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**NANYANG
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SINGAPORE

**IRON-BASED LOW-COST MAGNETOCALORIC MATERIALS
FOR NEAR ROOM TEMPERATURE MAGNETIC COOLING**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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VINAY KUMAR SHARMA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

2018

Statement of Originality

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

25-12-2018

A handwritten signature in blue ink, appearing to read 'Vinay', with a horizontal line drawn through the middle of the name.

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Date

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Vinay Kumar Sharma

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

25-12-2018

Raju V. Ramanujan

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Date

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Raju V. Ramanujan

Authorship Attribution Statement

This thesis contains material from the following journal paper published in the following peer-reviewed journals where I was the first author.

1. Magnetocaloric Properties and Magnetic Cooling Performance of Low-cost $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ Alloys, *MRS Communications* (2018) pp 1-7, doi:10.1557/mrc.2018.122
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- Prof R. V. Ramanujan provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Varun Chaudhary
- Sample synthesis, structural and magnetic property characterizations were performed by me at the Facility for Analysis, Characterization, Testing and Simulation and at the PPMS facility under SHARE program, CREATE. I conducted the data evaluation and thermodynamic modelling.

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- Prof R. V. Ramanujan provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I performed all the materials synthesis, collected X-ray diffraction patterns and magnetic measurements and conducted data evaluation.
- Dr. D.M. Repaka helped in Critical behavior analysis and magnetic measurements at PPMS facility in SHARE program, CREATE.
- Dr. Varun Chaudhary helped in refinement of the X-ray diffraction data.
- Scanning electron microscopy was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
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- Dr. Shashwat Shukla interpreted the EXAFS data and revised the manuscript.
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- Dr. H. Parmar performed the transmission electron microscopy at the Facility for Analysis, Characterization, Testing and Simulation.
- S. Pattanaik helped in performing the 2D Comsol modelling

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Abstract

Magnetic cooling relies on magnetocaloric materials (MCM). It is an emerging energy efficient, “green” thermal management technology which has the potential to replace conventional gas-compressor based cooling systems. Current research on MCM aims at developing low-cost, environmentally friendly materials which can be manufactured by simple processes and exhibit superior magnetocaloric effect (MCE) near room temperature. Many materials have been developed over the years which exhibit high MCE, however they suffer from disadvantages such as high cost of rare earth (RE) elements, low corrosion and oxidation resistance, tedious synthesis routes, strategic limitations etc. Hence, good performance and readily available MCM with high corrosion resistance and established manufacturing technology are urgently needed for cooling applications near room temperature.

In this thesis, the magnetocaloric properties of $(\text{Fe}, \text{Cr})_3\text{Al}$ and $(\text{Fe}, \text{Mn})_3\text{Al}$ alloys have been systematically explored with detailed investigation of their structure, magnetic and magnetocaloric properties. Binary Fe_3Al alloys exhibit a high Curie temperature (T_c), which is not suitable for near room temperature magnetic cooling. Addition of antiferromagnetic elements (Mn and Cr) and application of external hydrostatic pressure can be used to tune the MCE properties of Fe_3Al alloys by modifying the transition temperature, saturation magnetization and relative cooling power. Subsequently, magnetic fluids of $(\text{Fe}, \text{Cr})_3\text{Al}$ based alloys were also prepared and their magnetic cooling performance was demonstrated.

$\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ bulk alloys, prepared by arc melting, were found to exhibit high values of relative cooling power (RCP), which is an important figure-of-merit for a good MCM. $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ alloys exhibited RCP values of 395 Jkg^{-1} and 430 Jkg^{-1} at an applied field of 5 T, respectively and T_c values of 290 K and 250 K, respectively. Scaling analysis and local exponent analysis were performed on the thermodynamic data of these samples to study the nature of relevant phase transitions. We investigated the influence of annealing and external pressure on the structure, magnetic and MCE properties of $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ alloys. The T_c of $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ ribbons was tuned in a wide range, at an

annealing temperature of 1000 °C and optimum annealing durations, yielding technologically attractive values of T_c in the range of 277 K to 290 K. Optimal annealing conditions increased the MCE properties. Increasing hydrostatic pressure from 0 kbar to up to 11.5 kbar resulted in T_c and saturation magnetization (M_s) decreasing at a rate of $dT_c/dP \sim 1.8$ K/kbar and $dM_s/dP \sim 0.8$ emu/g/kbar. A magneto-structural transition was not observed in Fe_2MnAl alloys even at applied pressure up to 11.5 kbar.

The effect of Cr alloying on the MCE properties of Fe_3Al bulk alloys was explored. The T_c was tuned to near room temperature values. These samples exhibited RCP/US\$ values ~ 15 times higher than $Gd_2Si_2Ge_2$ alloys and ~ 24 times higher than the RCP/US\$ values of the “benchmark”, Gd. Synthesis routes can change the structure of these alloys, which is reflected in their magnetic and MCE properties. A notable enhancement of 54% in RCP and 33% in isothermal magnetic entropy change ($-\Delta S_m$) was observed for $Fe_{54}Cr_{21}Al_{25}$ ribbons compared to the bulk counterpart. This enhancement was attributed to a change in structural order and microstructure due to high cooling rates during melt spinning. The critical behavior of $Fe_{54}Cr_{21}Al_{25}$ ribbons conformed to a short-range order 3D Heisenberg model, with the values of critical exponents: $\beta = 0.345$, $\gamma = 1.316$ and $\delta = 4.63$. Fe-Cr-Al buttons were milled at high speeds for short durations and found to exhibit an unusual cyclic change in structural order. A thermodynamic reaction rate model was developed to calculate deduce the stored energy during high energy milling. An enhancement of 50 % in the M_s and 23 % in the RCP was observed in the Fe-Cr-Al samples milled for only 15 min.

Magnetic fluids of $Fe_{75-x}Cr_xAl_{25}$ nanoparticles were prepared by surfactant-assisted ball milling. These fluids were used to demonstrate magnetic cooling in a thermomagnetic cooling device (TMCD). Cooling was evaluated by optimizing several parameters such as Cr content, volume concentration and heat load. A maximum cooling of 5.4 °C was achieved at a heat load of 4 W, volume concentration of 0.8% and applied field of 0.3T for $Fe_{50}Cr_{25}Al_{25}$ magnetic fluids. The self-regulating and self-pumping nature of the TMCD was evident. These results were in good agreement with the modelling results.

Lay Summary

Nearly half of the total electricity consumption in a typical household in Singapore is consumed by refrigerators and air conditioners. These cooling systems may use chemical refrigerants which are harmful for the environment as they cause ozone depletion and increase global warming. Therefore, there is an urgent need for the development of alternative thermal management technology. Magnetic cooling is one such alternative cooling technology which relies on the MCE. The MCE is observed when a material gets heated up or cooled down due to the application or removal of a magnetic field. This temperature difference can be used to develop a thermal management system. To develop a magnetic cooling system, ready availability and superior MCE properties are major attributes of a magnetocaloric material. To exhibit high MCE, a material should display high magnetic entropy change and large values of relative cooling power. We developed Fe₃Al based magnetocaloric materials which were found to exhibit good magnetocaloric properties near room temperature.

Fe_{75-x}Mn_xAl₂₅ arc melted buttons displayed high values of relative cooling power with the values of Curie temperature near room temperature. Structural inhomogeneity was confirmed by theoretical modelling of the thermodynamic data using scaling laws and local exponent analysis. Annealing of Fe-Mn-Al melt-spun ribbons at 1000°C for suitable duration enhanced MCE properties as well as tuned T_c in a wide range. Hydrostatic pressure was found to tune the T_c and magnetic properties of Fe_{75-x}Mn_xAl₂₅ ribbon samples.

