MnNiSi based magnetocaloric alloys for cooling and energy harvesting applications

Kamble, Deepak

2019

Kamble, D. (2019). MnNiSi based magnetocaloric alloys for cooling and energy harvesting applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/136487>

<https://doi.org/10.32657/10356/136487>

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**MnNiSi BASED MAGNETOCALORIC ALLOYS FOR COOLING
AND ENERGY HARVESTING APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

MnNiSi BASED MAGNETOCALORIC ALLOYS FOR COOLING AND ENERGY HARVESTING APPLICATIONS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University in
partial fulfillment of the requirement for the degree of Doctor of
Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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5 July 2019

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Date

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Authorship Attribution Statement

This thesis contains material from 4 papers published in the following peer-reviewed journals in which I am listed as an author.

1. Figure of Merit and Improved Performance of a Hybrid Thermomagnetic Oscillator, *Applied Energy* 256, 113917 (2019).
2. Hybrid Thermomagnetic Oscillator for Cooling and Direct Waste Heat Conversion to Electricity, *Applied Energy* 233-234, 312-320 (2019)
3. Magnetocaloric Properties of Low-Cost Fe and Sn Substituted MnNiSi-based Alloys Exhibiting a Magnetostructural Transition Near Room Temperature, *IEEE Transactions on Magnetics* 54 (11), 2500805 (1-5) (2018)
4. Near Room Temperature Giant Magnetocaloric Effect in $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ Alloys, *Journal of Alloys and Compounds* 743, 494-505 (2018)

The contents of Chapter 4 is published as: K. Deepak and R. V. Ramanujan, "Near room temperature giant magnetocaloric effect in $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ alloys", *Journal of Alloys and Compounds* 743, 494-505 (2018). DOI: 10.1016/j.jallcom.2018.02.018

The contributions of the co-authors are as follows:

- Prof R. V. Ramanujan provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Prof. R. V. Ramanujan.
- Sample synthesis, structural characterization and magnetic measurements were performed by me at the Facility for Analysis, Characterization, Testing and Simulation (FACTS), NTU and at the PPMS facility under SHARE program, CREATE. I conducted the data evaluation and modeling of phase transition.

Chapter 5 is published as: K. Deepak and R. V. Ramanujan, "Magnetocaloric Properties of Low-Cost Fe and Sn Substituted MnNiSi-Based Alloys Exhibiting a Magnetostructural

Transition Near Room Temperature", *IEEE Transactions on Magnetics* 54 (11), 2500805 (1-5) (2018). DOI: 10.1109/TMAG.2018.2832090

The contributions of the co-authors are as follows:

- Prof R. V. Ramanujan provided the initial project direction and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised by Prof. R. V. Ramanujan
- I performed the materials synthesis, structural characterization, magnetic measurements and conducted data evaluation.
- X-ray diffraction at room temperature and high temperature were conducted by me at Facility for Analysis, Characterization, Testing and Simulation, NTU. Magnetic measurements were performed at the PPMS facility in SHARE program, CREATE.

Chapter 6 is published as:

- a) K. Deepak, V. B. Varma, G. Prasanna and R. V. Ramanujan, "Hybrid Thermomagnetic Oscillator for Cooling and Direct Waste Heat Conversion to Electricity", *Applied Energy* 233-234, 312-320 (2019).
DOI: 10.1016/j.apenergy.2018.10.057
- b) K. Deepak, M. S. Pattanaik and R. V. Ramanujan, "Figure of merit and improved performance of a hybrid thermomagnetic oscillator", *Applied Energy* 256, 113917 (2019). DOI: 10.1016/j.apenergy.2019.113917

The contributions of the co-authors are as follows:

- Prof R. V. Ramanujan provided the initial project direction and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised by Dr. V. B. Varma.
- I designed the setup of the prototype with the help of Dr. V. B. Varma. The synthesis of thermomagnetic material, geometry orientation, measurements of

temperature and electrical output and evaluation of figure of merit were performed by me.

- Data analysis and force balance calculations were done together by Dr. V. B. Varma and myself.
- G. Prasanna helped me to design the simulation model of the thermomagnetic oscillator in COMSOL Multiphysics and optimization of the material properties and device parameters.
- M. S. Pattanaik derived the expression for evaluating the energy generated by the thermomagnetic oscillator to be used for calculation of figure of merit.

25 November 2019

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Date

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Deepak Kamble

Abstract

Magnetic cooling and energy harvesting technology relies on magnetocaloric materials (MCM). It has several advantages over conventional cooling technology using vapour compression systems. The aim of current research on MCMs are to develop rare-earth free, high performance, low cost, environmentally friendly and readily available materials. Since the last two decades, various MCMs addressing to specific applications have been developed and some of these applications have also been commercialized in recent years. However, most of these materials suffer from various disadvantages such as high cost, low magnetocaloric properties, poor mechanical strength, corrosion, strategic limitations and tedious synthesis routes. Hence, there has been constant endeavors to develop MCMs exhibiting wide tunability of Curie temperature (T_C), good performance using low cost raw materials and simple synthesis steps. Such materials are very favorable for cooling and energy harvesting applications.

Among the MCMs investigated till date, it is observed that Mn based alloys have the property to exhibit giant magnetocaloric properties. Systematic tuning of the Mn-Mn interatomic spacing can be employed to induce ferromagnetic interactions. MnNiSi alloy was selected as the base material for the present work considering the cost of raw materials. This alloy exhibits both structural transformation and magnetic transition at 1200 K and 600 K, respectively. Substitutional alloying of MnNiSi can decrease the T_C and induce a coupling of magnetic and structural transition. Single element substitution by Fe can reduce the T_C upto 438 K. To further bring down the T_C to near room temperature, double element substitution, e.g., by Fe and Ge, is required.

(MnNiSi)_{1-x}(Fe₂Ge)_x alloys, synthesized by arc melting, exhibited a magnetostructural transition at temperatures ranging from 363 K to 218 K by varying x from 0.32 to 0.36, respectively. The heating and cooling cycles displayed a thermal hysteresis of ~15 K. The steep magnetic transition along with structural transformation resulted in a giant magnetocaloric response with $\Delta S_{\max} = 57.6 \text{ J kg}^{-1} \text{ K}^{-1}$, for a ΔH of 5 T at 301 K for x = 0.34. The alloy with x = 0.35 displayed an RCP of 480 J kg⁻¹. The phase transition was modeled

using Arrott plots, Landau theory and the Bean-Rodbell model to study the first order transition and identify the phase transition parameters.

Low cost, Ge-free MnNiSi based alloys, $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ were synthesized by arc melting. The T_C varied from 352 K to 255 K by varying the Sn content from $y = 0.12$ to $y = 0.18$. Magnetostructural coupling was observed for $y = 0.12$ to 0.16. A decrease in magnetostructural coupling during the first three heating and cooling cycles were observed due to Sn atoms hindering the martensitic phase transition. The magnetocaloric measurements showed reasonable values of $\Delta S_{\text{max}} = 8.6 \text{ Jkg}^{-1}\text{K}^{-1}$ for a field change of 5 T at 315 K for $y = 0.14$ and the highest RCP of 252 Jkg^{-1} was displayed by $y = 0.18$. Cost analysis of the raw materials revealed that the $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ are the most inexpensive magnetostructural alloys among MnNiSi alloys. The inexpensive raw materials and good performance makes it a suitable candidate for low cost, near room temperature applications.

A thermomagnetic oscillator prototype was fabricated to exploit the thermomagnetic response of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ alloys. The thermomagnetic alloy (TMA) oscillated between the heat sink and the heat load due to the heating and cooling cycles which changed the magnetic state of the TMA. A hybrid thermomagnetic oscillator was fabricated by coupling the movement of the TMA with another permanent magnet using a spacer. The coupled oscillations generated a voltage output of $\sim 10 \text{ V}$ and a cooling of upto 70°C per cycle. The material properties and device parameters were optimized using simulation models and a figure of merit analysis. The material showing the highest figure of merit, i.e., $(\text{MnNiSi})_{0.68}(\text{Fe}_2\text{Ge})_{0.32}$ was selected for a given heat load temperature to study the effect of spacer material on the performance. It was revealed that a flexible spacer can increase the oscillation frequency by 32 % and the voltage/cycle by 18% compared to a rigid spacer.

Lay Summary

More than half of the electricity consumption in Singapore is spent on cooling and air conditioning equipment. These cooling systems utilize harmful chemical refrigerants. Therefore, alternative thermal management technology is essential. Magnetic cooling is one such alternative technology relying on the magnetocaloric effect (MCE). The magnetocaloric materials used for MCE applications are materials that show a temperature dependent magnetic response. To develop efficient magnetic cooling devices, the MCM must possess high performance, low synthesis cost, be environmentally friendly and readily available. Considering these factors, we have studied MnNiSi based magnetocaloric alloys exhibiting a giant MCE effect and a wide range of T_C tunability near room temperature.

MnNiSi based alloys were synthesized using arc melting with no subsequent heat treatment steps. The $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ alloys were structurally characterized to study the crystal structure transition from the orthorhombic to the hexagonal phase along with a coupled magnetic transition from ferromagnetic to paramagnetic state, respectively. The Curie temperature was tuned from 363 K to 218 K by changing x from 0.32 to 0.36, respectively. An enhanced MCE effect was observed compared to other MnNiSi based alloys. The magnetostructural phase transition was modeled using theoretical models to analyze the order of the phase transition. In order to further decrease the materials cost, alloying additions of Fe and Sn were made. $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ alloys exhibited a magnetostructural transition near room temperature. The T_C was tuned from 352 K to 255 K by changing y from 0.12 to 0.18. The intensity of transition was lower compared to $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ due to the size of Sn atoms. The MCE values were comparable to the benchmark MCE material, Gadolinium. The cost analysis of raw materials revealed that $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ was the most cost effective among MnNiSi based alloys and are suitable for low cost applications near room temperature.

A thermomagnetic oscillator was demonstrated which utilizes the thermomagnetic response of magnetocaloric alloys. $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ was used as a thermomagnetic alloy (TMA) oscillating between the heat load at the top and the heat sink at the bottom of

a quartz tube. The prototype simultaneously cooled the heat load and generated electricity from the oscillations. The voltage output of ~ 10 V and a heat load cooling by upto 70°C per cycle was achieved. The electrical output was used to light up an LED. The optimization of the TMA properties and device parameters were performed using multiphysics simulations and figure of merit analysis for various alloys. The spacer material was optimized by replacing a rigid spacer by a flexible spacer to obtain an enhancement of 32% in the frequency and 18% in the voltage per cycle. Hence, the magnetocaloric properties of MnNiSi based alloys were investigated and used in a thermomagnetic oscillator prototype.

Acknowledgements

Foremost, I would like to express my deep sense of gratitude to my supervisor, Prof. Raju V. Ramanujan for his inspiring guidance, advice, encouraging support and patience throughout my PhD journey. He gave me his valuable time, believed in me and filled me with confidence. He has encouraged and inspired me in all the stages of this research work and allowed me to develop as an independent researcher.

I am thankful to my thesis advisory committee members, Prof. Dong Zhili and Prof. Rajdeep Rawat with whom I had fruitful discussions on my research work. They gave me timely and valuable suggestions.

This research would not have been possible without the financial support from the National Research Foundation, Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme on Nanomaterials for Energy and Water Management (NEW). I am thankful to all the staff members from CREATE, specially Dr. Ma Bing, Teh Chee Kuang and Jin Hongfang who helped me in every possible way to carry out research at CREATE labs. I am grateful to all the faculty members of the School of Materials Science and Engineering for providing a research conducive environment. I am also thankful to the MSE staff Swee Kuan, Patrick, Nelson, Gan Zi Li, Wilson, and Poh Tin for their kind help during the experiments. I am thankful to technical staff of the FACTS lab, especially Derrick, Alan, Yee Yan, Sam, Pio and Weiling. I am grateful for the assistance by staff at the CREATE lab, Metal Processing Lab, Heat Treatment Lab, Inorganic lab, Nanomaterials Lab and Computer Facilities Lab for their help in operating the equipment.

I am extremely thankful to my current lab members and alumni including Varun, Vijay, Vinay, Tan Xiao, Yaoying, Subhasish and Suneel who maintained a lively and cooperative environment in lab. I was considerably benefited with both scientific as well as non-scientific interactions with these colleagues.

I am indebted to my parents for their constant support, encouragement and advices throughout my life. My heartfelt thanks to my wife Snehal, who has been a constant source of support, love, trust and encouragement during this PhD journey. Last but not least, my extensive heartfelt gratitude to my spiritual master His Holiness Radhanath Swami whose teachings and guidance have given me a sublime direction and whose instructions have laid foundational principles and ideals in my life.

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Abbreviations

DSC	Differential scanning calorimetry
EDS	Energy dispersive spectroscopy
FM	Ferromagnetic
FOMT	First order magnetic transition
HTMO	Hybrid thermomagnetic oscillator
MCE	Magnetocaloric effect
MCM	Magnetocaloric material
PM	Paramagnetic
PPMS	Physical property measurement system
RCP	Relative cooling power
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy
SOMT	Second order magnetic transition
STMO	Single thermomagnetic oscillator
TEM	Transmission electron microscopy
TMA	Thermomagnetic alloy
TMO	Thermomagnetic Oscillator
VSM	Vibrating sample magnetometry
XRD	X-Ray diffraction

Chapter 1

Introduction

There is a growing need for energy efficient, environmentally friendly materials and technology in today's world. Nearly half of the energy is emitted as waste heat from the industries. The conventional cooling techniques have adverse effects on the environment. Technologies for waste heat management and energy efficient cooling have gained great demand. Magnetic cooling and energy harvesting is a potential technology which employs the thermomagnetic response of magnetocaloric materials. This chapter states the overview, motivation and problem statement of this thesis followed by the hypothesis, novelty and significance. The last section of this chapter contains the objective, organization and significant findings of this research work

1.1 Overview

Energy consumption has been continuously increasing all over the world. According to the National Research Foundation and National Climate change Secretariat, refrigeration and cooling devices consume more than half of the total energy utilized [1]. The statistics from the Global Energy Handbook states that electrical energy consumption across the world was 2.1×10^4 TWh in 2016 [2]. Industries discharge between 20 to 50% of energy in the form of waste heat [3]. There is a great demand for technology that can transform such low grade waste heat into useful energy. Conventional vapor compressor-based cooling systems may use harmful chloro-fluoro carbons (CFCs) that can deplete the ozone layer and increases the rate of global warming [4]. Magnetic cooling devices provide an energy efficient and environmentally friendly alternative to such conventional techniques [5,6]. Specifically, thermomagnetic devices can simultaneously be used for cooling and energy harvesting [7].

1.2 Motivation

There is a growing need to explore sustainable and unconventional forms of energy to mitigate environmental damage and reduce energy consumption. With the rapid growth of industries, the quantity of waste heat released to the atmosphere has been increasing. Heat loss transferred through conduction, convection and radiation from industrial products, equipment and processes contribute to the sources of waste heat. It is estimated that industries discharge about 20 to 50% energy as waste heat [3]. This waste heat not only causes harm to the environment but also reduce the durability of the equipment [8]. Conventional technologies generally consume lot of space, typically require cooling fans for operation; finally the waste heat is not converted into useful energy.

Apart from industries, household cooling systems such as air conditioners and refrigerators can use hazardous and harmful chemicals e.g., chloro-fluoro carbon (CFC), hydro-chloro-fluoro carbon (HCFC), hydro-fluoro carbon (HFC) etc., contributing to global warming and ozone layer depletion [4].

In order to overcome these drawbacks of conventional cooling technology, technologies which are environmentally sustainable and exhibit higher cooling efficiency are being explored around the world. Magnetic cooling systems using magnetocaloric materials can be a promising alternative technology offering various advantages: they are compact, have low maintenance cost, less vibration, no harmful emissions and do not include bulky compressors or pumps [9]. Magnetic cooling products have been commercialized e.g., a wine cooler developed has been developed by Astronautics Corporation of America (ACA) and BASF [10,11] and Haier achieving temperatures $\sim 8^{\circ}\text{C}$ [12]. Cooltech launched a magnetocaloric beverage cooling cabinet in 2016 at a Carrefour supermarket in Paris, France [13].

Extensive research is being performed to transform waste heat to electricity using the thermomagnetic response of magnetocaloric alloys [14-16]. Active devices generate electricity by alternately pumping hot and cold fluids over a thermomagnetic material. On the other hand, passive devices rely on waste heat to induce spontaneous mechanical oscillations of a suitable magnetic material. The movement of the magnetic material is then converted to electricity. Curie motors, thermomagnetic generators, hybrid devices etc., have been developed for conversion of waste heat to electricity [16-20].

Research in the field of magnetocaloric materials and their applications has been increasing rapidly in the recent decade [9]. The statistics from the ISI Web of Science (**Fig 1.1a**) shows the number of citations for the keyword “magnetocaloric” from the year 1900 to 2018. In the past two decades, there has been a large increase in the number of citations, which has reached 18000 citations per year in 2018. The Boolean search for the term “magnetocaloric AND magnetic cooling” in Patentscope database (**Fig 1.1b**) also shows the number of patents for magnetic cooling has been steadily increasing for the last 20 years and has reached over 80 patents per year in 2018.

Fig 1.1 (a) Number of citations for journals related to magnetocaloric materials since 1930 from ISI Web of Science database (www.webofknowledge.com). (b) Number of patents filed related to magnetocaloric and magnetic cooling since 1994 from Patentscope database (www.wipo.int/patentscope/en/).

1.3 Problem Statement

The performance of the magnetic cooling device critically depends on the properties of the magnetocaloric material (MCM) and device parameters. An ideal magnetocaloric material must possess high magnetic entropy change for the relevant phase transition (ΔS_M), high adiabatic temperature change (ΔT_{ad}), high relative cooling power (RCP), negligible hysteresis, wide working temperature span, non-toxic raw materials, facile synthesis and ready availability. The device parameters such as the temperature of the heat load and that of the heat sink, magnetic field strength of permanent magnet etc., can be optimized to obtain the best performance.

Gadolinium (Gd) is considered the benchmark MCM for magnetic cooling applications since it possesses a Curie temperature (T_C) of 294 K, close to room temperature [21]. This makes it suitable for various near room temperature cooling and refrigeration applications. However, Gd is very expensive, a strategic and prone to corrosion and oxidation. La based alloys were discovered as alternative magnetocaloric materials, but due to poor mechanical properties and the presence of the rare-earth element La, these alloys are not practical for large scale commercialization [22]. Low cost Fe based magnetocaloric materials such as Fe-Ni-Cr or Fe-Cr-Al, exhibiting large relative cooling power (RCP) values, are more practical than Gd [23,24]. However, for low-grade waste heat devices with working temperatures less than 200°C, the Fe-based magnetocaloric materials show low performance due to low ΔS_M values [25]. To obtain a rare-earth free alloy exhibiting better performance, MnNiSi based MCMs were studied to overcome the drawbacks of these classes of MCMs. **Table 1.1** lists the various drawbacks and challenges of current MCMs and the advantages of MnNiSi based MCMs over other counterparts.

Table 1.1 Comparison of current MCMs and MnNiSi based MCM

Composition of MCM	Drawbacks	MnNiSi based MCM
Gadolinium (Gd), Gd-Si-Ge [26]	Expensive, rare-earth, strategic element	No rare-earth elements used
La based alloys (La-Fe-Si, La-Fe-Si-H) [27,28]	Rare-earth, poor mechanical stability	Readily available, better stability
Fe based alloys (Fe-Ni-Cr, Fe-Mn-Al, Fe- Cr-Al) [23,24]	Low ΔS_M , poor performance over a narrow temperature range	High $\Delta S_M \rightarrow$ first order transition, good performance for narrow temperature range
Mn-Fe-P-As, Mn-Fe-P-Ge [29,30]	Toxic elements such as As and P. Hysteresis	No toxic elements involved in synthesis. Hysteresis
Mn-Co-Ge [31]	Geographical limitation of Co (strategic)	Raw materials are readily available

1.4 Hypothesis

The parameters which determine the feasibility of a magnetocaloric material for a given application include high performance, low cost, non-toxicity and ready availability. Elemental Mn and Cr exhibit antiferromagnetism. However, when these elements are in

alloys, Mn may show a tremendous enhancement in magnetization. The change in the Mn-Mn distance by alloying can play a key role in aligning the spins of the Mn atoms [32]. Mn based MnNiSi alloy was selected as the base alloy for our present study because it exhibits both a ferromagnetic to paramagnetic transition at ~ 600 K and a structural transition from orthorhombic (low temperature) to hexagonal (high temperature) at ~ 1200 K [33]. The requirement is to utilize these alloys for near room temperature applications, therefore the transition temperatures must be decreased to near room temperature by alloying addition. Single element substitution, such as Fe or Co, is insufficient to bring down the transition temperature below 450 K [34], therefore two element substitution is essential. The first hypothesis is that the magnetic and the structural transition could be coupled near room temperature by stabilizing the high temperature hexagonal phase by addition of Fe_2Ge to MnNiSi. The magnetostructural transition temperature (T_t) could indeed be tuned by addition of Fe_2Ge .

Replacement of Ge by a low cost element while maintaining the magnetostructural transition would be a promising alternative for low cost applications. Ge must be replaced by an element based on the site occupancy rule. Hence, the second hypothesis is that by replacing Sn in place of Ge and adjusting the Mn and Fe composition, the magnetostructural transition could still be maintained near room temperature. As Ge is 15 times more expensive than Sn [35], the cost would greatly decrease.

Finally, a prototype for cooling and energy harvesting would be designed. This prototype would utilize thermomagnetic response of MnNiSi based magnetocaloric materials to convert waste heat into electricity and for heat load cooling.

1.5 Novelty

Detailed studies of the magnetostructural transitions in MnNiSi based alloys have been performed [36-38]. Most of these studies focused on increasing the ΔS_M and reducing the hysteresis in alloys prepared by arc melting followed by annealing. The novelty of the present work has been summarized in **Table 1.2**. For the first time, the synthesis was performed by eliminating the annealing step for $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$. The arc melted

samples exhibited higher ΔS_M values than previously reported values for similar alloy compositions. The ΔS_M value of $57.6 \text{ J kg}^{-1} \text{ K}^{-1}$ obtained in this work for $x = 0.34$ was one of the highest among MnNiSi based alloys [39]. To reduce the materials cost, Ge-free alloys were synthesized for the first time. $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ alloys exhibited magnetostructural transition near room temperature which could be tuned by changes in the Sn content [40]. The cost of synthesis was estimated to be 88¢ per 10 g of alloy which was the most inexpensive among MnNiSi based alloys.

A novel thermomagnetic oscillator (TMO) for cooling and energy harvesting using waste heat was constructed based on the thermomagnetic response of these MnNiSi based alloys [7]. Previous thermomagnetic energy harvesters generally used pumps, blowers or piezoelectric connectors. This TMO is the first prototype which coupled thermomagnetic oscillation with electromagnetic induction to generate electricity. Further, this was the first time when simultaneous cooling and electricity harvesting was performed in a single prototype.

Table 1.2 Novelty of the thesis

Work	Previous reports	Novelty
Synthesis steps for MnNiSi based alloys	Arc melting + annealing	Eliminated annealing step. Use of direct arc melted alloys for applications
Magnetocaloric properties of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$	Reports show ΔS_{max} of $35.7 \text{ J kg}^{-1} \text{ K}^{-1}$	Higher value of ΔS_{max} ($57.6 \text{ J kg}^{-1} \text{ K}^{-1}$) obtained $\rightarrow$ highest among MnNiSi based alloys
Study of magnetostructural transition in $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$	No detailed modeling of transition	Detailed analysis and modeling of magnetostructural transition using Arrott plots, Landau equations and the Bean Rodbell model.
Synthesis of low cost Mn based alloys	Expensive Ge used in alloys. No reports on Ge-free MnNiSi alloys	Ge-free MnNiSi-Fe-Sn based alloy synthesized for the first time exhibiting magnetostructural coupling $\rightarrow$ most cost-effective among MnNiSi based alloys
Thermomagnetic energy harvesting prototype	Use of pumps, blowers or piezoelectric connectors giving low current output,	Use of thermomagnetic response + EM to generate electricity $\rightarrow$ high current. Efficient storage and dissipation using storage circuits and LED.

	No reports on energy storage and dissipation	
Multifunctional thermomagnetic oscillator prototype	No device for simultaneous cooling and electricity harvesting	Simultaneous cooling of upto 70°C per cycle and voltage of 10 V/cycle obtained by Hybrid TMO setup.
Figure of merit for TMO	No performance metric estimated for thermomagnetic devices	Derivation of figure of merit for TMO considering material properties and device parameters

1.6 Significance

Magnetic cooling and energy harvesting is environmentally friendly and a promising technology relying on magnetocaloric materials. The materials are expected to have high performance, low cost, non-toxic and readily available. Hence, we studied rare-earth free, low-cost, high performance MnNiSi based magnetocaloric materials. As a proof of concept, the thermomagnetic oscillator prototype based on the thermomagnetic response of the magnetocaloric alloys was constructed. The TMO prototype is significant for electricity generation from waste heat and can also serve as a temperature regulator for industrial equipment such as heat exchangers operating above room temperature.

1.7 Objectives and workflow

The aim of this research is to develop high performance, low cost magnetocaloric materials for cooling and energy harvesting. Mn based magnetocaloric materials can show better ΔS_M values and a wide Curie temperature window [37,41-43]. MnNiSi based alloys satisfy the criteria of rare-earth free, non-toxic and environmentally friendly MCMs. Therefore the focus of the research was to tune the magnetostructural transition temperature of MnNiSi based alloys to near room temperature by addition of Fe₂Ge and Sn. These alloys were then utilized as working material for thermomagnetic cooling and energy harvesting.

The specific tasks are summarized as:

- 1) Synthesis using arc melting of MnNiSi based alloys with Fe₂Ge and Fe-Sn addition to achieve coupling of magnetic and structural transition near room temperature.

- 2) Study the effect of composition on the magnetostructural transition of MnNiSi.
- 3) Structural characterization of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ and $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ alloys using XRD, DSC and TEM.
- 4) Identify the Curie temperature window and tune the magnetostructural transition temperature suitable for the prototype.
- 5) Measure the magnetocaloric properties such as ΔS_M and relative cooling power (RCP) for the alloys using physical property measurement system (PPMS) with VSM attachment.
- 6) Model the magnetic transition using Arrott plots, Landau theory and the Bean-Rodbell model.
- 7) Utilize the thermomagnetic response of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ based alloys to operate the thermomagnetic oscillator for cooling and energy harvesting. Enhance the voltage output by connecting a magnet with the alloy.
- 8) Perform simulation of the thermomagnetic oscillator using COMSOL Multiphysics and optimize the device parameters for maximum performance
- 9) Derivation of figure of merit for the thermomagnetic oscillator to compare the performance of various alloys and optimize the device parameters for a particular alloy.

