ Hz}$) and a low-band filter ($f_t = 200 \text{ Hz}$), then acquired through the DAQ at a sampling frequency of 10 kHz (Figure 5.2.c). It was verified that the magnetic field does not perturb the thermopile response. A short spike of electric noise appears, however, during the field change. This noise, independent of the sensor signal, is subtracted from the measurements.

The calibration of the sensor is performed for each sample, placing in contact with the back side of the sample, by a thermoconductive paste, a thermally controlled copper finger (thermal bath) with a Pt100 sensor and a resistive heater (on the left of the copper box in the sketch of Figure 5.2.b). An ITC503 temperature controller (Oxford Instruments) is used to stabilize the temperature of the finger, independently of T_b (which is kept constant), within 0.01 K. The calibrations are obtained by sweeping the temperature (on heating and on cooling) with a rate lower than 0.5 Kmin^{-1} to minimize the thermal gradient between copper finger and sample. The short temperature range (about 5 K above T_b) of every calibration makes possible to fit the obtained V(T) curve with a linear function T(V) = aV + b. Small variations of the coefficients have been observed on repeating the calibration. This contributes with an error of 0.1 K to the measured temperature. To reduce the error due to background IR radiation we repeated the calibration at every T_b . During the measurement of the adiabatic temperature variation, the copper finger is removed from the box and the sample remains thermally insulated from the environment.

This calibration procedure allows to reduce the errors in the temperature measurements due to different surface emissivity, which is peculiar of every measured specimen and depends on the emissivity coefficient, the surface area and state and the emitting angle. An alternative solution to overcome this drawback could be to cover the surface with a thin layer of black paint in order to maximize and standardize the emissivity for every sample to be measured. This allows using the same calibration when measuring different materials [139]. In this way however, we measure the temperature change of the black paint and not the direct effect of the sample surface [180,181].

5.3 Direct measurement of thin sheets

The instrument reliability has been tested by measuring the $\Delta T_{ad}(T)$ of a gadolinium bulk sample (Goodfellow 99.9% pure, dimensions: $5x3x2 \text{ mm}^3$, mass: 252 mg) induced by an internal magnetic field change $\mu_0 \Delta H = 1.75 \pm 0.1$ T. This value was estimated considering a demagnetizing factor of 0.2 and an external magnetic field of 1.9 ± 0.1 T. Figure 5.3 shows the comparison between the measured $\Delta T_{ad}(T)$ values, those obtained on the same sample by the setup for direct measurement based on a Cernox bare-chip temperature sensor (described in Chapter 3.5), and those derived by integrating in-field DSC data (Chapter 3.4) by using Equation 2.12.



Figure 5. $3 \Delta T_{ad}$ (T), in a $\mu_0 \Delta H=1.75 \pm 0.1$ T, for a bulk sample of gadolinium obtained from: present setup (green circles), probe based on a Cernox temperature sensor described in Chapter 3.5 (squares) and in-field DSC (line), described in Chapter 3.4. The dashed lines represent the error-bars on ΔT_{ad} deduced from elaboration of DSC measurement.

The agreement between the data demonstrates the reliability of the absolute ΔT_{ad} values obtained with the presented experimental setup. It can be also appreciated from Figure 5.3 that the direct techniques show smaller error-bars when compared to those obtained from calorimetry (dashed lines in Figure 5.3), which have been calculated following the standard method described in Ref. [127]. This confirms the suitability of the direct techniques for estimating the MC effect.

In order to probe the capability of this experimental setup to measure thin samples, which is the aim that led its development, ΔT_{ad} measurements have
been performed on a gadolinium sheet by progressively reducing its thickness (down to 13 µm). We preferred to smooth progressively the same starting sheet (Goodfellow, 99.9% purity, initial thickness: 100 μ m, surface: 5.7×7.0 mm²) to rule out the effect of unknown impurities content when comparing the ΔT_{ad} of samples with different thicknesses. Figure 5.4.a shows a single measurement of ΔT_{ad} at 292 K of a sample 58 ± 2 µm thick (mass: 18.0 ± 0.1 mg) for a magnetic field change $\mu_0 \Delta H = 2.00 \pm 0.05$ T. The magnetic field profile, measured with a Lakeshore 460 3-channel Hall-effect gaussmeter, is superimposed to the measurement. It can be appreciated that the sensor does not introduce a relevant delay in the measurement since its response time is faster than the magnetic field rise-time. Moreover, the relaxation of the sample temperature, after the application of the magnetic field, is very slow compared to the field change and that suggests the excellence of the adiabatic conditions achieved during the measurement. The ΔT_{ad} obtained (3.9 ± 0.2 K) is in agreement with other data reported in literature [62,138], considering the strong dependence of the effect from the presence of impurities and Gd oxide [182], emphasized in this case by the large surface-to-volume ratio.

The measured ΔT_{ad} of the same sheet with five different thicknesses (80 ± 2 µm, 58 ± 2 µm, 37 ± 2 µm, 27 ± 2 µm, 13 ± 2 µm) for $\mu_0 \Delta H = 1.00 \pm 0.05$ T and 2.00 ± 0.05 T are reported in Figure 5.4.b. All the measurements have been performed at 292.0 ± 0.2 K, at which temperature the MC effect is maximum. It can be observed that the measured values (3.8 ± 0.2 K, 2.2 ± 0.2 K) are constant within the experimental error down to 27 µm. The thinner sample (13 µm) shows a decrease of the measured effect due to the heat lost during the field sweep (field rise time $t \sim 1$ s).



Figure 5. 4 (a) Direct ΔT_{ad} measurement of a gadolinium sheet (58 µm thick) in $\mu_0 \Delta H = 2.0$ T both switching the field on and off. The magnetic field profile (red line) is superimposed to the temperature profile of the sample (green points). (b) ΔT_{ad} of a gadolinium sheet as a function of its progressively reduced thickness for $\mu_0 \Delta H = 1.0$ T (cyan circles) and 2.0 T (blues triangles). The results of a numerical simulation of the thermodynamic system (grey lines) are superimposed to the experimental data.

5.4 Heat transfer simulations

Heat transfer simulations have been performed to better explain the experimental results and to make a prediction about the possibility of measuring thinner samples. The thermal conductance within the material was considered much higher than the one between sample and environment. This fact allowed to assume a spatially uniform temperature inside the sheet. Two contributions to the heat exchange of the sample were taken into account: the MCE as a heat source developing inside the sheet for a time interval equal to the rise time of the external field (W_{MCE}) and the heat dissipated through radiation (W_{irr}). The first quantity was calculated by using the isothermal entropy change (ΔS_T) obtained from magnetic measurements by applying the Maxwell equation (Equation 2.3): $Q_{MCE} = \Delta S_T mT$, where m is the sample mass. Its time rate (Equation 5.1) has been obtained considering that the temperature variation is proportional to the applied field as reported in Ref. [162].

$$W_{MCE}(t) = Q_{MCE} \frac{1}{H_{max}^{2/3}} \frac{dH(t)^{2/3}}{dt}$$
(5.1)

The second contribution is the heat radiated from the sample surface:

$$W_{irr}(t) = \varepsilon \sigma S \left(T(t)^4 - T_b^4 \right) \tag{5.2}$$

where S is the sample surface, $\varepsilon = 0.3$ its emissivity, $c_p \approx 315$ Jkg⁻¹K⁻¹ an average of its specific heat over a small temperature range around the transition [135], T_b the box temperature and σ the Boltzmann constant. The temperature profile of the sample as a function of time has been calculated using equation (5.3).

$$T(i+1) - T(i) = \frac{(W_{MCE} - W_{irr})\Delta t}{c_p m}$$
(5.3)

The emissivity ε of gadolinium has been obtained through a best-fit of the decreasing part of the measured T(t), corresponding to the thermal relaxation after the peak value (see Figure. 5.5).

The outcome for a 27 µm thick gadolinium sheet ($m = 8.4 \pm 0.1$ mg) and a magnetic field change $\mu_0 \Delta H \ 1$ T is shown in Figure 5.5. The simulation follows the experimental data during the whole duration of the experiment. From these results, we can derive two conclusions. The first one is that the heat dissipated from the sample during the field change is negligible (less of the instrumental

error) thanks to the excellent quasi-adiabatic conditions achieved with this setup. This allows to perform properly the direct ΔT_{ad} measurement of a Gd sheet 27 µm thick, without the need of post-measurement corrections. Secondly, the experimental configuration makes negligible the heat dissipated as conduction and convection. The main source of heat losses is the emitted thermal radiation.



Figure 5. 5 Experimental (green points) and simulated (black line) temperature profiles of a gadolinium sheet (thickness: $27\mu m$) during and after a magnetic field change ($\mu_0 \Delta H = 1.0 T$).

The simulation has been repeated changing the thickness of the sheet to obtain the estimation of the maximum expected ΔT_{ad} by reducing the thermal mass of the sample. This calculation, reported in Figure 5.4.b (grey lines), confirms that just below a thickness of 20 µm the radiation heat losses prevent a correct estimation of the sample temperature change. To measure even thinner samples the only solution is to reduce the rise time of the magnetic field sweep together with the total measurement time-scale, provided to have a sensor with a response time shorter than such rise time.

The simulation presented above can be used to predict the fraction of detectable ΔT_{ad} as a function of the measurement time-scale. Keeping fixed the sheet surface ($S = 5.6 \text{x}7.0 \text{ mm}^2$), the simulation has been repeated, for every thickness, decreasing the time constant (τ) of the exponential field sweep:

$$H(t) = H_{Max}(1 - e^{-\frac{t}{\tau}}).$$
 (5.4)

The sensor response time has been considered negligible compared to τ . Figure 5.6 shows the fraction of ΔT_{ad} , which may be picked up in samples of gadolinium with thickness between 1 mm and 10 nm and with magnetic field time constants ranging from 10^2 s to 10^{-4} s. The black points represent the maximum time scale required to measure at least 95% of the ΔT_{ad} for a given thickness. This threshold

is imposed by a relative experimental error of about 5%. The area under this curve shows the combination of field time constant and sample thickness that allows the almost full measurement of ΔT_{ad} . The five cyan points drawn in Figure 5.6 represent the experimental measurements on the five thicknesses of the gadolinium sheet. As experimentally verified, four of these are enough to measure, within the experimental errors, about 95% of the ΔT_{ad} . The thinnest sample, instead, falls significantly above the curve. In this case we report $\Delta T_{ad} = 3.3 \pm 0.2$ K, equal to 87% (±5%) of ΔT_{ad} measured in the thicker sample, for which the heat dissipation during the field sweep is negligible.



Figure 5. 6 Simulation of the detectable fraction of ΔT_{ad} as a function of the sample thickness and time constant of the field change in case of gadolinium sheets. The black points mark 95% of ΔT_{ad} , while the cyan points are the experimental results also reported in Figure 5.4.b. Inset: linear dependence of the time constant of the field sweep as a function of the volume to surface ratio.

The inset of Figure 5.6 has been added to underline the proportionality between the time constant required to measure at least 95% of ΔT_{ad} and the sample volume-to-surface ratio (V/S). This outcome can be obtained by integration of Equation (5.3). The MCE is approximated as linearly dependent on the external magnetic field, while the heat emitted through radiation is considered proportional to the temperature difference between sample and environment (this is allowed for small temperature variations [183]).

$$t_{95\%} = (1 - 95\%) \frac{2c_p \rho}{\varepsilon \sigma T_b^3} \frac{V}{S}$$
(5.5)

This relation pinpoints that, for samples with large heat capacity and low transition temperature, the full ΔT_{ad} can be measured with longer time constants of the field change. On the other hand, in samples characterized by large surface, high emissivity and high transition temperature, radiation losses will be more pronounced, thus requiring faster field sweeps. In the case of first order transitions, which may be as well measured with this setup, the presence of latent heat would increase the ratio between the heat generated inside the sample and that dissipated from it, improving the quasi-adiabatic conditions and allowing the measurement of even thinner samples. This analysis, reproducible for different sample dimensions, materials and field sweeps, helps to figure out useful clues to design new experimental setups able to measure thinner systems.

5.5 Conclusions

In conclusion, in this chapter it was presented a new experimental setup, based on a commercial thermopile sensor, able to directly measure the magnetocaloric effect of bulk and thin sheet samples. This non-contact technique allows to reproduce very good quasi-adiabatic conditions needed to pick up the absolute ΔT_{ad} in gadolinium sheets as thin as 27 µm without the need of a complex postmeasurement elaboration. Simulations of the measurement system confirmed the experimental results and predicted the time-scale of the magnetic field change required for measuring thinner samples. Moreover, these calculations showed that in case of first order materials even thinner samples could be successfully measured thanks to the contribution of latent heat.

The designed technique is an ideal solution both to directly measure the MCE of samples with reduced thickness and to reproduce high frequency (up to 6 Hz, as deduced from the total response time of the sensor) thermomagnetic cycles for testing the material response in operating conditions. The use of thermopiles moreover can be extended to measure directly other caloric effects in thin samples. The proposed non-contact technique, when studying Electrocaloric, Barocaloric and Elastocaloric effects [115], may become an undeniable solution to isolate the temperature sensor from electric or mechanic stresses thus improving the measurement quality and the lifetime of the technique.

6. FAST MEASUREMENTS WITH PULSED MAGNETIC FIELDS

6.1 Fast magnetocaloric measurements

Why should we be interested in direct characterization of MCE induced by fast magnetic field changes?

The previous Chapter demonstrated that, even if good adiabatic conditions are achieved, the direct measurement of the MCE in very thin samples requires the reduction of the time needed to complete the magnetic field variation. Therefore, it is necessary to perform direct adiabatic temperature change measurements on short time scales. Moreover, performing fast MC measurements is fundamental to test the materials response to fast magnetic field stimuli and, consequently, to evaluate their exploitability in high frequency thermomagnetic cycles. Furthermore, fast measurements can be used to simulate, in a short time period, the whole lifetime of the MC materials subjected to cyclical transformations and to check the stability of their performances. Finally, fast measurements can give information about the kinetics of magnetic transitions.

The practical realization of fast direct MC measurements is not trivial. If on one hand, the adiabatic conditions are promoted by fast field changes, on the other hand the response time of temperature sensor can significantly affect the estimation of the ΔT_{ad} and the observation of possible kinetic effects. Different experimental setups were proposed in literature. All of them exploit pulsed magnetic fields to achieve fast field changes (usually in the time scale of milliseconds). The majority of reported experimental setups use thermocouples to detect the temperature variations of the sample [132,133,141]. Though this is the simplest solution, the response time of thermocouples depends on their dimensions and on the quality of the contact with the sample and it can introduce spurious effects on the measurement (a detailed analysis about this issue is reported in Chapter 6.2). An alternative solution was proposed by T. Kihara et al. and it consists in growing a thin-film resistive thermometer directly on the sample surface [184]. This method ensures a prompt time response of the temperature sensor but it requires a complex preparation of the samples that is not easy to reproduce with porous or irregular samples.

In this Chapter, a new solution is proposed. By exploiting a thermo-optical effect, named "Mirage Effect", an innovative experimental setup was built with the aim to directly probe the MC response of materials on magnetic field changes of the time order of milliseconds. This instrument allows to observe the dynamic response of magnetic phase transitions and to simulate operating conditions of a hypothetical machine performing thermomagnetic cycles up to 100 Hz.

6.2 Thermocouples and pulsed magnetic fields: an example

Thermocouples are the most used temperature sensors to perform direct MC measurements, thanks to their small size, low cost, good sensitivity and the ease of their signal acquisition and processing. However, their response time can be a problem in the case of fast magnetic field changes. Indeed, though their response time is shorter if compared to other standard temperature sensors, it can hardly drops below the milliseconds scale. As presented in Chapter 4.1, the thermocouples response time depends on their thermal mass and on the quality of the contact with the sample. The thermal mass of the junction is reduced by using very thin electrical wires. Instead, the sample-sensor thermal contact depends mainly on the area of the contact surface, which is reduced by the spherical shape of the thermocouples, and on the conditions of the sample surface. Moreover, the heat dissipated trough the metallic wires of the sensor increases the time needed to reach thermal equilibrium. All these elements make difficult to predict and to control the real response time of each different sensor and measured sample. If the response time is larger or comparable with the characteristic time of the field change, this introduces a delay in the temperature measurement that affects the final estimation of ΔT_{ad} and the evaluation of possible kinetic effects intrinsic of the studied material (as demonstrated in Chapter 4.1 for a resistive temperature sensor and a slow field change).

In order to verify this hypothesis, we compared heat transfer simulations and magnetic measurements with pulsed magnetic field performed on a Mn_3GaC sample with fast direct MC measurements reported in Ref. [185] (details about the sample preparation and its main characteristics are reported in Ref. [186]). This material, which crystallizes in an antiperovskite structure, displays a Curie transition at 246 K and a first-order magnetostructural transition at about 165 K between a low-temperature antiferromagnetic phase and a high-temperature ferromagnetic phase (details are reported in Appendix A). To this transition, characterized by a volume change without a variation in the crystal structure, is related a considerable inverse MCE [186]. Direct temperature change measurements, performed with pulsed magnetic fields, showed that the temperature variation of the material across the first-order transition is not able to follow a magnetic field change rate of 1000 Ts⁻¹ [185]. The authors explained this experimental observation with an intrinsic delay of the transformation induced by a so high fast magnetic field change.

In order to study the thermal system used to perform the direct measurements of MCE, heat transfer simulations were performed. The considered thermal system is a variant of the schematization reported in Figure 4.1 and it includes only the sample and the sensor, placed in ideal adiabatic conditions (Figure 6.1.a). All the heat exchanges with the surroundings are neglected. The sample is characterized by a temperature T_s and a thermal capacitance C_s much greater than that of the sensor C_t , so that the sample is treated like an infinite heat source with respect to the sensor. The temperature sensor, a chrome-constantan thermocouple, is schematized as a sphere placed inside the sample. It is characterized by a radius r, a temperature T_t and a thermal capacitance ($C_t = 4/3\pi r^3\rho c_t$) calculated starting from the average of the density (ρ) and of the specific heat (c_t) of chrome and constantan. Thus, the contact area between sample and sensor corresponds to the full sensor surface $A = 4\pi r^2$. The thermal contact conductance coefficient is difficult to be correctly estimated, and therefore we took a high value ($\alpha = 100$ kW m⁻² K⁻¹), lying within the range of values reported in literature for thermal contact between two pressed solid surfaces [187].



Figure 6. 1 (a) Sketch of the model considered to perform heat transfer simulations. (b) Time profile of the pulsed magnetic field utilized in simulations. (c) Corresponding sweep rate of the field.

The pulsed magnetic field profile, which is considered applied at the sample, is reported in Figure 6.1.b. The magnetic field pulse has a maximum amplitude of 10 T and a rise time of about 1 ms. The maximum sweep rate of the field is 15000 Ts⁻¹, during the increasing part of the pulse; the decrease of the field follows a lower field sweep rate (Figure 6.1.c).