Analysis of the MCE data of Fe_{75-x}Cr_xAl₂₅ bulk alloys revealed high values of RCP/US\$. The RCP/US\$ of Fe₅₆Cr₁₉Al₂₅ buttons was found to be ~15 times higher than that of Gd₂Si₂Ge₂ alloys and ~24 times higher than that of Gd. Melt-spun Fe_{75-x}Cr_xAl₂₅ ribbons exhibited 33% higher magnetic entropy change and 25 % higher RCP values compared to bulk samples. To determine the nature of the relevant phase transition, the Curie temperature and the MCE behavior in ribbon samples, a critical exponent analysis was carried out. The effect of short duration ball milling on the structure and MCE properties of Fe-Cr-Al alloys was investigated. An unusual cyclic structural ordering with milling

time was observed which was explored further using a reaction rate model. An enhancement of 50 % in saturation magnetization and 22 % in RCP was observed upon 15 min of milling. These results showed that processing methods such as melt spinning and high energy ball milling can effectively improve the MCE properties of Fe-Cr-Al alloys.

To demonstrate magnetic cooling, magnetic fluids of Fe-Cr-Al powders were prepared by surfactant-assisted ball milling. A self-pumping and self-regulating thermomagnetic cooling device was developed. Cooling (ΔT) by 5.4°C was obtained for an initial temperature of 125 °C, an applied field of 0.3 T and 4 W input heat load. The results showed that Fe-Cr-Al based magnetic fluids may be suitable for low-grade waste heat recovery.

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Abbreviations

Acronym	Expansion
AM	Arc melt
BCC	Body Centered Cubic
EDS	Energy Dispersive X-ray Spectroscopy
EXAFS	Extended X-ray Absorption Fine Spectrum
FCC	Face Centered Cubic
FOPT	First Order Phase Transition
FM	Ferro Magnetic
FWHM	Full Width at Half Maximum
H	Applied Magnetic Field
H_c	Coercivity
HBM	High Energy Ball Milled
HEA	High Entropy Alloys
HRTEM	High Resolution Transmission Electron Microscopy
K-F	Kouvel Fisher
MCE	Magneto Caloric Effect
MCM	Magneto Caloric Material
MF	Magnetic Fluid
M_s	Saturation magnetization
PM	Para Magnetic
PPMS	Physical Property Measurement System

RC	Refrigeration capacity
RCP	Relative cooling power
RE	Rare-earth Element
ΔS_m	Magnetic Entropy Change
SAD	Selected Area Electron Diffraction
SEI	Secondary Electron Images
SEM	Scanning Electron Microscopy
SOPT	Second Order Phase Transition
T	Temperature
T_c	Curie Temperature
TMCD	Thermo-Magnetic Cooling Device
VSM	Vibrating Sample Magnetometer
XRD	X-ray Diffraction

Chapter 1

Introduction

The world is struggling with climate change. Hence, researchers around the world are focusing on developing alternative energy sources, reducing energy consumption and mitigating global warming. One way to become less dependent on non-renewable energy sources is to reduce existing energy consumption by developing new technologies. Magnetic cooling is an energy efficient, environmentally friendly technology which relies on the magnetocaloric effect. 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 objectives, organization and significant findings of this research work.

1.1 Overview

Data from the National Climate Change Secretariat and the National Research Foundation (Singapore) states that out of the total energy consumption in a building, approximately half is due to the use of air conditioners and refrigerators [1]. The scenario is similar in other parts of the world. In the United States of America, vehicle air conditioners use nearly 7 to 10 billion gallons of gasoline every year. It is expected that China will surpass the USA and become the world's largest user of electricity for air conditioning by 2020 [2]. Conventional vapor compressor-based cooling systems can cause damage to the earth's atmosphere by releasing harmful ozone-depleting gases like chloro-fluoro carbons (CFCs), resulting in an increase in global warming potential (GWP). With greater economic development, more cooling systems are expected in the future, accompanied by an increase in the consumption of refrigerants [3]. Magnetic cooling is advantageous because it is environmentally friendly and an energy efficient alternative to conventional cooling technology [4].

1.2 Motivation

There is an urgent need to explore sustainable and efficient forms of energy to reduce environmental impact and energy consumption. In many cities, a high fraction of total energy is consumed by air conditioners and refrigerators. For Singapore, the National Environment Agency (NEA) data of the weighted energy consumption profile across all housing types, revealed that ~54% electricity consumption was from air-conditioners and refrigerators (figure 1.1 (a)) [5]. In 2011, according to the Energy Information Administration in the USA, 30 % of total electricity consumption was due to air conditioners and refrigerators [6]. Air conditioners and refrigerators may use various harmful and hazardous chemicals, e.g., chlorofluorocarbon (CFC), hydrofluorocarbon (HFC), hydro chlorofluorocarbon (HCFC) etc., which can contribute to ozone depletion and hence increase global warming. Air conditioners and refrigerants alone comprise ~ 30 % of the various sources contributing to ozone depletion (figure 1.1 (b)) [7]. Nearly 40 % of the total CO₂ emissions each year occur from residential and commercial buildings and ~ 5% of this CO₂ emission is contributed from air conditioners [8].

Figure 1.1 Pie chart showing the distribution of (a) weighted energy consumption profile across a household [5] and (b) Distribution of ozone-depleting agents[7].

Realizing the negative environmental impact of current thermal management technology, researchers around the world are exploring alternative environmentally friendly, “green”, sustainable cooling technologies. One such alternative is magnetic cooling which relies on the magnetocaloric effect (MCE). The magnetic cooling is being extensively researched as it offers various advantages compared to gas-compressor cooling systems. MCE based cooling systems are environmentally friendly since no ozone-depleting gases are used in their operation. These systems are safe as there is no leakage of hazardous gases or fluids. The best commercial refrigerators can reach only upto 40% ideal Carnot efficiency however, as demonstrated by BASF and Haier, the MCE based cooling systems can be 35% more energy efficient than conventional systems [9]. Magnetic cooling systems do not include a bulky compressor, are compact, display low noise levels (less than 35 dB), less vibration and low maintenance cost [10]. Realizing the high potential of magnetic cooling, many corporations have shown interest in developing commercial products e.g., a

commercial wine cooler was showcased at the Las Vegas Consumer Electronics Show (CES2015). The wine cooler developed by Astronautics Corporation of America, BASF and Haier was designed to attain a temperature of 8°C to 12°C in a room temperature environment [11].

The number of publications on the MCE and magnetic cooling exhibited rapid growth in the last few decades showing that the exploration of new magnetocaloric materials (MCM) has gained significant momentum. According to the ISI Web of Science, less than 20 articles based on “magnetocaloric AND magnetic refrigeration” Boolean search were published in the year 2000, ~100 in the year 2008 and more than 250 in the year 2017. Figure 1.2 (A and B) shows the number of publications during a time-span of last 20 years obtained from the ISI Web of Science database accessed on 10th December 2018. Figure 1.2 (C) shows the number of patents published on “magnetocaloric AND magnetic cooling” Boolean search in a span of last 20 years.

Figure 1.2 (A and B) Number of research articles published in a year with the web search string “Magnetocaloric”, accessed from ISI Web of Science database (www.webofknowledge.com/). (C) Number of patents published in a year searched in Patentscope database (<https://www.wipo.int/patentscope/en/>) with web search string “Magnetocaloric AND Magnetic cooling”.

1.3 Problem statement

The performance of a magnetic cooling system depends on the choice of MCM. An ideal MCM should possess superior performance metrics like a high isothermal change in

magnetic entropy (ΔS_m), high adiabatic change in temperature (ΔT_{ad}), wide working temperature span, high relative cooling power (RCP), negligible hysteresis losses, inexpensive processing, corrosion resistance and ready availability. Although considerable success has been achieved in developing MCM with superior properties, no material possesses all the desired characteristics. Gadolinium (Gd) is often considered to be the benchmark MCM due to its excellent magnetocaloric properties and useful transition temperature of ~ 290 K, which makes it suitable for various room temperature cooling applications [12]. However, the high cost of pure Gd and geopolitical limitations are still big hurdles to commercialize of magnetic cooling systems using Gd and related alloys. Various materials with first order phase transition exhibit “giant” magnetocaloric response but are limited by hysteresis loss and a narrow working temperature span [13]. To resolve such problems, intensive research is needed to develop novel MCM with good ΔS_m , large working temperature span and appropriate T_c near room temperature. Table 1.1 addresses various issues in existing MCM and potential solutions using Fe_3Al based MCM.