1.8 Organization of thesis

This PhD thesis is organized in 7 chapters as follows:

- ❖ **Chapter 1** provides an introduction along with a brief overview, problem statement, objectives, motivation, novelty, significance and workflow. The hypothesis and significant findings are also summarized.
- ❖ **Chapter 2** presents a literature review of the history and fundamentals of MCE. An overview of different types of magnetic materials exhibiting first order and second order transition is also discussed, followed by Mn based and MnNiSi based alloys. The equations for modeling of the magnetostructural transitions are mentioned. Thermomagnetic cooling and energy harvesting devices are described. Finally, the derivation of the figure of merit for the TMO is reported

- ❖ **Chapter 3** describes the experimental techniques used for synthesis, structural characterization and evaluation of magnetic properties. The experimental setup of the TMO is discussed along with the design and input parameters for COMSOL Multiphysics simulation of TMO.
- ❖ **Chapter 4** consists of experimental results to determine the MCE properties of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$. The structural transition was studied using XRD, high temperature XRD, DSC and TEM. The magnetic measurements were performed using PPMS with VSM attachment and magnetic measurements such as ΔS and RCP were determined. The phase transition was modeled using Arrott plots, Landau equations and the Bean-Rodbell model.
- ❖ **Chapter 5** comprises of MCE properties of Ge-free, low cost $(\text{Mn.Fe})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ alloys. The training effect exhibited by these alloys is studied. The structural and magnetic property evaluation is studied for alloys showing transition near room temperature by varying the amount of Sn. Finally, the cost per unit weight of various alloys are compared.
- ❖ **Chapter 6** presents the results of cooling and energy harvesting of the TMO. The enhancement in the performance by HTMO and flexible spacer are described. The results of COMSOL Multiphysics simulation for optimization of TMO are described. The analytical calculations of force balance, energy and frequency of oscillations leading to the figure of merit has been elucidated.
- ❖ **Chapter 7** presents the summary and future work.

Fig 1.2 Outline of the thesis and organization of research work.

1.9 Significant findings

This research led to several novel outcomes and significant findings:

1. An enhancement in the MCE properties of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ without the annealing step. The ΔS_{max} of $57.6 \text{ Jkg}^{-1}\text{K}^{-1}$ ($\Delta H = 5 \text{ T}$) for $x = 0.34$ was 38% higher than the value reported earlier [44]. The results indicated that heat treatment step could be eliminated for $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ and still retain good MCE properties.
2. The theoretical modeling of magnetostructural transition using Arrott plots, Landau equations and the Bean-Rodbell model was performed for MnNiSi based alloys. The first order transition was verified using modeling. Landau parameters for the M-H curves were determined and used to theoretically predict the M-H curves for intermediate temperatures.
3. All of the MnNiSi based alloys previously reported contained Ge which increased cost. Hence, a low cost Ge-free alloy $(\text{Mn,Fe})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ was synthesized for the first time with a cost 88¢ per 10 g of alloy. The alloys exhibited a magnetostructural transition near room temperature for $y = 0.12$ to $y = 0.16$. ΔS_{max} of $8.3 \text{ Jkg}^{-1}\text{K}^{-1}$ ($\Delta H = 5 \text{ T}$) was obtained for $y = 0.14$, which is comparable to ΔS_{max} for Gd. Hence, $(\text{Mn,Fe})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ provides a promising alternative to low cost MCE

applications.

4. A novel thermomagnetic oscillator prototype was developed for simultaneous cooling and energy harvesting using waste heat. Since the TMO is a passive system, it possesses several advantages such as low maintenance, no additional energy input, easy device setup etc. The TMO produced an output of 2 V/cycle using 20 g of working material.
5. A further enhancement in the design of TMO resulted in a Hybrid TMO which had NdFeB permanent magnet connected with the working material using a flexible spacer. It generates a voltage of ~ 11 V and cooling of heat load of upto 70°C per cycle. Electrical output of the HTMO was rectified and stored using a storage circuit connected to a capacitor. The stored energy was sufficient to light up LED for 50 seconds.
6. Equations for figure of merit using analytical calculations were derived for TMO. The figure of merit could predict the performance of various alloys in the TMO and accordingly optimize device parameters to achieve the best performance.

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Chapter 2

Literature Review

The magnetocaloric effect is the thermal response of a material in response to an external time varying magnetic field. The MCE possesses several advantages over conventional cooling technique. Hence, it has gained tremendous potential in future cooling technology. This chapter outlines the history and background of the MCE along with its fundamental aspects. Subsequently, MCE property measurements are described, followed by the types of magnetocaloric materials including Mn and MnNiSi based alloys. Several thermomagnetic cooling and energy harvesting prototypes have been elucidated. The last part of this chapter includes a discussion of the working principle of the thermomagnetic oscillator developed in this work and its figure of merit.

2.1 Background of MCE

2.1.1 History and important milestones

The first studies of the dependence of magnetic properties on temperature were performed by Emil Warburg in 1881 [1]. He measured heating in iron rods in the presence of a time varying magnetic field, which was an indication of magnetic hysteresis. The discovery of the MCE was attributed to Weiss and Piccard who reported the principles governing the MCE in 1917 and coined the French term ‘magnetocalorique’ [2]. Subsequently, Debye and Giaque proposed application of MCE cooling by the process of adiabatic demagnetization [3,4]. Giaque was awarded the Nobel Prize (Chemistry) in 1949 for this remarkable work on the adiabatic demagnetization of paramagnetic salts where he was able to reach a temperature of 0.25 K.

Studies to explore near room temperature MCE started in late 1960’s. In 1976, Brown designed a prototype for magnetic cooling based on the magnetic phase transition in Gd [5]. A significant breakthrough in magnetocaloric research emerged in 1997 when Pecharsky and Gschneidner discovered the giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ with an exceptional MCE response near room temperature [6]. This phenomenon was further used by the Astronautics Corporation, USA to design the world’s first room temperature magnetic refrigerator in 2001 [7]. This led to numerous other commercial magnetic refrigerators, as described in further sections.

Fig 2.1 Important milestones in MCE research

2.1.2 Thermodynamics of MCE

The thermodynamics of MCE relates the magnetic variables i.e. magnetization and magnetic field to temperature and entropy. MCE is an intrinsic property of any magnetic material, although the magnitude depends on the several factors such as atomic arrangement, microstructure, composition etc. MCE arises due to the coupling of the magnetic sublattice to the applied magnetic field, which changes the magnetic entropy of the solid. The change in the magnetic entropy due to alignment of magnetic moments affects the total entropy of the system [8]. The value of total entropy (S) of a ferromagnetic material at constant pressure is the sum of its magnetic entropy (S_M), lattice entropy (S_{lat}) and electronic entropy (S_{el}) given by:

$$S(T, H) = S_M(T, H) + S_{lat}(T, H) + S_{el}(T, H) \quad (2.1)$$

Eq.(2.1) represents the governing principle behind the thermodynamics of the material during the magnetocaloric cycle [9] described below:

(i) When the magnetic field is applied adiabatically, the magnetic moments tend to align in the direction of the field, resulting in a decrease of S_M . Since the total entropy of the material remains constant, S_{lat} has to change to compensate for the decrease in S_M .

Therefore, S_{lat} increases to maintain the total entropy of the material constant. Due to an increase in S_{Lat} , the temperature of the material increases, this adiabatic temperature rise (ΔT_{ad}) can be visualized as the isentropic difference in the corresponding entropy values.

(ii) The heat generated in the material can be extracted by a heat transfer medium while the magnetic field is present. When the magnetic field is removed adiabatically i.e. adiabatic demagnetization will lead to a decrease in the temperature of the material below the initial temperature. Thus the cooling can be utilized for magnetic refrigeration or cooling a heat load. The schematic representation of the MCE cycle is shown in fig 2.2:

Fig 2.2 The thermodynamic MCE cycle showing the variation in S_M with temperature of the material.

The expression for entropy in terms of change in the magnetization of the material can be derived by thermodynamic functions i.e., internal energy U , free energy F , Gibbs free energy G , specific heat C , entropy S , pressure p and absolute temperature T [10]. The internal energy can be represented as a function of Volume V and magnetic field H or magnetic moment M :

$$U = U(S, V, M \text{ or } H) \quad (2.2)$$

Eq. (2.2) can be represented in differential form as:

$$dU = TdS - pdV - HdM \quad (2.3)$$

The free energy can be expressed thermodynamically using the following expression:

$$F = U - TS \quad (2.4)$$

which assumes the differential form as follows

$$dF = -SdT - pdV - MdH \quad (2.5)$$

Under constant pressure, G can be represented in terms of T, p and H,

$$G = T - US + pV - MH \quad (2.6)$$

Eq. (2.6) can be expressed as:

$$dG = Vdp - SdT - MdH \quad (2.7)$$

Using the equation of states, the following equations can be deduced:

$$S(H, T, p) = -\left(\frac{\partial G}{\partial T}\right)_{H,p} \quad (2.8)$$

$$M(H, T, p) = -\left(\frac{\partial G}{\partial T}\right)_{T,p} \quad (2.9)$$

$$V(H, T, p) = -\left(\frac{\partial G}{\partial T}\right)_{H,T} \quad (2.10)$$

If the magnetic moment M is considered as an external variable,

$$H = -\left(\frac{\partial G}{\partial M}\right)_{T,p} \quad (2.11)$$

Combining the eq. (2.7) with eq. (2.8), (2.9) and (2.10) the Maxwell's relation can be obtained,

$$\left(\frac{\partial S}{\partial H}\right)_{T,p} = \left(\frac{\partial M}{\partial T}\right)_{H,p} \quad (2.12)$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,H} = -\left(\frac{\partial V}{\partial T}\right)_{H,p} \quad (2.13)$$

$$\left(\frac{\partial S}{\partial M}\right)_{T,p} = -\left(\frac{\partial H}{\partial T}\right)_{M,p} \quad (2.14)$$

At constant pressure, the entropy S of a magnetic material depends on H and T . Therefore, total entropy can be expressed in a differential form as,

$$dS = \left(\frac{\partial S}{\partial T}\right)_{H,p} dT + \left(\frac{\partial S}{\partial H}\right)_{T,p} dH + \left(\frac{\partial S}{\partial p}\right)_{T,H} dp \quad (2.15)$$

If the magnetic field is varied from $H = 0$ to H (H_i to H_f) under isothermal conditions, Eq (2.15) can be written in an integral form,

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \quad (2.16)$$

Eq. (2.16) is a crucial equation which decides the performance of MCM. The value of ΔS_M is one of the factors examined during the selection of a MCM.

The experimental analysis of ΔS_M can be performed by isothermally performing M vs H measurements at regular temperature intervals (T_j and T_{j+1}). The integral form of eq. (2.16) can be simplified for practical purposes,

$$\Delta S_{H1 \rightarrow H2} = \sum_i \frac{M_i(T_{j+1}, H_i) - M_i(T_j, H_i)}{T_{j+1} - T_j} \Delta H_i \quad (2.17)$$

ΔS_M is obtained for each temperature interval between field the range $H1$ to $H2$ using eq.(2.17). The temperature at which the ΔS_M yields highest value (ΔS_{Max}) is at the Curie temperature (T_C) for second order magnetic phase transition material.

2.1.3 Measurement of MCE

MCE is generally quantified by important parameters such as the adiabatic change in temperature (ΔT_{ad}), the isothermal entropy change (ΔS_M), and the relative cooling power (RCP). ΔS_M depends on the change in magnetization with temperature, whereas RCP is another figure of merit used to quantify MCM [10]. It is defined as the quantity of heat transferred between the hot end and the cold end during a cooling cycle. Both ΔS_M and RCP can be calculated using indirect measurements. Quantification of ΔT_{ad} requires direct measurements. The direct and the indirect measurement techniques are summarized below.

2.1.3.1 Direct methods

The direct method of MCE measurement involves the determination of ΔT_{ad} by subjecting the sample to a magnetic field and recording the variation in temperature using a thermocouple configuration [11]. As the magnetic field is switched from an initial to a final value, the thermocouple records the variation in temperature of the sample with respect to the applied magnetic field. The accuracy of the measurement depends on the sensitivity of the thermocouple, thermal surroundings, noise etc. Various developments have taken place in the direct measurement techniques e.g., measurement in static field by superconducting magnets and use of pulsed-magnetic fields or differential thermocouples. Direct measurements show significant values of ΔT_{ad} when there is a large change in entropy (ΔS_M) during application of magnetic field. Hence, this technique is suitable for materials exhibiting giant MCE or first order phase transition (FOPT). However, for second order phase transition (SOPT) materials having low values of ΔS_M , the sensitivity of the thermocouple needs to be high to measure temperature changes due to the application of magnetic field. Due to these limitations, MCE measurements for SOPT materials are performed using indirect methods [12].

2.1.3.2 Indirect methods

The magnetic properties are measured by determination of specific heat in indirect measurements [12]. The ΔS of a material is related to the change in the specific heat with temperature as shown in eq.(2.18). The magnetization of the sample is measured at regular

intervals of temperature at a constant and cyclic magnetic field yielding the M vs T and M vs H curves, respectively. Using the Maxwell's equation (eq.(2.16)), the ΔS_M value is derived at each temperature interval. The RCP is calculated as the area under the ΔS_M vs T curve equal to the product of full width at half maximum (FWHM) and ΔS_{Max} (eq.(2.19)) [13].

$$S(T, H) = \int_0^T \frac{C_p(H)}{T} dT \quad (2.18)$$

$$RCP = FWHM \times \Delta S_{max} \quad (2.19)$$

This method is suitable for samples with small mass. The advantage of indirect measurement is that it can be easily achieved using a magnetometer and is relatively quick, whereas the direct methods involve specialized instruments and calibration techniques [12].

2.2 Overview of magnetocaloric materials (MCM)

Magnetic cooling has been shown to be a promising technology compared to conventional cooling techniques. The performance of any magnetic cooling device is determined by the working material i.e., the magnetocaloric material. Selection of a suitable MCM for specific device parameters is the key to achieve the maximum efficiency. Several factors influence the choice of MCM including material and processing cost, availability of raw materials, tunable transition temperatures, excellent magnetic properties such as ΔS_M and RCP. Since most of practical cooling devices operate near room temperature, the T_C must be tunable to near room temperature. Further, coupling between the magnetic and structural transition can give rise to a giant magnetic transition with a large ΔS_M [14].

2.2.1 Classification of magnetic transition

The magnetocaloric transition is classified as first order phase transition (FOPT) or second order phase transition (SOPT). The FOPT are further classified into magnetostructural and magnetoelastic transitions (**Fig 2.3**) [15]. However, in the present work, we focus on the

magnetostructural transition which can be utilized for practical applications.

Fig 2.3 Classification diagram of solid-state phase transitions. Magnetostructural transitions are first order transitions undergoing crystal structure change during the transition [15].

2.2.1.1 First order phase transition (FOPT)

FOPT involves a coupling of the structural transformation and the magnetic phase transition. Usually, the low temperature structure exhibits the ferromagnetic phase and the high temperature structure exhibits paramagnetic phase (**Fig 2.4b**). The sharp magnetostructural transition results in a large ΔS_M values at the transition temperature. Due to the additional energy required for the structural transition, FOPT materials generally exhibit thermal hysteresis between the heating and the cooling cycles. The hysteresis is considered as a disadvantage in applications due to the additional energy needed during each temperature cycle [16]. However, applications have been developed for utilization of thermal hysteresis in the form of latent heat [17].

2.2.1.2 Second order phase transition (SOPT)

SOPT occurs when there is a gradual magnetic transition without any structural transition. Since SOPT can occur over a wide range of temperature, it lacks a well-defined T_C . Therefore the temperature at which the slope of the M vs T plot reaches maximum value is considered to be the T_C of the material (**Fig 2.4a**). The low values of ΔS_M exhibited by SOPT materials limits its usage in applications operating in a narrow temperature range [18]. For effective usage of SOPT materials, large gradient in magnetization must occur which requires a large temperature gradient. The advantage of SOPT over FOPT is the absence of thermal hysteresis between heating and cooling cycles.

Fig 2.4 Schematic of M vs T plot for MCM exhibiting (a) second order phase transition and (b) first order phase transition.

2.2.2 Materials exhibiting SOPT

The early thermomagnetic cooling and energy harvesting devices were based on SOPT materials with relatively high T_C such as Fe and Ni [19,20]. The benchmark MCM, gadolinium having a near room temperature T_C was utilized for the first time in 1968 by Brown for magnetic cooling application [5]. Since then numerous magnetocaloric materials exhibiting SOPT have been discovered as summarized in **Table 2.1**.

2.2.2.1 Gadolinium

Gd is a rare-earth metal considered as a benchmark MCM for near room temperature applications. Pure Gd metal possesses a hexagonal close-packed structure and orders ferromagnetically at $T_C = 294$ K [21]. Gd undergoes a SOPT from the ferromagnetic to the paramagnetic phase and displays a ΔS_{Max} of $-4.2 \text{ Jkg}^{-1}\text{K}^{-1}$ ($\Delta H = 1.5$ T) at T_C . The large MCE is due to the large change in C_P induced by magnetic transition. Since Gd had a suitable T_C at room temperature, it was the first choice until other alloys replaced it due to various disadvantages of Gd such as high cost, low availability, oxidation and corrosion issues.

2.2.2.2 Fe based alloys

Fe based amorphous material are extensively studied for their MCE properties since 1980s. Due to the ready availability of raw materials, tunability of T_C and high saturation magnetization, these alloys are preferred over Gd. Some of the Fe based alloys include Fe-Ni-Cr [22], Fe-Ni-B [23], Fe-Mn-Al [24], Fe-Cr-Al [25] and Fe-M-Zr (M = Al, Si, Ga, Ge and Sn) [26] alloy systems.

Although these alloys exhibit a much lower magnetic entropy (less than $2 \text{ Jkg}^{-1}\text{K}^{-1}$ for $\Delta H = 5$ T) and smaller adiabatic temperature change (ΔT_{ad}) than the benchmark Gd alloy, the cost of synthesis of Fe based alloys are about 5% of the cost of Gd. Fe based alloys are preferred in some low cost applications owing to their high RCP over wide range of temperature, high saturation magnetization and tunability of T_C [27].

2.2.2.3 High entropy alloys

MCE studies in high entropy alloys have been emerging recently. This class of MCM provides several advantages like good resistance to wear and tear, mechanical strength, corrosion resistance and tunability of T_C . The reports on MCE studies of FeCoNiCuMn high entropy alloy shows an attractive T_C of 300 K [28]. However, the low values of ΔS_{Max} (less than $1 \text{ Jkg}^{-1}\text{K}^{-1}$ for $\Delta H = 5$ T) is unattractive. Further research is being conducted for other high entropy alloy compositions [29,30].

2.2.3 Materials exhibiting FOPT

Cooling applications utilized Gd as a working material due to the high ΔS_M value near room temperature. However, a scientific breakthrough appeared when an alloy ($Gd_5Si_2Ge_2$) exhibiting giant MCE was proposed by Pecharsky and Gschneidner in 1997 [6]. This was the first study of the first order MCM having a coupled magnetic and structural transition. Since then, there have been extensive studies on FOPT alloys.

2.2.3.1 Gd based giant MCE alloys

The discovery of FOPT in $Gd_5Si_2Ge_2$ accelerated research interest in MCM. This alloy displayed ΔS_M of $36 \text{ Jkg}^{-1}\text{K}^{-1}$ for an applied field change of 5 T at 272 K [6]. The substitution of small amounts of Fe, Cu, Co, Ni, Ga, C and Al was investigated [31]. However, the substitution of these elements led to an increase in T_C and reduction of ΔS_M due to the loss of first order coupling during the transition. Study of the MCE properties by application of hydrostatic pressure indicated that the ΔS_M value shows a slight increase ($13 \text{ Jkg}^{-1}\text{K}^{-1}$ for $\Delta H = 5 \text{ T}$) by application of moderate pressure of 3 kPa [32].

MCE properties of other Gd based alloys such as $Gd_{55}Ni_{30}Al_{15}$ [33] and Gd-Fe-Al [34,35] have also been investigated. These alloys show good ΔS_{Max} values of $9.25 \text{ Jkg}^{-1}\text{K}^{-1}$ at 93 K and $7.14 \text{ Jkg}^{-1}\text{K}^{-1}$ at 149 K, respectively. Since the T_C values are much lower than room temperature and also due to the limitations of availability of Gd, the utility of Gd based alloys remains a challenge.

2.2.3.2 La based alloys

La based MCM are mainly based on the $LaFe_{13}$ alloy system. $La(Fe,Si)_{13}$ based alloys are of particular interest because of a small amount of a light rare earth element (La) used and a high Fe content resulting in a high magnetic moment. Various processing techniques such as melt spinning, ball milling, heat treatment etc [36] have been adopted to increase the mass fraction of 1:13 phase and overcome the challenge of α -Fe dendrite formation. Samples of $LaFe_{11.4}Si_{1.6}$ prepared by arc melting and subsequent annealing for 50 h at 1473 K displayed ΔS_{Max} of $19.4 \text{ Jkg}^{-1}\text{K}^{-1}$ under a field of 5 T at 208 K [37]. $LaFe_{11.6}Si_{1.4}$ prepared

using the ball milling shows a promising entropy value of $13 \text{ J kg}^{-1}\text{K}^{-1}$ ($\Delta H = 2 \text{ T}$) at $\sim 200 \text{ K}$ and negligible hysteresis ($\sim 1 \text{ K}$) [36]. Adding hydrogen to La(Fe,Si)_{13} is useful to expand the crystalline lattice of the 1:13 phase. However, $\text{La(Fe,Si)}_{13}\text{H}_x$ has drawbacks such as desorption of hydrogen, instability of hydride at room temperature, fatigue and cracking. Addition of Co increases the T_C to room temperature range, $\text{LaFe}_{11.7-x}\text{Co}_x\text{Si}_{1.3}$ alloys show a T_C of 265 K with $\Delta S_{\text{Max}} = 15 \text{ J kg}^{-1}\text{K}^{-1}$ ($\Delta H = 5 \text{ T}$), whereas $\text{LaFe}_{11.2-x}\text{Co}_{0.7+x}\text{Si}_{1.1}$ increases T_C to 294 K , with $\Delta S_{\text{Max}} = 13.5 \text{ J kg}^{-1}\text{K}^{-1}$ ($\Delta H = 5 \text{ T}$) [38]. Research has been ongoing to make La(Fe,Si)_{13} suitable for applications by improving the machinability to make structures such as packed bed, parallel plates, microchannels etc [39].

2.2.3.3 Other rare-earth (Dy, Er, Tb and Ho) based alloys

Similar to Gd and La based alloys, the other rare earth alloys exhibit MCE properties due to their magnetism, which is related to a partially filled 4f shell. A combination of rare-earth with a transition element gives rise to attractive magnetic properties. There are several well-known rare-earth (RE) based alloys i.e., $\text{RE}_2\text{T}_2\text{X}$ intermetallic compounds [40], RECo_2 Laves phases [41], bulk metallic glasses [42], REMnO_3 manganites [43,44] etc. Among the $\text{Re}_2\text{T}_2\text{X}$ intermetallics, $\text{Ho}_2\text{Cu}_2\text{Cd}$ displays the highest ΔS_{Max} of $20.3 \text{ J kg}^{-1}\text{K}^{-1}$ with an RCP of 481 J kg^{-1} (for $\Delta H = 5 \text{ T}$) at 30 K with a hysteresis of 15 K [40]. ErCo_2 is a widely studied alloy among the Laves phase compounds, it shows a T_C of $\sim 32 \text{ K}$ with $\Delta S_{\text{Max}} = 38 \text{ J kg}^{-1}\text{K}^{-1}$ (for $\Delta H = 5 \text{ T}$) [45]. Other alloys containing rare-earth elements have been introduced recently [15,46-48]. **Table 2.1** gives a summary of some of the important rare-earth alloys and their MCE properties. Most of the alloys containing rare-earth elements show a first order transition with T_C much lower than room temperature, hence they are more feasible for cryogenic applications.

2.2.3.4 AlFe_2B_2 alloys

The MCE of AlFe_2B_2 alloys were reported to have an attractive T_C of 307 K . As the raw materials used for synthesis are earth-abundant and light-weight elements, these alloys are quite promising FOPT alloys. Recent studies report a $\Delta S_{\text{Max}} = 7.7 \text{ J kg}^{-1}\text{K}^{-1}$ for $\Delta H = 5 \text{ T}$ and RCP of 162 J kg^{-1} [49], which are comparable to the corresponding values of Gd. The

calorimetric measurements indicated that the transition temperature is 274 K (cooling) and 280 K (heating) with a latent heat of 4.4 Jg^{-1} [50]. The MCE properties of AlFe_2B_2 can be enhanced by addition of Ge and Ga [51].

2.2.3.5 *Fe₂P based alloys*

The large MCE observed in Fe_2P -based compounds originates from a field-induced first-order magnetic phase transition. Usually, Mn substitutes for half of the Fe sites. The parallel alignment of the Mn and Fe moments results in high magnetization. The moments of Mn are much larger than those of Fe. The MCE properties of MnFe(P,Ge) , MnFe(P,As) and MnFe(P,Si) alloy systems have been studied. $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.74}\text{Ge}_{0.26}$ prepared by melt spinning displayed a ΔS_{Max} of $44.9 \text{ Jkg}^{-1}\text{K}^{-1}$ for $\Delta H = 5 \text{ T}$ at 323 K [52,53]. The transition temperature was tunable by varying the amount of P and Ge in the alloy. Similarly, in the case of $\text{MnFeP}_{1-x}\text{As}_x$ alloys, variation of the P/As ratio between 3/2 and 1/2 tuned the T_C between 200 K to 350 K. The value of ΔS_{Max} was reported as $18 \text{ Jkg}^{-1}\text{K}^{-1}$ for $\Delta H = 5 \text{ T}$ at 300 K for $\text{MnFeP}_{0.45}\text{As}_{0.55}$ [54]. However, for the purpose of cost and toxicity reduction there have been attempts to prepare Ge and As-free alloys such as MnFe(P,Si) and MnFe(P,Si,B) [55]. By concurrently changing Mn:Fe and P:Si ratios in $\text{Mn}_x\text{Fe}_{1.95-x}\text{P}_{1-y}\text{Si}_y$ compounds, the working temperature was maintained between 210 and 430 K for $x = 1.35$, $y = 0.46$ and $x = 0.66$ and $y = 0.42$, respectively. A steep transition and small hysteresis ($\sim 1.5 \text{ K}$) were observed [56]. High performance, relatively low cost and tunable transition temperature are advantages of Fe_2P based alloys.

2.2.3.6 *Heusler and half-Heusler alloys*

In the year 1898, Heusler discovered a series of ferromagnetic alloys which were characterized by remarkable magnetic properties [57]. Ferromagnetic alloys of general composition A_2BC are categorized as Heusler alloys (X and Y are 3d elements and Z is a group IIIA–VA element), whereas alloys with composition ABC are categorized as half-Heusler alloys. Ni based Heusler alloys, e.g., $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ show FOMT along with shape memory which results in high MCE with $\Delta S_{\text{Max}} = 20.4 \text{ Jkg}^{-1}\text{K}^{-1}$ for $\Delta H = 5 \text{ T}$ at 315 K

[58,59]. Inverse magnetocaloric effect has been observed in $\text{Ni}_{50-x}\text{Mn}_{39+x}\text{Sn}_{11}$ [60], $\text{Ni}_{50}\text{Mn}_{37+x}\text{Sb}_{13-x}$ [61], $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ [62] etc. which are a result of an antiferromagnetic to ferromagnetic transition. $\text{Ni}_{55.2}\text{Mn}_{18.6}\text{Ga}_{26.2}$ alloy has a transition temperature of 317 K with a structural change from cubic to tetragonal and ΔS_{Max} of $20.4 \text{ Jkg}^{-1}\text{K}^{-1}$ in a field of 5 T [63]. Other Heusler alloy systems studied for their magnetocaloric and magnetic properties are $\text{Co}_{2-x}\text{Fe}_x\text{VGa}$ [64], $\text{Cu}_{50}\text{Mn}_{25}\text{Al}_{25-x}\text{Ga}_x$ [65], Co_2MnX ($X = \text{Al, Si, Ge, Sn}$) [66], Zr_2PdT ($T = \text{Al, Ga, In}$) [67], Pd_2MnIn and Pd_2MnSn [68].