Simulations were carried out by considering the magnetic field be applied at the material near its Curie transition and near its inverse first-order transition. In the case of the Curie transition, the temperature of the sample varies with the applied magnetic field ($\Delta T_{ad} \propto H^{2/3}$). According to [185], we considered a maximum ΔT_{ad} of 2 K for a $\mu_0 \Delta H = 10$ T at 258 K. The field profile of the simulated temperature change in the sample, expressed by Equation 6.1, is reported with the red line in Figure 6.2.a.

$$T_s(H) = T_{start} + \Delta T_{max} \frac{H^{2/3}}{H_{max}^{2/3}}$$
(6.1)

Instead, when the magnetic field is applied at a temperature lower than the critical temperature of the first-order transition, the sample temperature does not change until a critical field H_{c1} is reached (see the blue line in Figure 6.2.a). Beyond this field, the transition starts and it is mainly completed in a magnetic field change of about 0.3 T (ΔH_{trans}) [185]. During the transition, an inverse MCE occurs. When the field decreases, the opposite effect develops at a different critical field H_{c2} , due to the presence of hysteresis. Following [185] and considering a starting temperature of about 150 K, we took a critical field H_{c1} = 2.6 T, by increasing the field, and $H_{c2} = 1.4$ T by decreasing the field. The maximum considered $\Delta T_{ad max}$ was 4 K. For simplicity, the transition was considered to occur over a 0.3 T field span with the temperature varying linearly with the field. The ΔT_{ad} was considered entirely reversible by applying and removing the field.

for
$$H_{c1} < H < H_{c1} + \Delta H_{trans}$$
 $T_s(H) = T_{H_{c1}} + \Delta T_{max} * \frac{H - H_{c1}}{\Delta H_{trans}}$ (6.2)

The time profile of the intrinsic temperature of the sample during the application of the pulsed field in adiabatic conditions was calculated (Figure 6.2.b) by considering the time profile of the magnetic field pulse (Figure 6.1.b) and the dependence of the sample temperature with the field $T_s(H)$ (Equations 6.1 and 6.2).



Figure 6. 2 (a) Sample temperature change as a function of the applied magnetic field for the second- (red line) and the first-order (blue line) magnetic transition. (b) Time profile of the sample temperature change near the second- (red line) and the first-order (blue line) magnetic transition.

After that, the contribution of the sensor, which measures the temperature, was simulated. A finite elements method was utilized to simulate the heat transfer between the sample and the sensor during the application of the magnetic field.

The outcomes of the simulations are reported as a function of time in Figures 6.3.a and 6.3.b and as a function of magnetic field in Figure 6.4.

Simulations were repeated considering different radii of the temperature sensor. Indeed, if we solved analytically the thermodynamic equation of the thermodynamic system with a step-like temperature drop of the sample we obtain that the characteristic time constant of the sensor is ruled by its specific heat, its density, its radius and the thermal conductance at the interface:



 $\tau = \frac{c_t}{\alpha A} = \frac{c\rho 4/3\pi r^3}{\alpha 4\pi r^2} = \frac{c_s \rho}{3\alpha} r$ (6.3)

Figure 6. 3 Sensor temperature change for the case of the second- (a) and the first-order (b) magnetic transition, obtained by finite-elements thermal simulations. Three temperature sensors are considered with different radius (r_i) . The temperature curves are superimposed to the magnetic field profile (grey dashed line).



Figure 6. 4 Temperature change as a function of the applied magnetic field for the secondorder (T = 258 K) and the first-order (T = 150 K) magnetic transition. The temperature curves, measured by three different sensors, are compared with the intrinsic temperature change of the sample (black dashed line).

By changing the radius of the thermocouple in the simulation, we are considering an increase of its thermal capacitance or a worsening of the thermal contact between it and the sample. Figures 6.3 and 6.4 report the results for three different values of sensor radius: 1.0, 4.0 and 10.0 μ m.

In the case of the MCE near the Curie temperature (Figure 6.3.a), we do not observe a clear difference between the outcomes of the three temperature sensors. On the contrary, in the case of the first-order transition (Figure 6.3.b) we appreciate a delay in the $T_t(t)$ measured by the biggest sensor. This difference becomes more evident if we plot the temperature change as a function of the magnetic field (Figure 6.4). The black dashed lines represent the intrinsic sample temperature as a function of the magnetic field in the case of a first- and a second-order transition. For the sample near T_c we observe a lenticular shape of the $\Delta T(H)$ curve for the biggest sensor (orange line), while the other two sensors show a small delay with respect to the sample temperature. On the contrary, in the case of the first-order transition the very strong field-dependence of temperature change brings to a time delay for the response of all the sensors, which increases with their radius. We observe also that in the decreasing part of the field pulse the delay is not so evident due to the lower field sweep rates. These simulated behaviours in the case of the first-order transition look very similar to the experimental results reported in Ref. [185] and they confirm the possibility that the characteristics of temperature sensor can affect the measurements.

Magnetic measurements with pulsed magnetic fields have been performed on a Mn₃GaC bulk sample in order to understand if the time-delay observed in ΔT_{ad} measurements reported in Ref. [185] is due to an intrinsic effect of the material's transition or it may be due to the temperature sensor. The measurements were performed at the IMEM-CNR Institute of Parma by Dr. R. Cabassi. The sample was placed inside a compensated pick-up coil, which signal, detected during the application of the magnetic field pulse, is proportional to the first time derivative of the sample magnetization. The magnetic field pulse is characterized by a rise time of about 0.4 ms. The peak amplitude of the field pulse is controlled, up to 25 T, by adjusting the capacitors bank voltage (Figure 6.5.a). The maximum sweep rate of the magnetic field is larger than 80000 Ts⁻¹. During the decreasing part of the field pulse, the sweep rate is lower and it is similar for all the applied voltages (Figure 6.5.b). The measurements were performed on a bulk sample in the temperature region near its first-order magnetic transition. Before performing each measurement, the sample was cooled down to 80 K to reset the low temperature phase. Once stabilized the temperature in the cryostat, the measurement was performed only after waiting further 15 minutes.

Measurements performed at different temperatures (136 K, 139 K and 151 K) and magnetic field sweep rates (70000 T/s, 50000 T/s and 30000 T/s) are reported in Figures 6.6.a and 6.6.b, respectively. In all the cases, the transition appears very sharp both on increasing and on decreasing the magnetic field, in agreement with the measurements reported in Ref. [188]. The transition starts and ends in a field interval of about 0.8 T. The values of critical field obtained from the performed measurements are comparable to the values reported in [185,188]. A small shift of the critical field is observed by increasing the magnetic field sweep rate. This can be explained considering the possible presence of a skin effect (with the used magnetic field sweep rates the penetration depth is of the order of a few millimetres) or, more simply, by small variations in the starting temperature of the measurement that significantly affect the critical field. The lenticular shape of the curves in the ferromagnetic region is due to a non-perfect compensation of the pick-up coil.



Figure 6. 5 (a) Time profile of the pulsed magnetic field by varying the capacitors bank voltage. (b) Corresponding sweep rates.



Figure 6. 6 (a) M(H) of a bulk Mn_3GaC sample, measured with a pulsed magnetic field (the field profile is shown with the brown line in figure 5.5.a) starting from different temperatures. (b) M(H) measurements performed at T = 151 K by changing the magnetic field sweep rate.

Anyhow, no broadening of the transformation, due to a possible kinetic delay, has been observed also with the used magnetic sweep rates, two times larger than the rate of the pulsed magnetic field exploited in measurements reported in Ref. [185]. These results, together with the thermal simulations, presented at the beginning of this paragraph, suggest that the use of thermocouples can be critical in measurements with pulsed magnetic fields. It is not possible to separate with certainty the effect due to the sensor and a time lag due to the intrinsic kinetics of the transformation. An alternative explanation for these results could be the existence of two different characteristic-times for the firstorder magneto-structural transformation and for the energy exchange between the structural and the vibrational systems. However, there are not, until now, experimental evidences of this hypothesis.

In conclusion, we argue that the reliability of direct measurement of ΔT_{ad} by using a contact temperature sensor in pulsed magnetic fields is limited by the response time of the sensor, due to its thermal mass and to the thermal contact between it and the sample. An alternative experimental solution has to be found to perform this kind of measurements with high reliability.

6.3 The Mirage Effect: a new way to perform fast MCE measurements

In the previous paragraph, it was demonstrated that the temperature sensor is a critical element in ΔT_{ad} measurements performed by using pulsed magnetic fields. Standard sensors can significantly affect measured values and the field dependence of the MCE.

In the following, an innovative and versatile non-contact setup for the MC characterization with pulsed magnetic fields is described. This new experimental setup is based on a thermo-optical effect, named "Mirage Effect", which consists in the deflection of a light beam by a thermal gradient. This effect has been already exploited to measure the thermal diffusivity and the thermo-optical absorption spectrum of materials (photothermal spectroscopy) [189–192]. In these experimental methods, the material's temperature change, induced by optical absorption or resistance heating, produces a time varying gradient of the refractive index in the surrounding medium (usually air), which can be detected by the deflection of a probe laser beam passing through the air layer immediately adjacent to the sample surface (Mirage Effect). Moreover, ultrasensitive techniques (thermal lensing spectroscopies) exploit this effect to measure the temperature change that is produced in a transparent sample (typically a

solution) by a laser pulse, as a result of non-radiative relaxation of the absorbed energy. By using fast pulsed laser beams, these techniques are used to study the kinetics of thermal-activated chemical and biological processes [193,194].

Our new experimental setup derives from the merging of the experimental solidstate photothermal techniques and of the experiences of kinetics studies by thermal lensing spectroscopies. The mirage effect gives the possibility to perform a fast measurement of the temperature rise of MC materials and so to test the kinetics of their magnetic transitions induced by a pulsed magnetic field.

Figure 6.7 shows a sketch of the realized experimental setup. It consists of a laser, a sample holder, a coil and an optical detector. The probe beam is a red ($\lambda = 632.8 \text{ nm}$) helium-neon laser, characterized by a long-term amplitude stability and low noise. The sample is glued with an insulating varnish onto a sample holder, whose temperature can be controlled and stabilized by a resistive heater and a Pt100 temperature sensor, complemented with an ITC503 temperature controller (Oxford Instrument). The sample holder is inserted inside a small coil (external diameter 3 cm) and mounted onto a micropositioning device, which allows an accurate alignment of the sample surface parallel to the laser beam. The magnetic field is generated by the controlled discharge of a capacitors bank (details on the pulsed magnetic field are reported in the following paragraph). Different magnetic field pulses of maximum amplitude $\mu_0 H = 1.2$ T and a rise time between 1 and 3 ms can be generated by varying the capacitance and the geometry of the coil (see below for details).

A single element silicon photoconductive detector picks up the deflection of the laser beam. In front of the sensor, a pinhole (0.5 mm diameter) is used to select only a small portion of the laser beam profile. A Hall probe tracks the magnetic field pulse and triggers the acquisition of the photodetector. The output signal of the detector is acquired, amplified and filtered by an oscilloscope. Between sample and detector, two mirrors extend the optical path of the laser beam as to amplify the resultant deflection at the detector position.

From geometric optics theory of photothermal spectroscopy, the deflection angle of the probe beam (Φ) in one dimension can be written as [195]:

$$\Phi(y,t) = \frac{1}{n} \frac{dn}{dT} \frac{\partial T(y,t)}{\partial y} d$$
(6.4)

where *n* is the refractive index of the deflecting medium, dn/dT is the temperature coefficient of the refractive index and *d* is the length of the laser path across the temperature gradient (in this case *d* is the sample length since each part of the sample experiences the same temperature change). For small

temperature variations, dn/dT can be assumed constant, while the temperature gradient $(\partial T/\partial y)$ is a function of sample temperature. The deflection angle (Φ) , and thus the change of intensity (ΔI) at the detector position, therefore depends on the temperature and on the length of the sample. When Φ is small, ΔI is directly proportional to Φ since a small portion of the Gaussian profile of the laser beam section at the detector position can be approximated as linear.



Figure 6. 7 Sketch (a) and photos (b,c,d) of the developed setup for direct ΔT_{ad} measurements with pulsed magnetic fields. On the top of the sketch: details of the sample holder inserted onto the coil and mounted above a micro positioning device. The magnetic pulsed field generates a temperature variation of the sample that deflects the laser beam, aligned close to its surface, of an angle Φ .

This allows us to assume that the measured laser intensity change by the photodetector (as a voltage signal ΔV) is proportional to the temperature variation of the sample (ΔT). This proportionality has been verified by measuring the ΔT_{ad} of a Gadolinium sample across its Curie transition (292 K) as a function of the amplitude of the magnetic field pulse (Figure 6.8). The achieved results are comparable with those obtained with the experimental setup based on a Cernox temperature sensor (Chapter 3.5). By using the Gd sample as reference material, the proportionality constant between the measured ΔV and the ΔT of the sample is obtained. Through this calibration, the absolute temperature change of the sample, induced by the magnetic field pulse, can be derived from the measured variation of the detector output (ΔV), provided that the calibration and measurements are carried out with the same geometrical configuration of the experimental setup (positions of laser beam, sample and detector).



Figure 6. 8 Voltage drop of the photodiode signal induced applying the magnetic field pulse with different amplitudes ($\mu_0 H$) at a Gd sample. The voltage drop is proportional to $\mu_0 H^{2/3}$.

The small measurement time constant is the key feature of this experimental setup. It is ruled mainly by the heat transfer through the medium in contact with the sample surface. The characteristic time for heat exchange between the sample surface and a point at a distance h in the deflecting medium is $\tau \approx h^2/4\alpha$, where α is the thermal diffusivity of the medium [196]. Considering that the present technique operates in air ($\alpha = 1.9 \cdot 10^{-5} \text{ m}^2 \text{s}^{-1}$) and that the laser beam is positioned within h = 0.1 mm above the sample surface, the resulting characteristic time constant of this setup can be calculated as $\tau \approx h^2/4\alpha \approx 0.5$ ms. Simulations of heat transfer and experimental tests carried out positioning the laser beam farther away from the sample surface confirm that the time constant (τ) is of the order of tenths of ms, making this experimental setup suitable to study the material's response at frequencies of hundreds of Hertz. In

these experimental conditions, we also estimated that the Joule heating induced by eddy currents in a Gd sample is less than 0.1 K.

6.3.a A portable system to generate pulsed magnetic fields

In order to generate the pulsed magnetic field, a laboratory-scale portable apparatus (overall dimensions: $20 \times 10 \times 8 \text{ cm}^3$) was realized. The magnetic field is generated by discharging a capacitors bank on a coil. Three different capacitors banks (*b*1, *b*2 and *b*3; with a capacitance of 18.70 mF, 2.20 mF and 0.47 mF, respectively) and three different coils (*coil*1, *coil*2, *coil*3; with inductance of about 4.4 10^{-4} H, 3.0 10^{-5} H, 6.2 10^{-6} H, respectively) were realized. The coils have a maximum external diameter of 35 mm, a length of 14 mm, an internal hole of 10 mm and they are composed of 180, 80 and 12 turns of an enameled copper wire with 1 mm diameter. The intensity and the characteristic time of the magnetic field are varied, as shown in Figure 6.9.a by changing the coil and the capacitors bank. In particular, the rise time of the magnetic field pulse depends on the inductance of the coil (*L*) and on the capacitance of the capacitors bank (*C*) (see the inset of Figure 6.9.a) [197]:

$$\tau_0 \propto \sqrt{LC} \tag{6.5}$$

With the combination of available coils and capacitances, the characteristic time can be varied from less than 1 ms to about 3 ms.

Instead, the peak intensity of the magnetic field pulse depends on the capacitance, on the voltage applied at the capacitors (V) and on characteristic factors of the coil-capacitors system (the inner radius of the coil (a_1) , a geometry factor $(\Phi(\alpha,\beta))$ and an attenuation factor k(d), which is a function of the damping factor $d = R^2 C/4L$, for more details see [197]). By fixing the coil features and the capacitance, the intensity of the magnetic field pulse is ruled by the applied voltage.

$$H_{max}(d) = V \sqrt{\left(\frac{2C}{a_1^3}\right)} k(d) \Phi(\alpha, \beta) \propto V$$
(6.6)

The linear behaviour of the maximum magnetic field with the applied voltage was experimentally verified and it is shown in Figure 6.9.b. The voltage does not modify the rise time of the magnetic field pulse (Figure 6.9.b). All the reported measurements were performed with a Lakeshore 460 Hall probe gaussmeter with the probe placed at the centre of the coil. With the same apparatus, the spatial homogeneity of the field was checked: within the coil, a region of about 1 cm along the coil axis shows a field homogeneity better than 10%.

An electronic circuit (reported in Figure 6.10) together with an Arduino Uno board is utilized for controlling the charge (through a relay) and the discharge (through a SCR) of the capacitor bank on the coil.



Figure 6. 9 (a) Time profile of magnetic field pulse generated by varying the capacitance of the capacitors bank and features of the coil. Inset: linear relationship between the characteristic time of the pulsed magnetic field and the root of LC. (b) Time profile of the magnetic field pulse by varying the voltage of the capacitors bank. The inset shows the linear dependence of the peak amplitude of the pulse with the applied voltage.



Figure 6. 10 Schematic of the control circuit of the pulsed magnetic field.

6.4 Response of Fe₂-based compounds to milliseconds magnetic stimuli

The experimental setup based on the mirage effect was exploited to test the MCE response to field changes on the millisecond time-scale of two Fe₂P based compounds: MnFeP_{0.45}As_{0.55} (As-sample) and Mn_{1.25}Fe_{0.7}P_{0.45}Si_{0.55} (Si-sample). These compounds are very promising materials for magnetic cooling thanks to ideal magnetocaloric properties, with large values of ΔT_{ad} and ΔS_T , and to a critical temperature tuneable with the composition [79,81,22,164,198]. The Assample is the precursor of the modern Si-substituted Fe₂P-based material family [79]. It displays a GMCE across the Curie transition at about 300 K. Its large MCE is due to a field-induced first-order isosymmetric magneto-elastic transition between a ferromagnetic and a paramagnetic phase [79]. The Sisample belongs to the family of (Mn,Fe)₂(P,Si) compounds that show a tuneable phase transition by partially substituting Mn for Fe and Si for P. The sample studied in this work, displays a weak first-order transition, characterized by a small jump in the lattice parameters at the transition [34,198]. Si-sample shows a lower thermal hysteresis (~ 0.4 K) and a lower dependence of the transition temperature with the applied magnetic field $(dT_t/dH = 3.1 \text{ KT}^{-1})$ compared to As-sample (Hyst. ~ 1.8 K and $dT_t/dH = 5.3$ KT⁻¹). Both samples exhibit a large and completely reversible MCE in a magnetic field change of 1 T near room temperature ($\Delta S_{T max} = 8.9 \pm 0.3$ Jkg⁻¹K⁻¹ at 305.5 K for the As-sample and $\Delta S_{T max} = 6.8 \pm 0.5 \text{ Jkg}^{-1}\text{K}^{-1}$ at 311.3 K for the Si-sample). Details on the samples preparation and on their magnetic, thermodynamic and MC properties, obtained from magnetometric and in-field DSC measurements, are reported in Appendix В.

Here, we report the results of direct adiabatic temperature change measurements of the two samples performed by means of the experimental setup based on the mirage effect. These measurements were done in order to probe the samples' response to a magnetic field change with a rate higher than 700 Ts⁻¹ and an amplitude ($\mu_0 \Delta H_{max} = 1$ T) typical of magnetic refrigeration prototypes. Figure 6.111 shows the output of the photodiode (ΔV), as a function of time, for a single measurement performed on the As-sample at 302 K. The same behaviour was found for the measurements performed on the Si-sample. The signal is normalized to the maximum ΔV and it is superimposed to the magnetic field profile. A delay of about 0.3 ms is evident between the detected signal and the magnetic field pulse profile, while the overall shapes of the two curves match well except for their "tails" on the right side. This delay between the detector signal and the magnetic field pulse corresponds to the characteristic time for heat exchange between the sample surface and the air layer to occur. This outcome highlights that, even in the fast dynamic regime, the heat transfer between the material and the surroundings is slower than the materials' response to the external field pulse, as previously observed for other systems at lower frequencies [199]. The faster decrease of temperature with respect to the reduction of the magnetic field is likely to be caused by the combination of the cooling due to the MCE and of the heat transfer to the sample holder.