Table 1.1 Issues in current MCM and solutions.

Issues in current MCM		Fe_3Al -based materials as a solution
1.	RE based MCM are expensive	Inexpensive, since the rare earth (RE) element is not used
2.	Geographical limitations e.g. Gd	Contains earth-abundant elements, ready Availability
3.	High hysteresis losses e.g. Gd-Si-Ge[13]	Negligible hysteresis
4.	Lower mechanical stability e.g. La-Fe-Si	High mechanical stability [14]
5	Narrow operating temperature range due to FOPT	The broad operating temperature range in Fe-Al alloys due to SOPT
6.	Low values of RCP with less control to tune the Curie temperature (T_c)	High values of RCP with tunable Curie temperatures
7.	Presence of toxic elements e.g., As in $MnFe(P_{1-x}As_x)$ alloys	No toxic elements

8.	Lower thermal conductivity	High thermal conductivity [15]
9.	Lower corrosion resistance e.g., Gd	Fe-Al alloys are corrosion resistant [14]

1.4 Hypothesis

For the selection of a suitable magnetocaloric material, ready availability, low-cost and superior magnetocaloric parameters are of utmost importance. Among earth-abundant materials, iron is an obvious choice owing to its widespread distribution and extremely well-established technology of extraction and use. Iron is a transition metal with high Curie temperature (1044 K) [16]. It exhibits ferromagnetism at room temperature. Fe-Al based intermetallics possess high magnetization and are soft magnetic, which is desirable in an MCM. The Fe rich region of the Fe-Al phase diagram is interesting as the magnetic properties are sensitive to the crystal structure. Fe₃Al composition possesses D0₃ crystal structure with a rather high T_c of ~ 710 K which is higher than room temperature T_c [17]. The Bethe Slater curve depicts the dependence of exchange energy and interatomic distance. It can be used to predict the antiferromagnetic behavior of Cr and Mn [18]. Hence, we hypothesize that adding Cr and Mn atoms to the Fe₃Al would reduce exchange interactions, lowering T_c to near room temperature.

The shape of the magnetization versus temperature (M-T) curve is important to achieve high ΔS and RCP. A sharp transition from the paramagnetic to ferromagnetic state (PM→FM) in the M-T curve will give sharper dM/dT . Hence high ΔS will be obtained but δT_{FWHM} values will be lower. The second hypothesis was that processing techniques such as melt spinning, ball milling etc. can be used to tune the magnetic transition (FM→PM) and improve the MCE values. Hydrostatic pressure is an external parameter which can modify local environment, exchange coupling and magnetic properties. Hence magnetocaloric properties can be tuned by this method [19]. We hypothesize that external hydrostatic pressure can be used to tune the magnetic and MCE properties of (Fe, Mn)₃Al alloys. Finally, due to their high thermal conductivity and sufficient magnetization, Fe₃Al

based alloys can be used to prepare magnetic fluids and demonstrate ferrofluid based magnetic cooling.

1.5 Novelty

Detailed studies of the structure and magnetic properties of iron aluminum (Fe_3Al) alloys have been performed over the years [17, 20]. However, the magnetocaloric properties of these alloys have not yet been reported. For the first time, we report the structure, magnetic and MCE properties of Fe_3Al alloys with Cr and Mn alloying addition for near room temperature applications. The novelty of this work is summarized in Table 1.2. The magnetocaloric properties of crystalline $(\text{Fe,Cr})_3\text{Al}$ and $(\text{Fe,Mn})_3\text{Al}$ bulk alloys have been reported for the first time. Processing techniques like melt spinning can significantly improve magnetic properties [21]. Appreciable enhancement in entropy change and RCP values was observed in $\text{Fe}_{3-x}\text{Cr}_x\text{Al}$ melt-spun ribbons. Ball milling is also a valuable technique to synthesize MCE materials. There are many reports on the effect of ball milling duration and speed on the magnetic and MCE properties of various alloys [22, 23], but there are no reports on the effect of short duration milling time (~ 15 min.) on structural order, magnetic and magnetocaloric properties of $\text{Fe}_{3-x}\text{Cr}_x\text{Al}$ alloys. External hydrostatic pressure can effectively tune magnetic properties [24]. For the first time, the effect of hydrostatic pressure on the magnetic and MCE properties of $\text{Fe}_{3-x}\text{Mn}_x\text{Al}$ alloys was studied. Synthesis of metal-based ferrofluids is challenging [25]. For the first time, we synthesized ferrofluids of $\text{Fe}_{3-x}\text{Cr}_x\text{Al}$ alloys with reasonable stability; a proof of concept magnetic cooling system using this magnetic fluid was demonstrated.

Table 1.2 Novelty of the thesis.

Work	Previous reports	Novelty	Summary
$\text{Fe}_{3-x}\text{Cr}_x\text{Al}$ bulk alloy series	No reports on MCE in this alloy	√	Composition effect studied. T_c tuned in a wide range. RCP/\$ analysis.
$\text{Fe}_{3-x}\text{Cr}_x\text{Al}$ bulk and ribbon	No reports of comparison of MCE in this material	√	Structural transition observed. Enhanced MCE. Critical analysis.
Short duration milling: effect on structural, magnetic and MCE properties	No work on short duration milling and its effect on structure and MCE	√	Unusual cyclic behavior in structural order Reaction rate model used RCP enhancement
$\text{Fe}_{3-x}\text{Mn}_x\text{Al}$ bulk alloy series	No reports on MCE on this material	√	High RCP values obtained Universal scaling analysis Near RT T_c values
Hydrostatic pressure effect on $\text{Fe}_{3-x}\text{Mn}_x\text{Al}$	No reports of pressure studies on $\text{Fe}_{3-x}\text{Mn}_x\text{Al}$	√	External pressure up to 11.5 kbar applied Fine tuning of T_c Low M_s and MCE
Annealing time effect on MCE of $\text{Fe}_{3-x}\text{Mn}_x\text{Al}$	No reports of annealing assisted enhancement of MCE in this material	√	Enhancement in MCE values Wide T_c range. Attractive $T_c \sim 273\text{ K}$.
Magnetic cooling using $\text{Fe}_{3-x}\text{Cr}_x\text{Al}$ magnetic fluids	No reports of Fe-Cr-Al fluid synthesis and its use in magnetic cooling prototype	√	Fairly stable alloy-based ferrofluid Optimized performance Max $\Delta T = 5.4^\circ\text{C}$

1.6 Significance

Magnetic cooling is an environmentally friendly and economical thermal management technology which mainly relies on suitable MCM. Challenges in commercialization of this technology include cost and ready availability of the magnetocaloric material. Hence, the materials studied in this thesis are rare-earth free, readily available and magnetically soft with negligible hysteresis losses, which make them suitable for near room temperature cooling applications. Fe and Al are easily available elements with well-established manufacturing techniques which makes them easy to process and inexpensive.

1.7 Objectives and workflow

One of the aims of this research is to develop Fe-based magnetocaloric materials with a focus on near room temperature cooling. The high abundance of Fe and Al may help to reduce the cost of resulting MCM. The main emphasis would be tuning the T_c of the material while retaining enough magnetization and low hysteresis. The effect of processing techniques, chemical composition, annealing treatment and external pressure on the magnetocaloric properties were investigated. Specific tasks include:

- 1) Selection of Fe_3Al as the base composition and synthesis of $(\text{Fe},\text{X})_3\text{Al}$ bulk alloys, $\text{X} = \text{Cr}$ or Mn .
- 2) Study of composition effects: Effect of Mn or Cr alloying on the crystal structure and magnetic properties.
- 3) Tune the Curie temperature (T_c) of the alloy over a wide range. Tuning T_c to near room temperature values.
- 4) Effect of processing techniques, i.e., arc melting, melt spinning and ball milling on the structural, magnetic and MCE properties.
- 5) Effect of heat treatment and external pressure on the structure and magnetic properties.
- 6) Characterization of the structure, morphology and magnetic properties using x-ray diffraction, scanning and transmission electron microscopy and the physical properties measurement system (PPMS) equipped with VSM head and a hydrostatic pressure cell.