Among the half-Heusler alloys, MnNiGe [69], MnCoGe [70] and MnNiSi alloy systems have been widely explored with addition of alloying elements to tune the T_C . $\text{Mn}_{0.89}\text{Cr}_{0.11}\text{NiGe}$ was reported to possess $\Delta S = 28 \text{ Jkg}^{-1}\text{K}^{-1}$ for $\Delta H = 5 \text{ T}$ at 280 K [71]. $\text{MnCo}_{1-x}\text{Ge}$ shows a peak of ΔS_M at 319 K with a value of $2.3 \text{ Jkg}^{-1}\text{K}^{-1}$ for $\Delta H = 1 \text{ T}$ [70], whereas vacancy-tuned $\text{Mn}_{1-x}\text{CoGe}$ show better MCE properties with peak ΔS_M value of $10 \text{ Jkg}^{-1}\text{K}^{-1}$ for $\Delta H = 2 \text{ T}$ [72]. Alloying elements such as Cu [73], Fe [74], Si [75], Cr [76], Zn [77] and Al [78] have been added to MnCoGe to enhance the MCE properties and improve the tunability of transition temperature. MnNiSi based half-Heusler alloy systems have gained tremendous interest in recent years due to its high performance, tunability of T_C and easy synthesis. The properties of MnNiSi and its alloying additions are discussed in the subsequent sections.

Table 2.1: MCE properties of some of prominent alloys categorized based on their alloy systems. (ND: No data available)

Base alloy system	Alloy composition	T_C range(K)	ΔS_{Max} ($\text{Jkg}^{-1}\text{K}^{-1}$)	RCP_{Max} (Jkg^{-1})	Ref.
Gd based	Gd (pure, Polycrystalline)	294	4.2 (1.5 T)	175.9	[21]
	$\text{Gd}_5\text{Si}_2\text{Ge}_2$	277	20 (5 T)	305	[6]
	$\text{Gd}_x(\text{Fe}_{0.56}\text{Al}_{0.44})_{100-x}$	212 - 280	7.2 (5 T)	744	[35]
La based	$\text{LaFe}_{11.6}\text{Si}_{1.4}$	196	22 (5 T)	169.9	[79]
	$\text{LaFe}_{11.4}\text{Si}_{1.6}$ annealed	208	19.4 (5 T)	ND	[37]
	$\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.6}$	333	21 (5 T)	ND	[80]

	$\text{LaFe}_{11.1}\text{Co}_{0.6}\text{Si}_{1.3}$	265	15 (5 T)	ND	[38]
Other rare earth based	$\text{Ho}_2\text{Cu}_2\text{Cd}$	30	20.3 (5 T)	481	[40]
	$\text{Tb}_{36}\text{Y}_{20}\text{Al}_{24}\text{Co}_{20}$	30	5.6 (5 T)	ND	[42]
	$\text{Dy}_2\text{Co}_2\text{Al}$	62	10.4 (5 T)	279	[81]
	ErCo_2	42	38 (5 T)	291	[45]
	Eu_2In	55	26 (5 T)	ND	[15]
AlFe_2B_2	AlFe_2B_2	274	7.7 (5 T)	162	[49]
	$\text{Al}_{1+x}\text{Ge}_x\text{Fe}_2\text{B}_2$	282 - 310	5.18 (2 T)	148	[51]
	$\text{Al}_{1.1}\text{Ga}_{0.05}\text{Ge}_{0.05}\text{Fe}_2\text{B}_2$	294	6.51 (2 T)	144	[51]
Fe based	$(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$	438 - 215	1.58 (5 T)	548	[22]
	$(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$	381	1.46 (5 T)	641	[23]
	$(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ Ribbons	330	1.16 (5 T)	305	[25]
	Fe-Zr-B Ribbons	286 - 390	1.13 (5 T)	135.6	[82]
High entropy alloys	NiFeCoCrPd_x	225 - 295	0.9 (5 T)	ND	[83]
	$\text{Fe}_x\text{CoNiCuMn}_{1-x}$	292 - 299	0.1 (1.5 T)	14	[28]
Fe_2P based	$\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.74}\text{Ge}_{0.26}$	248 - 345	18.2 (5 T)	483	[53]
	$\text{Mn}_x\text{Fe}_{1.95-x}\text{P}_{1-y}\text{Si}_y$	210 - 430	18 (2 T)	ND	[56]
	$\text{Mn}_{1.15}\text{Fe}_{0.85}\text{P}_{0.52}\text{Si}_{0.45}\text{B}_{0.03}$	205 - 251	19.8 (2 T)	208	[55]
	$\text{MnFeP}_{0.45}\text{As}_{0.55}$	306	18.3 (5 T)	390	[84]
Heusler alloys	$\text{Ni}_{50}\text{Mn}_{25+x}\text{Ga}_{25-x}$	258 - 340	9.56 (8 T)	ND	[58]
	$\text{Ni}_{50-x}\text{Mn}_{39+x}\text{Sn}_{11}$	280 - 300	10.4 (1 T)	ND	[60]
	$\text{Ni}_{50}\text{Mn}_{37+x}\text{Sb}_{13-x}$	273 - 298	19 (5 T)	32	[61]
	$\text{Co}_{2-x}\text{Fe}_x\text{VGa}$	275 - 345	3.3 (7 T)	ND	[64]

	$\text{Co}_{50-x}\text{Ni}_x\text{Cr}_{25}\text{Al}_{25}$	280 - 328	2.55 (5 T)	87	[85]
	$\text{Fe}_2\text{MnSi}_{1-x}\text{Ga}_x$	150 - 225	1.2 (2 T)	76	[86]
Half-Heusler alloys	$\text{Mn}_{1-x}\text{Cr}_x\text{NiGe}$	275	28 (5 T)	236	[71]
	$\text{MnCo}_{1-x}\text{Ge}$	293 - 325	2.3 (1 T)	58	[70]
	$\text{CoMnSn}_{1-x}\text{Cu}_x$	145 - 158	17.4 (5 T)	231	[87]
	$\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$	232 - 333	7.5 (5 T)	ND	[88]
	$\text{Mn}_{1-x}\text{Cr}_x\text{As}$	265 - 313	20.2 (5 T)	ND	[89]
	$\text{Mn}_{1.9-x}\text{Ni}_x\text{Ge}$	205	6.4 (5 T)	ND	[69]

2.2.4 Limitations of past MCMs

MCM serves as the heart of any magnetic cooling and energy harvesting device. Hence, selection of MCM should be based on several factors such as performance, cost, availability of raw materials, toxicity, mechanical strength etc.

The first cooling device using Gd as the working material was designed by Brown [5]. Since there was no option for the tunability of T_C in pure Gd, the device parameters had to be adjusted to suit the T_C of Gd. In 1997, $\text{Gd}_5\text{Si}_2\text{Ge}_2$ was discovered showing a first order giant MCE suitable for magnetic cooling applications [6]. However, first order MCM suffered from the drawback of hysteresis which consumed additional energy during every temperature cycle. Subsequent MCMs were discovered providing T_C tunability, mechanical strength and better magnetocaloric properties [90]. **Table 2.2** summarizes some of the drawbacks in each of the MCM.

Table 2.2 Drawbacks and challenges in MCM

Alloy System	Drawbacks and challenges
Pure Gd	1) No tunability of T_C 2) Rare-earth element : limited availability, high cost
Gd based alloys	1) Rare-earth raw material : limited availability, high cost 2) Challenges of impurity phases during synthesis : heat treatment necessary
La based alloys	1) Poor mechanical strength 2) Rare-earth raw material : limited availability, high cost 3) Impurity phases during synthesis
Fe based alloys	1) Low ΔS_M values : low performance 2) T_C is not well defined : approximated using the slope of M vs T plot
Fe ₂ P based alloys	1) Hysteresis during heating and cooling

2.2.5 MnNiSi based magnetocaloric alloys

MnNiSi is a half-Heusler alloy exhibiting a magnetic transition from a ferromagnetic (FM) state to a paramagnetic (PM) state at 622 K [91], and a structural transition between a low-temperature orthorhombic phase (TiNiSi-type structure, space group Pnma) to a high-temperature hexagonal phase (Ni₂In-type structure, space group P63/mmc) at 1200 K [92]. It is challenging to achieve magnetostructural coupling in MnNiSi due to this wide separation of the magnetic and the structural transition temperatures. It has also been shown that single-element substitution is insufficient to achieve the magnetostructural transition near room temperature [93,94]. Substitution of Fe and Co decreased T_C to ~450 K and ~550 K, respectively, but was unsuccessful in coupling the magnetic and structural transition (**Fig 2.5**). Hence, two element substitution is required to induce magnetostructural coupling in a temperature range known as the Curie temperature window (CTW). A wide CTW was achieved in MnNiSi by isostructural alloying with CoNiGe [95], MnFeGe [96], Fe₂Ge [97], CoFeGe [98], Co₂Ge [99] etc., (**Table 2.3**). The partial substitution of Fe, Co or Ni atoms

in Mn sites, and Ge or Sn atoms in Si sites stabilizes the hexagonal phase of MnNiSi, resulting in reduction of the structural transition temperature (T_t) to near room temperature values. Since the hexagonal structure is paramagnetic owing to its higher vibrational entropy, the magnetic phase changes (FM $\leftrightarrow$ PM) along with the structural transition, inducing a magnetostructural transition.

Fig 2.5 Curie temperature and transition temperature for single element (Fe, Co) substituted MnNiSi.

MnNiSi based alloys possess the highest ΔS_{Max} due to the rapid martensitic transition. $(\text{MnNiSi})_{1-x}(\text{FeCoGe})_x$ displayed a massive ΔS_{Max} of $143.7 \text{ Jkg}^{-1}\text{K}^{-1}$ for a field change of 5 T. $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ follows with a ΔS_{Max} of $57.6 \text{ Jkg}^{-1}\text{K}^{-1}$ obtained in the present work. In all the cases, double elemental substitution to MnNiSi show significantly higher ΔS_{Max} values compared to other alloy systems. The MCE properties and the CTW range for MnNiSi based alloys is summarized in **Table 2.3**.

Table 2.3 ΔS_{Max} and CTW of MnNiSi based alloys

Alloy composition	Elements added	CTW (K)	ΔS_{Max} ($\text{Jkg}^{-1}\text{K}^{-1}$)	Ref.
$\text{Mn}_{1-x}\text{Co}_x\text{NiSi}$	Co	541 - 622	40 (5 T)	[94]
$\text{Mn}_{1-x}\text{Fe}_x\text{NiSi}$	Fe	438 - 583	2.52 (5 T)	[93]
$(\text{MnNiSi})_{1-x}(\text{CoNiGe})_x$	Co, Ge	200 - 470	41.8 (5 T)	[95]
$(\text{MnNiSi})_{1-x}(\text{FeNiGe})_x$	Fe, Ge	174 - 420	11.5 (1 T)	[100]

$(\text{MnNiSi})_{1-x}(\text{MnFeGe})_x$	Fe, Ge	220 - 275	44 (5 T)	[96]
$\text{Mn}_{0.5}\text{Fe}_{0.5}\text{NiSi}_{1-x}\text{Al}_x$	Fe, Al	120 - 300	36.6 (5 T)	[101]
$\text{Mn}_{0.4}\text{Fe}_{0.6}\text{NiSi}_{1-x}\text{Ga}_x$	Fe, Ga	182 - 403	13.3 (3 T)	[102]
$\text{Mn}_{1-y}\text{Co}_y\text{NiGe}_{1-x}\text{Si}_x$	Co, Ge	125 - 446	40 (5 T)	[103]
$(\text{MnNiSi})_{1-x}(\text{Co}_2\text{Ge})_x$	Co, Ge	210 - 460	20.7 (5 T)	[99]
$\text{Mn}_{0.85}\text{Co}_{0.3}\text{Ni}_{0.85}\text{Si}_{1-x}\text{Ga}_x$	Co, Ga	239 - 542	29.8 (5 T)	[104]
$(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ga})_x$	Fe, Ga	219 - 504	48.8 (5 T)	[105]
$(\text{MnNiSi})_{1-x}(\text{FeCoGe})_x$	Fe, Co, Ge	235 - 355	143.7 (5 T)	[98]
$(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$	Fe, Ge	200 - 415	57.6 (5 T)	[97]
$\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$	Fe, Sn	248 - 343	8.64 (5 T)	[106]

2.3 Thermodynamic modeling of magnetocaloric transition

Thermodynamic models are described using variables obtained by fitting experimental results. These phenomenological models can provide a description of the phase transition and the effects of hysteresis. They are usually helpful for gaining understanding of the processes involved during phase transition [107]. In the present work, Arrott plots, Landau theory and the Bean-Rodbell model were used to analyze magnetostructural transition of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$. A brief description on each of the models are summarized below.

2.3.1 Arrott plots

Arrott plot relates to the square of the magnetization M^2 of a magnetic material to the ratio of the applied magnetic field and magnetization (H/M) at several fixed temperatures. It is used for identifying the order of the magnetic transition [108]. The Banerjee criterion [109] is applied to the Arrott plots to determine the order of the magnetic transition. A positive slope of M^2 versus H/M at all the temperatures indicates a SOPT, whereas a negative slope at any one of the temperature indicates a FOPT. The Arrott plots prove to be effective in determining the accurate T_C for SOPT, e.g., the 3D-Heisenberg model, the tricritical mean-field model, and the 3D-Ising model. **Fig 2.6** shows an example of an Arrott plot for arc melted and spark plasma sintered $\text{LaFe}_{11.6}\text{Si}_{1.4}$ alloy exhibiting FOPT and SOPT, respectively [110]. The negative slopes can be distinctly observed at different temperatures for FOPT.

Fig 2.6 Arrott plots of isotherms in the vicinity of T_C of (a) arc-melted sample showing FOMT and (b) spark plasma-sintered sample showing SOMT in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds [110]

2.3.2 Landau theory of phase transitions

The Landau theory of phase transitions is based on the free energy values expanded into a power series near a critical point. The magnetic free energy $F(M, T)$ is expressed as a function of magnetization (eq.(2.20)) [111]. The magnetic field (M) and temperature (T) of $F(M, T)$ determine the nature of the magnetic transition.

$$F(M, T) = \frac{A_1(T)}{2} M^2 + \frac{A_2(T)}{2} M^2 + \frac{A_3(T)}{2} M^2 + \dots - \mu_0 H M \quad (2.20)$$

where μ_0 is the permeability of free space and A_1 , A_2 and A_3 are the Landau coefficients. An equation of state linking the magnetic field (H) and the magnetization (eq.(2.21)) can be used to determine the Landau coefficients and by fitting this equation to experimentally determined values of $\mu_0 H$ versus M curves at different temperatures in the vicinity of the transition.

$$\mu_0 H = A_1(T)M + A_2(T)M^3 + A_3(T)M^5 \quad (2.21)$$

The two characteristic temperatures, T_C and T_0 can be identified using temperature dependent Landau coefficients A_1 , A_2 and A_3 . A positive minimum in A_1 represents the T_C and the temperature at which A_2 reaches zero represents T_0 . The values of T_C , T_0 and A_3

set the criteria for categorizing the order of the transition. For a FOPT, A_3 has a positive value and $T_C > T_0$ [112].

2.3.3 The Bean-Rodbell model

According to the Bean-Rodbell model, the lattice strain affects the magnetic ordering due to a change in the interatomic distance [113]. The T_C is given by eq. (2.22)

$$T_C = T_0(1 + \beta\omega) \quad (2.22)$$

where, T_0 is the Curie temperature without considering the lattice strain, β is the slope of dependence of T_C on the volume V and ω is the normalized volume change. β can be expressed as

$$\beta = \frac{d(\frac{T_C}{T_0})}{d(\frac{V}{V_0})} \quad (2.23)$$

Which yields $\omega = (V - V_0)/V_0$. The exchange interactions, distortion, Zeeman effect and a pressure effect are considered for expressing the Gibbs free energy per unit volume (eq.(2.24))[113].

$$G = -\frac{3J}{2(J+1)} Nk\sigma^2 T_C - H\sigma_s \sigma + \frac{1}{2K} \omega^2 + P\omega - TS \quad (2.24)$$

Where N is number of magnetic atoms per unit volume, k is the Boltzmann constant, K is the compressibility (reciprocal of the coefficient of thermal expansion (α)), σ_s is the saturation magnetization, J is the total ion angular moment, S is the magnetic entropy, H is the applied magnetic field and P is the pressure. σ is the relative magnetization given by $\sigma = \sigma_s / g\mu_B JN$, where μ_B is the Bohr magneton and g is the Lande factor.

Using eq. (2.22) and (2.24), the free energy can be minimized by volume factor, the volume

change under the influence of magnetization and pressure change, ω can be deduced:

$$\omega = \frac{(V - V_0)}{V_0} = \frac{3}{2} \frac{J}{(J + 1)} NKT_0 k\beta\sigma^2 - PK \quad (2.25)$$

Substitution of eq. (2.25) in eq. (2.24), the free energy term was minimized in terms of σ . H was set to zero to obtain the relationship between normalized spontaneous magnetization and temperature (T):

$$T = \frac{a_j\sigma T_0 + b_j\eta\sigma^3 T_0 + H\sigma_0/Nk}{-2\alpha\beta T_0\sigma - \frac{1}{Nk} \frac{\partial S_j(\sigma)}{\partial \sigma}} \quad (2.26)$$

Where, $a_j = 3J/(J + 1)$, $b_j = [9(2J + 1)^4 - 1] / [80 (J + 1)^4]$ and $\eta = [NkT_0K\beta^2 80 [J (J + 1)]^2] / [2[(2J + 1)^4 - 1] V_0]$

The order of the phase transition is determined by the phase transition parameter η , whereas volume change is related to the parameters α and β . For $\eta > 1$, the transition is FOPT. If $\eta < 1$, the transition is SOPT. The value of $\alpha\beta T_0$ can be evaluated by expressions for the Curie constant proposed by Blois and Rodbell [114].

$$C^* = C/(1 - \alpha\beta T_0) \quad \text{and} \quad T_0^* = T_0/(1 - \alpha\beta T_0) \quad (2.27)$$

where C is the Curie constant. The values of apparent Curie temperature T_0^* and apparent Curie constant C^* can be obtained by the reciprocal of susceptibility ($1/\chi$) vs temperature plot. The slope and the intercept on the temperature axis of the $1/\chi$ vs T plot in the paramagnetic regime was used to determine the value of C^* and T_0^* , respectively. The C^* and T_0^* substituted in eq. (2.27) gives the values of C and T . Solving the two equations for C^* and T_0^* (eq. (2.27)) at different temperature provides the value of $\alpha\beta T_0$. This value is substituted in eq. (2.26) to obtain the fitting equation to model the phase transition.

The entropy change for the transition can be modeled using the values of η obtained from eq.(2.26). By inserting eq. (2.25) in eq. (2.24) and minimizing the Gibbs free energy in

terms of σ , the magnetic state equation can be represented in terms of the Brillouin function (B_J) (eq.(2.28))[115]

$$\sigma = B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}Y\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}Y\right) \quad (2.28)$$

where

$$Y = \frac{1}{T} [3T_0\sigma \left(\frac{J}{J+1}\right) + \frac{g\mu_B J}{k} H + \frac{9[(2J+1)^4 - 1]}{80(J+1)^4} T_0\eta\sigma^3] \quad (2.29)$$

The inverse of the Brillouin function, $B_J^{-1}(x)$ determines the total magnetic entropy. The temperature, pressure and magnetic field dependence of entropy can be extracted using this relation. The expression for the magnetic entropy change (ΔS_M) [115] is given by:

$$\Delta S_{\text{mag}}(T, H) = S_{\text{mag}}(T, H_f) - S_{\text{mag}}(T, H_0) = R \left\{ \ln \frac{Z_{Hf}}{Z_{H0}} + T \left[\frac{\partial \ln(Z_{Hf})}{\partial T} - \frac{\partial \ln(Z_{H0})}{\partial T} \right] \right\} \quad (2.30)$$

where,

$$Z = \frac{\sinh(2Y)}{\sinh(Y)} = e^Y + e^{-Y} \quad (2.31)$$

H_0 and H_f are the initial and maximum applied field.

Using eq.(2.26), a fitting equation for the experimental M vs T curve can be derived and ΔS_M for each temperature interval can be predicted using eq.(2.30)

2.4 Applications of magnetocaloric materials

Magnetic cooling has emerged as a potential technology for various practical applications including cooling, refrigeration and energy harvesting. In the following sections, the chronology of the cooling and energy harvesting applications utilizing MCM are described.

2.4.1 Cooling devices based on MCE

The first magnetic cooling device was developed by Brown [5] using pure Gd as the working material oscillating between the heat sink and the heat load. Heat from the heat load was transported to the heat sink by externally induced oscillation of Gd. In 1992, Chubu electric and Toshiba Corp. developed a magnetic refrigerator operating at 25°C having a Carnot efficiency of ~53% and refrigeration capacity of 100 W [116]. In 1995,

ErNi alloy was used by Zimm et al. to demonstrate an active magnetic regenerator (AMR) for cooling a heat load of 1.6 W using a 3 T magnetic field and He gas as the heat exchanger [117]. In 1997, the Ames laboratory and Astronautics Corporation of America developed a reciprocating magnetic cooling device using 3 kg of Gd spheres attaining a cooling power of 600 W in 5 T magnetic field [118]. Carnot efficiency approached 60% and more than 10 K temperature difference was observed.

Among the rotary prototypes, Chubu Electric Power Co. demonstrated active cooling device using four AMR beds made from Gd based alloys. Magnetic field was applied using a rotating Nd-Fe-B magnet assembly providing a magnetic field of 0.77 T. Cooling power of 30 Wkg⁻¹ and 10 Wkg⁻¹ were obtained at heat sink temperatures of 283 K and 288 K, respectively [116]. Further prototypes were developed by Okamura et al. by increasing the magnetic field to 1.1 T yielding cooling power of 138 Wkg⁻¹ [119].

Curie motor is one of the prominent rotary prototypes using the thermomagnetic response of MCM for conversion of heat to mechanical energy [120]. The thermomagnetic response of magnetic fluids prepared using nanoparticles of Mn_{1-x}Zn_xFe₂O₄ and Fe₃O₄ have also been utilized for self-pumping magnetic cooling prototypes to achieve cooling of upto 30 K for a 5 W heat load [121]. This prototype has been further enhanced to achieve cooling in the kW range.

MCE cooling and refrigeration prototypes have been commercialized in recent years. in 2014, General Electric (GE) developed a magnetic cooling prototype capable of reducing temperature up to 80 K [122]. Subsequently in 2015, joint effort involving Haier, Astronautics Corporation and BASF resulted in a wine cooler based on magnetic refrigeration techniques [123]. Recently, Cooltech announced its partnership with supermarket chain Carrefour to implement their magnetic cooling system in a cold drinks cabinet [124]. Commercial magnetic cooling prototypes are shown in **Fig 2.7**.

Fig 2.7 Commercial prototypes based on MCE (a) Magnetic refrigeration system developed by Chubu Electric Power Co. Refrigerating performance of 540 W achieved with optimal permanent magnet positioning (2006) (b) The wine chiller is designed by Haier and BASF to achieve a temperature of 8 to 12°C in a normal room temperature environment (2015) (c) Wine refrigerator is designed GE capable of reducing temperature by 80 degrees. (2015) (d) Cold drinks cabinet at a supermarket in France using magnetic refrigeration application designed by Cooltech (2016).

2.4.2 Energy harvesting prototypes

The worldwide demand for energy results in an increasingly urgent requirement for highly energy efficient devices. Both active and passive devices can be used for electricity

generation. Active devices rely on external energy input to cause mechanical movement of the working material, producing electricity by electromagnetic induction or by a piezoelectric effect. The pyromagnetic generator proposed by Tesla [125] in 1890 used heat from a furnace to produce steam for alternate heating and cooling of iron pipes. The alternating heating and cooling of iron pipes produced a change in the magnetic flux in the circuit resulting in electricity output. In 1892, Edison [20] patented a different type of pyromagnetic generator. It consisted of iron tubes which rotated using a motor with hot and colds end on either side of the rotation axis. Alternate heating and cooling of the iron tubes changed their magnetization, generating current in the windings. Solomon [126] designed a thermomagnetic generator using Gd as the working material alternately subjecting Gd to a heat load and a heat sink, employing a cyclic magnetic field. The resulting change in the magnetic states of the Gd generated current in a coil wound around the working material. Recently, a pretzel-like configuration was found to give better performance due to sign reversal of the magnetic flux [127], drawbacks such as hysteresis, magnetic stray fields and complex geometries of the thermomagnetic material were also avoided in pretzel design.

However, all these devices require an additional pump or mechanical input to move the working material cyclically between the heat sink and the heat load. On the other hand, passive devices have advantages such as ease of maintenance and no external pumps are required. A thermomechanical actuator developed by Ujihara [128] used the oscillations of a Gd plate between a heat sink and a heat source. The plate was connected to a leaf spring which acts as a piezoelectric converter to generate electricity. A thermo-magneto-electric generator by [129] uses a similar principle to generate electricity, it uses flexible polyvinylidene difluoride (PVDF) instead of a leaf spring as the piezoelectric connector. Gueltig et al. [130,131] developed a thermomagnetic generator based on Heusler alloys, a Ni-Mn-Ga film with a pickup coil was mounted on a Cu-Zn cantilever. Electrical output was obtained when alternate heating and cooling changed the magnetic flux in the coil due to a variation in the magnetization of the Ni-Mn-Ga film. The passive devices mentioned above either use a piezoelectric connector or a thin-film working material, resulting in lower output power. The hybrid thermomagnetic oscillator (HTMO) [132] demonstrated in the present work is the only passive device exhibiting simultaneous cooling and

electricity harvesting functions. The recent thermomagnetic energy harvesting prototypes with device parameters, output and their limitations are summarized in **Table 2.4**.

Table 2.4: Thermomagnetic devices converting waste heat to electricity. Notations: electromagnetic induction (EMI), piezoelectric (PE), heat load temperature (T_{HL}), heat sink temperature (T_{HS}), Rare-earth element used (RE), not described (ND).

First Author	Device						Current (mA)	Voltage (V)	Limitations
	design	actuation	size(mm ³)	Material	T_{HL} (K)	T_{HS} (K)			
Present Work	EMI	Passive	5090	(MnNiSi) _{0.7} (Fe ₂ Ge) _{0.3}	453	298	15	10	--
Chen [133]	PE	Passive	63	Gd	300	280	4.7×10^{-6}	0.037	Low voltage, RE
Chen [134]	PE	Passive	35	Gd	308	279	ND	0.0304	Low voltage, RE
Chun [129]	4×PE cantilever	Passive	32	Gd	343	263	0.013	17	Small scale device, RE
Song [135]	PE cantilever	Passive	19	La _{0.85} Sr _{0.15} MnO ₃ + (Ni _{0.6} Cu _{0.2} Zn _{0.2})Fe ₂ O ₄	353	273	4.1×10^{-3}	2	Complex RE material
Chung [136]	PE	Passive	7	Gd	300	275	ND	0.0166	Low voltage, RE
Ujihara [128]	PE+spring	Passive	4.57	Gd + Au coating	323	273	ND	ND	Small scale, RE
Gueltig [131]	EMI+cantilever	Passive	0.02	Ni-Mn-Ga	433	295	0.18	ND	Small scale device
Gueltig [130]	EMI+cantilever	Passive	7.5×10^{-3}	Ni _{50.4} Co _{3.7} Mn _{32.8} In _{13.1}	433	295	0.01	0.001	Low voltage, small scale
Post [137]	PE+spring	Passive	ND	Ni ₄₅ Co ₅ Mn ₄₀ Sn ₁₀	443	393	ND	ND	PE required
Elliot [138]	EMI	Active	5000	Gd	300	277	ND	ND	RE & external pumps
Srivastava [139]	EMI	Active	3300	Ni ₄₅ Co ₅ Mn ₄₀ Sn ₁₀	375	298	ND	0.0006	Low voltage
Solomon [126]	EMI	Active	ND	Gd	310	280	ND	ND	RE & external pumps

2.5 Summary

Magnetic cooling is a potential emerging technology having numerous advantages over conventional cooling technology. Several MCM have been explored. MnNiSi based alloys

offer superior performance, are rare-earth free, display high ΔS_M and wide CTW for tuning the T_C . Double element substitution to MnNiSi has been effective in reducing T_C and inducing a magnetostructural transition near room temperature. The substitution of Fe and Ge to MnNiSi decreases the T_C to room temperature and couples the magnetic and structural transition over a wide CTW. The cost of synthesis was further reduced by replacing Ge with Sn. The thermomagnetic response of MCM has been utilized for energy harvesting applications by active and passive devices. Passive devices have advantages such as no external energy input in the form of rotors or pumps and low maintenance cost. The thermomagnetic oscillator demonstrated in the present work is one such passive device for simultaneous cooling and energy harvesting using waste heat, providing several advantages over other thermomagnetic energy harvesters.