Figure 6. 11 Normalized variation of the photodiode signal (green line) during the application of the magnetic field pulse (pink line) at the As-sample at 302 K.



Figure 6. 12 $\Delta T_{ad}(T)$ of the As-sample (a) and the Si-sample (b) directly measured with the mirage-based setup (blue squares) and with the Cernox based probe (Chapter 3.5) characterized by a rise time of the magnetic field of about 100 ms (red circles) or 1 s (yellow triangles). In all measurements: $\mu_0 \Delta H = 1$ T.

Figures 6.12.a and 6.12.b show the thermodynamic response of the two samples to the same magnetic field pulse ($\mu_0 H_{max} = 1$ T and $\tau = 1.3$ ms) as a function of temperature. The peak values of the measured ΔT_{ad} is 2.3 ± 0.2 K at 301.2 K for the As-sample and 1.3 ± 0.2 K at 308.3 K for the Si-sample, comparable with values reported in Ref.s [164,200]. The detector noise is the main source of error

and it induces an uncertainty on the measured ΔT_{ad} of about ± 0.2 K, while other sources of error (i.e. integration over the length of sample and proportionality between ΔI and Φ) are estimated to be negligible.

The results obtained with the mirage-technique (blue squares) are compared in Figures 6.12.a and 6.12.b with the measurements performed on the same samples with the setup, based on a resistive Cernox temperature sensor, described in Chapter 3.5. These latter direct measurements have been carried out by varying the magnetic field ($\mu_0 \Delta H = 1 \text{ T}$) in two different ways: moving the sample inside a static magnetic field by means of a pneumatic piston (field sweep $\approx 100 \text{ ms}$, red circles in Figure 6.14.a) or turning on a low inductive electromagnet (field sweep $\approx 1 \text{ s}$, yellow triangles in Figures 6.14.a and 6.14.b). The three measurements, characterized by different rise times of the magnetic field, give consistent results.

These measurements probe the magnetocaloric response of the two different Fe₂P-based materials to fast magnetic field pulses simulating high frequency (hundreds of Hertz) operating conditions. We observed that the response of these materials to different magnetic field change rates (1 Ts^{-1} , 10 Ts^{-1} , 750 Ts^{-1}) is the same. This means that the time for heat exchange within the material and from the material to the surroundings is longer than the intrinsic magnetocaloric response to the external field pulse. Thus, on the explored time scale there is no lag in the response to the magnetic field due to the dynamics of the phase transition (i.e. magnetocaloric effect) itself, making these materials capable of operating at the frequencies required for efficient magnetic refrigeration.

Moreover, this work shows that it is possible to correctly measure the dynamic response of very fast first-order phase transitions using a non-contact technique for the temperature measurement.

6.5 Direct magnetocaloric characterization of NiMn(In,Sn) ribbons

The experimental setup based on the mirage effect introduced in the previous paragraphs, does not just allow to probe materials' response to fast magnetic field changes but also permits the direct MC characterization of thin samples. Indeed, this technique combines a short measurement time with the absence of a thermometer in contact with the sample, reducing in this way the heat losses from the sample during the measurement (see Chapters 4 and 5). These features promote the direct measurement of the MCE in samples with a reduced thermal mass, which are not measurable with standard techniques.

In this paragraph, a direct MCE characterization of NiMn(In,Sn) ribbons is reported. The direct measurement of the ΔT_{ad} is required to probe the real MCE

of materials in form of thin sheets, which can be exploited as efficient active cooling elements in magnetic cooling devices (Chapter 2.2). The characterization of bulk materials with the same nominal composition does not ensure a correct estimation of the MCE in samples with different shapes and that have been subjected to different synthesis processes. Indeed, it was demonstrated that the materials processing routes can significantly alter their magnetic properties (see e.g. [168,169]). This effect has specially to be taken in consideration in the case of materials whose magnetic and MC properties are affected by the microstructure and by the presence of structural defects or chemical disorder, as in the case of Heusler alloys [201–204].

In the following, the results of direct ΔT_{ad} measurements are reported for a series of five Ni₅₀Mn₃₅(In_{1-x}Sn_x)₁₅ Heusler alloys, with x = 0, 0.25, 0.5, 0.75, 1 (the samples are labelled respectively: Sn0, Sn25, Sn50, Sn75, Sn100). This series of samples originates from the Ni₅₀Mn₃₅In₁₅ composition, which shows a considerable MCE at its Curie transition, little above room temperature [108]. Its saturation magnetization, about half of that of Gd, is the maximum observed for this class of alloys with a second-order transition near room-temperature and derives from the Mn and Ni magnetic moments. The substitution of In with Sn drastically reduces the starting cost of the material (more than 30 times) and gives the possibility to modify the transition temperature.

The samples were prepared in form of ribbons (thickness of about 10 μ m) with the melt-spinning technique (described in Chapter 3.1). All the ribbons were treated at 1073 K for 2 h in Ar atmosphere and subsequently they were quenched in cold water. This synthesis process results in a granular microstructure containing multiple shapes with a grains size that varies between a few micrometres and a few tens of micrometres (see Appendix C for details on sample preparation and on microstructural features of the ribbons).

Their composition, measured through energy dispersive spectroscopy (EDS) microanalysis, is shown in Table 6.1. The reported errors are the standard deviations calculated by repeating the EDS analysis on different points of the samples surface. A systematic and non-constant reduction of the Mn content is observed with respect to the nominal composition. Moreover, inhomogeneities (up to 0.7 at. %) were detected for the Mn and Ni contents. These inhomogeneities increase by raising the content of Ni (sample Sn75).

The five studied alloys present a stable austenitic phase in a large temperature range around room temperature (powder X-rays diffraction analysis of the alloys is reported in Appendix C). All the alloys show a second order magnetic transition from a ferromagnetic to a paramagnetic state near room temperature. The Curie temperature varies with the In/Sn ratio from 286.5 K (Sn0 sample) to 331.8 K (Sn100). On the contrary, their saturation magnetization progressively

decreases with the increase of Sn content (see Appendix C for details on magnetometric measurements). Sample S25 shows anomalous values of saturation magnetization and Curie temperature, probably due to the higher content of Mn with respect to the others samples. The isothermal entropy change (Figure 6.13), calculated from magnetometric measurements by applying the Maxwell relation, follows the composition dependence of saturation magnetization.

Sample	Composition (at.%)				
	Ni	Mn	In	\mathbf{Sn}	
Sn0	53.8 ± 0.4	31.2 ± 0.5	$15.0{\pm}0.1$	/	
$\mathbf{Sn25}$	52.1 ± 0.2	33.9 ± 0.2	10.5 ± 0.1	3.5 ± 0.1	
$\mathbf{Sn50}$	52.8 ± 0.4	32.7 ± 0.3	7.2 ± 0.1	7.3 ± 0.1	
$\mathbf{Sn75}$	54.2 ± 0.6	31.5 ± 0.7	3.5 ± 0.1	10.8 ± 0.2	
Sn100	52.6 ± 0.4	33.0 ± 0.2	/	14.4 ± 0.2	

Table 6. 1 Composition of the five $Ni_{50}Mn_{35}(In_{1-x}Sn_x)_{15}$ alloys, determined by EDS analysis and expressed as at.%. The reported error is the standard deviation estimated by mapping the composition on different points of the samples surface.



Figure 6. 13 Isothermal entropy change of the five alloys as a function of temperature calculated for a $\mu_0 \Delta H = 1$ T from isofield M(T) measurements.

The direct measurement of the adiabatic temperature change as a function of temperature of the five samples was performed with the setup based on the mirage effect. A pulsed magnetic field with an amplitude of 1 T and a characteristic time of 1.3 ms was used. Results are reported in Figure 6.14.a. The ΔT_{ad} shows a small decrease with the substitution of In, from $\Delta T_{ad} = 0.8 \pm 0.1$ K of the In-sample (S0) to $\Delta T_{ad} = 0.6 \pm 0.1$ K of the Sn-sample (S100), following the

behaviour of the isothermal entropy change with composition. The maximum value of the In-sample is lower than that of the corresponding bulk sample $(\Delta T_{ad} = 1 \pm 0.1 \text{ K}, \text{ discussed in Chapter 8})$, accordingly to the reduction of the saturation magnetization. The shape and the width of the $\Delta T_{ad}(T)$ curves are the same for the five samples and are comparable with those of the starting bulk alloy (described in Chapter 8) and of Gd. The comparison of the curves, normalized to their maximum values, is reported in Figure 6.14.b. All the curves collapse on the same, as predicted for the MCE across a second-order transformation [20].



Figure 6. 14 (a) Adiabatic temperture change in a $\mu_0 \Delta H = 1$ T as a function of temperature measured with the mirage-based setup. (b) Comparison between the normalized ΔT_{ad} (T) curves of the ribbons and those of bulk Gd and of a bulk Ni-Mn-In sample (Bulk, Chapter 8).

The obtained results demonstrate that it is possible to easily tune the peak of the MCE effect also across a second-order transformation near room temperature, and thus to realize, with these alloys, high-performance layered cooling elements. The high thermal conductivity of these metallic alloys and the possibility to realize thin foils promote the realization of cooling elements with high heat-exchange coefficients. However, the maximum MCE is still too low to really utilize these compositions in efficient devices. An increase of the saturation magnetization together with a reduction of the transition temperature could bring to a real use of these alloys as active elements in magnetic refrigerators.

From the instrumental point of view, it was demonstrated the suitability of the presented experimental setup, based on the mirage effect, to correctly and easily perform direct magnetocaloric characterizations of thin samples. To my knowledge, there are no other experimental techniques that can directly measure the adiabatic temperature change of a single ribbon a few micrometres thick, with a magnetic field change of the order of 1 T.

6.6 Conclusions

In summary, in this Chapter it was presented an innovative, simple and versatile non-contact temperature change measurement technique, based on the mirage effect, aiming at testing the response of magnetocaloric materials to fast magnetic field pulses, in this way simulating high frequency operating conditions. It has been shown that Fe₂P-based compounds not only present excellent standard magnetocaloric properties, but also an outstanding dynamic response, making them ideal for applications. The measurement technique itself represents a breakthrough: the measurement time constant is reduced below one millisecond allowing the measurement of the material's response in extreme operating conditions (1 T at a frequency of about 150 Hz). Moreover, its short measuring time ensures good adiabaticity, making this technique suitable for characterizing samples with low dimensionality (foils, ribbons and free-standing films), which represents a challenge using conventional techniques.

SECTION C - EXPERIMENTAL WORK

REDUCTION OF THE MAGNETOCALORIC EFFECT DUE TO BROADENING OF MAGNETIC TRANSITIONS

The search for suitable materials to be used in efficient magnetic cooling devices has converged to compounds, critical elements free, which show a weak first-order transition with a tuneable critical temperature near room temperature. The magnetization variation at the transition and the latent heat of the transformation have been optimized in a trade-off between large MC properties and a weak hysteretic character, in order to ensure a large effect exploitable in cyclical processes. However, to increase even more the materials performances and to reduce the necessary magnetic field change, another parameter has to be considered: the width of magnetic transitions. Indeed, the broadening of the transition, caused by intrinsic or extrinsic factors, can result in a significant alteration of the MC properties of materials.

In this section, the effect of the transition broadening on the MCE across first-order magnetic transformations is discussed on the basis of a phenomenological model of the transformation. The general outcomes of the model are compared with experimental results on a series of Heusler alloys across their magnetostructural transformation. Heusler alloys represent intriguing materials, in which the numerous potentialities, given by the flexible structure, clash with the difficulties to accurately control their properties. Together with the large hysteresis of the transition, which reduces the MCE exploitable in thermomagnetic cycles, also their large transformation width has a not negligible effect in reducing the MCE induced by relative low magnetic field changes.

The second part of this section, instead, reports about the negative effect of the broadening of magnetic second-order transformations. General conclusions, resulting from mean-field simulations, are followed by the analysis of a specific case: the degradation of the MCE at the Curie transition of Mn-based Heusler alloys caused by cold working. The effect on the magnetic and magnetocaloric properties of a manual crushing and subsequent heat treatments of a NiMnIn Heusler alloy are reported. The results of this study suggest a tight correlation between the magnetic system of the alloys and its microstructural features, which are deteriorated by the mechanical stresses induced with the cold working.

This work underlines that the detrimental effects of post-synthesis processes of materials have to be carefully analysed in the perspective of realizing complex high surface-area structures or smart composites for heat exchangers.

7. BROADNESS OF FIRST-ORDER MAGNETOSTRUCTURAL TRANSITIONS

7.1 From theory to real materials

Since a Giant Magnetocaloric Effect was discovered in the Gd₅Si₂Ge₂ compound. a great attention has been paid on materials showing first-order magnetic transitions near room temperature (Chapter 2.3). Indeed, though some drawbacks hinder their use in cooling devices, their MCE is much higher than that observed across second-order transitions, giving the possibility to increase the power and efficiency of magnetic refrigerators. As discussed in Chapter 2.1. the main parameters determining the intensity of the MCE at a first-order magnetic transition are the latent heat (L) of the transformation, the sensitivity of the transition temperature (T_t) to the applied magnetic field (dT_t/dH) and the magnetization change between the two phases at the transition (ΔM). The latent heat is characteristic of the first-order nature of the transition and it is related to the energy barrier at the transformation [205]. It fixes the maximum entropy change obtainable with a complete phase transformation. While, the maximum adiabatic temperature change is mainly determined by the sensitivity of the transition temperature to the external magnetic field, which depends on the coupling of the external magnetic field with the magnetic moments of the two phases and on the energy differences between the two phases. A large difference in magnetization between the two phases increases the shift of the transition temperature. Contrariwise, a large energy difference between the two phases, highlighted by a large latent heat of the transformation, makes difficult the shift of the transition temperature. So, a huge magnetization jump and an adequate value of latent heat are essential to design promising MC materials with a firstorder transformation [22].

However, these requirements are not enough to design promising GMCE materials. There are mainly two others key parameters that have to be considered: the hysteresis and the broadness of the transition. The hysteretic character of first-order transformations may drastically reduce the MCE exploitable in thermomagnetic cycles. Recently, many efforts have been made to study the origins of the hysteresis in MC materials and to design solutions for its reduction (see e.g. Ref.s [28,35,36,104]). Contrariwise, the width of transformation has been only marginally considered. Nevertheless, it has a primary role in determining the fraction of MCE exploitable with a definite magnetic field and the minimum magnetic field necessary to induce a complete phase transformation. Figure 7.1 shows a comparison between a schematization

of the MCE at an ideal first-order transition (a complete discussion is reported in Chapter 2.1) and experimental measurements performed on a $(Ni,Co)_2Mn(Ga,In)$ alloy across its first-order magnetostructural transformation. The jump discontinuities, theoretically predicted in magnetization and entropy at the critical temperature (Figures 7.1.a and 7.1.b), are not observed in the measured M(T) and in the entropy curves S(T) calculated from DSC data (Figures 7.1.d and 7.1.e, see Chapter 3.4 for experimental details).



Figure 7. 1 First row: schematization of temperature dependence of magnetization (a), entropy (b) and MCE (c) of an ideal "inverse" first-order magnetic transition. Second row: experimental data of a Ni42Co₃Mn₃₂Ga₁₄In₃ Heusler alloy. (d) Magnetization as a fuction of temperature under different applied magnetic fields. (e) Entropy versus temperature curves derived from in-field DSC data. (f) $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ for a $\mu_0 \Delta H = 1.8 T$.

Moreover, from Figures 7.1.c and 7.1.e it is evident as the broadening of the transformation has a direct effect on both $\Delta S_T(T)$ and $\Delta T_{ad}(T)$. Considering an ideal first-order transformation and assuming the same specific heat for the two phases, we expect a constant $\Delta S_T(\sim L/T)$ in the temperature range between the critical temperature at zero field (T_0) and that one under the applied magnetic field (T_1) (Figure 7.1.c). Instead, the $\Delta T_{ad}(T)$ shows an increasing value between T_1 and T_0 and reaches its maximum $(\sim \Delta H(dT_t/dH))$ at T_0 . This maximum value increases with the increase of the applied magnetic field until a field value enough to induce the complete phase transformation $(\Delta T_{ad_max} \sim L/c_p)$. Equation

2.9, Chapter 2.1). The broadening of the transformation reduces and spreads over a large temperature range both $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ (Figure 7.1.f).

Moreover, we have to consider that a broad first-order transformation requires larger magnetic field changes to complete the phase transformation and, accordingly, to exploit entirely the MC potentiality of materials. Looking at some of the most promising first-order MC materials we observe that the typical magnetic field used in cooling devices (~ 1 T) is often not enough to complete the phase transformation, with a resulting decrease of MCE, especially under adiabatic conditions (see e.g. Ref.s [91,22,206,207]). This is mainly due to the broadening of the transformation and it was observed also for pure single crystals [23,208]. This effect is more evident in the case of materials characterized by a large transition width, as is the case of the martensitic transition of Heusler alloys [90,134,158,209]. A deep study on the effect of the transition broadness on MCE and on the factors affecting such width could bring to a better control of materials' MC properties and to their improvement.

In this chapter, the effect of the transition broadness on the MCE is studied in a series of (Ni,Co)₂Mn(Ga,In) Heusler alloys showing a first-order magnetostructural transformation. The experimental results are discussed on the basis of a phenomenological model of the transformation built in the entropytemperature plane. This model provides a useful tool to correlate the MC parameters with a few thermodynamic and thermomagnetic features of the transformation, giving a general overview on the effect of the transition broadness on MCE. Moreover, in the second part of this Chapter, the correlation between the width of the transformation and the reversibility of the MCE in hysteretic transformations is discussed together with the role of possible factors in affecting the broadness. Finally, the Chapter reports a preliminary study performed on a martensitic transformation of a Heusler alloy with the aim of defining the length-scale characteristic of the transformation width.

7.2 A case of study: a series of NiCoMnInGa Heusler alloys

The effect of the transition broadening on the MCE across first-order magnetic transformations was investigated in a series of In- and Co-doped Mn-rich NiMnGa Heusler alloys. These alloys show a first-order magnetostructural transformation between a ferromagnetic cubic phase (austenite) and a low-symmetry, low-magnetization, low-temperature phase (martensite), at which an inverse GMCE is associated [93,210,209,211] (for details see Paragraph 2.3.e). The addition of Co and In allows to maximize the magnetization discontinuity at

the transformation and to reduce the critical temperature [209]. The possibility to explore several compositions and elements substitutions makes Heusler alloys very flexible systems, whose properties can be tuned and optimized for specific applications. However, the preparation of off-stoichiometry compositions increases the complexity of the material and can bring to problems of chemical homogeneity, chemical ordering and secondary phases growth (see e.g. Ref.s [212–214]). This can substantially modify the width of the structural transformation. Moreover, the large structural mismatch between martensite and austenite and the sensitivity of the transformation to microstructural features can contribute to the smearing of the transformation [102,215]. Leaving, for now, the discussion about the factors affecting the broadness of the transformation (see Chapter 7.5), we highlight only that Heusler alloys are, among the most promising MC materials, the ones that show the largest values of transition width. For this reason, they were selected for the present work.

The four studied (Ni,Co)₂Mn(Ga,In) samples have similar compositions, similar critical temperatures and a similar inverse magnetocaloric effect across their magnetostructural transformation. The samples, of general formula Ni_{50-x}Co_xMn_{50-y}(Ga,In)_y were prepared by arc-melting the starting elements and annealing the as-cast buttons for 72 h at 1173 K (details are reported in Chapter 3.1). Their composition, reported in Table 7.1, was experimentally determined through energy dispersive spectroscopy (EDS) microanalysis.