- 7) Modelling of the phase transitions and MCE using critical behavior analysis, universal scaling hypothesis and local exponent determination.
- 8) Studying the magnetocaloric properties of the material by determining ΔS_m , RCP etc.
- 9) To synthesize alloy-based ferrofluids and develop a magnetic cooling prototype.

1.8 Organization of thesis

This PhD thesis is organized in 7 chapters as follows:

- ❖ **Chapter 1** provides an introduction. It provides a brief overview, including problem statement, motivation, significance, novelty, objectives and workflow. The hypothesis and significant findings are also outlined.
- ❖ **Chapter 2** is a literature review of the magnetocaloric effect. A brief history of the use of MCE for magnetic cooling is presented. Fundamentals of MCE and methods to determine the MCE parameters are discussed. An overview of various MCM with Curie temperature near room temperature is presented, followed by a tabulated comparison of various Fe based, rare earth free, MCM. Modelling to evaluate the nature of the phase transition and MCE properties in Fe based MCM is also discussed. Finally, magnetic fluid based thermomagnetic cooling is elucidated.
- ❖ **Chapter 3** describes the experimental methodologies used for synthesis, structural characterization and magnetic property evaluation. The working principle of various experimental techniques and the design of the prototype are also included.
- ❖ **Chapter 4** contains the experimental results of Fe-Mn-Al alloys. The structure, magnetic and MCE properties of Fe-Mn-Al alloys were explored. The effect of heat treatment and external hydrostatic pressure on the structural and magnetic properties of these alloys was also investigated.
- ❖ **Chapter 5** describes the structure and MCE properties of Fe-Cr-Al alloys. The effect of Cr alloying on the Curie temperature and magnetocaloric properties is elucidated. A cost analysis (RCP/\$) is also discussed. Enhancement of MCE properties in melt-spun ribbons is discussed. The results of critical behavior analysis are also

elucidated. The effect of ball milling of bulk Fe-Cr-Al alloys on the structure, magnetic and magnetocaloric behavior is described. A reaction rate model is discussed to calculate the stored energies during high energy ball milling.

❖ **Chapter 6** describes Fe-Cr-Al based ferrofluid synthesis achieved by surfactant-assisted ball milling. Subsequently, it discusses the experimental and simulation results of the magnetic cooling performance.

❖ **Chapter 7** presents the summary and future work.

Figure 1.3 Organization of research work.

1.9 Significant findings

This research work has produced the following significant findings:

1. A promising enhancement of 33 % in magnetic entropy change and 25 % in the RCP value, resulting from high structural disorder, was obtained in $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ melt-spun ribbons [26]. The critical exponents obtained from an analysis of the magnetic phase transitions were close to the exponents obtained theoretically from the 3D-Heisenberg model. These results indicated that good magnetocaloric properties,

ease of availability of the constituent elements, established manufacturing techniques, low-cost, soft ferromagnetic nature, good corrosion resistance and good thermal conductivity make $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ ribbons suitable for near room temperature thermal management.

2. An interesting unusual cyclic behavior of structural order was observed in milled $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ alloys. The reaction rate model was used to study the cyclic behavior and the stored energy was calculated. Contrary to the common belief that ball milling leads to lower magnetization, we obtained enhancement in saturation magnetization after short duration ball milling. Significant enhancement of 50 % and 23 % in saturation magnetization and relative cooling power, respectively, compared to the bulk counterpart was observed. Short duration high energy ball milling can enhance magnetic and magnetocaloric properties of these alloys for magnetic cooling applications.

3. It is challenging to obtain larger working temperature span (δT_{FWHM}) and thus higher relative cooling power. We investigated the MCE properties of low-cost $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ alloys which exhibited high relative cooling power and Curie temperature near room temperature, making such alloys technologically attractive.

4. Annealing of Fe-Mn-Al ribbons provided a large window of useful Curie temperatures, e.g., yielding some very interesting values such as 277 K, 282 K and 290 K. ΔS_m and RCP values were also good, i.e. $1.2 \text{ J kg}^{-1} \text{ K}^{-1}$ and 425 J kg^{-1} , respectively.

5. T_c could be tuned at a rate of $dT/dP \sim 1.4 \text{ K/kbar}$ in $(\text{Fe}_{0.747}\text{Mn}_{0.253})_3\text{Al}$ ribbons at an applied pressure of upto 11.5 kbar.

6. We studied the MCE properties of $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($19 \leq x \leq 25$) bulk alloys and performed a cost analysis. The RCP/\$ of our alloys was found to be ~ 15 times higher than that of $\text{Gd}_2\text{Si}_2\text{Ge}_2$ and ~ 24 times higher than the RCP/\$ of Gd, which is considered a benchmark MCM.

7. Surfactant-assisted high energy ball milling was used to synthesize the magnetic fluids of $\text{Fe}_{50}\text{Cr}_{25}\text{Al}_{25}$ nanoparticles. A magnetic fluid with reasonable stability was obtained which was used in a thermomagnetic device to demonstrate magnetic cooling. Maximum cooling (ΔT) of 5.4°C was observed for $\text{Fe}_{50}\text{Cr}_{25}\text{Al}_{25}$ magnetic fluids with an initial load of 125°C , showing good prospects for waste grade heat recovery.

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Chapter 2

Literature Review

The MCE is the thermal response (heating or cooling) of a magnetic material under the influence of a time varying magnetic field. Interest in MCE has multiplied over the years due to its considerable potential to replace conventional vacuum compressor-based cooling technology. This chapter is structured accordingly, describing the history, major breakthroughs, thermodynamics of MCE, comparison between different types of magnetocaloric materials and MCE prototypes. First, we discuss the historical background of MCE, followed by theoretical considerations and measurement techniques. Subsequently, we discuss different types of MCE materials, focusing on rare earth free materials. A discussion of Fe-Al based alloys as a potential low-cost magnetocaloric material is included. A discussion of modelling methods relevant to MCE is also presented. Lastly, thermomagnetic cooling using magnetic fluids will be discussed.

2.1 Historical aspects of the MCE

The first studies of the MCE were performed by Emil Warburg in 1881. These experiments showed irreversible heating in iron due to magnetic hysteresis [1]. In 1905, Langevin reported a reversible change in temperature with change in magnetization [2]. The 1917 report of Weiss and Piccard established the physical principles governing the MCE, they coined the term ‘magnetocalorique’ in French [3]. Debye (1926) and Giauque (1927) independently proposed cooling via adiabatic demagnetization as an application of MCE [4, 5]. Giauque received the Nobel Prize in chemistry for this remarkable work in 1949.

The first experimental demonstration of magnetic refrigerator was made by Giauque and MacDougall in 1933 by demagnetization of gadolinium sulphate at cryogenic temperatures [6]. The studies on exploring MCE around room temperature began in the late 1960’s. In 1976, Brown showed that magnetic cooling could be used near room temperature by utilizing the ferromagnetic-paramagnetic phase transition in gadolinium [7]. Two major breakthroughs, in the year 1997 and 2001, boosted interest of researchers in this field. In 1997, Pecharsky and Gschneidner discovered a giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ with remarkable magnetocaloric response at room temperature [8]. In 2001, the Astronautics Corporation, USA made the world’s first successful room temperature magnetic refrigerator by replacing superconducting magnets with permanent magnets [9]. These breakthroughs were steps towards the commercialization of magnetic refrigerators. Table 2.1 shows the significant historical milestones in the magnetocaloric effect.

Table 2.1. Landmarks in the study of the magnetocaloric effect.