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Chapter 3

Experimental Methodology

This chapter provides a description of the techniques used for synthesis, characterization, measurements and modeling of MnNiSi based magnetocaloric alloys. The experimental flow is discussed using a flowchart, followed by sample synthesis using arc melting, structural characterization was performed by X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy with selected area electron diffraction (SAED) techniques. Magnetic measurement was carried out using a physical property measurement system (PPMS) with a vibrating sample magnetometry (VSM) attachment. The setup and working principle of the thermomagnetic oscillator is also elucidated followed by a description of the optimization of device parameters.

3.1 Overview of experimental methods

The flowchart of the experiments followed in the present work is shown in **Fig. 3.1**.

Fig. 3.1 Flowchart of the experimental plan

The first step of the experimental flow is the synthesis of materials using arc melting, followed by characterization using SEM to determine the composition. The crystal structure of sample was analyzed by SAED pattern in TEM as well as XRD analysis. Reitveld analysis was used to refine the XRD results and determine the lattice parameter. The structural transition temperature in the samples were determined by DSC peaks and high temperature XRD. Magnetic measurements were performed using PPMS with VSM

attachment and the values of ΔS_M and RCP were obtained using MATLAB and ORIGIN programs. Further analysis and simulations were performed using software tools such as COMSOL Multiphysics, VESTA and Labview.

3.2 Alloy Synthesis

$(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ and $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ were synthesized by arc melting using Mn chips (99.95 wt% purity), Ni powder (99.95 wt% purity), Ge powder (99.99 wt% purity), Fe chips (99.99 wt% purity), Si chips (99.95 wt% purity) and Sn shots (99.99 wt% purity). The mass of all elements was selected on the basis of the nominal composition. 5% by weight of excess Mn was taken to compensate the Mn loss by vaporization during arc melting. Since Mn is brittle and can scatter into small pieces while striking the arc, it was mixed with Ge and Ni powders and compressed to form a pellet. The compressed pellet was arc melted several times under argon atmosphere to ensure homogeneity. Alloys possessing magnetostructural transition temperatures higher than the room temperature spontaneously cracked due to the structural transition and turned into coarse powders inside the arc melter during cooling. Whereas, the alloys with below room temperature transition remained as button shaped pellets. The arc melted powders / buttons were used for characterization without any heat treatment.

Fig. 3.2 shows the arc melter (Buhler, MAM-1) consisting of a water cooled copper base and melting chamber connected to a 10^{-5} mbar turbo vacuum pump. It has a capacity of up to 20 g per charge and temperature range of ~ 3500 K depending on the material.

Fig. 3.2 Arc melter (Buhler, MAM-1) used in the present work

3.3 Characterization techniques

3.3.1 X-ray diffraction

The crystal structure analysis and phase determination was performed by X-ray diffraction. When X-rays scatter from a substance with a periodic arrangement of crystal lattice, interference can take place, resulting in a pattern of higher and lower intensities. The angle (2θ) at which the constructive interference occurs to give a peak is determined by Bragg's law (**Fig. 3.3c**).

Fig. 3.3 (a) Bruker D8 advance XRD instrument. (b) Goniometer with XRD source and the detector (c) Schematic of Bragg's law for constructive interference.

According to Bragg's law, interference from X-rays scattered by parallel planes of atoms will produce a diffraction peak if the relation given by eq. (3.1) is satisfied.

$$2d_{hkl} \sin \theta = \lambda \quad (3.1)$$

where, λ is the wavelength of the x-ray beam, d_{hkl} is the distance between two adjacent hkl planes and θ is half the scattering angle 2θ .

Fig. 3.3a and b shows the Bruker D8 advance XRD instrument used for room temperature XRD measurement operating at 40 kV, 30 mA and employing Cu K α radiation ($\lambda=1.54 \text{ \AA}$) as the X-ray source. The arc melted buttons were cut by diamond blade cutter (ISOMET 4000) and polished using SiC emery paper (800 grade). The prepared buttons and the powder samples were loaded into the XRD using their respective sample holders. The scan range was set from $2\theta = 20^\circ$ to 80° , the step size was 0.01 and the scan speed was $1^\circ/\text{min}$. The results obtained from XRD were further refined using Rietveld refinement by TOPAS 4.2 to remove the impurity peaks and determine the lattice parameters.

3.3.2 High temperature X-ray diffraction

Temperature dependent XRD was employed to determine the structure at various temperature intervals. Due to the presence of structural transition in the MnNiSi based alloys, the expected variation in the peaks were observed for XRD plots taken above the transition temperature. **Fig. 3.4** shows Bruker D8 Discover used for high temperature XRD analysis. The powder samples were compressed into pellets and sealed on both sides using a transparent tape to prevent scattering of powder. The prepared sample pellets were loaded into the XRD sample stage. The temperature of measurement was set suitably based on the transition temperature of the alloy. The data was collected from $2\theta = 20^\circ$ to 80° for each run with a step size of 0.01.

Fig. 3.4 Bruker D8 Discover used for high temperature XRD analysis

3.3.3 Scanning electron microscopy

The elemental composition of the arc melted samples were determined using energy dispersive X-ray spectroscopy (EDS) in a scanning electron microscope (JEOL JSM 6360LV) (**Fig. 3.5**).

Fig. 3.5 (a) SEM JEOL JSM-6360LV (b) Electrons and radiation emitted during the electron beam and sample interaction in scanning electron microscopy.

A focused electron beam is used to produce high magnification images. The primary electron beam can interact with the specimen to generate various emissions as shown in **Fig. 3.5**.

EDS detector attached to SEM can detect the X-ray emitted due to the relaxation of the ionized atoms by electron shell-to-shell transitions. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be

measured.

Different areas and spots on the sample were utilized and the average composition was calculated. The samples were further characterized only if the difference between nominal compositions before arc melting matched with the composition obtained from EDS within a tolerance limit of 5%.

3.3.4 Transmission electron microscopy

In transmission electron microscopy (TEM), an image is formed from the interaction of the electrons with the sample as the electron beam is transmitted through the specimen. The crystal structure of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ for $x = 0.32$ and 0.36 showing orthorhombic and hexagonal structure, respectively were obtained using a TEM JEOL JEM 2010 (Fig. 3.6). The electron beam was focused on the edge of the sample where the thickness of the sample was sufficient for the electron beam to pass through it. The area was selected such that a diffraction spot pattern was acquired. The spots were indexed using JEMS software and the d-spacing was calculated.

Fig. 3.6 (a) Photograph of the transmission electron microscope (TEM) (JEOL JEM 2010). (b) Electron beam path in TEM.

3.3.5 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermoanalytical technique to detect phase transitions in specimens. The Difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. The area under the peak was used to determine the latent heat of a structural transition and the temperature corresponding to the peak was regarded as the structural transition temperature of the sample.

The DSC measurements were performed on $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ and $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ alloys to confirm the structural transition. Around 5 – 10 mg samples were loaded into standard Aluminium pan and placed in the DSC chamber along with a reference pan. The temperature was cycled around the transition temperature with a heating and a cooling rate of 10 K/min and liquid nitrogen flow rate of 50 ml/min.

Fig. 3.7a shows the DSC Q-10 by TA instruments used in the present work with an operating temperature range of 200 K to 673 K. The schematic of the DSC chamber is shown in **Fig. 3.7b**.

Fig. 3.7 (a) DSC Q-10 (TA instruments) used for structural characterization. (b) DSC sample chamber containing the reference and the sample pan with heating module.

3.3.6 Physical property measurement system

The magnetic properties of the samples and their dependence on the temperature and the magnetic field were investigated using a Physical Property Measurement System (PPMS), (EverCool-II by Quantum Design, USA) equipped with a vibrating sample magnetometer (VSM) shown in fig (Fig. 3.8).

PPMS is used to investigate various properties of material such as magnetic properties, electrical resistivity, AC transport, heat capacity etc. The focus of present work was to investigate the magnetocaloric properties, hence the VSM attachment was used with PPMS. The original work by Simon Foner describes the working of a VSM [1].

A VSM works on the principle of Faraday's law of induction. When the sample is set in vibration between coils, a voltage is generated due to the varying magnetic flux between the pickup coils. The induced voltage is given by eq. (3.2):

$$V_{coil} = \frac{d\phi}{dt} = \frac{d\phi}{dz} \times \frac{dz}{dt} \quad (3.2)$$

where ϕ is the magnetic flux, t is the time and z is the vertical direction of the sample w.r.t the pickup coil. The sample is mounted on the VSM holder and set to vibrate inside the PPMS chamber containing superconducting pickup coils with a sensitivity of 10^{-6} emu. The induced voltage in the PPMS is given by,

$$V_{coil} = 2\pi f K M A \times \sin(2\pi f t) \quad (3.3)$$

where f , K , M and A are the frequency of oscillation, the coupling constant, the magnetic moment of the sample and the amplitude of oscillation, respectively. The sinusoidal voltage received from the pickup coils are captured and the magnetization of the sample is recorded.

The VSM attachment had a sensitivity of $<10^{-6}$ emu, oscillation frequency of 40 Hz and oscillation range of 0.1 mm – 5 mm. The operating temperature of PPMS ranges from 1.9 K to 400 K in a magnetic field from -9 T to 9 T. For the M vs H experiments, the magnetic field was cycled from 0 to 5 T to obtain the magnetization curve in the first quadrant. The Loop process was followed in M vs H measurement ensuring the complete magnetization or demagnetization of the sample before M vs H is measured for subsequent temperature interval [2]. This method results in elimination of any spurious ΔS_M peaks generated during property evaluation. The M vs T measurements were performed by applying a magnetic field of 0.1 T with a heating and a cooling rate of 4 K/min. **Fig. 3.8** shows PPMS (Evercool –II, Quantum Design) and the inner parts of the VSM attachment.

Fig. 3.8 (a) PPMS Evercool-II by Quantum Design. (b) The VSM probe used in the PPMS and the various parts in the VSM probe.

3.4 Property Evaluation

3.4.1 Structural analysis

The XRD patterns obtained at room temperature and high temperature were indexed using MATCH! 3.0 and the Reitveld refinement was performed using Total Pattern Analysis Solution (DIFFRACplus TOPAS) software. The XRD patterns were refined using the standard cif file of MnNiSi obtained from the Inorganic Crystal Structure Database (ICSD). The values of residual R_{wp} and R_{bragg} indicate the extent of discrepancy in the refinement [3]. The refinement parameters such as zero shift, sample displacement, Lorentz and Polarization (LP) factor and preferred orientation were adjusted to obtain R_{wp} and R_{bragg} values less than 10%. The comparison of relative intensities for the low temperature orthorhombic phase of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ sample with the pattern generated using ICDD PDF-4 database revealed a preferred orientation of (211). The lattice parameters of orthorhombic and hexagonal structures were also determined using the refinement.

3.4.2 MCE property evaluation

To evaluate the T_C of the sample, the magnetization values were measured during heating and cooling at the rate of 4 K/min at a constant applied field of 0.1 T. Due to the first order transition in the alloys, a sharp variation in the magnetization was observed during transition and the highest slope in the M vs T plot was regarded as the T_C . For investigation of MCE parameters, isothermal magnetization curves were obtained by sweeping the magnetic field from 0 to 5 T at regular temperature intervals of 5 K around T_C . The Maxwell's equation was used to evaluate the magnetic entropy, ΔS_M for a field change up to 5 T. From the experimentally measured values, the change in magnetic entropy was determined using the numerically integrated form of Maxwell's equation (eq.(3.4)):

$$\Delta S_M = \int_0^H \left(\frac{dM}{dT} \right)_H dH \quad (3.4)$$

The relative cooling power (RCP) is an important MCE parameter. The RCP is a useful metric to estimate the performance of a MCM. It is defined as the magnitude of heat transferred between hot and cold reservoirs during an ideal refrigeration cycle [4]. This is

obtained numerically by the area under the ΔS_M vs T curve given by:

$$\Delta S_{H1 \rightarrow H2} = \sum_i \frac{M_i(T_{j+1}, H_i) - M_i(T_j, H_i)}{T_{j+1} - T_j} \Delta H_i \quad (3.5)$$

Here, T_{Hot} and T_{Cold} are the temperatures of the hot and cold reservoirs, respectively and can be considered as the temperatures at higher and lower end of half maximum, respectively of the ΔS_M peak. In other words, the product of maximum entropy change and temperature at full width of half maximum (FWHM) in the ΔS_M vs T plot gives the value of RCP (eq. (3.6))

$$RCP = |-\Delta S_{max}| \times \delta T_{FWHM} \quad (3.6)$$

Quantitative methods were used to scale the field dependent magnetocaloric properties in order to evaluate the parameters at various applied field [5]. These values were used for force balance in the thermomagnetic oscillator prototype.

3.5 Thermomagnetic oscillator prototype

The setup and the design of the single and the hybrid thermomagnetic oscillator prototypes is described in the following sections. The enhancement in the voltage output was achieved by changing the spacer material. The circuit for the storage and the dissipation of electrical output from the thermomagnetic oscillator (TMO) is also highlighted.

3.5.1 Experimental setup of thermomagnetic oscillator

3.5.1.1 Single thermomagnetic oscillator (STMO)

The setup of STMO consisted of a quartz tube of height 9 cm and inner diameter 20 mm with a heat load at the top made from kanthal wires (resistance heating), and a heat sink at the bottom comprising of water filled upto 1/4th of the quartz tube. A copper coil of 1000 turns was wound around the quartz tube below the heat load. An NdFeB N52 grade permanent magnet (PM1) was placed above the tube as shown in **Fig. 3.9**.

The thermomagnetic alloy (TMA) of composition $(MnNiSi)_{0.7}(Fe_2Ge)_{0.3}$ having a T_C of

144°C (heating) and 128°C (cooling) was crushed into fine powder by mortar and pestle. 20 g of the alloy powder was wrapped in Al foil to form a cylinder of diameter 18mm. The weight of the alloy was selected on the basis of the upward force required to lift the TMA by PM1 for a given height of quartz tube. The TMA was further wrapped with multiple layers of Teflon tape to protect the alloy powder from oxidation due to water. The TMA was placed in the quartz tube ensuring a small air gap between the inner wall of tube and the cylinder to avoid friction.

Fig. 3.9 Schematic of the STMO setup showing the TMA at (a) the heat load and (b) the heat sink position.

The heat load was maintained at a constant temperature of 180°C before starting the experiment. When PM1 was introduced above the heat load, the TMA was pulled up due to the upward magnetic pull towards the heat load. The TMA heats up at the heat load and becomes paramagnetic, losing attraction to PM1 and falls towards the heat sink due to gravity. The heat from the TMA was transferred to the heat sink and the TMA becomes ferromagnetic again repeating the oscillations. The coil wound around the tube experiences a change in the magnetic flux due the oscillation of the TMA through it. This generated emf in the copper coil and was stored using electrical circuit.

3.5.1.2 Hybrid thermomagnetic oscillator (HTMO)

In order to achieve higher voltage output per cycle, the magnetic pull force experienced by TMA was utilized to pull another NdFeB magnet through a larger copper coil. The TMA was coupled with a cylindrical permanent magnet (PM2) having diameter of 15 mm using a spacer. The TMA and the PM2 oscillated through their respective Cu coils possessing 1000 and 6000 turns, respectively. The heat sink was externally connected to a reservoir to maintain the temperature of the heat sink. **Fig. 3.10** shows a schematic and experimental setup of the HTMO. Experimental investigations were performed by analyzing time-dependent voltage profiles obtained by Tektronix DPO5054B oscilloscope. High-speed imaging of the TMA oscillations was performed at 720p resolution and frame rate of 240 frames/s. For stable imaging, the camera was mounted by Manfrotto accessories, consisting a tripod (P/N: MT055XPRO3), a universal smartphone clamp (P/N: SKU MCLAMP), and a 3 axis gear head (P/N: 410). To determine TMA velocity, the recorded videos were analyzed in Fiji (ImageJ) software [6]. Numerical investigations were performed for the voltage and the velocity profile.

Fig. 3.10 The schematic setup of the HTMO showing the TMA at (a) the heat load and (b) the heat sink position. (c) Experimental setup of the HTMO.

3.5.2 HTMO with rigid and flexible spacer

The spacer material plays a significant role in the performance of the HTMO. The first set of experiments were performed using a rigid spacer (wooden stick) attached to the TMA and the PM2. In the case of the rigid spacer, a constant downward force due to the mass of the PM2 was experienced by TMA throughout the oscillation. To enhance the output, a flexible spacer made using a Teflon tape with a Young's modulus of 0.4 GPa, yield stress of 15 MPa [7] and maximum service temperature of 300°C [8]. The spacer was attached to the TMA and permanent magnet (PM2), the length of the spacer was slightly more than the distance between TMA and PM2, ensuring that the spacer is slack when the TMA is at the heat sink position and becomes taut when the TMA covers half of the distance upwards towards the magnet PM1. The schematic of the position of the TMA and the flexible spacer is shown in fig. 4a and 4b. The permanent magnet (PM2) attached to the flexible spacer moves upwards only when the flexible spacer becomes sufficiently rigid to pull it up. The magnetic force experienced by the TMA continuously increases as it moves upwards because the magnetic field acting on the TMA increases as it moves towards the magnet. The permanent magnet (PM2) is thus pulled up with a sudden, large force by the spacer, this rapid pull causes it to move upwards to a higher position than if a rigid spacer was used.

The rigid spacer restricts the upward motion due to its fixed length. PM2 reaches its topmost position when its kinetic energy is zero, at this point, flexible spacer again becomes slack. The potential energy of PM2 and the downward gravitational pull produces damped oscillations of PM2 in and out of the Cu coil generates additional output voltage compared to the rigid spacer setup. The position of the TMA, PM2 and the flexible spacer at each of these steps is shown schematically in fig 4 (a-e). A spring was also trialled as a spacer. However, the spring could not pull up PM2 when the TMA was pulled up towards the heat load, instead of lifting up PM2, the spring elongated absorbing part of the energy of the upward pull. Therefore, the spacer using Teflon was selected.

Fig. 3.11 Schematic diagram of the various stages of oscillations of a HTMO with a flexible spacer. (a) The TMA is situated at the heat sink and a slack flexible spacer connects it to a Nd-Fe-B N52 magnet (PM2) below. (b) The TMA is ferromagnetic and is pulled up by magnet PM1, the flexible spacer connected to PM2 becomes stiff when TMA reaches a distance of $L/2$ from the heat load. (c) PM2 is jerked upwards and lifted above the usual length which makes the spacer slack. (d) PM2 falls due to gravity but is stopped by the spacer (e) PM2 exhibits damped oscillations due to repeated stretching and slackening of the spacer.

3.5.3 Temperature and electrical measurements

The temperature at the heat load was logged at regular intervals of 10s per reading by a PCE-T390 digital thermometer (**Fig. 3.12a**). The temperature sensor was placed at the top surface of the heat load. The heat load temperature was plotted as a function of time for the first 25 oscillations to check the stability of the temperature cycles. The time-dependent

voltage output was measured by a Tektronix DPO5054B oscilloscope (**Fig. 3.12b**) at an interval of 5 ms per reading. The output current was measured using LabView software attached to a current measurement DAQ (National Instruments).

Fig. 3.12 (a) PCE-T390 digital thermometer for logging the heat load temperature. (b) Tektronix DPO5054B oscilloscope for recording time dependent voltage.

3.5.4 Electrical storage and dissipation

A capacitor based storage circuit was used to store the electricity from the HTMO. The voltage signal was rectified by 4 way Schottky diode (1N58191A) bridge rectifier and then stored in a 3.3 mF capacitor **Fig. 3.13**. The dissipation circuit consisted of an LED connected to a capacitor by means of a switch. The energy stored in the capacitor was calculated using the expression:

$$E = \frac{1}{2} CV^2 \quad (3.7)$$

where, C is the capacitance and V is the voltage across the capacitor. The energy stored for 65 min from the HTMO was sufficient to light up the LED for 50 seconds.

Fig. 3.13 Circuit diagram of the rectifier (D1), capacitor C1 (3.3mF) for storage, and a LED. The stored energy from this device was used to light up a LED by means of switch S1.

3.5.5 COMSOL simulation of TMO

The performance of the TMO as a function of material parameters such as thermal conductivity, mass and the device height was evaluated using a simulation model of the STMO coded in COMSOL Multiphysics 5.3a. The “AC/DC” module and the “magnetic fields –no current” module were used to design the STMO by applying a moving mesh with a mesh displacement method for the TMA oscillations. Extra-fine meshing was used for the whole geometry with a minimum element size of 3.5 μm . The velocity of the TMA was determined w.r.t the mass of the sample and the device height. The simulation results for STMO were in good agreement with the experimental results.

The COMSOL Multiphysics model of the HTMO was built taking account of the forces acting on the TMA i.e., upward magnetic force and gravitational force including forces by PM2 for both the rigid and the string spacer configuration. The temperature of the heat load and the heat sink were initially kept at 450 K and 25 K to mimic the experimental conditions, but could be varied the purpose of optimization. The “AC/DC” module, the “magnetic field –no current” module and the “structural mechanics” module were combined to design the HTMO simulation. Frequency of oscillation and the cooling performance for various alloys were evaluated by inputting their temperature dependent susceptibility values. A comparison of the performance due to the use of the rigid and the flexible spacer was modeled using the HTMO simulations.

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Chapter 4

(MnNiSi)_{1-x}(Fe₂Ge)_x Magnetocaloric alloys*

This chapter contains the results of the synthesis, characterization and property evaluation of (MnNiSi)_{1-x}(Fe₂Ge)_x alloys. The mechanism of Fe₂Ge alloying addition to MnNiSi is discussed in the first part, followed by the structural characterization and magnetic measurements for alloys with $x = 0.32$ to 0.36 . Coupling of the magnetic and the structural transition was observed near room temperature for all the compositions. An increase in the Fe₂Ge content from 0.32 to 0.36 decreased T_C from 363 K to 218 K. The magnetostructural coupling gave rise to a ΔS_{Max} value of $57.6 \text{ J kg}^{-1} \text{ K}^{-1}$ near room temperature $x = 0.34$, making such alloys technologically attractive. The magnetocaloric phase transition was modeled by Arrott plots, Landau equations and the Bean-Rodbell model. The chapter concludes with the principal outcomes of this work on (MnNiSi)_{1-x}(Fe₂Ge)_x alloys.

*This chapter is substantially published as: **K. Deepak**, R. V. Ramanujan, "Near room temperature giant magnetocaloric effect in (MnNiSi)_{1-x}(Fe₂Ge)_x alloys", *Journal of Alloys and Compounds* 743, 494-505 (2018).

4.1 Introduction

The increasing demand for energy efficient, green and environmentally friendly alternatives to conventional gas compression-based cooling techniques has led to an interest in magnetic cooling technology since two decades. Recently, commercial magnetic cooling devices have been launched by Haier, Astronautics Corporation of America, BASF and Cooltech [1,2]. The magnetic cooling based system is shown to be 35% more efficient than the cooling by vapour compression [3]. Additional benefits include less maintenance, no toxic emissions, no noise and vibrations, etc.

The properties of MCM determines the performance of magnetocaloric cooling system. The benchmark material Gd was first used by Brown [4] for the magnetic cooling prototype, thereafter several MCMs have been explored [5,6]. MCMs exhibiting second order transition have high RCP and low hysteresis, but suffer from low ΔS_M and low performance in a given range of operating temperature. On the other hand, the first order MCMs having “giant” magnetocaloric response are relatively better for narrow operating temperature range and low-grade waste heat recovery due to rapid switching of magnetic order with small temperature variation [7]. Another important consideration for the design of MCM is the cost effectiveness and availability. Many rare-earth based MCMs have a high cost of synthesis and also low availability. The MCMs having toxic elements such as As or P are not good option for environmental friendly technology. Hence, a quest for MCMs fulfilling the essential requirements of high performance, availability, cost and low toxicity leads us to explore the MnNiSi based MCMs.

MnNiSi based magnetocaloric alloys fall under the category of MnXX' ($X = \text{Co}, \text{Ni}$ and $X' = \text{Ge}, \text{Si}$) MCMs. The giant MCE and the tunability of transition temperature (T_t) in these family of alloys has been of considerable interest for magnetic cooling and energy harvesting technology [8]. MnNiSi undergoes a second order magnetic transition from ferromagnetic state to paramagnetic state at 662 K [9] and a structural transition from a low-temperature, orthorhombic TiNiSi -type structure to a high-temperature, hexagonal Ni_2In -type structure at 1200 K [10]. A large magnetocaloric effect can be attained by coupling of the magnetic and structural transition. Near room temperature transition and

tunability of T_t are desirable for important magnetocaloric applications such as refrigeration, harvesting low-grade waste heat and residential cooling systems [11,12]. However, magnetostructural coupling in MnNiSi is absent due to the broad separation between the magnetic and structural transition temperatures. This wide separation makes it challenging to achieve giant MCE effect and tunability near room temperature. The T_t can be lowered by substitutional addition of alloying elements that can stabilize the hexagonal phase to lower temperatures, hence decreasing the transition temperature. This decrease in transition temperature was achieved by single element substitution of Fe for Mn in the form of Mn_{1-x}Fe_xNiSi having T_C of 438 K [13]. Nevertheless, the most essential requirement for achieving the giant magnetocaloric response i.e., the coupling of structural and magnetic transition was not accomplished by the single element substitution. Hence, double element substitution was essential to obtain near room temperature magnetostructural coupling for MnNiSi-based alloys. The magnetostructural transition near room temperature occurred in MnNiSi-based systems such as MnNiSi-CoNiGe [14], MnNiSi-FeCoGe [15], MnNiSi-Fe₂Ge [16,17], (Mn,Fe)Ni(Si,Al) [18], MnNiSi-MnFeGe [19], (Mn,Fe)Ni(Si,Ga) [20], MnNiSi-FeNiGe [21] and MnNiSi-Co₂Ge [22].

This chapter focuses on the synthesis, characterization and magnetocaloric properties of (MnNiSi)_{1-x}(Fe₂Ge)_x. The alloys (x ranging from 0.32 to 0.36) were synthesized by arc melting, without any subsequent heat treatment step. The elimination of heat treatment greatly reduced the duration of synthesis of the alloy. The simpler processing technique was found to yield better magnetocaloric properties i.e., higher entropy change (ΔS_M) and better refrigeration capacity (RCP) at the magnetostructural transition compared to earlier reported values for (MnNiSi)_{1-x}(Fe₂Ge)_x alloys [16]. Since addition of Fe and Ge in specific ratio reduces the magnetostructural transition temperature, an increase in the value of x from 0.32 to 0.36 tuned the T_C from 363 K to 218 K. The one composition variable (x) provided greater flexibility for tuning the T_C to the required temperature based on the application.

The structural characterization was performed by XRD at room temperature and high temperature, SAED pattern obtained by TEM and DSC analysis. The magnetic properties

were measured by PPMS with a VSM attachment. The magnetic measurements were used for evaluating temperature dependent ΔS_M and RCP at various intervals of applied field. The values of M vs T and M vs H were utilized to model and determine the order of phase transition.