Sample	Composition (at.%)					
	Ni	Со	Mn	Ga	In	
S1	42.4 ± 0.2	7.1 ± 0.2	33.0 ± 0.2	15.3 ± 0.2	2.3 ± 0.2	
S2	41.7 ± 0.2	8.6 ± 0.3	32.3 ± 0.4	14.1 ± 0.2	3.3 ± 0.2	
$\mathbf{S3}$	40.0 ± 0.3	10.8 ± 0.2	31.4 ± 0.2	16.5 ± 0.2	1.4 ± 0.2	
$\mathbf{S4}$	41.7 ± 0.2	8.1 ± 0.3	33.3 ± 0.4	13.8 ± 0.2	3.2 ± 0.2	

Table 7. 1 Composition, measured by EDS analysis and expressed as at.%, of the four considered Heusler alloys. Reported error is the standard deviation estimated from compositional maps; the lower bound to the error is the instrument uncertainty of $\pm 0.1\%$.

Figure 7.2 shows the thermomagnetic analysis (TMA) of the four samples, performed with a purpose-built susceptometer (Chapter 3.3 for details). The temperature dependence of the magnetic susceptibility displays the presence, for all the samples, of a similar transformation between a paramagnetic-like martensite, characterized by a negligible null signal of the susceptibility, and a ferromagnetic austenite, evidenced by the high susceptibility region in the TMA curves. The evident thermal hysteresis reveals the first-order nature of this

transformation. The transformation temperatures, reported in Table 7.2, are all above room temperature and in a narrow interval, ranging between 350K for sample S2 and 388K for sample S1. At higher temperatures, between 430 K (sample S1) and 476 K (sample S3), the TMA curves show the Curie temperature of the austenite, which is mostly influenced by the Co content. Instead, the Curie transition of the martensite (not shown in Figure) occurs well below room temperature between 170 K and 223 K. We can also appreciate, from this preliminary thermomagnetic characterization, which among the four samples there are differences in the width and shape of the structural transformation.



Figure 7. 2 AC susceptibility as a function of temperature. To improve redability only the temperature range 300-500 K is displayed.

	T _{C Mart} (K)	$T_{CAust}(K)$	$T_{A-M}(K)$	Тм-а (К)
$\mathbf{S1}$	223	430	374	388
$\mathbf{S2}$	205	440	326	351
$\mathbf{S3}$	170	473	350	375
$\mathbf{S4}$	198	433	346	367

Table 7. 2 Magnetic (T_{CMart} , T_{CAust}) and structural (T_{A-M} , T_{M-A}) critical temperatures, estimated as the inflection points of the susceptinility curves.

Powder X-ray diffraction patterns, collected for each sample in a wide temperature range across the transformation, confirmed the presence of the structural transformation between the cubic austenite and a tetragonal martensite. The temperature dependence of the diffraction patterns proves the coexistence of the two phases in a large temperature interval, in agreement with the broadness of the structural transformations observed in TMA measurements (more details are reported in Appendix D).

Thermodynamic and thermomagnetic properties of the samples were explored through in-field calorimetric measurements, which were carried out by means of a homemade Differential Scanning Calorimeter (DSC), based on thermoelectric modules (described in details in Chapter 3.4). Figure 7.3 shows the temperature dependence of the heat flux measured for the four samples with temperature sweeps on heating and cooling at a rate of 2 K min⁻¹ in zero (solid lines) and in a 1.8 T applied magnetic field (dashed lines). The reported heat flux is normalized to the samples mass. DSC measurements were performed also under an applied magnetic field of 1 T but they are not shown in the graphs for clarity. The firstorder martensitic transition is displayed by the presence of a peak in the heat flux profile, which is due to the latent heat of the transformation. The large width of the peak confirms that the transitions is spread over a large temperature span. The peaks of the profiles collected on heating and on cooling are separated by the thermal hysteresis of the transformation. Whereas the magnetic field, as expected for inverse MCE alloys, promotes the high-temperature magnetic phase, thus shifting the transformation to lower temperature.



Figure 7. 3 In field DSC measurements of the four samples: heat flux as a function of temperature in $\mu 0H=0$ T (solid lines) and 1.8 T (dashed lines) measured with temperature sweeps on heating (red lines, right arrows) and on cooling (blue lines, left arrows).

The normalized heat flux values, measured before and after the transformation, correspond to the specific heat of the martensite and austenite phase, which is nearly the same for the four samples ($c_{pM} \approx 480 \text{ Jkg}^{-1}\text{K}^{-1}$ at 300K and $c_{pA} \approx 570 \text{ Jkg}^{-1}\text{K}^{-1}$ at 400K), and shows a slow variation with temperature. From the

shift of the heat flux peaks, we can deduce the values of dT_t/dH , which are reported in Table 7.3 for the transition on heating. The dT_t/dH calculated from the measurement performed with 1 T and 1.8 T applied magnetic field are the same, confirming that, up to 1.8 T, the transition temperature shift is proportional to the applied magnetic field. The peaks shape, width and height are different for each sample and does not seem to be correlated with the stoichiometric composition. The area under the peaks corresponds to the latent heat (L) of the fully transformed phase, which can be calculated by integrating the specific heat data after subtraction of the baseline between the start and finish temperature of the transformation (Chapter 3.4). The calculated latent heat values are comparable to those measured in samples with similar composition [209]. Other details on the thermodynamic properties of the studied samples are reported in Appendix D.

	T_p	L	dT₊/µ₀dH	Hyst.	FWHM
	(K)	(J kg ⁻¹)	(K T-1)	(K)	(K)
$\mathbf{S1}$	385.0 ± 0.3	2600 ± 80	-2.4 ± 0.6	10.4 ± 0.6	3.1 ± 0.3
$\mathbf{S2}$	351.9 ± 0.5	4700 ± 140	-4.6 ± 1.0	16.7 ± 1.0	10.0 ± 0.8
$\mathbf{S3}$	381.4 ± 0.5	4450 ± 130	-4.5 ± 1.0	21.5 ± 1.0	11.0 ± 1.0
$\mathbf{S4}$	366.6 ± 0.5	5150 ± 150	-3.5 ± 1.0	16.9 ± 1.0	7.7 ± 0.7

Table 7. 3 Thermodynamic and thermomagnetic features of the first-order transition of the four samples as obtained from DSC data: transition temperature (T_p) and latent heat of the transformation (L) in zero applied magnetic field on heating, magnetic field dependence of the transition temperature on heating $(dT_t/\mu_0 dH)$, thermal hysteresis in zero applied field (Hyst.) and transition width (FWHM, full width at half maximum of the heat flux peak at zero magnetic field on heating).

The comparison between zero and in-field specific heat data gives the possibility to obtain a complete MC characterization of the samples. The integration of the calorimetry data provides the entropy–temperature curves across the transition at different magnetic fields (Chapter 3.4). The adiabatic temperature change $\Delta T_{ad}(T)$ and the isothermal entropy change $\Delta S_T(T)$ are deduced from the obtained S(T) curves. The errors correlated with this numerical manipulation of specific heat data were estimated following the discussion reported in Chapter 3.4. The temperature behaviours of $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ for a $\mu_0 \Delta H$ of 1 T (yellow squares) and of 1.8 T (red triangles) are reported in Fgure 7.4. For clarity, the figure reports only the $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ calculated from measurements performed with temperature sweeps on heating. These results were compared to the $\Delta S_T(T)$ values derived from magnetic measurements using the Maxwell relation and to the $\Delta T_{ad}(T)$ directly measured with the probe described in Chapter 3.5 (see Appendix D). For all the samples, the results obtained from the different techniques turn out to be consistent, as we have already demonstrated in Ref. [125]. The peak values $\Delta S_{T peak}$ and $\Delta T_{ad peak}$ for a magnetic field span $\mu_0 \Delta H$ of 1.8 T across the transformation on heating are shown in Table 7.4 (the values for a $\mu_0 \Delta H$ of 1 T are reported in Appendix D). The $\Delta T_{ad peak}$ values measured in these samples are the highest among all the Ga-based Heuslers [125,209,210].



Figure 7. 4 $\Delta T_{ad}(T)$ and $\Delta S_T(T)$ for $\mu 0 \Delta H = 1$ T (yellow squares) and 1.8 T (red triangles) calculated from DSC data on heating.

	$\begin{array}{l} \pmb{\Delta S_{Tfull}} \\ (\mathrm{Jkg}^{\text{-1}}\mathrm{K}^{\text{-1}}) \end{array}$	$\Delta S_{T \ peak}$ (Jkg ⁻¹ K ⁻¹)	$\frac{\Delta S_{T peak}}{\Delta S_{T full}}$ (%)	ΔT _{ad max} (K)	ΔT _{ad peak} (K)	$\frac{\Delta T_{ad peak}}{\Delta T_{ad max}}_{(\%)}$
$\mathbf{S1}$	6.8	6.2 ± 0.5	91	-4.3	-2.5 ± 0.2	58
S2	13.4	7.7 ± 0.8	57	-8.3	-3.3 ± 0.3	40
$\mathbf{S3}$	11.7	6.5 ± 0.9	56	-8.1	-3.1 ± 0.4	38
$\mathbf{S4}$	14	7.5 ± 0.8	54	-6.3	-2.9 ± 0.3	46

Table 7. 4 Comparison between peak values of $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ in a $\mu_0 \Delta H = 1.8$ T, calculated from DSC data, and the maximum expected values ($\Delta S_{T full} \approx L/T_p$, $\Delta T_{ad max} = \Delta H(dT_t/dH)$).

Looking at Table 7.4, we observe that for all samples, the measured $\Delta S_{T peak}$ for a $\mu_0 \Delta H$ of 1.8 T results lower than the maximum entropy change of the fully induced phase, estimated from latent heat $\Delta S_{T full} \approx L/T_p$, where T_p is the temperature corresponding to the peak of the heat flux. This means that a magnetic field of 1.8 T is not enough to fully induce the transformation in these samples. Furthermore, there is no a close relationship between $\Delta S_{T peak}$ and $\Delta S_{T full}$ values: for instance, S4 has the biggest $\Delta S_{T full} = 14 \text{ Jkg}^{-1}\text{K}^{-1}$ among the four samples, but it shows a $\Delta S_{T peak}$ lower than that of S2. This fact underlines that further quantities characterizing the transition play a role in determining the ΔS_T and ΔT_{as} of real materials. A large $\Delta S_{T full}$, which, on the basis of the Clausius-Clapeyron relation (Equation 2.7, Chapter 2), is proportional to the magnetization difference between the two phases, is not enough to ensure a large $\Delta S_{T peak}$, induced by a finite magnetic field change. There is instead a correlation between $\Delta T_{ad peak}$ and (dT_t/dH) (Table 7.3); however, also in this case none of the samples reaches the maximum expected value of ΔT_{ad} , calculated as ΔH . (dT_t/dH) (Table 7.4).

The key to understand the behaviour of these materials is the transformation width (W): we can observe in Fgure 7.3 that, for all the samples, the transition occurs over a large temperature range rather than at a well-defined temperature, as expected, in principle, for a first-order transition. We estimated W from the calorimetric measurements as the *FWHM* of the transformation peaks (Table 7.3), because it is difficult to exactly determine the initial and final temperature of the transition. The quantity W assumes a relevant role in determining both the ΔS_T and ΔT_{ad} , induced in the studied materials. We can observe that S1, which has the narrowest W, is the sample in which the 1.8 T applied magnetic field manages to transform almost all the phase ($\Delta S_T_{peak}/\Delta S_T_{full} = 91\%$, Table 7.4). At the same time, this sample has the highest ratio (58%) between the measured $\Delta T_{ad peak}$ and the maximum exploitable ΔT_{ad} , as deduced from the relation $\Delta T_{ad max} = \Delta H (dT_t/dH)$ (Table 7.4).

These results suggest that the sharpness of transformation has, together with the shift of the transition temperature, a primary role in determining the phase fraction transformed with a defined magnetic field. Broaden transformations need higher magnetic field changes to transform the same phase fraction, and to induce the same MCE.
7.3 A phenomenological model of first-order magnetostructural transformations

In order to evaluate the influence of the transition width on the MC properties of materials, a phenomenological model of inverse first-order magnetic transitions, built in the entropy-temperature plane, is considered. This model allows to correlate the MCE parameters related to a first-order transformation to five thermodynamic and thermomagnetic features of the transformation. A similar model, based on magnetization data, has been introduced by G. Porcari et al. in Ref. [210], in order to correlate the isothermal and adiabatic features of the magnetocaloric effect. Here, its construction is generalized to take into account the broadness of the transformation. The model is built drawing the tangent lines at the inflection points of the two entropy curves across the transition, both in zero field and under applied magnetic field, and the tangent lines at the entropy curves below and above the transition region (Figure 7.5). In this way, the area in the S-T plane where the magnetocaloric effect is significant looks like a parallelogram. This construction considers, by a physical point of view, a linear variation of the phase fraction, the order parameter of the process, over a temperature range W centred at the peak temperature T_n of the DSC curve. Figure 7.5 shows the comparison between the measured heat flux data of sample S2 (Chapter 7.2) and the model constructed on such data. The heat flux peaks are approximated, in the model, by a rectangular shape, which after integration gives rise to the linear trend of the entropy curves at the transition. The rectangle width, W, is determined by the latent heat, which must remain the same obtained from the DSC data, and by the height of the heat flux peak, calculated as the peak value of a Gaussian best fit of the experimental curve. In this way, W approximately matches with the FWHM of a Gaussian interpolation of the heat flux peak and it is proportional to the standard deviation σ considered in the Gaussian model presented by Liu et al. in Ref. [90] ($W = \sqrt{2\pi\sigma}$). The temperature dependence of the specific heat below and above the transition is considered to be linear and the entropy curves outside the temperature range of the transformation with and without magnetic field are assumed to be overlapping. In this way, we are neglecting the possible effect of the magnetic field on the magnetic entropy of the ferromagnetic phase, resulting in a "classical" MCE. Actually, both positive ΔT_{ad} and negative ΔS_T contributions on the high-temperature peak-tails of the transformation were experimentally observed in the studied Heusler alloys (Figure 7.3) but they were below the experimental error. Therefore, the latent heat, represented as the segment DB' in Figure 7.6, is assumed to be the same in zero and applied magnetic field.

Although this approximation might seem far from reality, especially for weak first-order transformations [205], a possible field dependence of latent heat (leading to the S(T) curves not overlapping at high temperatures) would not affect the determination of peak values of both $\Delta T_{ad}(T)$ and $\Delta S_T(T)$. By model construction, peak values occur indeed before that the in-field transformation is finished. The only considered effect of the magnetic field is to shift the transition temperature T_p to lower temperatures.



Figure 7. 5 On the top: sketch of the proposed model of a first-order magnetic transformation superimposed to the S(T) curves of S2 sample calculated from DSC data on heating for $\mu 0H=0$ T and 1.8 T. On the bottom: comparison between the measured heat flux and the considered model of the transformation (dashed lines).



Figure 7. 6 Geometrical constructions based on the model in order to correlate the main parameters of the transformation.

For clarity reasons, we show in Figure 7.5 this construction applied on the entropy curves on heating, only. Curves on cooling and the effects due to thermal hysteresis can be introduced too, as was done by Gottschall et al. [33] (see Chapter 7.4 for a discussion about the relationship between transition broadness and hysteresis).

In this simplified model, five fundamental parameters are enough to describe the transition: the temperature of the transition peak in zero applied magnetic field (T_p) , the total latent heat of the transition (L), the shift of the transition temperature due to the applied magnetic field $\Delta H \cdot (dT_t/dH)$, the transition width (W) and the specific heat value of the low-temperature phase before the transition (c_p). Thanks to some geometrical proportions (Fgure 7.6), considering the triangles ABD, ACE and FC'E, we can link the maximum values of ΔT_{ad} and ΔS_T to these five parameters:

$$(\frac{dT_t}{dH}\Delta H):\Delta T_{ad\ max} = (\Delta S_T + CC'):\Delta S_T\ max$$
(7.1)

$$W: \Delta T_{ad\ max} = \left(\frac{L}{T_p} + BB'\right): \Delta S_{T\ max}$$
(7.2)

The segments CC and BB depend on the entropy rate before the transition and can be approximated as

$$BB' = ABtan \alpha \approx AB \frac{c_p}{T_p} = W \frac{c_p}{T_p}$$
(7.3)

$$CC' = ACtan \, \alpha \, \approx AC \frac{c_p}{T_p} = \frac{dT_t}{dH} \Delta H \frac{c_p}{T_p}$$
(7.4)

The validity of equation 7.1 for real materials was demonstrated in G. Porcari et al. [125] by comparing the ΔT_{ad} values obtained from 7.1 and those directly measured and derived from in-field DSC data. The proportions 7.1 and 7.2 are strictly valid only for purely first-order systems and when the field-induced transition shift is smaller than the transformation width [216]. The samples studied in Chapter 7.2 comply with these restrictions.

By inserting 7.3 and 7.4 in 7.1 and 7.2, we obtain

$$\Delta S_{T peak} = \frac{\left(\frac{dT_t}{dH}\Delta H\right)L}{T_p W} = \frac{L}{T_p} \frac{\left(\frac{dT_t}{dH}\Delta H\right)}{W}$$
(7.5)

$$\Delta T_{ad \ peak} = \frac{\left(\frac{dT_t}{dH}\Delta H\right)L}{L+Wc_p} = \frac{\left(\frac{dT_t}{dH}\Delta H\right)}{1+\frac{Wc_p}{L}}$$
(7.6)

These values correspond to the maximum isothermal entropy change and the maximum adiabatic temperature change related to the transformation schematized in the model. By combining Equations 7.5 and 7.6, these two values can be correlated:

$$\Delta T_{ad \ peak} = \frac{\Delta S_T \ peak}{L/W + c_p} \tag{7.7}$$

One can appreciate how Equation 7.7 deviates from previous derivations on the same matter [14]. The reason for such difference originates from the substantially different approximation employed to describe the first-order transformation. We must remark that the derivation appearing in Pecharsky et al. is obtained outside the range of validity of the present model, i.e., by assuming idealized sharp transitions (W = 0), where the application of the magnetic field is sufficient to complete the transformation, while in this study we are dealing with partial phase transformations and finite transition ranges. The denominator of Equation 7.7 represents an "effective specific heat" inside the transition region, as is shown in Figure 7.5, with a factor (L/W) taking into account a contribution of the latent heat, which is spread over the temperature range of the transition.

Equations 7.5 and 7.6 can be used to estimate the magnetocaloric features of materials from standard magnetometric and conventional zero-field DSC measurements. The only required parameters to perform the calculation are the specific heat before the transition, the latent heat of the transformation in zero applied field, the peak temperature of the transition, its span width and its change with the applied magnetic field.

To validate the outcomes of the model we compared the ΔS_T of 9 samples of Heusler alloys (listed in Tables 7.1 and 7.5), calculated using the model (Equation 7.5, $\Delta S_{T calc}$) and the maximum values obtained from in-field DSC data. Figure 7.7 shows the linear relationship between the measured values and those obtained from the model. The same comparison was made with the values of ΔT_{ad} . The values derived from the model show the same trend as the measured ones but they turn out to be overestimated by about 30%. This overestimation is due to the difference between the smoother trend of the experimental entropy curves when compared with the series of line segments of our geometrical model.

Sample	Composition* (at.%)				
	Ni	Со	Mn	Ga	In
$\mathbf{S5}$	45	5	30	20	/
$\mathbf{S6}$	45	5	31	19	/
$\mathbf{S7}$	45	5	31	19	/
S 8	41	9	32	16	2
S9	41	9	33	15	2

Table 7. 5 Nominal composition expressed as at.% of five Heusler alloys considered to validate the phenomenological model togheter with the alloys listed in Table 7.1.