S.No.	Research group	Significant findings	Year	Ref.
1	Warburg	Irreversible heating in iron due to magnetic hysteresis	1881	[1]
2	Langevin	Change in magnetization causes a reversible temperature change.	1905	[2]
3	Weiss and Piccard	Coined the term ‘magnetocalorique’	1917	[3]
4	Debye and Giaque et al. Independent research	Demagnetization under adiabatic conditions; Application of MCE	1926 and 1927	[4, 5]
5	Giauque and MacDougall	Demonstration of magnetic cooling for cryogenic applications	1933	[6]
6	Brown et al	Magnetic refrigeration used for ambient temperature applications	1976	[7]
7	Pecharsky and Gschneidner	Giant MCE in $Gd_5(Si_2Ge_2)$	1997	[8]
8	Zimm et al. Astronautics Corporation, USA	World’s first successful room temperature magnetic refrigerator employing permanent magnets	2001	[9]

2.2 Understanding the magnetocaloric effect (MCE)

2.2.1 MCE cycle

A cooling system is made by manipulating the entropy of the system. The entropy is dependent on temperature and parameters which can be used to absorb or release heat. In the case of conventional refrigerator, the external parameter is pressure whereas for magnetic refrigerators, the external parameter is magnetic field. Conventional cooling systems are based on changing the pressure on a working material to alter the entropy. As a result, heat is absorbed or released. On the other hand, magnetic refrigerators make use

of magnetocaloric materials as working bodies and magnetization/demagnetization processes instead of the compression/expansion process found in conventional refrigerators.

Magnetic cooling is based on the magnetocaloric effect (MCE). MCE is an intrinsic property of a magnetic material, it is displayed as a thermal response (increase or decrease in temperature) when the degrees of freedom of the magnetic sublattice of a material is altered by a time varying magnetic field [10]. It can be quantified by considering a system of spins, which is either ferromagnetic or paramagnetic, near the magnetic ordering temperature. The total entropy of such a system is a combination of lattice entropy and magnetic entropy. By applying the magnetic field adiabatically (adiabatic magnetization), the magnetic moments align and magnetic entropy decreases. To keep the total entropy of the system constant, the lattice entropy should increase. Increase in lattice entropy implies an increase in temperature of the system. A heat transfer medium can be used to extract the heat. Removal of magnetic field under adiabatic conditions (adiabatic demagnetization), will lead to the cooling of the system. A schematic description of magnetic cooling is shown in figure 2.1.

Figure 2.1 Schematic of a magnetic cooling cycle.

2.2.2 Thermodynamics of MCE

Entropy is a measure of randomness (disorder) in a system. The temperature directly influences the entropy of a system. When the temperature is increased, the thermal energy of electrons increases and as a result entropy also increases. The total entropy (S_t) of a magnetic material is the sum of lattice entropy (S_r) (due to lattice vibrations), magnetic entropy (S_m) (due to spin disorder) and the entropy of conduction electrons (S_e) [11].

At constant pressure, the total entropy can be represented as,

$$S_t(H, T) = S_r(T) + S_m(H, T) + S_e(T) \quad (2.1)$$

The lattice and electronic entropies are dependent on temperature (T) only, whereas the magnetic entropy is dependent on both the external magnetic field (H) and temperature (T). When a magnetic field is applied under adiabatic conditions ($dQ = 0$), the magnetic moment align in the same direction as the field and become ordered i.e., magnetic entropy is reduced. The lattice entropy increases to keep the total entropy of the system constant. This increase in lattice entropy causes a temperature (ΔT_{ad}) rise. Upon removal of the magnetic field, the magnetic spins randomize, increasing the magnetic entropy and thereby, decreasing lattice entropy, which leads to lower temperature. If a magnetic field is applied under isothermal conditions ($dT = 0$), the lattice entropy remains constant, whereas the magnetic entropy decreases, hence the total entropy of the system decreases.

To explain the thermodynamics of MCE, the following thermodynamic functions are required : internal energy U , Gibbs free energy G , free energy F , entropy S , absolute temperature T , pressure p and specific heat C [12]. The internal energy of a magnetic system can be represented as a function of volume V , entropy S and magnetic field H or magnetic moment M .

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

The corresponding total differential form of equation (2.2) can be written as,

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

The free energy F can be expressed in terms of thermodynamic parameters in the following form,

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

In total differential form,

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

The Gibbs free energy can be expressed in terms of T , p and H under constant pressure p ,

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

In total differential form,

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

Using the equation of state (EOS) we obtain the following equations:

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

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

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

When the magnetic moment M is chosen as an external variable,

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

Using the pair of equations (2.8) and (2.11), (2.8) and (2.9), (2.8) and (2.10), the Maxwell's relations can be obtained as follows,

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

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

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

The entropy S of a magnetic material is a function of H and T at constant pressure. The total entropy in differential form can be written as,

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

Under isothermal conditions and applied field change from $H=0$ to H (H_i to H_f), equation (2.12) can be written in integral form as,

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

Equation (2.16) is used to understand the behavior of MCE and to search new MCM. For a material to possess large MCE, the value of $\frac{\partial M}{\partial T}$ should be large.

To obtain a simplified equation for practical purposes, numerical integration of eqn. 2.16 for the case of isothermal magnetization condition yields:

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

Equation 2.17 is easy to use and yields the value of MCE from the experimental isothermal magnetization versus magnetic field curves.

2.2.3. Quantification of MCE

For quantification of the magnetocaloric effect, the most important parameters are the isothermal change in entropy (ΔS_m), relative cooling power (RCP) and adiabatic change in temperature (ΔT_{ad}) [12]. For second order phase transition materials, ΔS_m is used for MCE calculations and is given numerically by equation 2.17, which directly correlates to the rate of change in magnetization with temperature (dM/dT) and applied magnetic field (ΔH). The higher the value of dM/dT , the greater will be the isothermal change in entropy, resulting in larger MCE value. Relative cooling power (RCP) is another figure of merit to quantify magnetocaloric materials. It can be defined as the amount of heat transferred between the hot end and the cold end in a typical cooling cycle. It can be expressed

mathematically as the product of magnitude of the maximum magnetic entropy change and the temperature difference at full width of half maximum (*fwhm*) i.e., $RCP = |\Delta S_m| \times \delta T_{fwhm}$ [13]. For practical applications the RCP of a magnetocaloric material should be as high as possible. This implies that δT_{fwhm} i.e., the width of the entropy change curve is also an important parameter to compare various MCM.

2.2.4. Measurement of MCE

There are different strategies to measure the magnetocaloric effect. These can be divided into direct and indirect measurement methods.

2.2.4.1 Direct methods

The direct measurement of MCE involves the determination of ΔT_{ad} of the sample under an applied magnetic field, using a thermocouple configuration. This is a straightforward measurement technique wherein a magnetic material is put in contact with a temperature sensor. As the magnetic field is applied, the temperature change will be recorded. The accuracy of the direct measurements depend on the accuracy of the thermocouple, quality of thermal isolation of the sample, noise etc.[11]. Over the years, many developments have taken place in direct measurement of MCE using different strategies, e.g., measurement in varying magnetic field using pulsed-magnetic fields or differential thermocouples, and measurement in static field by superconducting solenoids. Direct MCE measurements are beneficial, specially, for the materials which exhibit large values of MCE, e.g., giant magnetocaloric effect (GMCE) materials, as well as materials exhibiting first order phase transitions (FOPT) or coupled magneto-structural transitions.

2.2.4.2 Indirect methods

Indirect measurement includes measurement of the MCE by determining magnetic properties or by determining specific heat. Measurements by determining the magnetic properties include measurement of field and temperature dependent magnetization curves. This leads to the determination of ΔS_M using the following:

$$\Delta S_M = \mu_0 \int_0^{H_m} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (2.18)$$

This method is quick and favored for samples with small mass. Another advantage of calculating the ΔS_M for MCE measurements is that it can be achieved easily using a magnetometer, whereas other methods for MCE measurements require specialized instruments.