4.2 Results and discussion

4.2.1 Structural analysis

The composition and the structure of the arc melted alloys were determined using XRD and electron microscopy techniques, whereas temperature dependent structural analysis was performed by high temperature XRD and calorimetry as described in this section.

4.2.1.1 Compositional analysis

Fig. 4.1 shows the EDS elemental mapping of the alloys with composition $x = 0.32$ to 0.36 . The average compositions in terms of mass fractions were determined by 5 such readings, combining both spot patterns and area mapping. The average mass fraction of each element obtained from EDS are shown in **Table 4.1**. The difference in the ideal composition and the composition after arc melting differed by $\pm 5\%$. Hence, further characterization was performed for these samples.

Fig. 4.1 EDS elemental mapping for (MnNiSi)_{1-x}(Fe₂Ge)_x for composition from $x = 0.32$ to 0.36

Table 4.1 Average mass percentage of (MnNiSi)_{1-x}(Fe₂Ge)_x for $x = 0.32$ to 0.36 obtained from EDS after the arc melting compared with the ideal calculated composition.

$x =$	0.32		0.33		0.34		0.35		0.36	
Elements	ideal	EDS	ideal	EDS	ideal	EDS	ideal	EDS	ideal	EDS
Mn	24.05	25.21	23.63	24.67	23.22	24.23	22.8	23.72	22.39	23.6
Ni	25.7	24.43	25.24	25.1	24.8	24.38	24.36	23.76	23.91	22.73
Si	12.3	12.14	12.08	11.8	11.87	11.59	11.66	11.24	11.45	11.07
Fe	23	22.9	23.66	23.53	24.32	24.16	24.96	24.5	25.6	26.13
Ge	14.95	14.58	15.38	14.9	15.80	15.7	16.22	16.3	16.65	16.51

4.2.1.2 X-ray diffraction analysis

XRD plots of (MnNiSi)_{1-x}(Fe₂Ge)_x alloys, with the compositions ranging from $x = 0.32$ to 0.36 , are shown in **Fig. 4.2a**. The alloys with $x = 0.32$ and 0.33 showed an orthorhombic structure, since the T_i of these alloys are higher than the room temperature. The peaks of $x = 0.34$ to 0.36 corresponded to a hexagonal structure, since they have T_i below the room temperature. The comparison of the relative intensities of peaks with the pattern generated using ICDD PDF-4+ database revealed a (211) preferred orientation for the orthorhombic phase of $x = 0.32$ sample (**Fig. 4.2b**).

Rietveld refinement was performed on the XRD plots to determine the lattice parameter of each alloy. The crystal structure transformation from hexagonal to orthorhombic structure produces three variants of orientation domains as shown in **Fig. 4.3**. Atomic rearrangement initiates mainly on the (0001) planes of hexagonal phase, therefore the unit-cell vectors can be defined in terms of the Cartesian coordinates as $\mathbf{a}_1 = a_o \mathbf{i}$ and $\mathbf{a}_2 = (1/2)a_o \mathbf{i} + (\sqrt{3}/2)a_o \mathbf{j}$. In the reciprocal lattice, the corresponding unit vectors can be interpreted as $\mathbf{a}_1^* = (1/a_o)\mathbf{i} - (1/\sqrt{3})a_o \mathbf{j}$ and $\mathbf{a}_2^* = (2/\sqrt{3})a_o \mathbf{j}$. To generate the three variants of the orthorhombic phase, the superlattice vectors are given by $\mathbf{k}_{o1} = (1/2) \mathbf{a}_2^*$; $\mathbf{k}_{o2} = (1/2) \mathbf{a}_1^*$; $\mathbf{k}_{o3} = -(1/2)(\mathbf{a}_1^* + \mathbf{a}_2^*)$; $-\mathbf{k}_{o1}$; $-\mathbf{k}_{o2}$ and $-\mathbf{k}_{o3}$ [23].

Fig. 4.2 (a) XRD pattern of (MnNiSi)_{1-x}(Fe₂Ge)_x alloys with compositions $x = 0.32, 0.33, 0.34, 0.35$ and 0.36 showing orthorhombic (o) and hexagonal (h) peaks (b) XRD pattern of random orientation, (211) preferred orientation (generated using ICDD PDF-4+ database) and $x = 0.32$ showing peaks corresponding to orthorhombic structure.

The lattice parameters of the orthorhombic and hexagonal phase are defined by a_{ortho} and c_{hexa} ; b_{ortho} and a_{hexa} ; c_{ortho} and $\sqrt{3}a_{\text{hexa}}$ based on the crystallographic nature of structural transformation. The relationship between the lattice parameters for the crystal structure transformation are $a_{\text{ortho}} \Leftrightarrow c_{\text{hexa}}$, $b_{\text{ortho}} \Leftrightarrow a_{\text{hexa}}$, and $c_{\text{ortho}} \Leftrightarrow \sqrt{3}a_{\text{hexa}}$. **Table 4.2** shows the lattice parameters of the orthorhombic and the hexagonal structures obtained by Rietveld refinement. The reduction of 11.2% from a_{ortho} to c_{hexa} and an increase of 10.3% from b_{ortho} to a_{hexa} was observed. c_{ortho} increased by upto 0.6% w.r.t $\sqrt{3}a_{\text{hexa}}$. Therefore, addition of Fe₂Ge to MnNiSi distorts the orthorhombic lattice, decreases a_{ortho} and increases b_{ortho} , leading to stabilization of the hexagonal phase at room temperature, which provides a driving force for the crystal structure transition. The coexistence of both orthorhombic and hexagonal phases were analyzed by reitveld refinement (**Fig. 4.4**). The composition with $x = 0.32$ consisted of 1.24% hexagonal fraction which increased to 96.3% for $x = 0.36$.

Fig. 4.3. Schematic illustration of (a) variants with three orientation domains for hexagonal to orthorhombic transition (b) Unit cell vectors of hexagonal phase and corresponding superlattice unit vectors (a_1^* and a_2^*) as well as superlattice vectors represented by dots.

Table 4.2. Lattice parameters of (MnNiSi)_{1-x}(Fe₂Ge)_x with $x = 0.32$ to 0.36 using Rietveld refinement of XRD data.

Composition	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)
<i>x</i> = 0.32	0.582	0.368	0.701
<i>x</i> = 0.33	0.581	0.367	0.699
<i>x</i> = 0.34	0.406	-	0.518
<i>x</i> = 0.35	0.402	-	0.516
<i>x</i> = 0.36	0.399	-	0.511

Fig. 4.4 Percentage of hexagonal phase for compositions ranging from *x* = 0.32 to 0.36

4.2.1.3 Differential scanning calorimetry

The DSC analysis (**Fig. 4.5**) shows the structural transition temperature (*T_t*) corresponding to the peaks and troughs; *T_t* decreased with content of Fe₂Ge from *x* = 0.32 to 0.36. Two heating and cooling cycles at a rate of 10 K/min, showed the transition at the same temperature for subsequent cycles. The observed transition temperatures were 367 K, 328 K, 301 K, 262 K and 216 K during heating and 352 K, 313 K, 285 K, 237 K and 199 K during cooling for *x* = 0.32 to 0.36, respectively. The thermal hysteresis of ~15 K was evaluated by calculating the difference between the heating and cooling *T_t*. The latent heat during the structural transformation was determined using the area under the peak of the

DSC curve. **Table 4.3** shows the values of latent heat for (MnNiSi)_{1-x}(Fe₂Ge)_x from $x = 0.32$ to 0.36 .

Fig. 4.5 DSC analysis plots of (MnNiSi)_{1-x}(Fe₂Ge)_x with $x = 0.32$ to 0.36 . The upper peak and lower trough represent exothermic and endothermic change, respectively.

Table 4.3. Latent heat of transformation during the heating and cooling of (MnNiSi)_{1-x}(Fe₂Ge)_x for values of $x = 0.32$ to 0.36 .

Composition (x)	Latent heat of crystal structure transformation (kJ/kg)	
	during heating	during cooling
0.32	17.56	17.83
0.33	17.13	18.14
0.34	18.49	19.62
0.35	16.27	10.56
0.36	13.68	9.9

4.2.1.4 High temperature X-ray diffraction

To analyze the temperature dependent structural transformation, the XRD analysis for a single alloy composition ($x = 0.32$) having T_i of 367 K was selected. The high temperature XRD was performed at temperatures ranging from 313 K to 393 K, acquiring XRD data at regular intervals of 20 K (**Fig. 4.6**). The XRD plots upto 353 K showed peaks

corresponding to the orthorhombic structure, the peaks corresponding to the hexagonal structure were observed at 373 K and 393 K. This confirmed the orthorhombic to hexagonal structural transformation occurring in (MnNiSi)_{0.68}(Fe₂Ge)_{0.32} at the T_i .

Fig. 4.6 High temperature XRD plots for with temperatures ranging from 313 K to 393 K for (MnNiSi)_{0.68}(Fe₂Ge)_{0.32}. Peaks corresponding to hexagonal (h) and orthorhombic (o) are indexed.

4.2.1.5 Selected area electron diffraction by TEM

Selected area electron diffraction (SAED) patterns of the single crystal (MnNiSi)_{1-x}(Fe₂Ge)_x samples with $x = 0.32$ and 0.36 were collected using TEM (in **Fig. 4.7**). SAED patterns indexed using JEMS software indicated that the diffraction pattern for $x = 0.32$ sample corresponded to the orthorhombic structure, whereas $x = 0.36$ sample corresponded to the hexagonal structure, revealing the change in crystal structure due to changes in the Fe₂Ge content added to MnNiSi.

Fig. 4.7 Bright field image and selected area diffraction (SAED) pattern of (MnNiSi)_{1-x}(Fe₂Ge)_x with $x = 0.32$ and 0.36 . The diffraction pattern of $x = 0.32$ corresponds to an orthorhombic structure whereas $x = 0.36$ corresponds to a hexagonal structure.

4.2.2 Magnetic measurements

Temperature dependent magnetization measurements were carried out for (MnNiSi)_{1-x}(Fe₂Ge)_x samples and the plots were used to determine the Curie temperature (**Fig. 4.8**). The measurements revealed a sharp transition from a high temperature, paramagnetic (PM) state to a low temperature, ferromagnetic (FM) state. The coupling of the magnetic transition and the crystal structure transition results in a steep change (0 emu/g to 25 emu/g at 0.1 T) in the magnetization states with decreasing temperature. The M vs H measurement upto 5 T for $x = 0.34$ reveals the soft magnetic character of the alloys and the saturation magnetization of 155 emu/g at 250 K. The T_C obtained from the highest slope of M vs T plots are shown in **Table 4.4**. A temperature hysteresis of ~ 15 K was determined by the difference between T_C during heating and cooling.

Fig. 4.8 (a) M vs T plots for $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ for compositions $x = 0.32, 0.33, 0.34, 0.35$ and 0.36 measured at a magnetic field of 0.1 T (b) M vs H curves for $x = 0.34$ with temperatures ranging from 250 K to 310 K for a field change of $0 - 5$ T.

Table 4.4. Latent heat of transformation during the heating and cooling of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ for values of $x = 0.32$ to 0.36 .

Composition (x)	Curie temperature (K)		Hysteresis (K)
	during heating	during cooling	
0.32	200	218	18
0.33	238	259	21
0.34	276	301	25
0.35	315	331	16
0.36	350	363	13

4.2.3 Analysis of magnetocaloric properties

The magnetic entropy values were evaluated using the Maxwell's relation in simplified form as shown in eq (2.17). Since the Curie temperatures for the orthorhombic and hexagonal phases for the MnNiSi alloy were reported to be $T_c^{\text{orth}} = 480$ K and $T_c^{\text{hexa}} = 200$ K, respectively [16], the T_C values of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ in the present analysis were within the temperature range to ensure magnetostructural coupling. Hence, the magnetostructural transition results in a higher entropy values for the compositions from $x = 0.32$ to 0.36 .

The entropy change for a field change of 2 T and 5 T were plotted against the temperature for each composition (**Fig. 4.9**). Maximum ΔS_M values of 47.3, 54.1, 57.6, 55.2 and 53.5 J K⁻¹K⁻¹ for $x = 0.32, 0.33, 0.34, 0.35$ and 0.36 , respectively were obtained for a field change of 5 T.

Fig. 4.9 ΔS_M vs T plots for (MnNiSi)_{1-x}(Fe₂Ge)_x with $x = 0.32$ to 0.36 measured at a magnetic field change of 2 T and 5 T.

The earlier reported ΔS_{max} value by Zhang et al. [16] for samples synthesized by arc melting, heat treatment and subsequent quenching were 36.9 Jkg⁻¹K⁻¹ ($\Delta H = 5$ T) for $x = 0.35$ composition. In the present work, arc melting and the addition of Fe₂Ge to MnNiSi stabilizes the hexagonal phase without subsequent heat treatment. The Fe atoms partially substitute the Mn and Ni atoms, whereas Ge partially substitutes the Si sites, according to the site preference rule resulting in a variation of Mn-Mn distance. Since the magnetic properties are sensitive to the distance between neighboring Mn atoms, tuning the Mn-Mn interatomic distance by alloying the MnNiSi with Fe and Ge varies the exchange interactions between adjacent Mn atoms [24].

The area under the ΔS_M vs T curve given by the product of the peak and full width at half maximum was evaluated to determine the RCP of alloys. The RCP values for (MnNiSi)_{1-x}(Fe₂Ge)_x samples were 376 Jkg⁻¹, 332 Jkg⁻¹, 342 Jkg⁻¹, 480 Jkg⁻¹ and 312 Jkg⁻¹ for $x = 0.32, 0.33, 0.34, 0.35$ and 0.36 , respectively.

0.33, 0.34, 0.35 and 0.36, respectively for a field change of 0-5 T. These values are substantially higher than the corresponding values for Mn_{1-x}Cr_xNiGe (236 Jkg⁻¹), melt-spun MnCoGe ribbons (218 Jkg⁻¹), Mn_{0.9}Co_{0.1}NiGe (159 Jkg⁻¹) and Mn_{0.64}Fe_{0.36}NiSi_{0.8}Ge_{0.2} (200 Jkg⁻¹) for a field change of 0-5 T [24-27]

4.2.4 Mechanism of magnetostructural transformation

In the MnM'X type of half Heusler alloys, the high temperature hexagonal and the low temperature orthorhombic structures possess covalent bonds between the adjacent Mn atoms and between M' and X atoms [28]. The stability of the crystal structure is dependent on the strength of these covalent bonds. The bond strength plays a key role in determining the dominance of among various structures. The structure possessing higher strength of covalent bonds dominates over the structure possessing lower covalent bond energies between the atoms [29]. Therefore, the analysis bond strengths in MnNiSi based alloys can provide insights for understanding the temperature dependent structural transformation. The sharpness of the magnetostructural transition and magnetization will depend on the relative amounts of the structural variants as observed in NiMnGa [30]. However, in the present scenario, the equiatomic MnNiSi composition resulted in orthorhombic and hexagonal variants. Due to the lower electronegativity difference between atoms, MnNiSi alloy consists of covalent Mn-Mn and Ni-Si bonds [13]. Since the electronegativity values of Ni ($\chi = 1.91$) and Si ($\chi = 1.9$) are identical, the Ni-Si covalent bond is preferred compared to either the Mn-Si or the Mn-Ni covalent bonds, due to the lower electronegativity of Mn ($\chi = 1.55$) than both Si and Ni.

The addition of alloying elements to the parent alloy varies the covalent bond strength. In the case of parent alloy MnNiSi, the T_t is ~1200 K [31], which decreases to 470 K for MnNiGe [32] due to the Ni-Ge covalent bonds in MnNiGe having a lower bond energy of 290.3 ± 10.9 kJ/mol compared to the value 318 ± 17 kJ/mol for Ni-Si covalent bonds in MnNiSi [33]. This suggests that T_t is a function of the bond energy between the atoms in the lattice. A similar trend has been previously reported in Co, Fe addition to MnNiSi in Mn_{1-x}(Co,Fe)_xNiSi alloys [13], addition of Fe to MnNiGe [34] replacing 3d element such

as Fe to MnCoGe in Mn_{1-x}Fe_xCoGe alloys [35] and substitutional addition of Al to MnNiGe [36].

Fig. 4.10 Schematic of the occupancy of atoms in the orthorhombic lattice (top) (upward vector: [100]; projection vector: [00-1]) and hexagonal lattice (bottom) (upward vector: [001]; projection vector: [0-10]).

In the case of addition of Fe₂Ge to MnNiSi, Ge atoms occupy Si sites resulting in Ni-Ge bond formation since the Ni-Si (318 ± 17 kJ/mol) bond has a higher energy than the Ni-Ge bond (290.3 ± 10.9 kJ/mol) [33]. As more of Ge is added to MnNiSi, the structural transition can be attained at lower transition temperature. Fe atoms occupying the Mn sites decrease the *c* axis of the hexagonal lattice due to smaller size of Fe atoms (atomic radius = 156 pm) than Mn atoms (atomic radius = 161 pm). This reduction in the *c* axis distance results in a change in the Mn-Mn distance, which stabilizes the hexagonal structure [37]. The Fe atoms occupying Ni sites replace the Ni-Si covalent networks resulting in small magnetic moments, whereas Mn/Fe carry the main magnetic moment [13]. As temperature increases, vibrational amplitude of the atoms increases due to the thermal energy. A higher

structural entropy change causes atoms to have greater amplitude of vibration from their equilibrium positions driving the structural transition [38].

A schematic of the occupancy of atoms in the orthorhombic and hexagonal structures for Fe_2Ge substituted MnNiSi is shown in **Fig. 4.10**. The martensitic transformation of the orthorhombic lattice results in a hexagonal lattice when the temperature reaches T_t .

4.2.5 Theoretical modeling of magnetostructural transition

4.2.5.1 Arrott plots

Arrott plots were used to determine the nature and order of the magnetic transition. Arrott plots represent the variation of square of the magnetization (M^2) with respect to $\mu_0 H/M$.

The Arrott plots for $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ with $x = 0.32$ to 0.36 at low magnetic fields were plotted. The magnetization values were derived from the values obtained from M vs H measurements (**Fig. 4.11**).

According to the Banerjee criterion [39], a negative slope in the Arrott plots indicates a first order magnetic transition. The negative slopes were observed within an initial range of M^2 in the Arrott plots for all the compositions.

Fig. 4.11 Arrott plots (M^2 vs $\mu_0 H/M$) for (MnNiSi)_{1-x}(Fe₂Ge)_x with $x = 0.32$ to 0.36 at low magnetic fields. The negative slopes near the magnetostructural transition temperature indicate the first order transition according to the Banerjee criterion.

4.2.5.2 Landau theory of phase transition

The characteristic temperatures T_C and T_0 were identified from the plots and the Landau criteria was used to determine the order of phase transition. According to the criteria, the condition for first order transition must satisfy $T_0 > T_C$ and $A_3 > 0$. Both the conditions for first order phase transition were satisfied in alloys with $x = 0.32$ to 0.35 . However, for the $x = 0.36$ alloy, it was observed that $T_0 = T_C$ and $A_3 < 0$ at all temperatures (**Table 4.5**) indicating a gradual reduction in the magnetostructural coupling closer to the boundary of the Curie temperature window (CTW) ($T_C^{\text{hexa}} \sim 200\text{K}$) [16] below which the coupling between structural and magnetic transition ceases.

The Landau coefficients A_1 , A_2 and A_3 were plotted against temperature (**Fig. 4.12**) using the experimental M vs H values and eq (2.21).

Table 4.5. Characteristic temperatures T_C and T_0 and the maximum value of coefficient A_3 obtained by Landau theory for (MnNiSi)_{1-x}(Fe₂Ge)_x ($x = 0.32$ to 0.36).

Composition	T_C (K)	T_0 (K)	$(A_3)_{\text{max}}$
0.32	355	360	157.58
0.33	305	315	0.254
0.34	290	300	0.523
0.35	250	255	0.223
0.36	215	215	-0.018

Fig. 4.12 Landau coefficients A_1 , A_2 and A_3 for the alloys $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ ($x = 0.32$ to 0.36) at the vicinity of transition temperatures.

4.2.5.3 Bean-Rodbell model

The values of apparent Curie constant (C^*) and Curie temperature (T_0) shown in **Table 4.6** were evaluated by substituting the experimental values of $1/\chi$ at various temperatures in eq. (2.25). The magnetization measurements performed at 5 T yielded a saturation magnetization (σ_s) of $3.014\mu_B/\text{f.u.}$ for (MnNiSi)_{1-x}(Fe₂Ge)_x alloys. Setting the value of Lande factor (g) to the theoretical value of 2 and assuming that the number of atoms per fractional unit (N) is 2, the value of the total ion angular momentum (J) was calculated as 3/2. Using the modeling parameters and the values of $\alpha\beta T_0$, eq.(2.26) can be expressed as

$$T = \frac{1.8\sigma T_0 + 0.734\eta\sigma^3 T_0 + \left(\frac{H\sigma_s}{Nk}\right)}{1.8\sigma + 0.734\sigma^3 + 0.6\sigma^5 - 2\alpha\beta T_0\sigma} \quad (4.1)$$

Table 4.6. Values of C^* and T_0^* obtained from T_0 , $\alpha\beta T_0$ and $1/\chi$ vs T curves. Phase transition parameter (η) was evaluated by the Bean Rodbell model for (MnNiSi)_{1-x}(Fe₂Ge)_x alloys

Composition	Apparent Curie constant, C^* [TKg(Am ² K) ⁻¹] $\times 10^{-2}$	Apparent T_0^* (K)	T_0 (K)	$\alpha\beta T_0$	Phase transition parameter, η
0.32	1.25	320	319	0.0015	1.35
0.33	1.21	293	274	0.066	1.25
0.34	1.19	287	263	0.083	1.37
0.35	0.57	233	226	0.030	1.35
0.36	0.44	204	192	0.057	1.28

Fig. 4.13 Temperature dependent relative magnetization plots at 1 T external magnetic field for $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ alloys (curve with symbols) compared with the results obtained from the Bean-Rodbell model for a range of η values.

The order parameter (η) was evaluated by fitting eq (4.1) to the temperature dependent saturation magnetization plots (T vs σ_s) for $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ with $x = 0.32$ to 0.36 (Fig. 4.13). The values of other resulting parameters shown in Table 4.6 were obtained using the

Bean Rodbell model. The value of η was greater than 1 for all the compositions from $x = 0.32$ to 0.36 , indicating a first order transition consistent with the experimental results.

The entropy change (ΔS_M) for the magnetostructural transition was modeled by utilizing the values of η obtained from the best fit in M vs T plots. By inserting the values of η in eq.(2.30), the ΔS_M for (MnNiSi)_{1-x}(Fe₂Ge)_x ($x = 0.32$ to 0.36) was plotted in the vicinity of the T_t . The experimental and the theoretical values of the ΔS vs T plots (**Fig. 4.14**) had a reasonable match. The experimental results were in good agreement with the modeling predictions in the present studies of the magnetostructural transition in (MnNiSi)_{1-x}(Fe₂Ge)_x ($x = 0.32$ to 0.36) alloys.

Fig. 4.14 Comparison between ΔS_M vs T ($\Delta H = 0$ to 5 T) determined experimentally (dotted lines denoted by E) and by the Bean-Rodbell model (solid lines denoted by M) for (MnNiSi)_{1-x}(Fe₂Ge)_x ($x = 0.32$ to 0.36).

4.3 Principal outcomes

- Synthesized rare-earth free, environmentally friendly and high performance (MnNiSi)_{1-x}(Fe₂Ge)_x magnetocaloric alloys by arc melting without subsequent heat treatment.

- Magnetostructural coupling was tuned near room temperature range by changing the Fe₂Ge content in (MnNiSi)_{1-x}(Fe₂Ge)_x. The crystal structure transition from high temperature, hexagonal structure to low temperature, orthorhombic structure was observed. The transition temperature decreased from 363 K to 218 K by changing x from 0.32 to 0.36.
- (MnNiSi)_{0.66}(Fe₂Ge)_{0.34} exhibited $T_C = 301$ K with a $\Delta S_{\max} = 57.6 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\Delta H = 5$ T, higher than the previously reported value. (MnNiSi)_{1-x}(Fe₂Ge)_x show a much higher $\Delta S_{\max}$ values than other MnNiSi based alloys.
- The first order phase transition was modeled by Arrott plots, Landau theory and the Bean-Rodbell model. The T_C and the ΔS_M values derived from the Bean-Rodbell model were in good agreement with experimental findings.
- **Fig. 4.15** shows the summary of the transition temperatures and the MCE parameters for (MnNiSi)_{1-x}(Fe₂Ge)_x (x = 0.32 to 0.36)

Fig. 4.15 $\Delta S_{\max}$ and RCP for compositions from $x = 0.32$ to 0.36 . Variation of magnetostructural transition temperature during heating and cooling with change in alloy composition x in (MnNiSi)_{1-x}(Fe₂Ge)_x

4.4 Conclusion

Magnetocaloric measurements and structural characterization were carried out on arc melted (MnNiSi)_{1-x}(Fe₂Ge)_x alloys ($x = 0.32$ to 0.36), without subsequent heat treatment steps. Addition of Fe₂Ge to MnNiSi resulted in decrease of transition temperature and coupling of magnetic and structural transition enhancing the magnetocaloric properties. A sharp paramagnetic to ferromagnetic transition near room temperature (286 K during cooling and 301 K during heating) was observed for $x = 0.34$, with $\Delta S_{\max} = 57 \text{ J kg}^{-1} \text{ K}^{-1}$ for a field change of 5 T. The structural transition was characterized using XRD, DSC and TEM, whereas the magnetic measurements were performed using PPMS with VSM attachment. The wide CTW with a giant magnetostructural coupling near room temperature are useful for various applications. The ease of tunability of T_t from 365 K to 200 K by changing single variant x from 0.32 to 0.36 gives it an added advantage over other MnNiSi alloys. (MnNiSi)_{0.65}(Fe₂Ge)_{0.35} alloys exhibited an RCP of $\sim 480 \text{ J kg}^{-1}$ displaying higher performance compared to other MCMs. Theoretical models such as Arrott plots, Landau theory and the Bean-Rodbell model were used to model the phase transition in these alloys, There was a good agreement between the experimental and theoretical models for the magnetostructural transition in these alloys.

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Chapter 5

(Mn, Fe)Ni(Si_{1-y}Sn_y) Magnetocaloric alloys *

This chapter describes the synthesis, characterization and magnetocaloric properties of (Mn, Fe)Ni(Si_{1-y}Sn_y) alloys. The Mn:Fe ratio was fixed at 45:55 based on previous studies. The replacement of Ge by Sn makes it a better alternative for low cost applications. The substitution of Sn in the place of Si reduced the T_C from 343 K (for $y = 0.12$) to 248 K (for $y = 0.18$). The coupling of magnetic and structural transition was observed for alloys from $y = 0.12$ to 0.16. The magnetostructural transformation was observed near room temperature for $y = 0.14$, with a maximum entropy change (ΔS_{max}) of $8.64 \text{ J kg}^{-1} \text{ K}^{-1}$ for a field change of 5 T. Cost analysis revealed that the $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ alloys are the most inexpensive (88¢/10 g) compared to other MnNiSi based alloys. Hence, $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ alloys are promising candidates for low cost, near room temperature, magnetocaloric applications.