Figure 7. 7 Comparison of the maximum isothermal entropy change for a $\mu_0 \Delta H = 1.8$ T, of the 9 samples listed in Tables 7.1 (red circles) and 7.5 (yellow squares), calculated by using Eqation 7.5 ($\Delta S_{T calc}$) and derived from DSC data ($\Delta S_{T peak}$).

From Equations 7.5 and 7.6 we can derive simple indications on how the various parameters of the transformation affect the $\Delta S_{T max}$ and $\Delta T_{ad max}$ values. Firstly, these relations confirm that higher values of (dT_t/dH) and L increase both $\Delta S_{T max}$ and $\Delta T_{as max}$. The former has a primary role in determining the $\Delta T_{ad max}$ and it represents its upper limit when the product $W \cdot c_p$ tends to zero or $L >> W \cdot c_p$. The broadening of the transformation reduces the $\Delta T_{ad max}$ whereas large values of L limit this negative effect. Regarding instead $\Delta S_{T max}$, it reaches its maximum value, limited by the entropy variation of the fully induced phase (L/T_p) , when the ratio $(\Delta H(dT_t/dH))/W$ tends to 1. For a lower width of the transition, this model is no longer valid: anyhow, the value of $\Delta S_{T max}$ cannot grow more and it is expected to remain constant over a finite temperature range which is enlarged by the increase of $\Delta H(dT_t/dH)$.

These general considerations can be visualized in Figure 7.8. Figure 7.8.a shows a series of possible S-T diagrams differing in the transition width W. All the other parameters $(dT_t/dH, T_p, c_p, L)$ are kept constant and equal to those of sample

S2 (described in Chapter 7.2). Figures 7.8.b, and 7.8.c report the variations of $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ curves on changing the *W* value. As discussed above, we can observe that ΔS_T reaches its upper limit when $W = \Delta H \cdot (dT_t/dH)$ (= 8.3 K, in this case), while ΔT_{ad} continues to grow for *W* tending to zero. It is evident indeed that the transition width *W* plays a key role in changing the $\Delta S_T \max$ and $\Delta T_{ad} \max$ values as compared to their upper limit. From Figures 7.8 we can appreciate also the evolution, widening the transformation, of the temperature dependence of the MCE. Indeed, in broader transformations, the temperature range in which the MCE is maximum decreases; whereas the total temperature range, in which the MCE is sizable, increases. This has to be considered for the development of AMRs working over a large temperature range.



Figure 7. 8 (a) Simulation of different S(T) diagrams on varying the width of the transition temperature span; ΔS_T and ΔT_{ad} are pointed out with arrows. (b,c) Variations of the $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ as a function of the transition width W.

To summarize, we can argue that there is a combined effect of the transformation width, the shift of the transition temperature and the total latent heat of the transformation in determining the MC features at first-order transformation. Although the maximum predicted ΔS_T and ΔT_{ad} are mainly defined by L and $\Delta H(dT_t/dH)$, the transformation width determines the fraction of MCE induced by a definite magnetic field change. The ratio between W and L limits the ΔT_{ad} whereas the ratio between W and $\Delta H(dT_t/dH)$ limits the ΔS_T . Indeed, by considering the series of Heusler alloys studied in Chapter 7.2, we can observe (Table 7.4) that the samples with the larger percentage of induced ΔT_{ad} are S1 and S4, which have the lowest transformation width (S1) and the largest latent heat (S4). Whereas the sample with the maximum percentage of developed ΔS_T is S1, which shows the largest ratio between $\Delta H(dT_t/dH)$ and W. This is related to the fraction of phase that transforms due to the change of the applied magnetic field. The transformation can be fully induced in isothermal conditions only if the shift of the transition temperature $(\Delta H(dT_t/dH))$ is larger than the transformation width. Tending W to zero, an infinitesimal magnetic field change is enough to completely induce the transformation. Therefore, sharp transformations allow to reduce the magnetic field change needed to exploit the whole MCE of materials. Instead, regarding adiabatic processes, the transformation can be completed only with an applied magnetic field that results in:

$$\Delta H(dT_t/dH) > L/c_p + W \tag{7.8}$$

As an example, let us consider the values of sample S2 used to obtain the results of simulation presented in Figure 7.8. If we simulate, for this sample, a sharper transformation, with W tending to 0, we can appreciate that a 1.8 T applied magnetic field is enough to complete the phase transformation under isothermal conditions ($\Delta H(dT_t/dH) = 8.3 \text{ K} > W \rightarrow 0$) but not under adiabatic conditions ($\Delta H(dT_t/dH) = 8.3 \text{ K} < L/c_p = 9.8 \text{ K}$). On the contrary, sample S1, characterized by a quite sharp transition (W = 3.1 K), shows an almost complete phase transformation under isothermal conditions ($\Delta H(dT_t/dH) = 4.3 \text{ K} > W$) but just about 50% of the transformation under adiabatic conditions ($\Delta H(dT_t/dH) = 4.3 \text{ K} > W$) but

To complete this discussion we consider, as an example of a different MC material, a Mn_3GaC compound, which shows a first-order transition from an antiferromagnetic to a ferromagnetic state accompanied by a discontinuous volume contraction without change of symmetry [217]. At this transformation an inverse giant MCE occurs [185,186,218]. This compound, characterized by a very sharp structural transformation ($W \approx 1.2$ K, see Appendix A or Ref.s [186,188]),

represents an opposite case with respect to the broad martensitic transformation of Heusler alloys. We can appreciate from Ref. [218] that a magnetic field change of 1 T is enough to fully induce the transformation under isothermal conditions. This is in agreement with the predictions derived from the model, indeed if we look at the shift of the transition temperature due to a 1 T applied magnetic field of this compound, we obtain: $\Delta H(dT_t/dH) \approx 4.3 \text{ K} >> W = 1.2 \text{ K}$ (see Appendix A). Whereas, a magnetic field change of 2 T induces a complete transformation also under adiabatic conditions ($\Delta H(dT_t/dH) \approx 8.6 \text{ K} > (L/c_p + W) = 6.2 \text{ K}$, calculated using the values reported in Ref.s [218,219]), leading to the maximum adiabatic temperature change, as it has been demonstrated with direct measurements, which are reported in Figure A.2.b of Appendix A.

To conclude, by using the predictions obtained from a general phenomenological model and the experimental results of different materials with a first-order transformation, it turns out that the transformation width is a fundamental parameter to determine the MCE exploitable with a definite applied magnetic field. Moreover, this model allows also to deduce the magnetic field needed to fully induce the phase transformation, thus exploiting the maximum MC performance of materials.

7.4 Broadness of transformation, hysteresis and reversibility of MCE

In the discussion of previous paragraph we have neglected the effect of the typical hysteretic character of first-order transformations. The effect of the hysteresis in reducing the MCE exploitable in repeated thermomagnetic cycles and the possibility to exploit a reversible MCE trough minor loops of the transformation are widely discussed in literature (see e.g.: [32,35,90,104]). This possibility is strictly linked with the broadness of the transformation.

Indeed, sharp transformations consent a reversible MCE only if the $\Delta H(dT_t/dH)$ is larger than thermal hysteresis of the material. However, broaden transformations allow to obtain a reversible MCE also in the opposite case. To discuss this assertion, we consider, as an example, a Ni₅₀Mn₃₄In₁₆ Heusler alloy. Figure 7.9.a shows the DSC measurements performed on the sample with temperature sweeps on heating and on cooling (red and blue curves, respectively) in zero (continuous lines) and under a 1.8 T applied magnetic field (dashed lines). We can appreciate, considering the heat flux peaks, that the thermal hysteresis is larger than the shift of the transition temperature due to the applied magnetic field. Therefore, in principle, we do not expect a reversible MCE with a magnetic field change of 1.8 T. Indeed, looking at the phase diagram of the material as a

function of temperature and magnetic field (Figure 7. 10.a), if we assume the following process: (1) cooling down of the material, initially in the austenitic phase, under an applied magnetic field (arrow 1 in Figure 7. 10.a) and (2) removing the magnetic field (arrow 2 in Figure 7. 10.a), we expect that the material transforms into martensite and a positive temperature change develops. When the magnetic field is applied again (arrow 3 in Figure 7.11.b), the equilibrium line of the inverse transformation (red line) is not crossed and we do not expect a transformation and a MCE to occur.



Figure 7. 9 (a) In field DSC measurements of a $Ni_{50}Mn_{34}In_{16}$ sample across its martensitic transition: heat flux as a function of temperature in $\mu 0H = 0$ T (solid lines) and 1.8 T (dashed lines) measured with temperature sweeps on heating (red lines, right arrows) and on cooling (blue lines, left arrows). (b) Direct meaurement of the sample temperature variations due to cyclical applications and removals of a 1.8 magnetic field. Before the first removal of the field the sample was cooled down from 310 K in 1.8 T applied field.



Figure 7. 10 Phase diagram of the $Ni_{50}Mn_{34}In_{16}$ alloy (details in the main text). The arrows draw the loops followed by the material during the direct measurement reported in Figure 7.9.b.

However, directly measuring the sample temperature during the reproduction of this cycle, a reversible MCE is detected (Figure 7.9.b). This is allowed by the broadness of the transformation, which converts the equilibrium lines in superimposed equilibrium areas (Figure 7.10.c), which consent partial transformations of the material between mixed states. Therefore, the condition to have a partial reversible MCE is modified in:

$$\Delta H(dT_t/dH) + W > \Delta T_{hyst.} \tag{7.9}$$

For materials that show a $\Delta H(dT_t/dH)$ larger than the thermal hysteresis, a reversible effect is always expected (with the magnetic field change ΔH) in a temperature range defined by $\Delta H(dT_t/dH) - \Delta T_{hyst}$. In this case, the broadening of the transformation reduces the fraction of transformed phase, as discussed in the previous paragraph and as is evident for example in the case of Mn₃GaC sample (see Appendix A).

These general statements were very recently verified by using a spatially resolved numerical model of inhomogeneous materials with a first-order magnetic transition [220]. The authors demonstrated that it is possible to simulate minor loops in the S - T diagram only if a chemical inhomogeneity, resulting in a distribution of the critical temperatures, is included in the model. A complete numerical and experimental study of the combined effect of hysteresis and width of the transformation on the MCE under isothermal and adiabatic transformations will provide important information for the design of efficient thermomagnetic cycles useful for cooling devices.

7.5 A preliminary study on the width of martensitic transition on a microscopic scale

In previous paragraphs, it has been demonstrated the negative role of the broadening of first-order transformations on the MC performance of materials. The possibility to obtain materials with sharp transformations would increase the MCE exploitable with a definite magnetic field variation and would reduce the magnetic field necessary to complete the phase transformation. As in the case of hysteresis [28], several factors can contribute to the smearing of the transformation, both extrinsic and intrinsic to the material. Which of them plays a main role has not yet been clearly identified. Understanding the factors that

determine the transformation width can be one of the major goals to improve materials properties exploitable in magnetic refrigerators.

In this paragraph, we report a preliminary study, carried out with the aim to find out the characteristic length scale of the broadness of the martensitic transformation of Heusler alloys. The proposed optical microscopy-based method leads to a first selection of the factors affecting the transformation width. Indeed, such factors act on specific length-scales, which can be macroscopic, microscopic or atomic.

Macroscopic compositional inhomogeneity, caused either by an improper synthesis procedure (an example is reported in Appendix E) or by phase splitting due to solubility limits of the various elements in the alloy [212-214], can represent the main contribution to the transformation smearing [220,221]. Indeed, in Heusler alloys, small compositional variations (< 1%) can, in some cases, shift the martensitic critical temperature for tens of degrees [96]. On the other hand, microstructural features, such as defects and grain boundaries, strongly influence the martensitic transformation process that proceeds through nucleation and growth of one phase into the other, following an avalanche criticality type of path [215]. Moreover, the lattice mismatch between martensite and austenite phases and the large volume discontinuity at the transition, of the order of 1-2 % in these alloys [211], can produce local stresses and internal pressure variations (exceeding 100 MPa near phase boundaries [222]). These result in a variation of the local free energy due to an elastic strain term, which has an important role to define the thermal hysteresis [102] and could influence also the width of the transition. Finally, on the atomic scale, a chemical disorder, which is responsible for competing ferromagnetic and antiferromagnetic interactions, can locally vary the magnetic and structural properties of the alloys changing the transformation temperature due to the alteration of the local energy differences between the two phases [201,221,223].

Here we report a study performed on the martensitic transformation of the sample S2 presented in Chapter 7.2. A piece of 62.1 mg (dimensions: about 4x3x2 mm³) was characterized by in-field DSC measurements (reported in Chapter 7.2) and isofield magnetic measurements (Figure 7.11), carried out with a SQUID magnetometer. All these characterizations were performed with temperature sweeps on heating and on cooling at 2 Kmin⁻¹ at different applied magnetic fields. Calorimetric and magnetic measurements show a transformation in temperature that spreads over a temperature range larger than 20 K.

Afterwards, the transformation was studied through an optical microscope characterization of the sample surface as a function of temperature. The Differential Interface Contrast (DIC) method was used to observe very small variations of relative height on the sample surface. Images of different portions of the sample surface were collected during temperature sweeps between 300 K and 380 K, on heating and cooling at 2 Kmin⁻¹ (for experimental details see Chapter 3.3).



Figure 7. 11 Magnetization as a function of temperature of sample S2 measured with temperature sweeps on heating and on coling in $\mu_0 H = 0.1, 0.5, 1.0, 1.5, 2.0 T$.

Figure 7.12 reports a sequence of images collected during temperature sweeps on heating (first row) and on cooling (second row). In the Supplementary Materials of Ref. [224], a video displays all the images taken during the temperature cycle. The flat surface at high temperature (370 K) corresponds to the sample mainly in the austenitic phase: in fact, the surface lapping was performed at 400 K with the sample in the austenitic phase (details on the sample preparation are described in Chapter 3.2). Decreasing the temperature, the images show the appearance of the variants microstructure typical of the martensitic phase [102]. In the video (Sup. Mat. of Ref. [224]), it is possible to appreciate how the transition proceeds with the transformation and the growth of elongated segments of the sample surface evenly distributed. The portion of the images at 320 K in the upper right does not clearly show the variants because they grow parallel to the surface with a reduced variation in the height of the surface. The most evident variation on the sample surface occurs around 350 K on warming the sample and between 340 K and 330 K during the temperature sweep on cooling. The comparison of the warming and cooling sequences reveals that the portions of the sample surface that transform last on warming are the first to appear on cooling. The observations were repeated three times with cycles in temperature: the sequence of appearance of the different variants (Figure 7.13) is the same in all the cycles, in contrast to the observations of Ref.s indicates nucleation [104, 225].This that the and growth of the martensitic/austenitic phase proceed all times in the same order, from the same positions and along the same orientations.



Figure 7. 12 DIC phase-imaging pictures of sample S2 surface catched during temperature sweeps on heating (first row) and on cooling (second row) across the martensitic transition.



Figure 7. 13 Optical microscopy pictures of the sample surface catched during the heating sweep of three different subsequent cycles in temperature.

An elaboration of the collected images was performed to analyse quantitatively the transformed phase on varying temperature. We subtracted from each image the one acquired at higher temperature (380 K) and then, with a light-intensity filter, we estimated the transformed fraction of the sample surface. A low-limit intensity level was used to eliminate the effect of sample height change due to thermal expansion. Figure 7.14.a shows (blue triangles) the phase fraction as a percentage of the transformed sample surface, estimated from the microscope images, as a function of temperature for the heating and cooling sweeps. It confirms the presence of thermal hysteresis of about 17 K and the broadening of the transformation in a temperature span wider than 20 K. This analysis was repeated for images collected during different temperature cycles (Figure 7.14.b) and in different portions of the sample surface (Figure 7.15): all the results are similar. This means that the temperature dependence of the transformation does not change during subsequent thermodynamic cycles and that it is the same in every observable area of the sample surface, though they show different microstructural configurations of martensitic variants (Figure 7.15.b).

The results of the magnetic and calorimetric measurements performed on the entire volume of the sample were superimposed with the temperature dependence of the transformed phase fraction obtained by the microscope observations (Figure 7.14.a). The transformed phase fraction was estimated from DSC measurements by integrating the heat flux peak across the transition after subtraction of the baseline of the specific heat outside the transition.



Figure 7. 14 (a) Phase variation as a percentage of the sample S2 as a function of temperature on heating and on cooling derived from: microscopy analysis (blue trinagles), calorimetric measurements (pink squares) and magnetization data in $\mu_0 H = 0.1 T$ (green circles). (b) Comparison of the phase variation as a function of temperature obtained from the analysis of the three cycles reported in Figure 7.13.



Figure 7. 15 (a) Comparison of the phase variation as a function of temperature obtained from the microscopy analysis of two different portions (site A and site B) of the sample surface. (b) Optical microscopy images of the two different areas of the sample surface at 315 K and 375 K.

We considered the transformed phase fraction to be directly proportional to the latent heat of the transition, which develops over a wide temperature span. The transformed phase fraction was determined from the M(T) curves performed at 0.1 T by subtracting from M(T) the magnetization of the martensitic phase at the transition starting temperature, and by normalizing for the magnetization values of the austenite at the transition finishing temperature. In this case, we approximated the net magnetization of the entire sample as the weighted sum of the magnetization of the two phases. We cannot exclude the presence of a sample fraction that does not transform. However, it would have no effect on the estimation of the relative transformed phase fraction from the three techniques. The results obtained with the three techniques are consistent, as can be seen in Figure 7.14.a, in particular if one considers the different thermal inertia that can affect all the experiments and that the magnetic measurements were performed with a 0.1 T applied magnetic field. The result of this comparison demonstrates that the broadness of the martensitic transition is characteristic of a submillimetric length scale, lower than the average grains and martensite variants dimensions. Moreover, it is the same over all the sample and it does not vary in repeated thermodynamic cycles across the transition. On the other hand, we have verified that the sample surface can be considered an adequate statistical system to extrapolate the properties of the entire volume of the bulk sample, as observed in Ref.s [160,226] for field-induced transitions.

To understand if compositional inhomogeneities could have a primary role in the transition broadness (as in the case of sample S9, reported in Appendix E), maps of the local composition were performed through the EDS technique on different portions of the sample surface. It was chosen to probe surface areas with size similar to the one observed with the optical microscope. The compositional map (Figure 7.16) does not show the presence of extended areas (at least a few square micrometres) on the sample surface characterized by evident compositional variations, within the limit of sensitivity of EDS analysis (about 0.1%).

This preliminary study, which compares results from bulk and spatially resolved techniques, presents a methodology to firstly discriminate macroscopic causes of the transformation broadness. Moreover, it highlights as it is necessary to explore smaller length-scales to understand what leads to the spreading of the martensitic transition and whether its control is possible. Microstructural features, effect of local pressures, of chemical order and of local magnetic configuration need to be deeply investigated with proper experimental techniques (electron and magnetic microscopies and high resolution diffraction), compared with bulk measurements as a function of temperature, magnetic field and pressure.



Figure 7. 16 Superposition of EDS compositional maps of the alloy atoms (Ni, Co, Mn, Ga and In) on SEM electron image. Inset: overall EDS spectrum of the map.

7.5 Conclusions

In this chapter, we investigated the role of the transformation broadness in determining the MCE across first-order magnetostructural transitions. Exploiting a phenomenological model of the transformation, built in the entropy-temperature plane, it was demonstrated that the broadening of the transformation is always unfavourable to the magnetocaloric performance of materials, reducing both isothermal entropy change and adiabatic temperature change obtainable in a given magnetic field change and increasing the value of the minimum field needed to fully induce the transformation. The outcomes of the model were compared with results of a complete thermomagnetic characterization of a series of $(Ni,Co)_2Mn(Ga,In)$ Heusler alloys, characterized by similar compositions, critical temperatures and high inverse magnetocaloric effect across their martensitic transformation, but different transition widths. The experimental results confirm the general outcomes of the model.