Determination of MCE using specific heat is considered as the most accurate method. The entropy of a material is related to specific heat as follows,

$$S(T, H) = \int_0^T \frac{C_p(H)}{T} dT \quad (2.19)$$

2.2.5. Applications of MCE and industrial interests

MCE has emerged as a technology of immense interest and finds applications in various areas (figure 2.2). The applications mainly depend on the transition temperature of the magnetocaloric material (MCM). The most explored areas for MCE applications are room temperature cooling and air-conditioning systems. From a materials perspective, Gd is a benchmark MCM due to its T_c near room temperature (294 K) and good MCE properties [14]. The first laboratory scale prototype operating at room temperature, using Gd as the MCM, was demonstrated by Brown [7]. Many prototypes have since been reported for near room temperature cooling. In 2002, Chubu Electric and Toshiba Corp. demonstrated a magnetic refrigerator operating at 25°C with a refrigeration capacity of 100 W and a Carnot efficiency of ~53 % [15]. Cooltech Applications (France) in the year 2005, reported a magnetic refrigerator composed of Nd-Fe-B magnets, Gd plates and a heat exchanger fluid, working close to room temperature with a cooling capacity between 100 W to 360 W [16]. Besides refrigeration and air conditioning applications, various heat pumps based on the MCE have also been reported. Kirol and Dacus developed a rotating type heat pump providing a maximum cooling of 11 K [17].

In the low temperature regime, MCE has been used to attain cooling to ultra-low temperatures. Barclay *et al* developed a prototype working in temperatures ranging from 20 K to 4 K. They used DyPO₄ single crystals and attained cooling power of upto 1 W [18]. Zimm *et al* in 1995 demonstrated an active magnetic regenerator, using ErNi alloy, 3 T

magnetic field and He gas as the heat exchanger resulting in cooling of a 1.6 W heat load at 3.5 K [19]. Matsumoto *et al* proposed MCE based hydrogen liquefaction at 20 K which could cool down and extract hydrogen from natural gas [20]. Kishore *et al* investigated MCE application in harnessing low-grade waste heat [21]. MCE can be also be used in hyperthermia treatment and drug delivery. Li *et al* investigated the MCE in $\text{Mn}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ based nanocarriers for drug delivery triggered by hyperthermia [22].

Figure 2.2. Applications of the magnetocaloric effect.

2.3. A brief comparison of cooling technologies

Vacuum compressor-based refrigeration is the most commonly used commercial technology. In this section, a brief comparison of alternate thermal management technologies is presented. Thermoelectric cooling has been commercialized in various markets like automotive power supply, electronic gadget cooling, Peltier coolers, thermoelectric generators etc. Thermoelectric cooling possesses advantages such as

environmental friendliness, long lifetime, flexible design, large cooling density etc. [23], but suffers from drawbacks like low efficiency and comparatively higher cost compared to gas-compressor technology. Among thermoelectric materials, Bi_2Te_3 based bulk alloys are most commonly used as refrigerants. Researchers claim that thermoelectric cooling has scope to enter commercial household refrigeration if a breakthrough in thermoelectric materials is achieved in the near future. Elastocaloric cooling is a relatively new technology which manifests as the change in latent heat upon stress induced phase transformation in shape memory alloys [24]. It is still in its nascent stages with the possibility of reaching a theoretical maximum Carnot efficiency of $\sim 50\%$ upon maximum strain applied to Ni-Ti-Cu-V shape memory alloys [25]. Alternate cooling technologies, including magnetocaloric, elastocaloric and thermoelectrics are ecologically compatible and green, they do not use global warming potential (GWP) refrigerants like CFCs, HCFCs etc.

Table 2.2. Selected cooling technologies in terms of material, efficiency, cost, environmental impact and market status.

Technology	Coolant	Cost	Environmental impact	Status	Ref.
Gas compressor	CFC, HCFC	Low	Harmful	Well established	[26]
Thermoelectric	Bi-Sb-Te	Moderate	Friendly	Commercial	[23]
Elastocaloric	Ni-Fe-Ga	Moderate	Friendly	Lab stage	[24]
Magnetocaloric	MCM	Moderate	Friendly	Prototype stage	[27]

2.4 Magnetocaloric materials with near room temperature Curie temperature

Magnetocaloric materials (MCM) can be broadly classified into various categories based on the nature of the phase transitions, i.e., first order phase transition (FOPT) or second order phase transition (SOPT), type of rare earth element (e.g. Gd or La.), crystallinity

(amorphous or crystalline), transition temperature value, and morphology (bulk, powder, thin films and multilayers). The following section discusses the MCE properties of materials with transition temperature near room temperature, which is desirable for many applications like wine coolers, household refrigeration, cold storage etc. Gadolinium (Gd) is a rare earth element exhibiting SOPT, with Curie temperature near room temperature (294 K) [14]. Gd is a benchmark material for lab-scale cooling prototypes due to its suitable T_c , negligible hysteresis and high ΔS . However, high cost, poor corrosion and oxidation resistance and strategic limitations make Gd unsuitable for practical applications. The discovery of the giant magnetocaloric response in $Gd_2Si_2Ge_2$ by Pecharsky and Gschneidner accelerated research interest in MCM. This alloy showed a high ΔS of $12 \text{ J kg}^{-1} \text{ K}^{-1}$ at an applied field of 1T, as a result of a coupled magneto-structural transition at 272 K. Many attempts have been made to tune the MCE values as well as the T_c of $Gd_2Si_2Ge_2$ based alloys by varying the ratio of Si and Ge [28]. Despite having high MCE and desirable value of T_c , thermal hysteresis ($\sim 10 \text{ K}$) is rather high in $Gd_2Si_2Ge_2$ based alloys. Tseng and co-workers have used hydrostatic pressure to tune the MCE in $Gd_5(Si_{0.375}Ge_{0.625})_4$ alloys and explored the relationship between Si content, applied pressure and volume change [29].

$(Mn,Fe)_2P$ based alloys also exhibit interesting MCE properties because of their first order phase transitions, as reported by Tegus *et al* in 2002 [30]. Although a high ΔS value of $13 \text{ J kg}^{-1} \text{ K}^{-1}$ at an applied field of 1T and T_c of 303 K was found in $MnFeP_{0.45}As_{0.55}$, the presence of As makes this compound less feasible for practical applications due to toxicity issues. Addition of Si, instead of As, lowers the cost and eliminates toxicity issues but hysteresis as high as 75 K was observed [31]. Subsequent research shows that addition of boron was useful to some extent in reducing hysteresis from $\sim 75 \text{ K}$ to $\sim 2.5 \text{ K}$, but the material showed cracking and fatigue over multiple cycles of heating and cooling [32]. Mn-Fe-P-Si-B based melt-spun ribbons are considered to be one of the feasible choices for MCE based practical systems, as this was used by BASF, Haier and Astronautics Corporation of America for their wine cooler [33].

Another interesting material class showing near room transition temperatures are Heusler alloys with a general formula X_2YZ , where X and Y are transition metals and Z is an

element from the IIIA-VA group. Heusler alloys exhibit a first order martensitic transformations from an austenite phase to a martensite phase, resulting in high values of magnetic entropy change (ΔS) [34, 35]. Khovaylo *et al* reported a T_c of 281 K and an inverse magnetic entropy change of $-13.8 \text{ Jkg}^{-1}\text{K}^{-1}$ at 2T field in Ni-Mn-Co-Sn alloys, although this was accompanied by a large hysteresis of 16.5 K [36]. The same research group reported higher MCE response in Heusler type $\text{Ni}_{53.3}\text{Mn}_{20.1}\text{Ga}_{26.6}$ alloys, as a result of a first order magnetostructural transition at 320 K, with a magnetic entropy change of $27.6 \text{ Jkg}^{-1}\text{K}^{-1}$ at 1.2T and $\sim 5 \text{ K}$ thermal hysteresis. The difference in ΔT_{ad} upon heating and cooling cycles is quite significant in Heusler alloys, reducing their overall usefulness for practical applications.