*This chapter is substantially published as: **K Deepak**, R V Ramanujan, "Magnetocaloric Properties of low-cost Fe and Sn substituted MnNiSi-based alloys exhibiting a magnetostructural transition near room temperature", *IEEE Transactions on Magnetics* 54 (11), 2500805 (1-5) (2018)

5.1 Introduction

Magnetic cooling technology has attracted lot of attention in recent years due to its advantage over conventional cooling methods. The magnetic cooling utilizes magnetocaloric material (MCM) having a Curie temperature (T_C) tuned to the device operating temperature. The MCM must possess high ΔS_M , non-toxic elements and easy availability [1]. The cost of raw materials plays a key role in the cost effectiveness of the magnetic cooling device. Gd was first used for magnetic cooling due to its room temperature T_C [2]. However, due to non-tunability of T_C and high cost, various other rare-earth free MCMs based on Fe, Ni and Mn were discovered [3,4].

Materials exhibiting first order magnetic transition are of high interest owing to their high ΔS_M and RCP for a particular temperature range. The family MnXX' (X = Ni, Co and X' = Si, Ge) based alloys such as MnCoGe, MnNiGe and MnNiSi exhibit both magnetic and structural transition [5,6]. The added advantage is the tunability of the transition temperature by alloying addition. The isostructural alloying additions to MnXX' result in a high ΔS_M values due to the magnetostructural coupling. Especially, MnNiSi is preferred due to the absence of Ge, which can reduce the cost of synthesis by upto 15 times. MnNiSi exhibits a magnetic transition from a ferromagnetic (FM) state to a paramagnetic (PM) state at 622 K [7] and a structural transition between a low-temperature orthorhombic (TiNiSi-type structure, space group Pnma) and a high temperature hexagonal phase (Ni₂In-type structure, space group P63/mmc) at 1200 K [8]. The high structural and transition temperature are impractical for room temperature applications. However, by substitutional alloying, the T_C of MnNiSi can be decreased substantially. Addition of Co or Fe to MnNiSi can bring down the T_C below 500 K. It has also been shown that Fe addition reduces the T_C more rapidly than Co addition. The T_C of 438 K was reported in single element substitution having a composition Mn_{0.45}Fe_{0.55}NiSi [9]. Nevertheless, the T_C achieved by single element substitution was much higher than room temperature. Hence, double element substitution has been explored to tune the T_C to near room temperature range. The MnNiSi based alloy systems such as MnNiSi-Fe₂Ge [10], MnNiSi-CoNiGe [11], MnNiSi-MnFeGe [12], (MnNiSi)_{1-x}(Fe₂Ga)_x [13], MnNiSi-FeCoGe [14], (Mn,Fe)Ni(Si,Ga) [15], (MnNiSi)_{1-x}(Co₂Ge)_x [16] and MnNiSi-FeNiGe [17] having double element substitution

have been reported to exhibit a tunable T_C near room temperature. Although these alloys do not contain rare-earth elements, but the presence of Ge increases the cost of synthesis.

In this chapter, MCE properties of low cost Ge-free (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) alloys are reported. The cost analysis was carried out to establish the cost effectiveness of the alloy. The alloys were characterized by SEM, DSC and PPMS. Training effect of magnetization was observed during the first 3 temperature cycles. The magnetic measurements taken after the stabilization yielded a ΔS_M of 8.64 Jkg⁻¹K⁻¹ for a field change of 5 T. The subsequent sections describe the synthesis, characterization, the training effect and the cost analysis of (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) alloys.

5.2 Results and discussion

5.2.1 Structural analysis

5.2.1.1 X-ray diffraction analysis

The XRD patterns obtained at room temperature for (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) ($y = 0.12$ and 0.18) are shown in **Fig 5.1a**. The peaks show a mixture of orthorhombic and hexagonal phases in all the compositions. For a lower concentration of Sn ($y = 0.12$ and 0.14), the peaks corresponding to the orthorhombic structure dominate, whereas for higher Sn concentration ($y = 0.16$ and 0.18), the peaks corresponding to the hexagonal structure show higher intensity. Hence, the variation in the crystal structure can be achieved by changing the amount of Sn in (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y). **Fig 5.1b** shows XRD patterns at high temperature, ranging from 303 K to 423 K taken at intervals of 30 K for the composition $y = 0.12$ alloy. The indexed pattern reveals the hexagonal peaks predominated at higher temperatures (393 K and 423 K). Whereas, orthorhombic peaks were observed at 363 K, 333 K and 303 K, thus heating of the alloy beyond the transition temperature gives an orthorhombic to hexagonal crystal structure transition.

Fig 5.1 (a) XRD patterns of Mn_{0.45}Fe_{0.55}NiSi_{1-y}Sn_y with y = 0.12 to 0.18. The hexagonal peaks (h) and orthorhombic peaks (o) are indicated (b) High Temperature XRD for y = 0.12 sample from 303 K to 423 K, the pattern at higher temperatures showed hexagonal peaks and patterns at lower temperature consisted of orthorhombic peaks.

5.2.1.2 Differential scanning calorimetry

DSC analysis was performed for both heating and cooling cycles with a ramp rate of 10 K/min to determine the structural transition temperatures (**Fig 5.2**). Structural transition peaks at 325 K, 360 K and 382 K for the heating cycle and 260 K, 305 K and 330 K for the cooling cycle were observed for y = 0.16, 0.14, 0.12, respectively. The broad peak for y = 0.16 indicated a gradual structural transition with temperature variation. No peak was observed in the DSC analysis for y = 0.18, suggesting that the first order transformation ceases when the Sn content is below y = 0.16. Thus, substitution of Si by Sn reduces the transformation temperature of (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) alloy.

Fig 5.2 DSC plots with a ramp rate of 10 K/min for Mn_{0.45}Fe_{0.55}NiSi_{1-y}Sn_y ($y = 0.12, 0.14$ and 0.16) showing the heating and cooling cycles.

5.2.2 Magnetic measurements

The temperature dependent magnetization measurements were performed at a constant applied field of 0.1 T for $y = 0.12, 0.14, 0.16$ and 0.18 compositions (**Fig 5.3**). The M vs T plots were repeated for 4 cycles of temperature due to the training effect observed in the first three cycles. A ferromagnetic (FM) to paramagnetic (PM) transition was observed in all the alloy compositions with significant temperature hysteresis. The increase in Sn content from 0.12 to 0.18 weakens the first order transition, resulting in a shift of T_c to lower temperature. The T_c of the alloys during heating and cooling cycles are shown in **Table 5.1**.

The magnetic moment of (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) alloys were measured to obtain M vs H plots at each temperature interval for temperatures in the vicinity of the magnetostructural transition. The M vs H plot for Mn_{0.45}Fe_{0.55}NiSi_{0.88}Sn_{0.12} is shown in (**Fig 5.3b**) during cooling from 355 K to 310 K for every 5 K interval. A significant variation of magnetization was observed during increasing and decreasing field near the transition temperature, arising due to the lattice constraint which prevents the magnetic moments from flipping back when the field is reduced.

Fig 5.3 (a) M vs T plots for (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) (y = 0.12 to 0.18) measured at a constant field of 0.1 T (b) M vs H plots (0 to 5 T) measured at 5 K intervals for y = 0.12 for temperatures ranging from 310 K to 355 K.

Table 5.1 Curie temperatures during heating and cooling obtained from M vs T plots for (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) (y = 0.12 to 0.18)

Composition (y)	T _c Heating (K)	T _c Cooling (K)	Hysteresis (K)
0.12	355	343	12
0.14	332	312	20
0.16	301	263	38
0.18	275	248	27

5.2.1.1 Training effect

The M vs T measurement for the arc melted samples showed variation in T_c during the initial heating and cooling cycles. There was negligible variation in T_c after the third cycle.

Fig 5.4 shows the M vs T plots for the first three heating and cooling cycles for (Mn_{0.45}Fe_{0.55})Ni(Si_{0.86}Sn_{0.14}). The similar training effect was observed previously in (Mn,Fe)₂(P,Ge) [18,19], MnAs based alloys [20], MnCoGe [21], (Mn,Fe)₂(P,Si,Ge) [22] and Mn_{0.53}Fe_{0.47}NiSi_{0.53}Ge_{0.47} [23] alloys. The training effect occurs due to the presence of a metastable state that is preserved in the as-prepared sample resulting in an irreversible structural transformation when the alloy is cooled/heated during temperature cycling. This metastable phase gradually transforms to the low and high temperature phase upon

repeated heating and cooling cycles, respectively. A similar phenomenon was observed in the present study due to the bulky Sn atoms forced into the MnNiSi lattice, increasing the energy barrier for transformation between the high temperature hexagonal structure and the low temperature orthorhombic structure during the first three cooling cycles. After three such heating/cooling cycles, the Sn atoms are suitably positioned in the lattice and the T_C stabilizes during subsequent heating and cooling cycles.

Fig 5.4 M vs T plot of the first three heating and cooling cycles showing the training effect in (Mn_{0.45}Fe_{0.55})Ni(Si_{0.86}Sn_{0.14}) alloy.

5.2.3 Mechanism of transformation

In MM'X alloys, the nature and strength of the local the chemical bonds between atoms determine the magnetic and the structural properties [24]. Particularly, the strength of the covalent bonds formed between M' and X atoms determine the stability of the structure [25]. A stable structure corresponds to higher strength of covalent bonds between the atoms and can exist prominently compared to other structural counterparts. In MnNiSi alloys, Ni

and Si have identical bond energies(χ) of 1.9 whereas Mn has lower χ of 1.55, hence Ni-Si bonds are preferred due to higher covalency compared to Mn-Ni or Mn-Si bonds [26]. By substitution of other alloying elements in the place of Mn and Si creates new bonds between the alloying element and the parent alloy. This trend has been previously observed in the case of replacement of Si by Ge in MnNiSi ($T_t = 1200\text{K}$) to obtain MnNiGe ($T_t = 470\text{ K}$), substitutional addition of Al to MnNiGe [27], addition of Fe to MnNiGe [28], Mn_{1-x}Fe_xCoGe alloys [29] and Mn_{1-x}(Co,Fe)_xNiSi alloys [9].

In the case of (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y), Fe and Sn were added MnNiSi parent alloy. Fe atoms occupy Mn and Ni sites, whereas Sn atoms occupy Si sites according to the site preference rule. The Ni-Sn bonds possess lower bond energy (180.4 kJ/mol) compared to Ni-Si bonds ($318 \pm 17\text{ kJ/mol}$) resulting in lowering of structural transition temperature by increasing the Sn content [26]. The Fe atoms occupying the Mn sites decrease the length of the c axis in the orthorhombic lattice due to the difference in the atomic radius of Fe (156 pm) and Mn (161 pm), resulting in a change in Mn-Mn interatomic spacing, stabilizing the hexagonal structure [11] at lower temperature than the parent alloy. The increase in vibrational amplitude of the atoms w.r.t temperature creates a driving force for the structural transformation [30]. At T_t , the vibrational entropy increases beyond the stability of the orthorhombic structure resulting in rearrangement of atoms to form the hexagonal structure. Due to the arrangement of atoms with higher vibrational entropy, the ferromagnetic state is transformed to the paramagnetic state as the temperature increases beyond T_t .

5.2.4 Analysis of magnetocaloric properties

The temperature dependent ΔS_M was determined for (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) using the Maxwell's equation given by eq. (2.17). The ΔS_M vs T for a field change of 2 T and 5 T are shown in **Fig 5.5**, the values of magnetocaloric parameters $\Delta S_{\max}$ and RCP are shown in **Table 5.2**.

Fig 5.5 ΔS_M vs T plots for $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ ($y = 0.12, 0.14, 0.16$ and 0.18) for field change of 2 T and 5 T.

Table 5.2 Values of $\Delta S_{\max}$ and RCP for a field change of 5 T and 2 T and transition temperature for 5 T field change obtained from ΔS_M vs T plots.

y	$\Delta S_M (\text{Jkg}^{-1}\text{K}^{-1})$ $\Delta H=2\text{T}$	$\Delta S_M (\text{Jkg}^{-1}\text{K}^{-1})$	Peak T for $\Delta H=5\text{T}$	RCP(Jkg^{-1}) $\Delta H = 5\text{T}$
0.12	2.96	7.36	335	116
0.14	3.28	8.64	317.5	79
0.16	1.24	3.00	262.5	133
0.18	0.59	1.35	155	156

The values of $\Delta S_{\max}$ are comparable with those other magnetocaloric alloys e.g., $\text{Mn}_{0.4}\text{Fe}_{0.6}\text{NiSi}_{0.94}\text{Ga}_{0.06}$ ($7.7 \text{ Jkg}^{-1}\text{K}^{-1}$) [15], $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ ($5.15 \text{ Jkg}^{-1}\text{K}^{-1}$) [31], $\text{LaFe}_{10.6}\text{Si}_{2.4}$ ($5.85 \text{ Jkg}^{-1}\text{K}^{-1}$) [32], $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ ($9.4 \text{ Jkg}^{-1}\text{K}^{-1}$) [33], $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.7}\text{Ge}_{0.3}$ ($5 \text{ Jkg}^{-1}\text{K}^{-1}$) [34] and are much higher than some of the Fe based second order MCMs such as $(\text{Fe}_{70}\text{Ni}_{30})_{99}\text{Cr}_1$ ($1.58 \text{ Jkg}^{-1}\text{K}^{-1}$) [35], $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ ($1.16 \text{ Jkg}^{-1}\text{K}^{-1}$) [36] and $\text{Fe}_x\text{Cu}_{100-x}$ ($1.04 \text{ Jkg}^{-1}\text{K}^{-1}$) [37]. Although the entropy values are lower than some MnNiSi giant magnetocaloric alloys, the cost of synthesis of $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ is much lower since Sn is much cheaper than Ge, Ga or other rare earth elements.

The RCP values for (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) obtained by the product method (eq.(3.6)) were 116 Jkg⁻¹, 79 Jkg⁻¹, 133 Jkg⁻¹, 156 Jkg⁻¹ for y = 0.12, 0.14, 0.16 and 0.18, respectively. The RCP values are comparable to other MnNiSi based alloys e.g., Mn_{0.4}Fe_{0.6}NiSi_{0.96}Ga_{0.04} (136 Jkg⁻¹) [15] and (MnNiSi)_{0.62}(CoNiGe)_{0.38} (169 Jkg⁻¹) [11].

5.2.5 Cost of raw materials used for synthesis

Cost effectiveness is one of the crucial factors for selection of MCM for any practical application. The rare-earth based alloys consist of Gd, La and other rare-earth elements which significantly increase the cost of synthesis. **Table 5.3** shows the cost of pure elements [38], Gd and La have relatively higher price/kg than other elements. The MnNiSi based alloy system utilizes most inexpensive elements for synthesis, making it one of the most cost effective for practical applications.

A comparison of cost of raw materials for 10 g of MnNiSi based alloys are shown in **Table 5.4**. Since Ge and Ga are 10-15 times much expensive than Sn, the cost of synthesis is higher in the alloys containing these elements. Although alloys containing single element substitution have lower cost, they do not exhibit a magnetostructural coupling near room temperature. The alloys (MnNiSi)_{1-x}(FeNiGe)_x, and (MnNiSi)_{1-x}(MnFeGe)_x and costs up to 7.68 and 9.38 \$/10g, respectively. This makes commercializing of these MCM difficult for low cost applications. Therefore, the Fe and Sn substitution having a cost of 88¢/10 g of alloy was found to be the most cost effective among all the other MnNiSi based alloys exhibiting magnetostructural transition near room temperature.

Table 5.3 The cost of pure elements used as raw materials for synthesis of MCM in USD per kg [38]

Metal	Price (USD/Kg) Pure element
Aluminum	157.2
Cobalt	210
Gadolinium	4500

Gallium	2200
Germanium	3600
Iron	72
Lanthanum	8000
Manganese	65
Nickel	77
Tin	240
Silicon	54

Table 5.4 Cost of raw materials for preparation of 10 g of MnNiSi based MCMs calculated according to the ratios of elements in each alloy

Alloy	x	y	Cost for 10g alloy (USD)
Mn _{1-x} NiSi _{1-y} Fe _x Sn _y	0.55	0.14	0.88
Mn _{1-x} NiSiCo _x	0.4	--	0.92
Mn _{1-x} NiSiFe _x	0.55	--	0.69
Mn _{0.36} Fe _{0.6} Ni _{0.98} Si	0.6	--	0.70
(MnNiSi) _{1-x} (FeNiGe) _x	0.44	--	7.68
Mn _{0.4} NiSi _{1-x} Fe _{0.6} Ga _x	0.06	0.6	1.32
Mn _{1-x} NiSi _{1-y} Co _x Ge _y	0.2	0.25	5.15
(MnNiSi) _{1-x} (Fe ₂ Ge) _x	0.35	--	6.42
(MnNiSi) _{1-x} (FeCoGe) _x	0.39	--	7.16
(MnNiSi) _{1-x} (MnFeGe) _x	0.54	--	9.38

5.3 Principal outcomes

- Synthesized low cost, Ge-free (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) alloy exhibiting magnetostructural transition near room temperature for y = 0.12 to 0.16.

- The transition temperature was tuned from 355 K to 275 K during heating and 343 K to 248 K during cooling by changing y from 0.12 to 0.18. The crystal structure transition from the high temperature hexagonal to the low temperature orthorhombic accompanied the magnetic transition from the paramagnetic state to the ferromagnetic state, respectively.
- The ΔS_{Max} of 8.64 Jkg⁻¹K⁻¹ was observed for $y = 0.14$ for a field change of 5 T at 317.5 K. The highest RCP of 156 Jkg⁻¹ was recorded for $y = 0.18$. The training effect was prevalent during the first 3 cycles due to the substitution of bulky Sn atom in the place of Si, hindering the transition.
- The cost of raw materials used for synthesis was compared for various MnNiSi alloys. The alloy with Fe and Sn substitution, i.e., (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) stands out to be the most economical (88¢/10 g alloy) among other alloys exhibiting magnetostructural transition near room temperature.
- **Fig 5.6** shows the summary of the transition temperatures and the MCE parameters for (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) ($y = 0.12$ to 0.18)

Fig 5.6 Summary of the MCE properties and the transition temperature for (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) with compositions varying from $y = 0.12$ to 0.18

5.4 Conclusion

The magnetocaloric effect of low cost Fe and Sn substituted MnNiSi alloys was studied for the first time. (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) ($y = 0.12, 0.14$ and 0.16 alloys) exhibited a first order magnetostructural phase transition. Increasing the Sn content decreased the T_C from 343 K (for $y = 0.12$) to 248 K (for $y = 0.18$). A wide Curie temperature window was obtained near room temperature for a range of Sn composition. A magnetostructural transition displayed a $\Delta S_{\max}$ of $8.64 \text{ J Kg}^{-1} \text{ K}^{-1}$ at 317.5 K for $y = 0.14$ and an RCP of 156 J Kg^{-1} for $y = 0.18$. The cost analysis revealed that the Ge-free alloy, (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) is the most economical among MnNiSi alloys. These rare-earth free, low cost alloys exhibiting relatively good magnetocaloric properties are promising for near room temperature MCE applications.

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Chapter 6

Development of a Thermomagnetic Oscillator for Cooling and Electricity Harvesting *

A thermomagnetic oscillator prototype is described in this chapter. It utilizes the thermomagnetic response of the magnetocaloric material for simultaneous cooling and electricity harvesting. The principle of operation, performance and figure of merit of the thermomagnetic oscillator are described. The hybrid thermomagnetic oscillator having the thermomagnetic alloy coupled with a permanent magnet produced a voltage output of upto 10 V and a cooling of upto 70°C per cycle. $(\text{MnNiSi})_{0.68}(\text{Fe}_2\text{Ge})_{0.32}$, with the highest figure of merit of 4.2 Js^{-1} , was selected to show that the flexible spacer enhanced the frequency by 32% and the voltage/cycle by 18%. COMSOL simulations and force balance analysis was used to derive the figure of merit for optimization of material properties and device parameters for achieving maximum energy output.

*This chapter is substantially published as:

- 1) **K. Deepak**, V. B. Varma, G. Prasanna and R. V. Ramanujan, "Hybrid Thermomagnetic Oscillator for Cooling and Direct Waste Heat Conversion to Electricity", *Applied Energy* 233-234, 312-320 (2019)
- 2) **K. Deepak**, M. S. Pattanaik and R. V. Ramanujan, "Figure of merit and improved performance of a hybrid thermomagnetic oscillator", *Applied Energy* 256, 113917 (2019).

6.1 Introduction

Thermal energy is the most ubiquitous form of energy because the other forms of energy, e.g., electrical, magnetic, mechanical, metabolic, etc. eventually degrade to thermal energy. The energy consumption throughout the world, especially electrical energy consumption has been rising dramatically, to 2×10^4 TWh in 2016 [1]. The “waste” heat from the electrical equipments occurs in a wide range of applications. Between 20 to 50% of industrial energy consumption is discharged as waste heat [2]. Most automobiles discharge 55-80% energy as waste heat [3]. The i7 computer processors and data centers dissipate 140 W and 400 MW energy, respectively as waste heat [4]. Hence, the interest in waste heat harvesting technology is increasing. Particularly, generation of electricity from waste heat is a significant way of regeneration of energy [5]. Recent applications include electricity harvesting utilizing heat from human body [6] [7], electronic devices [8] and solar energy [9] [10]. Recovery and conversion of waste heat to electricity [11] has been performed by piezoelectric [12,13], thermoelectric [3,14-16], pyroelectric [17-19], thermoacoustic [20], triboelectric [21,22], and hybrid devices [23-27].

The challenge of increasing and unsustainable worldwide demand for energy can be mitigated by highly energy efficient cooling and energy harvesting devices [1]. Both active and passive devices can be used for electricity generation. Active devices rely on external energy input, e.g., to induce mechanical movement of the working material, producing electricity by electromagnetic induction or by the piezoelectric effect. The pyromagnetic generator proposed by Tesla [28] used heat from a furnace to produce steam for alternate heating and cooling of magnetic iron pipes. This resulting temperature change of the pipes produced a change in the magnetic flux of a suitable arranged circuit, resulting in electrical output. Edison [29] patented a different type of pyromagnetic generator. It consisted of rotating iron tubes, one half of the circumference of the tube was placed in a hot region, while the other half was placed in a cold region. Alternate cooling and heating of the tube caused a change in the magnetization, which generated current in suitably placed windings. Gd was used as the working material for an active magnetic heat pump developed by Brown [30]. Using external mechanical power, Gd was oscillated between a heat load and a heat sink. The resulting variation in the magnetization of the Gd during these oscillations

caused adiabatic demagnetization, giving rise to magnetocaloric cooling. Solomon [31] designed a thermomagnetic generator, using Gd as the working material. He subjected Gd alternately to a heat load and a heat sink, employing a cyclic magnetic field. The resulting change in the magnetic states of Gd generated current in a coil wound around the working material. Recently, a pretzel-like configuration was found to yield better performance due to sign reversal of the magnetic flux [32], drawbacks such as magnetic stray fields, hysteresis and complex geometry of the thermomagnetic material were also avoided in this pretzel design.

However, all these devices require a pump or mechanical input to move the working material cyclically between the heat sink and the heat load. On the other hand, passive devices have advantages such as ease of maintenance and no pumps are required. A thermomechanical actuator developed by Ujihara [33] used the oscillations of a Gd plate between a heat sink and a heat source. The plate was connected to a leaf spring which acts as a piezoelectric converter to generate electricity. Another system was developed using a similar principle to generate electricity, it uses flexible polyvinylidene difluoride (PVDF) instead of a leaf spring as the piezoelectric connector [24]. Gueltig et al. [34] [35] developed a thermomagnetic generator based on Heusler alloys. A Ni-Mn-Ga alloy film with a pickup coil was mounted on a Cu-Zn cantilever. Electrical output was obtained when alternate heating and cooling changed the magnetic flux in the coil due to a variation in the magnetization of the Ni-Mn-Ga film. The passive devices mentioned above use either a piezoelectric connector or a thin-film working material, resulting in lower output power. The thermomagnetic effect can be effectively utilized to harvest electricity from waste heat. Hence, a thermomagnetic oscillator (TMO) was developed to convert waste heat to electricity while simultaneously accomplishing cooling of the heat load. The hybrid thermomagnetic oscillator (HTMO) [36] is the only passive device which demonstrated both cooling and electricity harvesting.

6.2 Working principle

6.2.1 Single thermomagnetic oscillator

The single thermomagnetic oscillator (STMO) device (**Fig. 6.1**) contains a thermomagnetic alloy (TMA) in the form of a cylinder oscillating between a heat load (HL) and a heat sink (HS) due to its thermomagnetic response.

Fig. 6.1 Schematic diagram of the working of STMO. (a) The ferromagnetic TMA rises to heat load due to the upward magnetic pull force. (b) The TMA absorbs heat from the heat load and becomes paramagnetic. (c) The paramagnetic TMA loses attraction towards the magnet and falls to the heat sink due to gravity. (d) TMA releases the heat to the heat sink and becomes ferromagnetic.

The thermomagnetic effect is summarized in four stages illustrated in **Fig. 6.1**. (a) Initially, TMA temperature is below its Curie temperature (T_C). Due to the attraction of the TMA by the permanent magnet (PM1) placed above the HL, the TMA rapidly rises towards the HL. The movement of the ferromagnetic TMA under the influence of a magnet through the coil changes the magnetic flux inside the coil resulting in electricity generation. (b) The TMA absorbs heat from the HL, resulting in cooling of the HL and increase in the temperature of the TMA. Due to continuous supply of heat to the HL, subsequently, the temperature of the TMA reaches T_C . (c) The TMA becomes paramagnetic at T_C , loses the magnetic attraction towards PM1 and falls due to gravity, towards the heat sink. (d) The TMA cools down below T_C by transferring heat to the heat sink. When it is sufficiently cool, it becomes ferromagnetic and the magnetic force between the TMA and the PM1 is sufficiently large to lift the TMA, repeating the cycle. These oscillations result in cooling of the heat load and electricity generation.

The TMA oscillates between hot and cold regions alternatively. The temperature variation causes change in the magnetic state of the TMA. **Fig. 6.2** shows the M vs T plot of the $(\text{MnNiSi})_{0.7}(\text{Fe}_2\text{Ge})_{0.3}$ alloy measured at a constant magnetic field of 0.1 T. The T_{CH} and T_{CC} are the Curie temperatures during heating and cooling, the difference in T_{CH} and T_{CC} accounts for the thermal hysteresis of the TMA. The thermomagnetic cycle of the STMO starts when the TMA is at the heat sink (HS). The TMA at the HS is at room temperature, below its T_{CH} . Therefore, TMA exhibits ferromagnetic response and is lifted up to the heat load (HL) due to the magnetic force on the TMA due to PM1. At the HL, the heat is transferred from the HL to the TMA. The TMA heats up above T_{CH} , becomes paramagnetic and loses magnetic attraction to PM1. This paramagnetic TMA fall to the HS due to gravity and transfers the heat from the HL to the HS. When the temperature of the TMA is sufficiently below T_{CC} , the upwards magnetic force overcomes the gravitational force, the TMA gets pulled up by the magnet PM1 and the cycle repeats.

Fig. 6.2 M vs T plot of the $(\text{MnNiSi})_{0.7}(\text{Fe}_2\text{Ge})_{0.3}$ alloy measured at a constant magnetic field of 0.1 T, T_{CH} and T_{CC} represent the Curie temperature during heating and cooling.

6.2.2 Hybrid thermomagnetic oscillator

The HTMO was constructed by connecting an NdFeB magnet PM2 (type: N52, diameter: 1.3 cm and height: 2 cm) to the TMA by a spacer. The spacer length was adjusted to position the magnet PM2 below coil 2 (**Fig. 6.3**). In the STMO configuration, only coil 1 generated the output voltage due to the movement of the TMA, whereas in the HTMO configuration, the voltages from both coils 1 and 2 connected in series contributed to the resultant output voltage. The voltage was generated in coil 1 and 2 due to the simultaneous movement of TMA and PM2, respectively. **Table 6.1** summarizes the device parameters utilized for the STMO and HTMO configurations.