On the other hand, large values of transformation width are useful in the case of materials characterized by thermal hysteresis larger than the shift of the transition temperature due to the applied magnetic field. In this case, the broadening of the transformation allows to obtain a reversible MCE under repeated thermomagnetic cycles, by following minor loops between metastable mixed states of the two phases.

Finally, a preliminary study regarding the factors affecting the broadness of the martensitic transformation of Heusler alloys was presented. The comparison of spatially resolved microscopy analysis and bulk characterization techniques demonstrated that the broadness of the transformation is characteristic of a submillimetric length scale and cannot be ascribed to grains or variants dimensions or to macroscopic chemical inhomogeneities. This study fixes a research direction with the aim to understand which factors determine the width of the martensitic transformation of Heusler alloys.

Understanding the origin of the transformation broadness and how to control it, will bring significant indications in order to increase the MC performance of materials and to lead to the scaling up of their synthesis routes.

8. DETRIMENTAL EFFECTS ON THE MCE AT SECOND-ORDER TRANSITIONS

8.1 Introduction: broadening of Curie transition

In previous Chapter it was demonstrated the degrading role of the transition broadening on the MCE at first-order magnetic transitions. This negative effect can occur also in materials exploiting a second-order magnetic transformation. Indeed, chemical inhomogeneities or local variations of the magnetic system, caused for example by microstructural features, can modify the critical temperature, spreading the transformation over a finite temperature range, bringing thus to a reduction of the MCE [227,228].

By using a mean-field approach, it is possible to simulate the effect of broadening of the Curie transition on the related MCE [227,229]. Figure 8.1 reports the results of simulations performed considering as reference system a Ni₅₀Mn₃₄In₁₆ Heusler alloy, which shows a considerable direct MCE at the Curie transition [108]. The Figure shows the entropy variation as a function of temperature calculated for a field span $\mu_0 \Delta H = 1$ T by following a classical mean-field approach (details are reported in Appendix F). The broadness of the transition was included by considering a Gaussian distribution of the Curie temperature, centred at the mean value T_c , and characterized by a standard deviation σ . By changing the σ value (from 1 K to 20 K) we simulated different widths of the transformation. From Figure 8.1, we can appreciate that an increase of transformation width brings to a decrease of the maximum entropy change of the material, without any advantage in terms of useful temperature span of the MCE.

Though broadness of second-order transitions is less evident than that of firstorder transformations, it cannot be neglected. Indeed, many typical situations can lead to changes in the magnetic properties of materials, which include a possible broadening of the transformation. The first and simpler cause of broadening of the transformation can be a compositional inhomogeneity produced in the material during the synthesis process [227]. Moreover, microstructural features and chemical disorder on the atomic scale, depending also to the synthesis of material, can affect magnetic transformations [230,231]. Furthermore, also post-synthesis processes can modify the magnetic properties of materials, by changing the saturation magnetization or the critical temperature [168]. This occurs especially for materials whose magnetic properties are strongly sensitive to microstructural features and to the application of external mechanical stresses, as in the case of Heusler alloys.



Figure 8. 1 Entropy change as a function of temperature obtained through mean-field simulations of a $Ni_2Mn_{1.4}In_{0.6}$ Heusler alloy for a $\mu_0\Delta H = 1$ T. The graph reports results for different Gaussian distributions of the Curie temperature, centred at the mean value (320 K) and characterized by different widths (σ).

In this Chapter, we report, as an example, the effect of cold working on the MCE of a NiMnIn Heusler alloy, which shows the Curie transition near room temperature. The result of manual crushing and subsequent heat treatments on the magnetic and magnetocaloric properties of a Ni₅₀Mn₃₄In₁₆ sample are presented. Both the decrease of the saturation magnetization and the broadening of the Curie transition due to cold working result in a significant reduction of the MCE shown by the material. The degrading effect of crushing is discussed on the basis of magnetic and structural measurements. A plausible explanation of this effect is reported, looking at the correlation between the magnetic behaviour of the material and the structural defects introduced by the grinding process.

As in the case of the broadness of first-order transformations discussed in the previous chapter, the study of the connection between microstructure and magnetic properties of these materials represents a key point for the improvement of Heusler MC performance and for the development of industrial routes for materials preparation and processing. On the other hand, this study can result in a better understanding of the physical properties of Heusler alloys and of experimental results on laboratory-scale samples. Indeed, cold working and further annealing processes of samples may introduce relevant alterations of their properties, giving rise to inconsistent results for the same nominal

composition. This effect can represent a possible explanation for the spread of values reported in literature concerning the magnetic properties of nominally identical samples (see for example the case of Ni₅₀Mn₃₅In₁₅ described in several papers [90,108,134,232–235]).

8.2 Degradation of the MCE of Heusler alloys due to cold working

Here, we test the effect of manual crushing of a $Ni_{50}Mn_{34}In_{16}$ sample on its magnetic and MC features. This composition was selected because it represents the prototypical combination showing a large saturation magnetization, a suitable Curie temperature and the cubic parent phase which is stable down to 2 K [108]. In this way, a possible martensitic transition induced by mechanical stresses, as observed by Singh et al. [236] in a $Ni_{45}Mn_{45}In_{10}$ sample and by Belesi et al. in a $Ni_{50}Mn_{25}Ga_{25}$ sample [237], is reasonably avoided.

The studied sample was prepared by arc melting the stoichiometric amount of high-purity (99,99%) elements. First, two ingots of Ni-Mn and of Ni-In were melted. An excess of 5% Mn and In were added to compensate the evaporation of these two elements. Afterwards, the two ingots were melted together. The sample was flipped and re-melted three times for every side to improve homogeneity. Then it was annealed at 1173 K for 72 h in Ar atmosphere and quenched in cold water. The final composition of the sample (Ni_{49.1}Mn_{33.9}In₁₇) was determined through energy dispersive spectroscopy (EDS) microanalysis.

The temperature dependence of the magnetization at different magnetic fields, measured on a single fragment of the sample (mass = 5.53 mg) with a SQUID magnetometer, is reported in Figure 8.2.a with red triangles.

The sample undergoes a magnetic transition at 319 K between the ferromagnetic and the paramagnetic state. The measurement of the magnetization as a function of the magnetic field at 5 K (Figure 8.2.b) shows that the magnetization is almost saturated at a field of 2 T. The saturation magnetization at 5K is 128 Am^2kg^{-1} . The magnetization as a function of temperature measured in a magnetic field of 0.01 T (inset of Figure 8.1.a) does not show the presence of other transitions down to 5 K.

The MC properties of the sample were collected on a fragment by both direct and indirect methods. The isothermal entropy change ΔS_T was derived from isofield M(T) measurements by applying the Maxwell relation (Equation 2.3 Chapter 2). The $\Delta S_T(T)$ for an external magnetic field change $\mu_0 H = 2$ T is reported in Figure 8.3.a (red triangles). It presents a maximum of 3.3 ± 0.2 Jkg⁻¹K⁻¹ at 318 K. Direct measurements of the adiabatic temperature change $\Delta T_{ad}(T)$ (Figure 8.3.b) were

obtained by using the dedicated experimental probe described in Chapter 3.5. Both ΔS_T and ΔT_{ad} are in agreement with the results of Ref. [108].



Figure 8. 2 (a) Magnetization as a function of temperature in a magnetic field of 2 T of a $Ni_{50}Mn_{34}In_{16}$ fragment, untreated powder and annealed powder from the same sample. Inset: their magnetic behaviour in a low magnetic field ($\mu_0H = 0.01$ T). (b) Isothermal M(H) curves at 5 K.



Figure 8. 3 (a) Isothermal entropy change of a fragment, untreated powder and annealed powder for a magnetic field change of 2 T. (b) Adiabatic temperature variation of the $Ni_{50}Mn_{34}In_{16}$ fragment measured near its Curie transition with a magnetic field change of $\mu_0\Delta H = 2$ T and 1 T.

A part of the ingot was manually crushed in an agate mortar. Half of the powder was annealed for 24 h at 773 K in Ar atmosphere (by following indication of Ref. [236]). The temperature dependence of magnetization of the untreated powder and of the annealed powder are reported in Figure 8.2.a with green squares and yellow circles. The M(T) of the powdered sample shows a significant reduction of the saturation magnetization (about 26%) and a widening of the transition, shifted to lower temperatures ($T_c = 317$ K). The annealed powder presents a partial, but not complete, restoration of the low-temperature saturation magnetization typical of the original fragment. Moreover, the heat treatment reduces the width of the transition, which was induced by cold-working. We considered also the effect of the annealing process (773 K for 24 h) on a fragment of the bulk sample (Figure 8.4). The annealing does not have a substantial effect on the magnetization and on the Curie temperature of the alloy. This is in agreement with Ref. [238], which shows that a noticeable atomic rearrangement takes place only with heat treatments at temperatures higher than 773 K.



Figure 8. 4 Magnetization as a function of temperature in a magnetic field of 1 T of a fragment of the starting alloy (red triangles) and of a fragment subjected to a heat treatment at 773 K for 24 h (cyan circles). Inset: their magnetic behaviour in a low magnetic field ($\mu_0 H = 0.01$ T).

 $\Delta S_T(T)$ curves, derived from isofield M(T) measurements, for untreated powder and annealed powder are reported in Figure 8.3.a. The remarkable decrease of the maximum ΔS_T of about 50% in the case of untreated powder can be attributed to both the decreasing of the saturation magnetization (about 26%) and to the broadening of the transition. The annealing process permits to restore almost entirely the original values of magnetic entropy-change for the fragment before crushing, though the saturation magnetization remains 10% lower, highlighting that the broadness of the transformation has a key role in determining the MCE reduction.

Powder X-rays diffraction data were collected at room temperature for the untreated and for the annealed powder sample. The corresponding profiles are shown in Figure 8.5.a. Rietveld analysis performed with JANA2006 confirms the austenitic $L2_1$ structure shown in Figure 8.6.a (reliability factors of the refinement of the annealed powder: Rp 3.34, wRp 5.72). The 4a and 8c Wyckoff positions result to be occupied by Mn and Ni atoms, respectively. The excess Mn atoms occupy randomly, instead, the In site (4b). The XRD pattern of the untreated sample shows broad diffraction peaks that after the annealing at 773 K become much sharper. Comparing the two patterns, no significant relative intensity variations or shifts of the line positions are observed. The asymmetry

of the main reflections is a clear indication of the presence of multiple austenite phases having compositional variations. Two main phases are evident (inset of Figure 8.5.a) corresponding to lattice parameters of 6.0104 Å and 6.0357 Å. Nevertheless, this chemical inhomogeneity has no substantial effect on the magnetic behaviour of the sample, confirming a weak dependence of the Curie temperature on the composition.



Figure 8. 5 (a) Rietveld refinements of room-temperature X-rays diffraction patterns of the $Ni_{50}Mn_{34}In_{16}$ untreated powder (top) and annealed powder (bottom). Ticks represent the Bragg peaks positions of two austenitic phases with a different lattice parameter. Arrows point at the peaks of an unknown secondary phase, which grew with the heat treatment. Inset: enlargement of the main peak (220) of the X-rays diffraction patterns of annealed powder. (b) Neutron diffraction data collected on fragments, untreated powder and annealed powder.

Neutron diffraction data, collected with the PEARL diffractometer at TU Delft (Figure 8.5.b), confirm the same results. The patterns collected after and before annealing do not show a relevant variation of the intensity due to change of atomic occupancies or of the magnetic moment on the Mn site. All these results suggest the presence in the crushed sample of a relevant density of defects and lattice deformations.

The annealed powder X-rays diffraction profiles present also some new peaks that actually are not ascribable to known crystalline phases. Such unidentified phases have been likely developed during the annealing after the crushing. The possible segregation of secondary phases or the creation of a compositional inhomogeneity could be a drawback of post-synthesis heat treatments, which has to be considered very carefully.

Summarizing the results, the grinding of the Heusler sample introduces in the material a large density of structural defects without a clear modification of the atomic chemical ordering, a substantial reduction of the saturation magnetization and a broadening of the Curie transition, with a resultant halving of the MCE. A heat treatment at a relative low temperature (much lower than the temperature used for the post-synthesis annealing) allows to restore the saturation magnetization, the shape of the transition in temperature and the MCE shown by the material.

8.3 Cold working, microstructure and magnetic interactions

The effect of cold working on Heusler alloys is well known. Since the 70's of the last century, heat treatments were prescribed in order to eliminate dislocations and lattice deformations introduced during sample crushing [238,239]. The effect depends on the brittleness of the material. Brittle alloys, like NiMnSb with C_{1b} structure, tend to easily break rather than assume a plastic deformation and therefore evident effects of cold working on the material properties are not shown [240]. The L_{21} cubic Heusler alloys have a higher degree of plasticity that permits the accumulation of a large number of dislocations, deformations and, in particular, antiphase boundaries (APB) being induced by cold working [240]. The observed symmetrical line broadening of the X-rays diffraction pattern of the untreated powder confirms the presence of a relevant density of structural defects and deformations. The annealing treatment permits to partially release the deformations and the defects, while it has no significant effect on the atomic order. Previous works demonstrated that the annealing at 773 K allows the

relaxation of at least part of mechanically induced deformations, while the temperature is not high enough to promote the atomic displacements through diffusion processes and thus it has a weak effect on the atomic disorder and on the phase structure [241]. This negligible effect of the heat treatment on the degree of atomic order is also confirmed by the observed Curie temperature. Indeed, Ref. [201] shows that an increase of atomic order in a Ni-Mn-In alloy enhances the magnetic character of austenite, thus increasing its Curie temperature of almost 20 K. In the present case, the Curie temperature of the starting bulk sample, of the annealed powder and of a bulk fragment treated at 773K for 24 h are the same (Figures 8.2.a and 8.3).

The focus of this work is to highlight how defects and deformations induced by cold working may transform the magnetic interactions within the material and thus have a degrading effect on MC properties. The partial amorphization of the alloy, observed in nanometric powders synthetized by high-energy ball-milling, in principle could justify such a decrease of magnetization. However, the presented results and literature works [203] do not support the formation, through a manual crushing, of a so large amount of amorphous phase such as to determine a 26% decrease in magnetization. Other hypotheses are considered in literature to explain the reduction of magnetization by cold working in Mn-based intermetallic alloys [241–243]. Ultimately, the interpretation shared by all such hypotheses is based on the antiferromagnetic coupling of Mn atoms in presence of structural defects.

Following the hypothesis of Ref. [242], atomic disorder or structural defects may compromise the Mn/In ordering in the Heusler scaffold, with a consequent increase of the number of antiferromagnetically coupled Mn atoms. The antiferromagnetic coupling of Mn atoms that occupy the two adjacent sites 4b e 4a is confirmed by theoretical calculations [244] and it was experimentally observed in other Heusler alloys [245]. The net value of saturation magnetization can be expressed as the sum of the magnetic contribution of the $(N_0 - N)$ Mn atoms in the 4a site and of the N atoms in the 4b site [242]:

$$M_0 = (N_0 - N)\vec{\mu}_{Mn} + N\vec{\mu'}_{Mn}$$
(8.1)

where μ_{Mn} and μ'_{Mn} are the magnetic moment of the regular (4a) and irregular (4b) Mn atoms, respectively. The variation of magnetization caused by cold working becomes proportional to the relative amount of Mn atoms in the 4b sites, due to their reduced magnetic moment. This amount depends on the dislocation density produced by the plastic deformation of the material, which changes the

local environment of Mn atoms. However, Mössbauer and NMR measurements demonstrated that the amount of antiferromagnetically coupled Mn atoms on the *4b* sites is too small to account for the observed reduction in magnetization [240,241].

Another interpretation proposes that the crushing procedures enable the introduction of APBs generating local antiferromagnetic regions [241,242]. A layer shift of 1/2 along the 001 direction moves the Mn atoms to the In regular sites. The view of the 110 plane (Figure 8.6.b) shows how the shifted Mn atoms are close to the Mn atoms in the 4a sites, resulting in an antiferromagnetic coupling. Hence a ferromagnetic region limited by two APB's is coupled antiferromagnetically with the other domains [242]. The total magnetization is given by the sum of the contribution of the two regions that are antiferromagnetically coupled, $(N_{\uparrow} - N_{\downarrow})\vec{\mu}_{Mn}$, where $N_{\uparrow} + N_{\downarrow} = N_0 - N$, and of the different moment (μ'_{Mn}) of the N Mn atoms in 4b sites near the APBs:

$$M_0 = (N_{\uparrow} - N_{\downarrow})\vec{\mu}_{Mn} + N\vec{\mu'}_{Mn}$$
(8.2)

This hypothesis may conciliate the observed reduction of magnetization with the low number of antiferromagnetic Mn atoms deduced from local probe measurements. In a first approximation, by considering the contribution of the reduced magnetic moment of Mn atoms near the structural defects to be negligible, we can estimate 17% of Mn atoms to occupy the regions with reverse magnetic moment in the powder.



Figure 8. 6 (a) Unit cell of $Ni_{50}Mn_{34}In_{16}$. Local magnetic moments on the Mn site, deduced from neutron powder diffraction, are marked by arrows. (b) Sketch of the possible antiferromagnetic coupled regions between two antiphase boundaries.

Concerning the transition temperature, the mean field theory defines the Curie temperature (T_c) as:

$$T_c = \frac{zJs(s+1)}{3k_B} \tag{8.3}$$

where z is the number of nearest-neighbour moments, s the localized spin on Mn atoms, J the exchange interaction between Mn atoms and k_B the Boltzmann's constant. Assuming that the localized spin of Mn atoms in 4b sites is the same as that of Mn atoms in 4a sites and that the local exchange interaction varies only near the APBs and not inside the AF regions, we can understand why we observe only a weak variation of T_c compared with the large reduction of magnetization. The broadening of the transition in the powder can be explained with a local distribution of the exchange interaction as a function of the local amount of lattice defects and of the presence of Mn atoms in the 4b sites.

Suitable heat treatments can reduce the density of structural defects and eliminate part of the AF regions pinned to the APBs, with a resultant recovery of magnetization [241]. However, heat treatments temperature and duration have to be selected very carefully in order to avoid the segregation of secondary phases, as in the case of the sample measured in this work.

The great difficulty to directly observe the APBs makes it very hard to experimentally verify the above hypothesis. Indeed, diffraction data collected with conventional measurements are not sufficiently resolved to provide reliable information on the local atomic disorder affecting the Heusler superstructure. Detailed assessments on the nature and density of intrinsic lattice defects such as antiphase boundaries (APB's), stacking faults or point defects require specific structural investigation strategies involving a series of complementary experimental techniques. Only recently, with a combination of Lorentz microscopy, electron holography and high-angle annular dark-field scanning transmission electron microscopy (HAADF-TEM), it was possible to demonstrate the magnetic degradation in the APBs regions of a Ni₅₀Mn₂₅Al_{12.5}Ga_{12.5} Heusler alloy [246,247]. More accurate and systematic studies, based on a synergic use of TEM, electron crystallography and high-resolution diffraction experiments collected with synchrotron radiation, are necessary to statistically extend these local observations to the entire volume of a bulk material and to correlate them with the macroscopic magnetic and MC properties. Furthermore, the correlations between structural defects and functional properties have to be investigated as a function of the adopted synthesis protocols, including the annealing processes, and of the mechanical stresses introduced by manufacturing.