Lanthanum based MCE materials ($\text{LaFe}_{13-x}\text{M}_x$) which crystallize in a NaZn_{13} type structure, have also emerged as potentially useful MCM. Depending upon the content of M, which is usually Si or Al, a ferromagnetic transition can be obtained from 200 K to 250 K along with high MCE values. For values of $x > 1.8$ in $\text{LaFe}_{13-x}\text{Si}_x$, the first order transition is replaced by a second order transition, whereas for $x < 1.6$, a strong itinerant electron metamagnetic (IEM) transition is observed, as indicated by “S” shaped Arrott plots [37]. Hu *et al* observed high values of MCE, which they attributed to contraction in the lattice, leading to a metamagnetic transition [38]. Insertion of hydrides was a beneficial strategy implemented by Lyubina *et al*, to achieve near room temperature transitions and preserving high magnetic entropy change [38]. La-based compounds are advantageous in terms of cost and scalability of production, but poor corrosion resistance needs to be addressed to make them usable in practical cooling devices.

Manganites are another class of MCM with general formula $\text{R}_{1-x}\text{M}_x\text{MnO}_3$ (R = rare earth element), which offer advantages like high chemical stability, scalable production capabilities and low-cost precursors, but the MCE response is not very high owing to the second order magnetic transition [39]. Tlili *et al*. reported a near room temperature MCE response in $\text{La}_{0.7}(\text{Sr}, \text{Ba})_{0.3}\text{MnO}_3$ with RCP of 286 Jkg^{-1} at 5 T. $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ is an exceptional manganite which exhibits a FOPT, yielding a high magnetic entropy change of $6.9 \text{ Jkg}^{-1}\text{K}^{-1}$ at 2T, accompanied by a thermal hysteresis of 5K [40].

High entropy alloys (HEA) are an emerging class of magnetocaloric materials which offer advantages like high mechanical strength, resistance to wear and tear, good corrosion resistance and tunable magnetic properties [41]. Perrin *et al* reported the magnetocaloric properties of FeCoNiCuMn high entropy alloys with a technologically attractive Curie temperature of 300 K [42]. In conclusion, considerable research has been done to explore the MCM with Curie temperature values near room temperature. Since every class of materials has some disadvantages, the search for better MCM continues.

Table 2.3. Magnetocaloric materials with Curie temperature (T_c) near room temperature. The MCE parameters are magnetic entropy change (ΔS), adiabatic temperature change (ΔT_{ad}), relative cooling power (RCP), thermal hysteresis ($H_{ys.}$)

Class of MCMs	Author	Material	T_c (K)	MCE Parameters	Ref
Gd-based	Pecharsky <i>et al.</i>	Gd ₂ Si ₂ Ge ₂	272	$\Delta S = 12 \text{ Jkg}^{-1}\text{K}^{-1}$ (1T) $H_{ys.} = 10 \text{ K}$	[43]
	Lyubina <i>et al.</i>	Gd (polycrystalline, pure)	294	$\Delta S = 5.2 \text{ Jkg}^{-1}\text{K}^{-1}$ (2T)	[14]
	Gschneidner <i>et al.</i>	Gd ₅ Si ₄	326	$\Delta T_{ad} = 7 \text{ K}$ (5T)	[44]
(Mn,Fe)₂P based	Tegus <i>et al.</i>	MnFeP _{0.45} As _{0.55}	303	$\Delta S = 13 \text{ Jkg}^{-1}\text{K}^{-1}$ (1T)	[30]
	Thanh <i>et al.</i>	MnFeP _{0.55} Si _{0.3} Ge _{0.15}	292	$\Delta S = 6 \text{ Jkg}^{-1}\text{K}^{-1}$ (2T)	[45]
	Bruck <i>et al.</i>	Mn _{1.25} Fe _{0.7} P _{0.5} Si _{0.5}	274	$\Delta S = 9 \text{ Jkg}^{-1}\text{K}^{-1}$ (1T) $H_{ys.} = 75 \text{ K}$	[31]
	Bruck <i>et al.</i>	MnFe _{0.95} P _{0.582} Si _{0.34} B _{0.078}	289	$\Delta S = 9 \text{ Jkg}^{-1}\text{K}^{-1}$ (1T) $H_{ys.} = 2.5 \text{ K}$	[32]
	Khovaylo <i>et al.</i>	Ni ₅₀ Mn ₃₆ Co ₁ Sn ₁₃	281	$\Delta S = -13.8 \text{ Jkg}^{-1}\text{K}^{-1}$ (2T)	[36]

Heusler based (FOPT)				$H_{ys.} = 16.5 \text{ K}$	
	Basso <i>et al.</i>	$\text{Ni}_{53.3}\text{Mn}_{20.1}\text{Ga}_{26.6}$	320	$\Delta S = 27.6 \text{ Jkg}^{-1}\text{K}^{-1} (1.2\text{T})$ $H_{ys.} = 5.2 \text{ K}$	[46]
	Krenke <i>et al.</i>	$\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$	295	$\Delta S = -18 \text{ Jkg}^{-1}\text{K}^{-1} (5\text{T})$	[47]
	Barman <i>et al.</i>	$\text{Ni}_{50.2}\text{Mn}_{36.7}\text{Sb}_{11.9}\text{Al}_{1.2}$	345	$\Delta S = 11.8 \text{ Jkg}^{-1}\text{K}^{-1} (2\text{T})$ $\text{RCP} = 126 \text{ Jkg}^{-1}$	[48]
La-based	Rosendahl <i>et al.</i>	$\text{LaFe}_{11.14}\text{Co}_{0.76}\text{Si}_{1.1}$	267	$\Delta S = 7.2 \text{ Jkg}^{-1}\text{K}^{-1} (1\text{T})$	[49]
	Lyubina <i>et al.</i>	$\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.6}$	333	$\Delta S = 21 \text{ Jkg}^{-1}\text{K}^{-1} (5\text{T})$	[50]
	Barcza <i>et al.</i>	$\text{LaFe}_{11.35}\text{Mn}_{0.39}\text{Si}_{1.26}\text{H}_{1.5}$ 3	295	$\Delta S = 12 \text{ Jkg}^{-1}\text{K}^{-1} (1.6\text{T})$	[51]
Manganite based	Jerbi <i>et al.</i>	$\text{Pr}_{0.5}\text{Na}_{0.05}\text{Sr}_{0.45}\text{MnO}_3$	270	$\Delta S = 1.6 \text{ Jkg}^{-1}\text{K}^{-1} (5\text{T})$ $\text{RCP} = 266 \text{ Jkg}^{-1}$	[52]
	Radaelli <i>et al.</i>	$\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$	268	$\Delta S = 6.9 \text{ Jkg}^{-1}\text{K}^{-1} (2\text{T})$ $H_{ys.} = 5\text{K}$	[40]
	Tlili <i>et al.</i>	$\text{La}_{0.7}(\text{Sr, Ba})_{0.3}\text{MnO}_3$	322	$\Delta S = 2.75 \text{ Jkg}^{-1}\text{K}^{-1} (5\text{T})$ $\text{RCP} = 286 \text{ Jkg}^{-1}$	[53]
Order-order transitions (FOPT)	Nikitin <i>et al.</i>	FeRh	315	$\Delta S = -12.5 \text{ Jkg}^{-1}\text{K}^{-1} (1\text{T})$ $H_{ys.} = 10 \text{ K}$	[54]
Fe-based	Law <i>et al.</i>	$\text{Fe}_{75}\text{B}_{12}\text{Cr}_8\text{Ce}_5$	295	$\Delta S = 1.1 \text{ Jkg}^{-1}\text{K}^{-1} (1.8\text{T})$	[55]
	Min <i>et al.</i>	$\text{Fe}_{84}\text{Nb}_7\text{B}_9$	299	$\Delta S = 1.44 \text{ Jkg}^{-1}\text{K}^{-1} (1.5\text{T})$	[56]