Fig. 6.3 The schematic setup of the HTMO showing the TMA at (a) the heat load and (b) the heat sink position. (c) Experimental setup of the HTMO

Table 6.1 The design parameters and TMA properties used in the HTMO setup

Sets	Set 1	Set 2	Set 3
Configuration	STMO	STMO	HTMO
TMA composition	$(\text{MnNiSi})_{0.7}(\text{Fe}_2\text{Ge})_{0.3}$		
Mass (g)	15	20	20
TMA cylinder dimensions diameter $\times$ height (mm $\times$ mm)	18 $\times$ 15	18 $\times$ 20	18 $\times$ 20
Heat load temperature($^{\circ}\text{C}$)	180	180	180
Heat sink temperature($^{\circ}\text{C}$)	25	25	25
PM2 dimension diameter $\times$ height (mm $\times$ mm)	-	-	13 $\times$ 20

6.3 Performance of STMO

The voltage profile obtained for both the 15 g and the 20 g of TMA is shown in **Fig. 6.4a-c**. The heat load was set at a temperature of 180 $^{\circ}\text{C}$ before the magnet was introduced to

induce oscillations. A maximum voltage of 0.35 V was obtained for the 15 g TMA (Fig. 6.4(a-c)) with an oscillation time period of ~ 2 min. The velocity and voltage profile of one of these signals were analyzed by experiments and numerical simulations (Fig. 6.4b and c). During the upward movement of the sample towards the HL, the smaller peak of 0.1 V corresponded to the TMA entering into coil 1, followed by a larger peak of -0.3 V corresponding to the TMA exiting coil 1. The maximum velocity was 2.6 m/s was recorded when TMA reaches the HL. The simulations and the experimental results for the voltage and velocity are in good agreement.

Fig. 6.4 Voltage output recorded for 10 min for (a) 15 g and (b) 20 g of TMA. Velocity of the TMA during its movement towards the heat load for (a) 15 g and (b) 20 g of TMA.

A peak voltage of 0.75 V was obtained for the 20 g TMA, with an oscillation time period of ~160 s (**Fig. 6.4** (d-f)). A single voltage profile was analyzed by experiments and simulations (**Fig. 6.4e** and f). During the upward movement of the sample towards the HL, the voltage peak of 0.38 V corresponding to the TMA entering coil 1 was observed, followed by a larger peak of -0.75 V corresponding to the TMA exiting coil 1. The velocity profiles indicated a lower velocity (1.6 ms^{-1}) was observed for the case of the 20 g TMA compared to the case of the 15 g TMA. The lower velocity in the case of 20 g TMA is due to the higher mass of the TMA resulting in higher downward force due to gravity. The simulation results showed a good agreement with the experimental voltage profile. The velocity determined by experimental analysis exhibits a quasi-linear profile, whereas the velocity obtained by simulations follows a nonlinear profile, hence a slight deviation was observed. The mismatch may also be partly due to the nonlinear response of the TMA at lower magnetic fields, this non-linearity becomes significant at lower magnetic volume force. The voltage profile shows a higher value of the peak corresponding to the exit of the TMA from coil 1 is due to the higher velocity of the TMA when it leaves the coil compared to the velocity when it enters into the coil. No significant peaks were obtained during the fall of the TMA due to the negligible magnetic flux of the paramagnetic TMA.

6.4 Performance of HTMO

The HTMO generates voltage due to the oscillation of both the TMA as well the magnet PM2 oscillating in their respective coils. The magnetic flux change due to PM2 was ~9 times higher compared to the flux change due to the TMA, this significantly enhances total voltage output. The following section describes the electricity harvesting and cooling performance of the HTMO device.

6.4.1 Electrical output

Fig. 6.5a shows the voltage profile obtained from a HTMO for a time period of 50 min. The upward motion of the TMA and the PM2 results in a peak voltage of -10 V, whereas the peak voltage generated during the downward motion are in the range of 3 V to 5 V. In

Fig. 6.5a, small peaks (≤ 0.5 V) in the positive direction were due to the TMA moving up through the coil 1 towards the heat load.

Fig. 6.5b shows the current through the coil for one of the voltage profiles in the HTMO device measured by LabView. The current profile exhibited a 15mA peak current corresponding to each of the voltage peak of 10 V. This magnitude of the generated current from the HTMO device is significantly higher compared to other energy harvesting approaches. Specifically, for piezoelectric devices, though peak voltage and the frequency are on the higher side, the current values are in the range of pA to μ A [34], which are at least 10000 times less than the current generated by the HTMO. The low current values in these devices limits the storage and dissipation of electrical energy using these devices, whereas the storage and dissipation of electricity is performed for the HTMO in the present demonstration.

Fig. 6.5 (a) Voltage output of HTMO recorded for 50 min and (b) the current in the coil corresponding to one of the voltage peaks.

6.4.2 Cooling performance

The heat load temperature profile was collected for the first 25 oscillations of the TMA (**Fig. 6.6a**). The initial cycles showed small variations in the peak temperatures (**Fig. 6.6b**) which stabilized after the 13th cycle. A constant peak temperature was observed during each cycle after stabilization of the HL temperature cycles (**Fig. 6.6c**).

The path AB corresponds to the cooling profile of the heat load, this cooling occurs due to absorption of heat by the TMA from the HL. The temperature of the TMA at point A is T_{CC} , and gets heated up due to the HL (path BC). At point C, the temperature of the TMA reaches T_{CH} , becomes paramagnetic and loses magnetic attraction to PM1.

Fig. 6.6 (a) The temperature of the heat load recorded for the first 25 cycles of the HTMO. (b) The temperature profile for the first 13 cycles with transient cooling cycles, inset shows one of the temperature cycle corresponding to position of the TMA (A, B, C and D). (c) The temperature profile from the 14th cycle having stabilized cooling cycle.

The paramagnetic TMA falls towards the HS under the influence of gravity. At the HS, the TMA transfers the heat absorbed from the HL to the HS until the TMA reaches the temperature T_{CC} . After the TMA falls towards the HS, a small cooling of HL (path CD)

was observed due to cooler air replacing the volume occupied by the TMA at the heat load. The HL is cooled by air during the path CD in **Fig. 6.6c**. Subsequently, HL reaches a steady state temperature value without the TMA upto point A. The TMA at HS becomes ferromagnetic and is lifted to the HL by magnetic force due to PM1. Path AB (**Fig. 6.6c**) exhibited a cooling of upto 70°C, this cooling was attained during every cycle when the TMA from the HS was lifted and came in contact with the heat load (point A) under the action of the magnetic force (F_M) due to PM1.

6.4.3 Energy storage and dissipation

The electrical output from the HTMO was stored in a 3.3 mF capacitor via a full wave rectifier circuit (**Fig. 3.13**). The capacitor stores the energy generated during each thermomagnetic cycle. The capacitor was charged upto 2 V after 65 minutes of the HTMO operation (**Fig. 6.7a**). The total energy of upto 6 mJ was stored in the capacitor, which was calculated from eq. (3.7), shown in **Fig. 6.7b**.

The stored energy can be utilized for various applications. For e.g., in the present demonstration, the stored energy was used to light up a LED which was connected to the capacitor via a switch (**Fig. 3.13**). The stored energy gradually discharged across the LED, lighting it for ~50s (**Fig. 6.7c**). Power density is a crucial parameter for an energy harvesting system. Considering the energy stored in the capacitor during the first thermomagnetic cycle (0.4 mJ in 180 s), a power density of $0.6 \mu\text{W}/\text{cm}^3$ was obtained. The significance of the present HTMO prototype is the self-actuation or passive system without the need of a fluid pump, cooling fans or piezoelectric connectors for electricity generation.

Fig. 6.7 (a) The voltage across the 3.3 mF capacitor connected to the HTMO via rectifier (b) The corresponding energy stored in the capacitor for 65 min of HTMO operation (c) The voltage discharge profile of the 3.3 mF capacitor connected to an LED by a switch.

6.5 Optimization of device parameters

The performance of the STMO and the HTMO is determined by the generated voltage and the resulting cooling of the HL. Both the generated voltage and the heat load cooling depend on the thermomagnetic response of the TMA. The role of various parameters on the STMO performance was analytically modeled. Numerical simulations were also performed.

6.5.1 Force balance analysis

The upward magnetic force experienced by the TMA [37] is given by:

$$F_M = C\chi_H (\mathbf{B} \cdot \nabla \mathbf{B}) / \mu_0 \quad (6.1)$$

Where, C is the volume of the TMA, χ_H is the susceptibility of the TMA, $\mathbf{B}$ is the magnetic flux density of the permanent magnet and μ_0 is the permeability of the free space.

The net force experienced by the TMA for its upward motion, due to the combined effect of the magnetic force (eq. (6.1)) and gravitational force (F_g), can be written as,

$$F_{eff}(z) = F_m - F_g = C\chi_H (\mathbf{B} \cdot \nabla \mathbf{B}) / \mu_0 - mg \quad (6.2)$$

where, m is the mass of the TMA and g is the acceleration due to gravity. Eq. (6.2) was used to determine the profile of the magnetic and the gravitational force acting on the TMA during the thermomagnetic cycle (**Fig. 6.8**).

Fig. 6.8 Analytical investigation of the competing forces acting on the TMA. The TMA rises towards the heat load (HL) when the magnetic force at the heat sink F_{m1} exceeds the gravitational force F_g (at $m1$). The TMA drops to the heat sink (HS) when F_g exceeds the magnetic force at the heat load F_{m2} (at $m2$).

The magnetic force F_m (in positive y-direction) and the gravitational force F_g (in negative y-direction) oppose each other. For the ferromagnetic state of the TMA (below T_{CC}), the force F_m exceeds force F_g , resulting in upward motion of the TMA. The force F_g exceeds F_m when the TMA is paramagnetic (temperature $\geq T_{CH}$), resulting in downward motion of the TMA. A force greater than 196 mN is required for the upward movement of the 20 g TMA towards the heat load (point $m1$ in **Fig. 6.8**). The TMA, initially located at the heat load, falls when F_g exceeds the F_m at the HL (point $m2$).

6.5.2 Numerical simulations: effect of mass, height and magnetic field

We employed numerical simulations to investigate STMO behavior (**Fig. 6.9**). The simulation model has been described earlier. A reference point $(x, y, z) \equiv (0, 0, 0)$ was

defined at the center of the coil. The y-direction indicates the vertical axis of symmetry, +y corresponds to the up direction and the negative y-direction points down.

We first investigated the effect of magnetic field strength of the permanent magnet PM1 on the device performance (**Fig. 6.9a**).

Fig. 6.9 STMO performance showing voltage over a range of (a) magnetic fields, (b) sample mass, and (c) device height. The experimental device dimensions were used for (a, b). The experimental magnetic field of PM1 was used for (b,c). TMA mass of 20 g was used for (a, c).

The magnetic volume force F_m acting on the TMA is determined by the field strength of PM1. At higher field strength of PM1, the velocity of TMA will be larger. Also, for greater magnetic field strength of PM1, the magnetic flux in the coil is higher because of larger magnetization of the TMA passing through this coil. Hence, oscillations of the TMA for the higher field strength of PM1 will result in greater voltage. A slow increase in voltage was observed for magnetic fields ≤ 0.4 T. For magnetic fields higher than 0.4 T, a sharp

increase in generated voltage was observed. At magnetic field of 1.2 T, voltage attains the maximum value of 7 V for the STMO configuration. Hence, voltage increases nonlinearly with increasing magnetic field.

The effect of TMA mass was studied (**Fig. 6.9b**). A large increase in voltage was obtained with increasing mass from 10 g to 250 g. After 150 g, voltage saturates at ~4.5 V.

The effect of device height was investigated (**Fig. 6.9b**) for all simulated sets. The device height was changed while keeping the coil at the centre and heat load at the top. We found that an optimized device height of 50 mm is required to generate a maximum voltage of 2.5 V, for a fixed sample mass of 20g and magnetic field strength of 0.4 T. The voltage exhibits a sharp increase until an optimum device height is reached, followed by a slow decrease after this optimum height.

Hence, the generated voltage of the STMO increases significantly with increasing magnetic field, mass and exhibits a sharp increase with increasing device height until an optimum height.

6.5.3 Numerical simulations: role of thermal conductivity

Our simulation model was used to determine the role of factors affecting the heating rate of the TMA. The heating rate ((b) and (d) in **Fig. 6.6**) determines the oscillation frequency of the TMA. Hence, the time for heating of the TMA has been determined (**Fig. 6.10**). We compared our experimental results with the simulation model results (**Fig. 6.10a**), Time-dependent simulations were performed, the simulated temperature profile (**Fig. 6.10a**) is in good agreement with the experimental profile (**Fig. 6.6c**). Both the experimental results and the simulation profiles follow a similar temperature profile and similar time constant.

We then used this model to investigate the role of thermal conductivity ratio (λ) of the TMA (**Fig. 6.10b**) and the heat load temperature (THL) value (**Fig. 6.10c**). The thermal conductivity ratio λ is the ratio $\lambda_{\text{sim}}/\lambda_{\text{exp}}$, where λ_{sim} and λ_{exp} are the simulation and experimental thermal conductivities (in $\text{Wm}^{-1}\text{K}^{-1}$). The experimental thermal conductivity

was $\lambda_{\text{exp}} = 20 \text{ Wm}^{-1}\text{K}^{-1}$. **Fig. 6.10b** shows the effect of λ on the temperature profiles. Numerical investigations were performed for λ values in the range of 0.5 to 10. We found that, with increasing λ value, the heating rate of the TMA increases, increasing cycle frequency. The rate of TMA heating increases significantly for λ values from 0.5 to 2.5, reducing heating time of the TMA from $\sim 360 \text{ s}$ (at $\lambda = 0.5$) to $\sim 60 \text{ s}$ (at $\lambda = 2.5$). For $\lambda > 2.5$, the temperature profiles start to saturate. Hence, heating duration decreases with increasing λ .

Fig. 6.10 Numerical simulation of the effect of thermal conductivity and heat load (HL) temperature on heating of TMA. Temperature profiles of the path BC: (a) Experimental and simulation (b) Effect of thermal conductivity ratio (λ) varied in the range from 0.5 to 10. (c) Effect of HL temperature, in the range from 200°C to 600°C for $\lambda = 1$ (solid lines) and $\lambda = 5$ (dashed lines).

The effect of HL temperature on the temperature profiles, for λ values of 1 and 5 is depicted in **Fig. 6.10c**. The HL temperature was varied in the range from 200°C to 600°C. **Fig. 6.10c** shows decreasing initial slopes with increasing HL temperatures, indicating reduction in heating rate of the TMA, for λ values of 1 and 2. The decrease is more significant at $\lambda = 1$

compared to $\lambda = 5$. At 200°C, saturation is reached in ~ 15 s for both λ values, whereas at 300°C it is reached at 30 s for $\lambda = 5$ and at 120 s for $\lambda = 1$. For an increase in HL temperature from 300°C to 600°C, heating time of the TMA increases from ~ 120 s to ~ 240 s for a λ value of 1. The duration of heating of the TMA increases with increasing HL temperatures, especially at $\lambda = 1$.

Hence, superior performance of the STMO can be obtained at higher magnetic field strength, larger TMA mass, optimized device height, higher thermal conductivity of the thermomagnetic alloy, and lower heat load temperatures.

6.6 Figure of merit for TMO

Low-grade thermal energy harvesting technologies are mainly based upon the pyroelectric [17-19], thermoelectric [15,16] or thermomagnetic effect [31,33,35,36,38]. These energy harvesters utilize waste heat to generate useful energy. Thermoelectric devices are based on the Seebeck effect [39], the Thomson effect [40] and the Peltier effect [41]. The figure of merit (FoM) for thermoelectric devices (ZT) is given by:

$$ZT = \frac{\alpha^2 \sigma T}{k} \quad (6.3)$$

where α , σ , k and T represent the Seebeck coefficient, electrical conductivity, thermal conductivity and temperature respectively.

Similarly, the efficiency (η_{TM}) of thermomagnetic cycles [42] is given by :

$$\eta_{TM} = \frac{\mu_0 \oint H dM}{\rho \int_{T_C}^{T_H} C_P(T) dT} \quad (6.4)$$

where μ_0 is permeability of free space, ρ is the density, H is the applied magnetic field, and M is magnetization of the material. Although the above relationship defines the efficiency of the thermomagnetic material for various magnetic field strength and temperature values, there is a necessity to find the performance metric for a specific device. The combination of material properties with device parameters can facilitate the optimization of material and device geometry. Therefore in the following sections, the figure of merit, relating the energy and the frequency of the oscillation, has been derived for a thermomagnetic

oscillator (TMO). Using this FoM for the TMO, optimization of the device parameters or material properties based on the device can be analyzed.

In this analysis, the energy output generated by the TMO was considered as a suitable figure of merit (FoM). The FoM was calculated using the product of energy generated per oscillation and the frequency of the oscillation. The FoM calculations included both material properties as well as the device parameters. The following sections highlight the derivation of the FoM.

6.6.1 Derivation of Energy generated per Oscillation

The energy obtained from the TMO is due to the induced emf in the coil as the ferromagnetic TMA passes through it during its oscillation.

The energy harvested in a coil due to the motion of the TMA through the coil is given by:

$$E_{osc} = \frac{V^2 t_{coil}}{R} \quad (6.5)$$

where, V , R and t_{coil} are the induced emf, resistance of the coil and the time which the TMA takes to move through the coil, respectively.

The induced emf due to the motion of TMA can be written as,

$$V = -NA \frac{dB_{TMA}}{dt} \quad (6.6)$$

where, N is the number of turns of the coil, A is the cross sectional area of the coil, B_{TMA} is the magnetic flux density associated with the coil due to the motion of the TMA and t is the time.

The magnetic flux density of the TMA is a function of the magnetic field of the permanent magnet 1 (PM1) and the magnetization of the TMA, and is given as,

$$B_{TMA} = \mu_0 H_{magnet} + \mu_0 M_{TMA} \quad (6.7)$$

Hence, the time rate of change of magnetic flux density linked with the coil takes the form,

$$\frac{dB_{TMA}}{dt} = \mu_0 \left(\frac{dH_{magnet}}{dt} + \frac{dM_{TMA}}{dt} \right) \quad (6.8)$$

The magnetic field due to PM1 varies along the direction of motion of the TMA, i.e., the z -direction. The magnetization of the TMA is related to this magnetic field of PM1. Hence, eq.(6.8) takes the form,

$$\frac{dB_{TMA}}{dt} = \mu_0 \frac{dz}{dt} \left(\frac{dH_{magnet1}}{dz} + \chi \frac{dH_{magnet1}}{dz} \right) \quad (6.9)$$

The magnetic force experienced by the TMA [37] is given by eq. (6.1).

Fig. 6.11 . Free body diagram of the TMA inside the heat load. The downward gravitational force (F_g) and the upward magnetic force (F_m) act on the TMA. F_m is due to the effect of the applied magnetic field due to PM1. The TMA is separated by the heat load by quartz tube (thickness = r_{glass}) and an air gap (r_{air}).

The net force experienced by the TMA is given by eq. (6.2)

Eq. (6.2) can be simplified as,

$$F_{eff}(z) = ma = \frac{C\chi_H}{\mu_0} (B \cdot \nabla B) - mg \quad (6.10)$$

The acceleration (a) of the TMA is the double differentiation of displacement (z) with respect to time, thus eq. (6.10) can be rearranged

$$\frac{d}{dt} \left(\frac{dz}{dt} \right) = \frac{C\chi_H}{\mu_0 m} (B \cdot \nabla B) - g \quad (6.11)$$

Eq. (6.11) can be integrated within the time limits of start of TMA motion and the time it takes to transit through the coil and the corresponding coil length was taken as displacement limits. $z = 0$ and z_{coil} correspond to the TMA position at the entrance and exit of the coil, respectively.

$$\left(\frac{dz}{dt} \right)_{z=z_{coil}} - \left(\frac{dz}{dt} \right)_{z=0} = \int_{t=0}^{t=t_{coil}} \left(\frac{C\chi_H}{\mu_0 m} (B \cdot \nabla B) - g \right) dt \quad (6.12)$$

The velocity of the TMA at $z = 0$ is assumed to be zero since $F_g \geq F_m$. In addition, the magnetic flux density due to the permanent magnet is independent of time for a constant z . Hence, the integral in eq. (6.12) takes the form,

$$\left(\frac{dz}{dt} \right)_{z=z_{coil}} = \frac{C\chi_H}{\mu_0 m} B_z \frac{\partial B_z}{\partial z} t_{coil} - g t_{coil} \quad (6.13)$$

The value of χ_H can be different for different magnetic samples. If χ_H is higher, the time required for the TMA to reach the coil (t_{coil}) will be lower and vice versa.

The time taken to lift the TMA depends on the magnetic susceptibility, mass, applied magnetic field strength and the temperature of the heat load. During the lift, the mass of the TMA, applied field strength and the temperature of heat load remains constant. The time of lift of the magnetic material is inversely proportional to the root magnetic susceptibility. This proportionality was taken into account while calculating the t_{coil} for various alloys.

$$t_{coil} \propto \frac{1}{\sqrt{\chi}} \quad (6.14)$$

Hence, substituting eq. (6.13) in eq. (6.9),

$$\frac{dB_{TMA}}{dt} = \mu_0 t_{coil} \left(\frac{dH_{magnet}}{dz} + \chi \frac{dH_{magnet}}{dz} \right) * \left(\frac{C\chi_H}{\mu_0 m} B_z \frac{\partial B_z}{\partial z} - g \right) \quad (6.15)$$

Using eq. (6.15), eq. (6.6) for the induced emf can be written as,

$$V = -NA\mu_0 t_{coil} \left(\frac{dH_{magnet}}{dz} + \chi \frac{dH_{magnet}}{dz} \right) * \left(\frac{C\chi_H}{\mu_0 m} B_z \frac{\partial B_z}{\partial z} - g \right) \quad (6.16)$$

The emf obtained from eq. (6.16) was substituted in eq. (6.5) to obtain energy generated by TMO per unit time (E_{osc})

6.6.2 Derivation of Frequency of Oscillation

The frequency of oscillation depends on the rate of heat transfer from and to the TMA at the heat sink and the heat load, respectively. Heat is transferred to the ferromagnetic TMA at the heat load which reduces its magnetic susceptibility until the gravitational force exceeds the magnetic attraction force between TMA and PM1. Hence, from **Fig. 6.12**, the temperature of the TMA must be raised from T_{FM} to T_{PM} at the heat load including the latent heat for structural transformation (in alloys exhibiting first order transformation). T_{FM} and T_{PM} are the temperature of TMA during lift and fall, respectively. They were calculated using the force balance eq. (6.1) and eq. (6.2).

Fig. 6.12 . Magnetization vs Temperature plot showing the temperature of TMA during lift (T_{FM}), temperature of TMA during fall (T_{PM}), temperature of heat load (T_{HL}) and temperature of heat sink (T_{HS})

The amount of heat required for this transition is given by Q_H :

$$Q_H = mC_P\Delta T_H = mC_P(T_{PM} - T_{FM}) \quad (6.17)$$

The same quantity of heat must be absorbed by the heat sink during cooling to change the magnetic state of the TMA from the paramagnetic to the ferromagnetic state to overcome the force of gravity. The heat absorbed at the heat sink is also given by Q_H .

The rate of conductive heat transfer from the heat load (at temperature T_{HL}) to the TMA (at temperature T_{FM}) is described by the formula for heat transfer due to conduction per unit time given by eq. (6.18). Similarly, the rate of heat transfer from paramagnetic TMA (at temperature T_{PM}) to the heat sink (at temperature T_{HS}) is given by eq. (6.19):

$$\frac{dQ_{HL}}{dt} = \frac{k_{eff}A_C \Delta T}{r_{eff}} = \frac{k_{eff}A_C (T_{HL} - T_{FM})}{r_{eff}} \quad (6.18)$$

$$\frac{dQ_{HS}}{dt} = \frac{k_{eff}A_C \Delta T}{r_{eff}} = \frac{k_{eff}A_C (T_{PM} - T_{HS})}{r_{eff}} \quad (6.19)$$

where, A_C is the area of contact, k_{eff} and r_{eff} is the effective coefficient of thermal conductivity and effective distance, respectively. The air gap is necessary to avoid friction between the glass tube and the TMA during the oscillation, therefore k_{eff} and r_{eff} are calculated considering the thickness of the quartz glass ($r_{glass} = 1$ mm) and a small air gap ($r_{air} = 0.5$ mm) (**Fig. 6.11**). Since the air gap is filled with water when the TMA is at the heat sink, $r_{air} = r_{water}$ was considered. The ratio of r_{eff}/k_{eff} of the TMO was calculated using the formula for conduction through dissimilar media at the heat load given by eq. (6.20) and at the heat sink given by eq. (6.21)

$$\frac{r_{eff}}{k_{eff}}(\text{at HL}) = \frac{r_{glass}}{k_{glass}} + \frac{r_{air}}{k_{air}} + \frac{r_{TMA}}{k_{TMA}} \quad (6.20)$$

$$\frac{r_{eff}}{k_{eff}}(\text{at HS}) = \frac{r_{water}}{k_{water}} + \frac{r_{TMA}}{k_{TMA}} \quad (6.21)$$

where, k_{glass} , k_{air} , k_{water} are the coefficient of thermal conductivities for glass, air and water with the values $1.4 \text{ Wm}^{-1}\text{K}^{-1}$, $0.0262 \text{ Wm}^{-1}\text{K}^{-1}$ and $0.608 \text{ Wm}^{-1}\text{K}^{-1}$, respectively [43]. k_{TMA} was calculated using rule of mixtures, r_{TMA} is the radius of the TMA cylinder (7.2 mm).

The time taken to heat the ferromagnetic TMA at temperature T_{FM} to the temperature T_{PM} is the ratio of heat required for transformation to the heating rate. The time taken for the heat transfer at the heat load (t_{HL}) and the heat sink (t_{HS}) is given by:

$$t_{HL} = \frac{mC_P(T_{PM} - T_{FM}) r_{eff}}{k_{eff}A_C (T_{HL} - T_{FM})} \quad (6.22)$$

$$t_{HS} = \frac{mC_P(T_{PM} - T_{FM}) r_{eff}}{k_{eff}A_C (T_{PM} - T_{HS})} \quad (6.23)$$

The total time per taken per oscillation is the sum of t_{HL} and t_{HS} . We neglect the time required by the TMA to travel from the heat load to the heat sink and vice versa, as they are negligible compared to t_{HL} and t_{HS} . Therefore, the frequency of thermomagnetic oscillation (f_{tmo}) was determined using the reciprocal of time taken per oscillation.

$$f_{tmo} = \frac{1}{t_{HL} + t_{HS}} \quad (6.24)$$

6.6.3 Figure of Merit analysis for various thermomagnetic alloys

The figure of merit for the TMO can be calculated as the product of energy per cycle (eq. (6.5)) and frequency (eq. (6.24)).

$$FoM_{TMO} = E_{Osc} \times f_{TMO} \quad (6.25)$$

The calculation of FoM was performed for various magnetocaloric alloys given in **Table 6.2**. The latent heat for crystal structure transformation was calculated using the DSC plots. The values of thermal conductivity, C_P were calculated using the rule of mixtures, and the temperatures T_{PM} and T_{FM} were obtained using the force balance analysis.