8.4 Conclusions

In conclusion, in this chapter we have discussed the degrading effect of the broadening of second-order Curie transition on the related MCE. Mean-field simulations demonstrated the substantial negative effect on the MCE due to the increase of the transition broadness. Moreover, the particular case of the effect of cold working on the magnetic and magnetocaloric properties of a NiMnIn Heusler alloy across its Curie transition was considered. The detrimental effect of cold working on the MC properties of a Ni₅₀Mn₃₄In₁₆ sample was demonstrated. The induced stressed state of the sample decreases the saturation magnetization and broadens the Curie transition, resulting in a drastic reduction of the magnetic entropy change. This effect could be likely due to the presence of domains limited by APBs, antiferromagnetically coupled with the rest of the sample. Annealing treatments can partially release the strain and recover the initial magnetization. This fact is of great importance for the technological application of this class of allovs as active element in magnetic refrigerators. Furthermore, an open fundamental issue is to understand in detail the link between structural disorder and the magnetization reduction, in order to control it. This could lead to a better reproducibility in sample preparation, thus allowing the comparison of samples synthesized in different laboratories. Moreover, this could offer a new parameter that can be tuned in engineering of functional materials.

9. CONCLUSIONS AND OUTLOOKS

The aim that has driven this Thesis was the development of new experimental methodologies for the characterization of functional materials to be used as active elements in magnetic cooling systems at room temperature. The attention was mainly paid to the test of magnetocaloric features of materials in shapes and under conditions closer to those of real applications. Moreover, the necessity to precisely control the magnetocaloric performance of materials, moved me to investigate the effect of several properties of magnetic transitions, which can be modified during materials' synthesis and manufacturing and which have a key role in determining the exploitable magnetocaloric effect.

The main goal of this Thesis was the realization of two innovative experimental setups to directly measure the MCE, as adiabatic temperature change, in thin samples and with fast magnetic field changes.

In the first realized instrument, based on a non-contact IR temperature sensor, very good quasi-adiabatic conditions were obtained, thus allowing the measurement of field-induced temperature variations in gadolinium sheets with a thickness down to 27 μ m. Thermal simulations of the measurement system confirmed the experimental results and allowed to estimate the time-scale of magnetic field change required for measuring thinner samples. The designed technique represents an ideal solution both to directly measure the MCE of samples with reduced thickness and to reproduce high frequency (up to 6 Hz) thermomagnetic cycles for testing the material response in operating conditions. The use of thermopiles moreover can be extended to directly measure other caloric effects in thin samples. The proposed non-contact technique, when studying Electrocaloric, Barocaloric and Elastocaloric effects, may become an undeniable solution to isolate the temperature sensor from electric or mechanical stresses, thus improving the measurement quality and the lifetime of the technique.

The second designed experimental setup represents an original idea, which takes advantage of the thermo-optical "Mirage effect" to directly measure the adiabatic temperature change induced in a magnetocaloric material by a pulsed magnetic field. This innovative, simple and versatile non-contact technique allows to test the response of magnetocaloric materials to fast magnetic field changes, in this way simulating high frequency operating conditions (1 T at a frequency of about 150 Hz).

Measurements performed on some Fe₂P-based compounds, demonstrated the suitability of the realized experimental setup and the outstanding dynamic response of these materials, which makes them ideal for applications at high frequencies. Moreover, the reduction of the measurement time constant below one millisecond ensures very good adiabatic conditions, making this technique suitable also for characterizing samples with low dimensionality (foils, ribbons and freestanding thin films). This possibility was proved through the direct characterization of the magnetocaloric effect near the Curie transition of a series of NiMn(In,Sn) ribbons.

The combination of the principles of the two presented instruments, may bring, in the future, to the development of experimental setups in which IRtemperature sensors and magnetic field pulses are exploited to investigate the MCE induced by very fast magnetic stimuli. This may offer important information to design innovative technological applications and to extend the understanding of the kinetics of magnetic transformations.

The second main result of this Thesis was the demonstration of the negative influence on the MCE of the broadening of first- and second-order magnetic transitions. This conclusion has been reached by exploiting phenomenological and numerical models of the transformations and complete magnetocaloric characterizations performed on different MC materials. In particular, the magnetostructural martensitic transition and the Curie transition of (Ni,Mn)based Heusler alloys were investigated. Concerning the magnetostructural transformation of these alloys, the combination of bulk measurements techniques and microscopy analysis demonstrated that the broadness of the transition is characteristic of a microscopic scale and cannot be ascribed to macroscopic chemical inhomogeneities. Moreover, the study of the degrading effect of cold-working on the MCE of a NiMnIn Heusler alloy at the Curie transition suggested the existence of a correlation between the density of structural defects, and in particular of antiphase boundaries, with the magnetic and magnetocaloric features of these alloys.

For both the transitions, it resulted evident a strong relationship between the magnetic and magnetocaloric properties of these alloys with their structural and microstructural features. A thorough study is needed to understand these correlation. Results from bulk measurement techniques have to be compared with local direct observations (e.g.: high resolution electron microscopy and crystallography, Lorentz microscopy, magnetic atomic force microscopy) and experiments with statistical probes of local states (e.g.: high-resolution X-rays diffraction, elastic and inelastic neutron diffraction and solid-state nuclear magnetic resonance). Furthermore, these studies have to be carried out

considering different synthesis protocols, annealing processes and mechanical stresses induced by cold manufacturing. This work would result fundamental in the perspective to optimize the MC performance of materials and to develop mass production routes with the scaling-up of synthesis protocols. Moreover, the idea of realizing complex structures consisting of layered magnetocaloric materials, or of their smart composites, requires a careful evaluation of the manufacturing influence on the functional properties of materials.

Finally, an unresolved topic that has still to be studied is the correlation between hysteresis and broadness of first-order transformations. Partial transformations between metastable mixed-states, induced by temperature or by magnetic field under different conditions have to be explored on both the macroscopic and the microscopic scale, in order to optimize the thermomagnetic cycles exploitable in energy conversion applications. Moreover, this study would result in a clearer understanding of the kinetics of first-order magnetic transformations.

APPENDIX

A. Adiabatic temperature change of Mn₃GaC

This appendix presents direct adiabatic temperature change measurements performed on Mn_3GaC and $Mn_3GaC_{0.85}N_{0.15}$ compounds. These materials belong to a family of compounds (Mn_3MC , M = Al, Zn, Ga, Ge, Sn, In) that crystallize in the antiperovskite structure and show interesting magnetic ordering configurations and structural transitions [188,217,218,230]. Here, the attention is focused on the magnetocaloric effect displayed by the Mn_3GaC compound at its first-order magnetostructural transition between an antiferromagnetic (AFM) and a ferromagnetic (FM) state (~ 160 K) and at the Curie transition of the FM phase (~ 250 K) [186,218]. The partial substitution of C with N decreases the Curie transition temperature and increases the temperature of the structural transition, thus determining the convergence of the two transitions [217,248].

The studied samples (Mn₃GaC and Mn₃GaC_{0.85}N_{0.15}) were prepared by Ö. Çakir (Yildiz Technical University, Istanbul, Turkey) by solid state reactions of starting elements powders (for details see Ref.s [186,248]).

The temperature dependence of magnetization of the two samples is reported in Figures A.1.a and A.1.b for different values of applied magnetic field ($\mu_0 H = 0.001$ T, 1 T and 2 T). The Mn₃GaC compound shows a sharp first-order magnetostructural transition, between an AFM and a FM state, at about 161 K, which is characterized by a thermal hysteresis of about 3.5 K (Figure A.1.a). The transition temperature is shifted by the applied magnetic field to lower temperatures with a rate of about -4.3 KT⁻¹. The Curie transition of the ferromagnetic state, not shown in Figure, occurs at 250 K. Instead, the N-doped sample shows the structural transition at about 182 K, almost superimposed to the Curie transition (Figure A.1.b). The thermal hysteresis is reduced to nearly zero.

Direct adiabatic temperature change measurements were performed on the two compounds, by using the probe described in Chapter 3.5 with magnetic field changes of 2 T and 5 T, reaching magnetic field rates of about 20 Ts⁻¹ and 200 Ts⁻¹, respectively. Before performing each measurement, the sample was cooled down to T_{reset} , in order to completely reset the antiferromagnetic state of the material (for Mn₃GaC: $T_{reset} < 130$ K for measurements in $\mu_0 H = 2$ T and $T_{reset} < 110$ K in 5 T; for Mn₃GaC.₂₅N_{0.15}: $T_{reset} < 150$ K for measurements in 2 T and $T_{reset} < 130$ K in 5 T). In each measurement, after stabilizing the starting

temperature, the sample was cyclically inserted and extracted three times from the magnetic field region (see examples reported in Figure A.3.a).



Figure A. 1 Temperature dependence of magnetization of (a) Mn_3GaC and (b) $Mn_3GaC_{0.85}N_{0.15}$ under $\mu_0H = 1 \text{ mT}$ (right scale), 2 T and 5 T (left scale).

Figure A.2.a reports the $\Delta T_{ad}(T)$ of Mn₃GaC sample for a $\mu_0 \Delta H = 2$ T obtained with the first insertion and extraction of the material from the applied magnetic field. We can appreciate the large inverse MCE at the structural transition $(\Delta T_{ad} = -3.1 \pm 0.1 \text{ K at } 158 \text{ K})$ and the lower direct MCE at the Curie transition $\Delta T_{ad} = 0.9 \pm 0.1$ K at 248 K). Figure A.2.b compares the $\Delta T_{ad}(T)$ for a $\mu_0 \Delta H = 2$ T and 5 T measured during the first and the second application of the magnetic field. The magnetic field change of 2 T is enough to fully induce the phase transformation under adiabatic conditions in a narrow temperature range. The reduction of the ΔT_{ad} with the 5 T magnetic field is due to the alignment of the magnetic moments of the ferromagnetic phase, which results in a classical direct MCE superimposed to the inverse effect of the first-order transformation. The difference between the $\Delta T_{ad}(T)$ curves obtained with the first and the second application of the magnetic field is related to the hysteretic character of the transition. The hysteresis reduces indeed the MCE exploitable with a cyclical application of the magnetic field in the temperature range of the hysteretic shift of thermal transition in zero applied field (the orange area in Figure A.2.b). In this temperature range, the MCE is nearly completely irreversible both in the 2 T and in the 5 T magnetic field change. Instead, at temperatures lower than about 156 K the MCE is completely reversible also with the lower magnetic field change. At these temperatures, both the application of the magnetic field and its removal induce the same phase transformation. Figure A.3.a reports, as an example, some cyclical direct ΔT_{ad} measurements performed at different temperatures. We observe the difference between the fully reversible ΔT_{ad} of measurement number 3 (at 154.9 K) and the almost completely irreversible ΔT_{ad}

of measurement number 1 (at 160.5 K). Looking at the schematization of these measurements in the phase diagram of the compound (Figure A.3.b, built from magnetization data), we see that in measurement 1 only the AFM \rightarrow FM equilibrium line is crossed, while in measurement 3, the 2 T magnetic field is enough to induce both the transformations.

The very sharp shape of the structural transformation defines the clear distinction between the reversibility and irreversibility regions. Indeed, as discussed in details in Chapter 7, in presence of sharp transformations the temperature range in which cyclical partial transformations between mixed states are allowed is restricted.



Figure A. 2 (a) $\Delta T_{ad}(T)$ of Mn_3GaC , directly measured by applying (field on, red squares) and removing (field off, brown triangles) a $\mu_0 H = 2T$ magnetic field, following the "reset" protocol described in main text. (b) Comparison between the $\Delta T_{ad}(T)$ obtained with the first (red and blue symbols) and the second (yellow and cyan symbols) application of a $\mu_0 H = 2$ T (squares) and 5 T (triangles). The orange area highlights the temperature range of the thermal hysteresis in zero applied magnetic field (from magnetization measurements).



Figure A. 3 (a) Examples of some ΔT_{ad} measurements performed on the Mn₃GaC sample with the cyclical application and removal of the 2 T magnetic field. (b) Schematization of the measurements number 1 and 3 in the phase diagram of the material built from magnetometric data.
Figures A.4.a and A.4.b report the results obtained for the N-doped sample. We can appreciate that the direct and indirect MCE are very close in temperature and they limit themselves. However, a very narrow hysteresis makes the MCE completely reversible also across the first-order transformation. The ΔT_{ad} at the first-order transition measured with $\mu_0 \Delta H$ of 5 T shows values larger than those obtained with the 2 T magnetic field span. This is due to the shift of the transition temperature to lower temperatures, which allows the material to reach a higher magnetization state (Figure A.1.b), with a resulting increase of the MCE.



Figure A. 4 (a) $\Delta T_{ad}(T)$ of $Mn_3GaC_{0.85}N_{0.15}$, directly measured by applying (field on, red squares) and removing (field off, brown triangles) a $\mu_0 H = 2$ T magnetic field, following the "reset" protocol described in main text. (b) Comparison between the $\Delta T_{ad}(T)$ obtained with the first (red and blue symbols) and the second (yellow and cyan symbols) application of a $\mu_0 H = 2$ T (squares) and 5 T (triangles).

B. Magnetic and calorimetric properties of MnFeP(As,Si) compounds

This appendix reports the magnetic and calorimetric characterization of samples $MnFeP_{0.45}As_{0.55}$ (As-sample) and $Mn_{1.25}Fe_{0.7}P_{0.45}Si_{0.55}$ (Si-sample), which are discussed in Chapter 6.4. The samples were prepared by L. Caron and X. F Miao (TU Delft, The Netherlands) by ball milling and subsequent annealing of high purity elements. The As-sample was made by milling for 1 h in Ar atmosphere the starting elements in adequate proportions. The resulting powder was pressed into pellets under a force of 5 kN. The pellets were then annealed at 1273 K for 100 h then at 923 K for 120 h in Ar atmosphere. The Si-sample was prepared as described in Ref. [34,81].

Isofield magnetization curves of the two samples are reported as a function of temperature in Figure B.1. The measurements have been performed, using a SQUID magnetometer, across the magnetic transition with temperature sweeps on heating and on cooling at a rate of 1 Kmin⁻¹. The As-sample shows a firstorder magnetoelastic transition, characterized by a narrow thermal hysteresis (1.8 K) and a strong dependence of the transition temperature on the magnetic field $(dT_t/dH = 5.3 \text{ KT}^{-1})$. These results are in agreement with literature data [79,164]. The Si-sample displays a transition with a weaker first-order character. The observed thermal hysteresis is lower than 0.4 K, which can be due to a thermal delay of the experimental setup. In addition, the dependence of the transition temperature from the magnetic field is lowered $(dT_t/dH = 3.1 \text{ KT}^{-1})$. Insets of Figures B.1.a and B.1.b report the isothermal entropy change $(\Delta S_T(T))$ of the two samples, which was calculated using the Maxwell relation (Equation 2.3). The entropy change exhibits a peak of 8.9 ± 0.3 Jkg⁻¹K⁻¹ at 305.5 K for the As-sample and of 6.8 ± 0.5 Jkg⁻¹K⁻¹ at 311.3 K for the Si-sample (for a $\mu_0 \Delta H = 1$ T), in agreement with Ref. [164]. The heating and cooling $\Delta S_T(T)$ curves overlap, for both samples, across their peak value, showing the complete reversibility of the MCE for this magnetic field span. This has been confirmed by measuring the adiabatic temperature change of subsequent thermomagnetic cycles, where no differences between the first and the following branches were observed.

In-field DSC measurements (Figures B.2.a and B.2.b) confirm the results obtained from magnetometry data. Figures B.2.a and B.2.b report the heat flux of the two samples measured with temperature sweeps of 1 Kmin⁻¹ on heating (red lines) and on cooling (blue lines), in a zero (continuous lines) and in a 1 T applied magnetic field (dashed lines). The larger thermal hysteresis of DSC data is due to a thermal lag of the calorimeter, which is amplified by the large dimensions and the low thermal conductivity of the measured samples. The

peaks in the DSC data of the Si-sample broaden with the application of the magnetic field, while the total amount of latent heat of the transition remains constant. This effect, which is not observed in the As-sample supports the assumption of weakening of the first-order nature of the transformation, with a decrease of the energy barrier associated with the phase transition [13,198].



Figure B. 1 Isofield measurements of the As-sample (a) and of the Si-sample (b), performed at different magnetic fields on heating (filled symbols) and on cooling (empty symbols). Insets: isothermal entropy variation for a magnetic field change of 1 T on heating (red circles) and on cooling (blue triangles).



Figure B. 2 In-field DSC measurements of the As-sample (a) and of the Si-sample (b), performed in zero applied magnetic field (dashed lines) and in a $\mu_0 H = 1T$ applied magnetic field (continuous lines), with temperature sweeps on heating (red lines) and on cooling (blue lines). Insets: isothermal entropy variation for a magnetic field change of 1 T on heating (red circles) and on cooling (blue triangles), derived from the DSC data.

The ΔS_T values, obtained by integrating DSC data (Chapter 2.4) and plotted in the insets of Figures B.2.a and B.2.b, are consistent with the results of magnetometric measurements (ΔS_T peak values: 8.7 ± 0.7 Jkg⁻¹K⁻¹ for As-sample and 6.1 ± 0.6 Jkg⁻¹K⁻¹ for Si-sample). On the contrary, the ΔT_{ad} values derived from DSC data (peak values of 2.9 ± 0.2 K for As-sample and 1.9 ± 0.2 K for Sisample) are larger compared to the results obtained from direct measurements (reported in Figures 6.12.a and 6.12.b of Chapter 6.4). This discrepancy was already observed by Engelbrecht et al. [200] and it is in contrast with other works that demonstrate the convergence of MC characterizations obtained with direct and indirect methods in different materials [22,125]. It has to be underlined that this discrepancy cannot be ascribed to thermal hysteresis, because the ΔT_{ad} values obtained following the resetting and the continuous protocols (Chapters 2.4 and 3.5) are the same. This unresolved task will be the object of a specific future research activity.

C. Structural, microstructural and magnetic features of Ni,Mn(In,Sn) ribbons

In the following, the results of structural, microscopy and magnetometric characterization are reported for a series of five $Ni_{50}Mn_{35}(In_{1-x}Sn_x)_{15}$ Heusler alloys ribbons, with x = 0, 0.25, 0.5, 0.75, 1 (the samples are labelled respectively: Sn0, Sn25, Sn50, Sn75, Sn100). The MC characterization of these alloys is presented in Chapter 6.5.

The samples were prepared in form of ribbons (thickness of about 10-20 μ m) with the melt-spinning technique (described in Chapter 3.1). The Sn0 sample was prepared starting from a Ni₅₀Mn₃₅In₁₅ bulk sample synthetized with the arcmelting technique. The other four samples were prepared by melting the starting elements (99.99% purity) directly in the inductance oven of the melt-spinner. An excess of 1% Mn, In and Sn was added to compensate the evaporation during the melting. Later, the ribbons were sealed in quartz tubes, annealed for 2h at 1073 K in Ar atmosphere and subsequently quenched in cold water. The composition of the samples, measured through SEM-EDS microanalysis, is reported in Table 6.1 of Chapter 6.5.

Figures C.1.a and C.1.b show the magnetization as a function of temperature of the five alloys in a field span $\mu_0 H = 0.01$ T (Figure C.1.a) and 2.0 T (Figure C.1.b), measured, with a SQUID magnetometer, by following the zero-field cooling (ZFC), the field cooling measured on cooling (FCC) and on warming (FCW) protocols. The magnetic field was applied parallel to the ribbons surface, in order to minimize the effect of the demagnetizing field. The five samples display a Curie transition near room temperature, which is shifted to higher temperatures with the increase of Sn content (Table C.1 and green circles in Figure C.2.a). On the contrary, the substitution of In with Sn brings to a decrease of the low temperature magnetization of the samples in a $\mu_0 H = 2$ T (Table C.1, blue squares in Figure C.2.a). M(H) measurements demonstrated that the magnetization at 5 K is almost saturated with a 2 T magnetic field. The S25 sample does not follow the composition dependences of T_c and saturation magnetization, showed by the others four samples (open symbols in Figure C.1; red symbols in Figure C.2.a). The higher values of saturation magnetization and transition temperature are likely due to the higher content of Mn (Table 6.1, Chapter 6.5) with respect to the others samples.

Samples S100 and S25 present, at low temperature, a structural transformation between a low-temperature martensitic phase and the ferromagnetic austenitic phase. This first-order transformation is characterized by an evident thermal hysteresis. The martensitic transformation fixes a limit to the Mn content of the alloy. Indeed, a higher content of Mn, at the expense of In-Sn content, leads to an increase of the martensitic transformation temperature up to room temperature, with a resulting disappearance of the austenite Curie transition [232,249]. In the case of studied samples, the martensitic transformation is still far away from room temperature and it does not affect the presented results at the Curie transition.



Figure C. 1 ZFC and FCC magnetization measurements in a $\mu 0H = 0.01 T$ (a) and FCC, FCW in $\mu 0H = 2 T$ (b) of the five alloys.



Figure C. 2 (a) Curie temperature (cyrcles), saturation magnetization (squares) and cell parameter (triangles) of the five $Ni_{50}Mn_{35}(In_{15-x}Sn_x)_{15}$ alloys as a function of Sn content. The red symbols represents the data of the Sn25 sample. (b) X-rays powder diffraction patterns for the five alloys.

The observed magnetic features of the samples are quite in agreement with those reported for bulk samples [232,249]. A small reduction of Curie temperatures and saturation magnetization can be ascribed to the decrease of the Mn/Ni ratio with respect to the stoichiometric composition.

The opposite trends, with the Sn content, of T_c and of saturation magnetization derive from the complex magnetic configuration of these Heusler alloys. Their magnetic state is the result of the interactions between the magnetic moments of Mn and Ni atoms; but it is also strongly influenced by the electronic structure, by structural and microstructural features and by the chemical order of the alloy [201,203,204,223,250]. The deep understanding of the individual and crossed contributions of these factors, which is the subject of a research activity in progress, would bring to a better design of functional magnetic Heusler alloys, with the aim of tuning and improving their magnetic and MC properties.

Powder X-rays diffraction analysis at room temperature, reported in Figure C.2.b, confirms the $L2_1$ cubic structure (Fm3m) for all the samples. Cell parameters (Table C.1, Figure C.2.a), obtained by Rietveld refinement of the diffraction data, do not show an evident trend with the composition.

	e/a	c (Å)	M (Am ² kg ⁻¹)	T _C (K)	ΔT_{ad} (K)	T_p (K)
Sn0	8.014	5.998	105.7	286.5	0.81	288.5
$\mathbf{Sn25}$	8.038	6.003	117.2	309.8	0.74	310.8
$\mathbf{Sn50}$	8.077	5.990	101.2	303.7	0.78	301.2
$\mathbf{Sn75}$	8.162	5.994	90.1	316.7	0.66	314.9
Sn100	8.146	6.006	87	331.8	0.65	328.4

Table C. 1 Valence electron concentrations per atoms (e/a), lattice parameters of the cubic unit cell (c) at room temperature, magnetization at 5 K in $\mu_0 H = 2$ T (M), Curie temperatures, adiabatic temperature change in a $\mu_0 \Delta H = 1$ T (T_c), temperatures corresponding to the peaks of ΔT_{ad} (T) curves (T_p) of the five alloys.



Figure C. 3 Electron microscopy images of three different microstructure observed in the NiMn(In,Sn) ribbons.

Electronic microscope observations reveal for the five ribbons a similar granular microstructure containing multiple shapes (grains with different size, a tree leaflike structure, examples of which are reported in Figure C.3) with a grains size that varies between a few micrometres and a few tens of micrometres. The average grain size is lower than that observed in bulk materials prepared with by arc-melting technique (see e.g. [232]). The microstructure of the surface suggests the presence of columnar grains perpendicular to the ribbon surface, grown in the direction of heat flow during the rapid solidification process (as already observed for example in Ref. [251]).

D. Structural, calorimetric and MC properties of NiCoMnGaIn Heusler alloys

This appendix reports supplementary information about the series of (Ni,Co)₂Mn(Ga,In) samples discussed in Chapter 7.2 (listed in Table 7.1). Structural properties of the samples were evaluated by X-rays powder diffraction experiments, performed in a wide temperature range across the structural transformation of each sample. The powder used for the experiments was heat treated to reduce stresses and structural defects induced by grinding. The collected data confirm the presence in all samples of a structural transformation from cubic austenite to tetragonal martensite, spreaded over a large temperature interval and characterized by a considerable cell volume change. The diffraction patterns have been fitted through the Lebail algorithm to extrapolate the lattice parameters of the two phases as a function of temperature. Table D.1 reports the obtained values of: the volume change at the transition $(\Delta V/V)$, the tetragonal distortion of the martensitic lattice $(t = c_M/a_M \sqrt{2})$, where a_M is the lattice parameter of the tetragonal plane and c_M is the tetragonal axis) and the middle eigenvalue of the transformation matrix for the cubic-tetragonal transformation $(\lambda_2 = a_M \sqrt{2}/a_A)$, which is a good parameter for describing the lattice mismatch at the transformation invariant plane [100,211].

	ΔV/V (%)	$t=c_M/a_M\sqrt{2}$	$\lambda_2 = a_M \sqrt{2}/a_A$
$\mathbf{S1}$	0.6 ± 0.1	1.200 ± 0.005	0.940 ± 0.002
S2	1.2 ± 0.1	1.210 ± 0.005	0.933 ± 0.002
$\mathbf{S3}$	0.85 ± 0.05	1.205 ± 0.005	0.936 ± 0.001
$\mathbf{S4}$	0.88 ± 0.025	1.202 ± 0.005	0.937 ± 0.001

Table D. 1 Values of the relative volume change ($\Delta V/V$), tetragonal distortion of the martensitic cell (t) and middle eigenvalue of the transformation matrix λ_2 , obtained for the four samples from X-rays powder diffraction data.

The volume change together with the change in symmetry between the two phases can be one of the main causes of the large thermal hysteresis and of the large width of the transformation observed for these alloys (see Chapter 7.2). The volume change $(\Delta V/V)$ varies significantly within the series of samples: the maximum volume discontinuity is $\approx 1.2 \pm 0.1$ % for sample S2, while the smallest one is $\approx 0.6 \pm 0.1$ % for sample S1, which displays the smallest broadness of the transformation. On the contrary, S1 has the highest values of the middle

eigenvalue of the transformation matrix λ_2 . Instead, the values of the tetragonal distortion *t* of the martensitic phase show a much smaller variance in the series. Tables D.2-5 collect values of thermodynamic and thermomagnetic characteristics of the martensitic transition of the four studied samples, complementary to the data reported in Chapter 7.2. All these data were derived from DSC measurements, showed in Figure 7.4 of Chapter 7.

From Table D.2 we appreciate that, for all the samples, the dT_t/dH across the cooling transformation is higher than that in the heating branch. This confirms the already reported behaviour [209,252] according to which the magnetic field shifts more the transformation temperature on cooling due to the larger magnetization jump. Moreover, the different field sensitivity of the cooling and heating critical temperatures affects also the thermal hysteresis: the in-field hysteresis is indeed larger than the zero-field one (Table D.2).

	dT₊⁄µ₀dH	dT₁⁄ µ₀dH	Hyst.	Hyst.	
	heat.	cool.	$\mu_0 H = 0 \mathrm{T}$	$\mu_0 H = 1.8 \text{ T}$	
	(K T-1)	(K T-1)	(K)	(K)	
$\mathbf{S1}$	$\textbf{-}2.4\pm0.6$	-2.7 ± 0.6	10.4 ± 0.6	11.6 ± 0.6	
S2	-4.6 ± 1.0	-5.9 ± 1.0	16.7 ± 1.0	19.1 ± 1.0	
$\mathbf{S3}$	-4.5 ± 1.0	-5.9 ± 1.0	21.5 ± 1.0	24.0 ± 1.0	
$\mathbf{S4}$	-3.5 ± 1.0	-4.3 ± 1.0	16.9 ± 1.0	18.4 1.0	

Table D. 2 Magnetic field dependence of the transition temperature $(dT_t/\mu_0 dH)$ on heating and on cooling; thermal hysteresis of the transformation (Hyst.) in zero and in 1.8 T applied magnetic field.

	L	L	L	L
	0 T heat.	1.8 T heat.	0 T cool.	1.8 T cool.
	(J kg ⁻¹)			
S 1	2600 ± 80	2280 ± 70	2450 ± 70	2230 ± 70
$\mathbf{S2}$	4700 ± 140	4040 ± 120	3730 ± 110	3420 ± 100
$\mathbf{S3}$	4450 ± 130	4070 ± 120	3940 ± 120	3940 ± 120
$\mathbf{S4}$	5150 ± 150	4550 ± 130	3810 ± 110	3440 ± 100

Table D. 3 Latent heat of the structural transformation of the four samples calculated from DSC data for temperature sweeps on heating and on cooling in zero and in 1.8 T applied magnetic field.

Looking at the values of latent heat, collected in Table D.3, we observe that both the application of magnetic field and the shift to lower temperatures of the transformation observed in the cooling curves result in a sizeable reduction of L. The strong action of the magnetic field on the latent heat was already observed in Ni-Mn-Co-Ga-In [209]. This effect is reduced by decreasing the In content and it disappears in the parent ternary Ni₂MnGa alloy [209]. Comparing the values of latent heat of the transformation on heating in zero applied magnetic field, we observe that S1 shows the lowest value. This is in agreement with the trend of the volume change and of the transformation width. In general, the reported values of latent heat are lower than that of the parent $Ni_{50}Mn_{30}Ga_{20}$ alloy (L ~ 7000 J kg⁻¹ [209]), which shows a magnetostructural transition from a ferromagnetic martensite to a paramagnetic austenite accompanied by a lower volume change ($\Delta V/V \sim 0.2$ % [209]). This indicates as the enhancement of magnetization and volume jump, by the Co- and In-doping, which contribute to increase the sensitivity of transition temperature to the magnetic field, has a depressive effect on the maximum entropy change $(\sim L/T_t)$ [209].

	ΔS_f	ΔS_p	$\Delta S_p / \Delta S_f$	ΔS_p	$\Delta S_{p} \Delta S_{f}$
		$\mu_0 \Delta H = 1.0 \text{ T}$	$\mu_0 \Delta H = 1.0 \text{ T}$	$\mu_0 \Delta H = 1.8 \text{ T}$	$\mu_0 \Delta H = 1.8 \text{ T}$
	(J kg ⁻¹ K ⁻¹)	$(J \text{ kg}^{-1} \text{ K}^{-1})$	(%)	(J kg-1 K-1)	(%)
$\mathbf{S1}$	6.8	3.5 ± 0.5	52	6.2 ± 0.5	91
S2	13.4	4.2 ± 0.8	31	7.7 ± 0.8	57
$\mathbf{S3}$	11.7	3.8 ± 0.9	32	6.5 ± 0.9	56
$\mathbf{S4}$	14	3.7 ± 0.7	26	7.5 ± 0.8	54

Table D. 4 Comparison between the peak values of $\Delta S_T(T)$ for a $\mu_0 \Delta H$ of 1 T and 1.8 T, calculated from DSC data, and the maximum expected values ($\Delta S_f \approx L/T_p$).

	ΔT_{max}	ΔT_p	$\Delta T_{p/} \Delta T_{max}$	ΔT_p	$\Delta T_{p/} \Delta T_{max}$
		μ ₀ ΔΗ =1.0 T	μ ₀ ΔΗ =1.0 T	μ ₀ ΔΗ =1.8 T	μ ₀ ΔΗ =1.8 T
	(K)	(K)	(%)	(K)	(%)
S 1	4.3	1.3 ± 0.2	30	-2.5 ± 0.2	58
$\mathbf{S2}$	8.3	1.7 ± 0.3	20	-3.3 ± 0.3	40
$\mathbf{S3}$	8.1	1.7 ± 0.4	21	-3.1 ± 0.4	38
$\mathbf{S4}$	6.3	1.3 ± 0.3	21	-2.9 ± 0.3	46

Table D. 5 Comparison between the peak values of $\Delta T_{ad}(T)$ for a $\mu_0 \Delta H$ of 1 T and 1.8 T, calculated from DSC data, and the maximum expected values ($\Delta T_{max} = \Delta H(dT_t/dH)$).

Unlike latent heat, hysteresis and sensitivity of the transition temperature to the magnetic field, the width of the transformation is, for all the samples, almost unchanged under the applied magnetic field.

Moreover, we have verified that the width of the transformation is almost insensitive also to the application of an external pressure. Indeed, by performing M(T,H) measurements of NiCoMnGaIn alloys under high hydrostatic pressure (up to 1.1 GPa; at the ASCR Institute of Physics, Prague, Czech Republic), we observed a significant modification of the critical temperature of structural transitions, of the thermal hysteresis and of the sensitivity of transition temperature to the applied magnetic field but no variation in the width of the transformation (for details see Ref. [253]).

Finally, Figure D.1.a and D.1.b report, as an example, the comparisons, for the S2 and S4 samples, of the $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ derived from in-field DSC data and the values of $\Delta S_T(T)$ calculated from M(T,H) curves and those of $\Delta T_{ad}(T)$ directly measured with the probe described in Chapter 3.5, respectively. The direct measurements have been performed by following the "reset" protocol described in Chapter 2.4. As we already demonstrated in Ref. [125], results of the three techniques converge to the same values, providing that right measurement protocols are followed and the same samples are measured with the different techniques.



Figure D. 1 (a) Comparison of the $\Delta S_T(T)$ of sample S2 for a $\mu_0\Delta H$ of 1 T and 1.8 T on heating and on cooling derived from DSC data (circles) and calculated from $M(T)_H$ curves by applying the Maxwell relation (triangles). (b) Comparison of the $\Delta T_{ad}(T)$ of sample S4 for a $\mu_0\Delta H$ of 1.8 T on heating obtained from DSC data (circles) and directly measured (triangles). Inset: example of a single ΔT_{ad} measurement at 365 K.

E. An example of transition broadening due to compositional inhomogeneity

Here, it is reported an example of transformation broadening caused by a macroscopic chemical inhomogeneity resulting from a wrong synthesis process. The studied sample is a $Ni_{41}Co_9Mn_{33}Ga_{15}In_2$ Heusler alloy (sample S9 in Chapter 7.3), which shows a broad martensitic transformation (FWHM ~ 5 K) at about 385 K.



Figure E. 1 (a) Chemical composition, as at.%, resulted from SEM-EDS analysis of 8 different points of the sample surface, which are stated in photograph (b). (c) Microscopy images of 3 portions of the sample surface corresponding to the regions A, B and C in photograph (b).

Investigation of the spatial distribution of the chemical composition was carried on through SEM-EDS analysis of 8 different areas on the sample surface. In the histogram of Figure E.1 we can appreciate the presence of three distinct regions of the sample surface (highlighted in Figure E.1.b as: A, B and C) characterized mainly by a different content of Ni and Co. Ni and Co are among the constituent elements the ones with the higher melting temperature and this can result in a improper melting process. In particular, region B shows the presence of a not melted piece of Co. The other two regions (A and C) present Co variations of about 7 % and Ni oscillations up to 5 %. This can bring to a shift of the martensitic critical temperature higher than 20 K [93].

Microscopy images, reported in Figure E.1.c, display that different microstructures correspond to these three regions with different composition. Regions A and C display a microstructure typical of a martensitic phase, probably characterized by different modulations of the crystal structure (as observed for Ni-Mn-Sn alloys in Ref. [254]). On the contrary, region B shows a microstructure similar to that observed in Co-rich alloys [255].



Figure E. 2 DSC measurements of the sample S9 (continuous lines) and of a fragment of it (dashed lines), obtained with temperature sweeps on heating (red and orange lines) and on cooling (blue lines) in zero and in a 1.8 T applied magnetic field.

	<i>Тр</i> (К)	<i>L</i> (J kg ⁻¹)	<i>dT</i> _t / μ₀ <i>dH</i> (K T ⁻¹)	W (K)	ΔS_{Tpeak} (Jkg ⁻¹ K ⁻¹)	ΔT _{ad peak} (K)
S 9	387.0 ± 0.5	2530 ± 90	-2.3 ± 0.6	5.0 ± 0.4	3.9 ± 0.4	-1.9 ± 0.2
Frag	385.0 ± 0.3	2600 ± 80	-2.4 ± 0.6	3.1 ± 0.3	6.2 ± 0.5	-2.5 ± 0.2

Table E. 1 Peak temperature of the magnetostructural transition (T_p) , latent heat of the transformation (L), magnetic field dependence of the transformation temperature $(dT_t/\mu_0 dH)$, width of the transformation (W), peak values of $\Delta S_T(T)$ and $\Delta T_{ad}(T)$ derived from DSC data of the starting sample S9 and of a fragment of it.

The reported large macroscopic variations of the composition are probably reflected in a distribution of the temperature of the structural transformation, thus resulting in the broadening of the transformation. This is confirmed by the DSC measurements performed on a fragment of the initial bulk sample. The fragment (about $1x2x1 \text{ mm}^3$) was taken from region C and its chemical

homogeneity was verified within 0.5 %. Figure E.2 reports DSC measurements performed on the initial sample and on the fragment. The width of the transformation is almost halved, while the latent heat of the transformation and the field sensitivity of the transition temperature are almost unchanged (Table E.1). The reduction of the transition width results in a substantial increase of the MCE, as ΔS_T and ΔT_{ad} (Table E.1).

F. Mean field simulations of the MCE

Chapter 8.1 reports the results of simulations demonstrating the negative role of transformation broadening on the MCE across a second order magnetic transition. Simulations were performed by numerically implementing a molecular mean-field approach for the calculation of the magnetization of the system as a function of temperature and external magnetic field [16]. To simulate the broadness of the transformation, the system was considered divided in n not interacting portions, each characterized by a critical temperature T_i ($1 \leq 1$ $i \leq n$). A Gaussian distribution of the critical temperatures was chosen to simulate a random disorder in the system, due for example to a chemical or structural distribution around a mean value [227]. This distribution implies, in the mean-field perspective, a distribution of the mean-field exchange parameter λ ($T_C = \lambda C$, where C is the Curie constant). $M(T)_H$ curves were independently calculated for each portion of the total system with different external magnetic fields (up to 1 T) and from them the $\Delta S_i(T)$ was calculated by using Maxwell relation. The total $\Delta S_T(T)$ of the system, reported in Figure 8.1 (Chapter 8), was calculated as the weighed mean of the $n \Delta S_i(T)$ obtained for each portion, with the Gaussian weight:

$$w_i(T_i) = \frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{(T_i - T_c)}{2\sigma^2}}$$

where T_c is the mean value of the critical temperature distribution and the standard deviation σ permits to simulate different degrees of disorder.

To obtain the results presented in Chapter 8.1, the simulation was performed considering as a reference system a Ni₂Mn_{1.4}In_{0.6} Heusler alloy ($T_c = 320$ K, saturation magnetization $M_0 = 126$ Am²kg⁻¹, number of unit cells for unit mass = 2.28 10²⁴ kg⁻¹). M(T) curves were calculated for 21 values of applied magnetic field from 0.025 T to 1 T, in the temperature range 260 – 380 K, with a temperature step of 1 K.

Eight values of the standard deviation of the Gaussian distribution were considered: 1, 3, 5, 7, 9, 12, 15, 20 K. The distribution was numerically discretized with a temperature step of 0.1 K. The simulation performed with $\sigma = 1$ gave the same results of that in which it was not considered a distribution of critical temperatures.

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