Table 6.2 Calculation of FoM for various magnetocaloric alloys using the device parameters and material properties. NA: no oscillation due to insufficient heating/cooling of TMA

Alloy [Ref]	Comp	Device Temperatures		Material Temperatures		Time / oscillation s	Frequency mHz	Energy/ cycle mJ ($\times 10^{-2}$)	FoM J.Hz or Js ⁻¹ ($\times 10^{-6}$)
		Heat Load (T _{HL}), K	Heat Sink (T _{HS}), K	for lift (T _{FM}), K	for fall (T _{PM}), K				
(MnNiSi) _{1-x} (Fe ₂ Ge) _x [44]	0.3	453	298	401	421.3	230	4.3	50.7	2.2
	0.32	453	298	345.7	364	122.7	8.1	51.4	4.2
	0.33	453	298	320.5	350.3	145.2	6.9	49.7	3.4
MnFeP _(1-x) Ge _x [45,46]	0.26	453	298	327.6	358	155	6.4	45.1	2.9
	0.3	453	298	362	403	169	5.9	44.8	2.7
	0.32	453	298	424.7	449	337.3	3	41.8	1.2
Mn _{2-x} Co _x Ge [47]	1.07	453	298	324	345.5	119.8	8.3	49.9	4.2
	1.06	453	298	346	381.6	158.2	6.3	38.8	2.4
	0.85	453	298	295	327	NA	0.0	45.4	0
	0.86	453	298	302	336	314.2	3.2	52.5	1.7
Mn _{1.3} Fe _{0.7} P _{1-x} Si _x [48]	0.54	453	298	312	330.5	187.7	5.3	39.6	2.1
	0.55	453	298	316.4	332	175.6	5.7	38.8	2.2
Fe _{75-x} Mn _x Al ₂₅ [49]	15	453	298	359	488	NA	0.0	41.6	0
	17.5	453	298	305.5	498.6	NA	0.0	43.2	0
	15	553	298	359	488	191.9	5.2	41.6	2.2
	17.5	553	298	305.5	498.6	756.6	1.3	43.2	0.6

The FoM was compared for some of the first order magnetic transition alloys i.e., (MnNiSi)_{1-x}(Fe₂Ge)_x [44], Mn_{2-x}Co_xGe [47], MnFeP_{1-x}Ge_x [45,46], Mn_{1.3}Fe_{0.7}P_{1-x}Si_x [48] and second order alloy Fe_{75-x}Mn_xAl₂₅ [49]. The transition temperature of these alloys were suitable for the experimental heat load and heat sink temperature. From the FoM values, it was observed that the alloys exhibiting first order transformation are quite effective for a temperature difference of ~150 K between the heat load and the heat sink. The second order alloys, having no hysteresis, show a lower FoM due to a gradual magnetic transition with respect to temperature and lower ΔS_M values. To obtain a better FoM using a second order

alloy, the heat load temperature must be high which limits the usage of second order alloys for harvesting low-grade waste heat. The FoM for $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ is zero when the heat load temperature is 453 K because the T_{PM} is higher than the heat load temperature. Therefore the temperature is insufficient for the material to become sufficiently paramagnetic for it to fall. Similarly, in the case of $\text{Mn}_{2-x}\text{Co}_x\text{Ge}$ ($x = 1.06$), the T_{PM} is less than the heat sink temperature. $(\text{MnNiSi})_{0.68}(\text{Fe}_2\text{Ge})_{0.32}$ shows the highest FoM of 4.2, predominantly due to the high ΔS_{max} ($47.3 \text{ J kg}^{-1} \text{ K}^{-1}$) [44] compared to other Mn based magnetocaloric materials and possesses a suitable T_{PM} and T_{FM} for the device operating temperatures.

According to the FoM analysis, an ideal working material for the TMO should possess a steep magnetic transition between the heat load and the heat sink temperature range, high ΔS_{M} , negligible hysteresis and high thermal conductivity. Most of the Mn based first order materials possess high ΔS_{M} , however the hysteresis poses a drawback where additional energy needs to be supplied in each oscillation for structural transition. In many second order materials the change in the magnetization is insufficient within the given temperature range due to gradual change in the magnetization with respect to temperature. Therefore, it is necessary to select a material having T_{C} between the heat load and the heat sink temperature. From the device point of view, it is essential to have a reasonable temperature difference between the heat load and the heat sink, sufficient magnetic field of the permanent magnet and optimal height to lift the TMA towards the heat load. Hence, both the device parameters and the material properties contribute to the performance of the TMO. The FoM is an indicator for deciding the optimum material for a particular set of device parameters.

From the above analysis, $(\text{MnNiSi})_{0.68}(\text{Fe}_2\text{Ge})_{0.32}$ and $\text{Mn}_{0.93}\text{Co}_{1.07}\text{Ge}$ yielded the highest FoM among other alloys for the given heat load and the heat sink temperature. To further enhance the performance, spacer material was optimized by comparing a rigid spacer and a flexible spacer described in the subsequent sections using $(\text{MnNiSi})_{0.68}(\text{Fe}_2\text{Ge})_{0.32}$ as the TMA.

6.7 Enhancement of TMO performance by flexible spacer

6.7.1 Voltage output

The voltage readings with the flexible spacer is shown in **Fig. 6.13**. The HTMO produces a voltage of up to 1.5 V when the TMA along with magnet PM2 falls to the heat sink due to gravity (indicated as A in **Fig. 6.13a**). The maximum contribution to this voltage comes from PM2 because the TMA is paramagnetic during its fall to the heat sink. A voltage signal indicated as B in **Fig. 6.13a** is produced when both TMA and M2 are pulled up towards the heat load, a voltage of ~ 11 V is produced across the two Cu coils. This voltage signal is higher the value obtained using a rigid spacer (9 V), this is due to the sudden pull of M2 into the coil which gives rise to a rapid change in the magnetic flux inside the coil. The voltage signal indicated as C in **Fig. 6.14b** and the subsequent damped voltage signals are due to the oscillations of magnet PM2 inside the Cu coil

Fig. 6.13 Voltage vs time measurements of HTMO with flexible spacer. The voltage signal obtained when TMA falls to heat sink is represented by A, the voltage signal during the rise of TMA towards the heat load is shown as B and the voltage signal C and the successive small peaks are generated due to the oscillation of magnet M2.

Fig. 6.14 Comparison between a single voltage signal obtained during the rise of TMA towards heat load for a rigid (red) and flexible (black) spacer. Additional voltage signals due to oscillations of M2 and a higher voltage output of 11 V is generated in case of a flexible spacer.

Comparison between the voltage signal obtained using rigid spacer and a flexible spacer is shown in **Fig. 6.14**. An additional voltage signal of 3 V was obtained during the first oscillation of PM2 inside the coil and subsequently lower voltage signals. The higher voltage (11 V) obtained due to flexible spacer when compared to rigid spacer (9 V) can be attributed to the sudden pull with a higher force experienced by PM2 when the flexible spacer becomes stiff. In the case of a rigid spacer, PM2 is pulled up with a lower force due to the larger distance between TMA and PM1. In the case of a flexible spacer, PM2 is pulled up with greater force since the TMA is closer to PM1 and experiences a greater upward pull force when the flexible spacer is taut. Hence according to Faraday's law (eq. (6.26)), the sudden upward jerk experienced by PM2 increases the rate of change of flux (ϕ) resulting in higher EMF.

$$\text{EMF} = -\frac{d\phi}{dt} \quad (6.26)$$

6.7.2 Force balance

Fig. 6.15 shows a comparison between the forces experienced by the TMA using either flexible or rigid spacer at various operating temperature of the HTMO. The TMA situated at the heat load experiences a downward force due to gravity. As the TMA temperature increases, the upward magnetic pull force decreases due to a decrease in the magnetic susceptibility of the TMA. When this force reaches point R (**Fig. 6.15**), the gravitational force (due to both TMA and PM2) exceeds the magnetic force and TMA falls to the heat sink. During cooling in the heat sink region, the susceptibility of the TMA increases. It undergoes a ferromagnetic transition, the upward magnetic force increases beyond the gravitational force (P for rigid spacer and Q for flexible spacer in **Fig. 6.15**), and the TMA jumps up towards the heat load. The difference in temperature of lift i.e., P and Q in the rigid and flexible spacer case respectively, is due to the difference in the downward force experienced by the TMA. In the case of a flexible spacer, the downward force is due to the weight of the TMA. In the case of a rigid spacer, the downward force is due to the combined weight of TMA and PM2. A sufficiently large upward force is required for the TMA to overcome the downward force due to gravity. Since the downward force is higher in the case of rigid spacer, the TMA must possess higher susceptibility to gain the required value of upward force. Therefore the TMA is cooled down to lower temperature (point P in **Fig. 6.15**) to attain the upward force required to overcome the gravitational force of both TMA and PM2. Whereas in the case of a flexible spacer, the upward force required for lift is lower due to absence of the downward force from PM2. Hence, the TMA is lifted up to the heat load at relatively higher temperature (point Q in **Fig. 6.15**). The time taken to cool the TMA upto point P in the case of the rigid spacer results in lower oscillation frequency. An additional cooling of 4°C per cycle (length of PQ in **Fig. 6.15**) is obtained if rigid spacer is used instead of a flexible spacer.

Fig. 6.15 Force experienced by the TMA with respect to temperature at heat load and heat sink positions. A higher downward force is experienced by the TMA in the case of a rigid spacer (red) compared to a flexible spacer (blue) during cooling. The upward magnetic force decreases as temperature increases (pink). The temperature at which the TMA with rigid spacer and flexible spacer are lifted up are given by P and Q respectively. The TMA drops to the heat sink at point R. Forces acting on TMA are given by F_M : upward magnetic pull force, F_{gM2} : downward gravitational pull force due to weight of M2, F_{gTMA} : downward gravitational force due to weight of TMA.

6.7.3 Simulation model for frequency analysis

Fig. 6.16 shows the force balance of the TMA during the oscillations for the rigid spacer case and the flexible spacer case. Due to a higher downward force in the case of the rigid spacer, a higher magnetic force of 46 N is required to pull the TMA towards the heat load. Whereas, in the case of a flexible spacer, the downward body load due to PM2 is experienced only after TMA rises to a certain distance, therefore only 7 N is required to pull the TMA upwards. Once the TMA travels some distance upwards, the upward force

is sufficiently high to easily pull the magnet PM2. The downward force on the TMA remains constant in the case of a rigid spacer (**Fig. 6.16a**), whereas in the case of a flexible spacer, the downward force due to PM2 is not experienced by the TMA when it is at the heat sink (**Fig. 6.16b**). The frequency in the case of rigid spacer was 1.19 Hz (14 min per oscillation), whereas in case of a flexible spacer, the frequency increases by 32% to 1.75 Hz (9.5 minutes per oscillation) which is in good agreement with the experimental results (**Fig. 6.16a**). The higher frequency leads to higher voltage per unit time, increasing performance.

Fig. 6.16 Simulated force balance of the TMA in the case of (a) Rigid spacer, A and B indicate the point where the TMA is lifted towards the heat load and falling to the heat sink due to gravity, respectively (b) Flexible spacer where A' and B' indicate the point where the TMA is lifted towards the heat load and the TMA falling to the heat sink due to gravity, respectively. The downward force of TMA and PM2 due to gravity (red) and upward magnetic force due to PM1 (blue)

Therefore, the type of spacer was found to play a significant role in the performance of the HTMO device. Using a flexible spacer generated additional voltage signals and significantly increased oscillation frequency of the HTMO.

6.8 Principle outcomes

- The integration of thermomagnetic oscillations with electromagnetic induction to generate electricity was implemented for the first time. The novel design for simultaneously cooling the heat load and electricity harvesting was demonstrated.

The TMO is a passive device utilizing waste heat to generate electricity without any external pumps, cooling fans or piezoelectric connectors.

- The STMO device generated a voltage output of upto 0.75 V whereas HTMO generated upto 10 V during the lift and upto 5 V during the fall. The heat load was cooled from 180°C to 110°C during every cycle. Transient behavior of temperature profile was observed for the first 13 cycles and the temperature profile stabilized after the 13th cycle.
- The HTMO generated an energy of 6 mJ during 65 min of operation. The energy was stored in a 3.3 mF capacitor and dissipated through an LED which lighted up for upto 50 seconds.
- The effect of mass of TMA, height of the device and the magnetic field strength was investigated using simulation of STMO. It was revealed that the generated voltage of the STMO increases significantly with increasing magnetic field, mass and exhibits a sharp increase with increasing device height until an optimum height.
- The figure of merit (FoM) was derived as the product of energy generated per cycle and the frequency of the HTMO. The FoM was determined for various alloys based on their properties and the device parameters. The Mn based alloys such as $(\text{MnNiSi})_{0.68}(\text{Fe}_2\text{Ge})_{0.32}$ and $\text{Mn}_{0.93}\text{Co}_{1.07}\text{Ge}$ displayed the highest FoM of 4.2 Js⁻¹ for a heat load and a heat sink temperature of 453 K and 295 K, respectively.
- The material with the highest FoM, i.e., $(\text{MnNiSi})_{0.68}(\text{Fe}_2\text{Ge})_{0.32}$ was used as TMA to study the effect of flexible spacer on the performance of HTMO. The flexible spacer increased the oscillation frequency by 32% and voltage/cycle by 18% compared to the rigid spacer.

6.9 Conclusion

The thermomagnetic cycles of $(\text{MnNiSi})_{0.7}(\text{Fe}_2\text{Ge})_{0.3}$ was successfully utilized to generate electrical energy using the vertical movement in the prototype. An instantaneous voltage of upto 10 V and a cooling of upto 70°C per cycle was achieved. 6 mJ of energy was stored in a 3.3mF capacitor by running the prototype for 65 min which could to light up LED for about 50 seconds. The experimental results were in good agreement with the COMSOL Multiphysics simulations. The simulations were used to study the effect of material

properties and device parameters along with the evaluation of figure of merit. $(\text{MnNiSi})_{0.68}(\text{Fe}_2\text{Ge})_{0.32}$ and $\text{Mn}_{0.93}\text{Co}_{1.07}\text{Ge}$ displayed the highest FoM of 4.2 Js^{-1} for a heat load and a heat sink temperature of 453 K and 295 K, respectively. The flexible spacer enhanced the performance of the HTMO with an increase in the frequency by 32% and output voltage by 18%. Thus, the thermomagnetic oscillator was demonstrated to possess an enormous potential for cooling and energy harvesting applications.

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Chapter 7

Conclusion and Future work

This chapter presents a brief summary of the present work highlighting the significant results in this thesis. The MCE properties of MnNiSi based magnetocaloric materials were studied with two sets of alloying additions i.e., Fe₂Ge and Fe-Sn. Giant magnetocaloric properties were obtained near room temperature in (MnNiSi)_{1-x}(Fe₂Ge)_x and the cost analysis revealed that the (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) has lowest cost among MnNiSi based alloys. A thermomagnetic oscillator prototype was demonstrated utilizing the thermomagnetic response of the MnNiSi based alloys. The performance of the prototype was optimized using simulations and figure of merit analysis. Based on these results of MnNiSi based alloys, the scope for future work is discussed.

7.1 Summary

This chapter draws together the important outcomes of this thesis. The investigation of magnetocaloric properties of high performance, low cost, rare-earth free and environmentally friendly MnNiSi based magnetocaloric materials was performed. The objective of the present work was to achieve better MCE properties in the alloys and reduce the cost of synthesis by using inexpensive raw materials. In this regard, MnNiSi was alloyed with Fe₂Ge to tune the coupling of magnetic and structural transition near room temperature. The structural and magnetic characterization revealed higher ΔS_M and RCP for the arc melted samples without further heat treatment than previously reported values. To further reduce the cost of synthesis, Ge-free alloy (Mn_{0.45}Fe_{0.55})Ni(Si_{1-y}Sn_y) was synthesized by substituting Sn for Si. The magnetostructural transition was tunable near room temperature by varying the Sn content. The thermomagnetic response of (MnNiSi)_{1-x}(Fe₂Ge)_x was used to construct a thermomagnetic oscillator for simultaneous cooling and energy harvesting. The hybrid thermomagnetic oscillator was optimized by calculation of figure of merit and the performance was enhanced by selecting the accurate materials for the spacer. Overall, the good magnetocaloric properties, ready availability, easy tunability of T_C near room temperature and low cost of synthesis provides a wide range of useful applications to the MnNiSi based alloys.

The major conclusions of the thesis are summarized as follows:

1. The magnetocaloric properties of (MnNiSi)_{1-x}(Fe₂Ge)_x were studied by elimination of heat treatment step after arc melting. The structural characterization and magnetic measurements revealed that the (MnNiSi)_{1-x}(Fe₂Ge)_x alloys with composition $x = 0.32$ to 0.36 exhibit first order magnetostructural coupling between 363 K to 218 K (heating cycle) and 350 K to 200 K (cooling cycle).
2. The alloy composition (MnNiSi)_{0.66}(Fe₂Ge)_{0.34} showed the highest ΔS_{max} of 57.6 Jkg⁻¹K⁻¹ for a field change of 5 T at 301 K. This value of ΔS_{max} was one of the highest among Mn based magnetocaloric materials. The RCP value of 480 Jkg⁻¹ was determined for (MnNiSi)_{0.65}(Fe₂Ge)_{0.35} establishing its potential for high performance applications.
3. The phase transition in MnNiSi based alloys was modeled using theoretical

modeling for the first time. The theoretical models such as Arrott plots, Landau equations and the Bean-Rodbell model were employed to verify the first order phase transition in $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ alloys. The phase transition parameters were used to predict the MCE properties of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ alloys. The experimental and the modeled values of ΔS_M were in good agreement for all the compositions.

4. The magnetocaloric properties of low cost, Ge-free alloy $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ was studied for the first time. The magnetostructural transition temperature was tuned from 355 K to 275 K (heating cycles) and 343 K to 248 K (cooling cycles) by varying the Sn content from $y = 0.12$ to 0.18 . A ΔS_{max} of $8.64 \text{ Jkg}^{-1}\text{K}^{-1}$ was obtained for a field change of 5 T at 317.5 K and the RCP of 156 Jkg^{-1} was achieved for $y = 0.18$. Training effect of magnetization was observed during first 3 temperature cycles.
5. The cost analysis for various MCMs was carried out based on the raw materials used for synthesis. $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ being rare-earth free alloy displayed the lowest cost of synthesis (88¢/10 g) among other MnNiSi based alloys. The inexpensive materials used for synthesis makes it a potential material for low cost applications near room temperature.
6. A thermomagnetic oscillator for simultaneous cooling of the heat load and electricity harvesting was demonstrated for the first time. The novel prototype utilized the thermomagnetic response of $(\text{MnNiSi})_{0.7}(\text{Fe}_2\text{Ge})_{0.3}$ alloy to induce mechanical oscillations between the heat load and the heat sink. The mechanical oscillations generated electricity in the coils by Faraday's law of induction. A single thermomagnetic oscillator having 20 g of alloy generated an output voltage of upto 2 V/cycle, whereas the hybrid thermomagnetic oscillator generated upto 10 V/cycle due to the coupled oscillation of alloy and the permanent magnet. Cooling of heat load from 453 K to 383 K was achieved during each cycle.
7. The figure of merit, given by the product of energy per cycle and the frequency of oscillation was identified and evaluated using various alloys' properties for the hybrid thermomagnetic oscillator. The figure of merit combined the material properties and device parameters giving a flexibility to optimize both features for

maximum efficiency. The analysis showed that the alloys exhibiting high ΔS_M between the heat load and the heat sink temperatures and low temperature hysteresis has the maximum figure of merit. Among the alloys studied, $(\text{MnNiSi})_{0.7}(\text{Fe}_2\text{Ge})_{0.3}$ and $\text{Mn}_{0.93}\text{Co}_{1.07}\text{Ge}$ displayed a figure of merit of 4.2 Js^{-1} for a heat load and a heat sink temperature of 463 K and 295 K, respectively.

8. The alloy with the maximum figure of merit, i.e., $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ was selected to study the effect of spacer material on the performance of thermomagnetic oscillator. It was observed that the flexible spacer enhanced the voltage output by 18% and the oscillation frequency by 32% compared to the rigid spacer.

7.2 Future work

The possible future work are categorized based on the magnetocaloric properties of MnNiSi based alloys and device parameters of the thermomagnetic oscillator to enhance the performance.

7.2.1 MnNiSi based alloys

- MnNiSi based alloys exhibit a martensitic transition from a low temperature, orthorhombic structure to a high temperature, hexagonal structure. The understanding of the mechanism of such a rapid transition requires a deeper insight into the occupancy of atoms. Particularly, in the $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ alloy, the transition between the magnetic states takes place within 5 K temperature interval. The exact occupancy of Fe and Ge in the MnNiSi lattice requires further crystallographic study to interpret how the crystal structure transition affects the magnetic moments in the alloy during the transition. Advanced characterization techniques such as neutron diffraction, electron holography and synchrotron studies can provide insights into other crystallographic and magnetic details underlying in the atomic arrangements.
- Since the grain boundaries play a very vital role in the structural and magnetic transition, the study of MCE properties on single crystal MnNiSi based alloys can provide better understanding of the dependence of properties on grain size. The

synthesis of single crystals of MnNiSi based alloys can be accomplished by Czochralski process, Bridgeman technique, optical floating zone method, etc. The MCE properties of rare-earth based manganite single crystals such as $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [1], TbMnO_3 [2], HoMn_2O_5 [3] have been studied extensively. The MCE was larger in single crystalline rather than polycrystalline manganites. Single crystals of the Heusler alloy Ni_2MnGa exhibiting an inverse magnetocaloric transition has also been studied [4]. Hence, there is a wide scope of improving the MCE properties and reduction of hysteresis for $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ and $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ alloys to make it more efficient for practical applications.

- Most of the Mn based magnetocaloric materials also exhibit magnetoresistive, magnetostrictive and ferroelectric properties. The main focus of this thesis was the magnetocaloric properties of MnNiSi based alloys. However, due to the structural transformation and the variation in the lattice parameters in $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ during transformation, it is expected to possess magnetostrictive properties. The magnetostriction effect has been previously observed in MnCoSi [5] and NiMnSn [6] alloys having similar half-Heusler structure as MnNiSi. Magnetoresistive properties are also explored in some of the Heusler alloys such as $\text{Co}_2(\text{Mn,Fe})\text{Si}$ [7] and NiMnSb [8]. The multiferroic properties of MnNiSi based alloys have not been studied till date. Hence, an extensive investigation of other essential multiferroic properties can open a wide range of applications for MnNiSi based alloys.

7.2.2 Thermomagnetic oscillator

- The hybrid thermomagnetic for simultaneous cooling and energy harvesting was demonstrated in the present work. The frequency of the oscillator depends on the heating and cooling rate of the TMA. The higher mass of the TMA gives higher voltage output but increases the time for reaching the T_C due to volume reducing the frequency. In order to increase the frequency, multiplexing of the TMO would be beneficial. Multiplexing would consist of multiple TMO units connected in series to each other and the overall frequency would be multiplied according to the number of units. **Fig. 7.1** shows the setup of multiplexed TMO. The heat load is distributed throughout the multiplexed unit covering a larger area of the heat load.

The cooling performance would increase due the larger contact area between the TMA units and the heat load surface.

Fig. 7.1 Schematic of the multiplexed TMO units connected in series with distributed heat load.

- The voltage output of the TMO depends on the TMA properties, i.e., mass and magnetic susceptibility. Increasing the mass of the TMA would require a stronger magnet to generate sufficient upward pull force to overcome gravitational force. In the present work, 20 g of $(\text{MnNiSi})_{0.7}(\text{Fe}_2\text{Ge})_{0.3}$ alloy was selected to balance the magnetic pull force to overcome gravity in the ferromagnetic state of the TMA. Due to the restriction in the magnetic field strength (maximum of 1.4 T for NdFeB), an optimized mass must be selected by balancing the upward magnetic force and the gravitational force for an alloy. Scale up of the device can be achieved using higher magnetic field strength by Halbach arrays [9] or stacking of permanent magnets [10]. A large number of magnets can also be used in a multiplexed setup (**Fig. 7.1**). However, these magnets require careful handling and specific fixtures to prevent damage to the setup or the handling personnel.
- The increasing demand for technologies in the field of waste heat recovery provides a promising future for the thermomagnetic oscillator. Since the TMO utilizes waste heat and requires minimal maintenance, it possesses enormous potential. For example, cooling of heat exchangers usually require faster dissipation of heat for their effective operation, the excess heat slows down the system and may cause

damage to the equipment if the temperature exceeds the safe operating range. Hence, the multiplexed TMO unit can be installed at the excess heat region for regulating the temperature to a safe range, additionally generating electricity using waste heat. A large area of the heat load can be cooled effectively using multiplexed TMO system with array of magnets (**Fig. 7.2**). Due to the simple operating principle and easy maintenance of the TMO, the geometry and device parameters can be adjusted according to the application.

Fig. 7.2 Schematic of the potential application of the TMO for cooling the heat exchanger and generating electricity from the excess heat.

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7.3 Publications and conferences

The following articles were published as a part of this thesis:

1. **K. Deepak**, M. S. Pattanaik and R. V. Ramanujan, "Figure of merit and improved performance of a hybrid thermomagnetic oscillator", *Applied Energy* 256, 113917 (2019).
2. **K. Deepak**, V. B. Varma, G. Prasanna and R. V. Ramanujan, "Hybrid Thermomagnetic Oscillator for Cooling and Direct Waste Heat Conversion to Electricity", *Applied Energy* 233-234, 312-320 (2019).
3. **K. Deepak** and R. V. Ramanujan, "Magnetocaloric Properties of Low-Cost Fe and Sn Substituted MnNiSi-Based Alloys Exhibiting a Magnetostructural Transition Near Room Temperature", *IEEE Transactions on Magnetics* 54 (11), 2500805 (1-5) (2018).
4. **K. Deepak** and R. V. Ramanujan, "Near room temperature giant magnetocaloric effect in $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ alloys", *Journal of Alloys and Compounds* 743, 494-505 (2018).

The work was presented at the following conferences/invited talks:

1. "MnNiSi based magnetocaloric alloys for cooling and energy harvesting applications", **K. Deepak** and R. V. Ramanujan, Invited talk, *Leibniz Institute for solid state and materials research (IFW)*, Dresden, Germany, November 2019.
2. "Hybrid Thermomagnetic Oscillator for Simultaneous Cooling and Electricity Harvesting Using Waste Heat", **K. Deepak**, V.B. Varma and R.V. Ramanujan, *10th International Conference on Materials for Advanced Technologies (ICMAT)*, Singapore, June 2019, Oral presentation.
3. "Magnetocaloric properties of $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ and $(\text{Mn}_{0.45}\text{Fe}_{0.55})\text{Ni}(\text{Si}_{1-y}\text{Sn}_y)$ alloys", **K. Deepak** and R. V. Ramanujan, *Joint MMM-INTERMAG 2019 Conference*, Washington D.C. (USA), January 2019, Oral presentation.
4. "Hybrid Thermomagnetic Oscillator for cooling and energy harvesting", **K. Deepak**, V B. Varma and R. V. Ramanujan, *IEEE Magnetics Symposium*, NTU (Singapore), October 2018, Oral presentation, **Chair's special award**
5. "Giant Magnetocaloric effect in $(\text{MnNiSi})_{1-x}(\text{Fe}_2\text{Ge})_x$ alloys near room temperature", **K. Deepak** and R. V. Ramanujan, *Asia-Pacific Conference for Energy Storage and*

Conversion 2018, Singapore, July 2018, Oral presentation

6. “MnNiSi based magnetocaloric materials”, **K. Deepak** and R. V. Ramanujan, *IEEE Summer School*, Universidad San Francisco de Quito, Ecuador, June 2018, poster presentation.
7. “Near room temperature magnetocaloric effect in Fe₂Ge and Fe-Sn substituted MnNiSi”, **K. Deepak** and R. V. Ramanujan, *The IEEE International Magnetic Conference (INTERMAG)*, Singapore, April 2018, Oral presentation
8. “Giant Magnetocaloric effect near room temperature in (MnNiSi)_{1-x}(Fe₂Ge)_x”, **K. Deepak** and R. V. Ramanujan, *IEEE Magnetics Symposium*, NTU (Singapore), October 2017, Oral presentation