(SOPT)					
	Sharma <i>et al.</i>	(Fe _{0.72} Cr _{0.28}) ₃ Al	330	$\Delta S = 1.16 \text{ Jkg}^{-1}\text{K}^{-1}$ (5T) RCP = 305 Jkg ⁻¹	[57]
HEA	Lucas <i>et al.</i>	FeCoCr _x N	220	$\Delta S = 0.35 \text{ Jkg}^{-1}\text{K}^{-1}$ (2T) RCP = 43 Jkg ⁻¹ (1.5)	[58]
	Perrin <i>et al.</i>	FeCoNiCuMn	300	$\Delta S = 0.11 \text{ Jkg}^{-1}\text{K}^{-1}$ (0.55T) RCP = 36 Jkg ⁻¹ (1.5)	[42]

2.5. Iron-based, rare earth (RE) free, magnetocaloric materials

For a magnetic cooling system the cost of the magnetocaloric material is an important factor. Gadolinium, which is the benchmark material, is limited in terms of geographical availability, high cost etc. For other rare earth based MCM which exhibit high MCE response, similar problems of high cost and availability remain unsolved. Hence, many research groups have explored rare earth free, iron-based magnetocaloric materials. Flores *et al* explored the MCE properties of amorphous Fe_{88-2x}Co_xNi_xZr₇B₄Cu ribbons prepared by melt spinning, which exhibited a magnetic entropy change of 1.98 Jkg⁻¹K⁻¹ and RCP of 166 Jkg⁻¹ at 1.5 T. With addition of Co and Ni in Fe₈₈Zr₇B₄Cu, an increment of 40% in RCP compared to Gd₅Si₂Ge_{1.9}Fe_{0.1} alloy was obtained [59]. Waske *et al* investigated the magnetocaloric properties of amorphous Fe-B based alloys and systematically adjusted the T_c, to near RT values of 329 K and higher values such as 462 K, by adding Nb in Fe-B system [60]. Zhong *et al* reported high RCP values and tunable T_c in Fe₇₅Ta₅B₁₀Zr₉Cu₁ melt-spun ribbons [61]. Yang *et al* claimed extraordinary MCE values in Fe₈₀P₁₃C₇ alloys prepared by quenching technique obtaining entropy change of 2.2 Jkg⁻¹K⁻¹ and RCP of 126 Jkg⁻¹ at 1.5 T [62]. Apart from these amorphous Fe based alloys, several other research groups have investigated MCE properties in crystalline Fe based alloys and nanoparticles. Repaka *et al* explored the MCE properties of ball milled Fe_{100-x}Cu_x binary nanoparticles and emphasized their low-cost, high conductivity and superior mechanical properties [63].

Chaudhary *et al* investigated MCE properties of Fe-Ni based bulk alloys and nanoparticles and highlighted very high RCP values [64] [65].

Although Fe based RE free MCMs exhibit relatively low values of entropy change due to a SOPT, there are various other advantages associated with these systems. Due to their transition temperature distributions, the RCP values are usually higher than those of FOPT based MCM. These alloys are mechanically robust, low-cost, possess negligible hysteresis and low coercivity.

Table 2.4. List of iron-based rare earth free magnetocaloric materials. The MCE parameters, preparation method and major claims are listed.

Material	Preparation method	ΔS_m (Jkg ⁻¹ K ⁻¹)	RC (Jkg ⁻¹)	T _c (K)	Major claims	Ref.
Fe _{88-2x} Co _x Ni _x Zr ₇ B ₄ Cu	Melt spinning	1.98 (1.5T)	166 (1.5 T)	~525	<ul style="list-style-type: none"> • 40% high RCP w.r.t. Gd₅Si₂Ge_{1.9}Fe_{0.1} • Tunable T_c from 287 K to 626 K 	[59]
Fe ₈₈ B _{12-x} Nb _x (x=8, 9, 10) Fe _{86-x} B ₁₄ Nb _x (x=2, 4, 6, 8)	Melt spinning	1.75 (2T) 1.5 (2T)	-----	329 462	<ul style="list-style-type: none"> • systematic adjustment of T_c with doping in Fe-B ternary system 	[60]
Fe ₇₅ Ta ₅ B ₁₀ Zr ₉ Cu ₁	Melt spinning	2.03 (5T)	242 (5T)	313	High RC, tunable T _c for application from 310-410 K	[61]
Fe ₈₀ P ₁₃ C ₇	J-quenching, Single roller melt spinning	2.2 (1.5T)	126 (1.5T)	579	Extraordinary values of MCE	[62]
Fe ₈₄ Mn ₆ Zr ₁₀	Melt spinning	2.25 (5T)		220	More uniform entropy change	[66]

					Suitable for Ericson-cycle	
$(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Zr}_7\text{B}_4$	Ball milling	2.8 (5T)	330 (5T)	342	High RCP Promising for RT applications	[67]
$(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$	Arc melting	1.46 (5T)	641 (5T)	381	RCP larger than other bulk MCM	[68]
Fe_3ZnC_x	Direct elemental reaction	2.67 (5T)	385 (4.5T)	358	Large RCP, inexpensive raw materials	[69]
$\text{Fe}_{32}\text{Cu}_{68}$	Ball milling	0.86 (5T)	206 (5T)	298	Low-cost binary alloy, T_c at RT	[63]
$\text{Fe}_{70}\text{V}_{10}\text{B}_{12}\text{Si}_8$	Melt spinning	1.165 (2T)	113.5 (2T)	435.5	V tunes the MCE properties	[70]
$(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$	High energy ball milling	1.58 (5T)	548 (5T)	398	High RCP, low-cost	[64]
$(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$	High energy ball milling	0.6 (1.5T)	125 (1.5T)	340	High RCP, minimal hysteresis	[65]

2.6 Tuning the MCE properties

The magnetocaloric response of a material can be tuned in various ways like alloying, external pressure, applied magnetic field and processing techniques. In this section, we discuss these methods, highlighting the advantages and disadvantages of each method.

2.6.1 Alloying

The magnetic properties and transition temperature of an alloy or compound are strongly dependent on the composition. Kamilov *et al* explored the effect of Ag in LaMnO_3 manganites [71]. The Ag atoms occupied the A-type vacancies in the La sublattice. Depending on the Ag concentration, the MCE response and Curie temperature was tuned in the temperature range from 260 to 310 K. Campos *et al* studied the effect of Fe on the hysteresis and MCE response of MnAs-based materials [72]. Fe was chosen due to the similarities in behavior of Fe and Mn and their mutual solubility. The Fe atoms occupy the

Mn sites in MnAs, resulting in lower lattice parameter and cell volume. A large drop in saturation magnetization as well as MCE was observed in $\text{Mn}_{1-x}\text{Fe}_x\text{As}$ for $x > 0.0125$. Thermal hysteresis exhibited a linear behavior with increasing alloy content, increasing from 10 K to 28 K for $x = 0$ to 0.015 in $\text{Mn}_{1-x}\text{Fe}_x\text{As}$ alloys. Similarly, the addition of Ce and La in EuTiO_3 influences the antiferromagnetic to ferromagnetic ordering, thereby altering the magnetocaloric response [73].

2.6.2 Processing techniques

Many groups have explored the effect of synthesis and processing routes on the MCE. Khlifa *et al* studied the difference in MCE properties in $\text{Pr}_{0.8}\text{K}_{0.2}\text{MnO}_3$ alloys prepared by sol-gel routes and solid-state reaction and suggested that their physical properties strongly depend upon the synthesis routes [74]. The samples prepared by the sol-gel route exhibited larger ΔS_m and RCP compared to those prepared by the solid-state route. This enhancement was attributed to greater ferromagnetism on the surface of nanoparticles prepared by the sol-gel route. Many researchers have reported an enhancement in the MCE response of amorphous ribbons compared to their bulk counterparts. Yu *et al* reported a higher MCE in amorphous $\text{Gd}_{55}\text{Co}_{25}\text{Al}_{20}$ ribbons as a result of short-range order [75]. Processing methods also affect the structure, magnetic and MCE properties. Annealing is a common technique to stabilize the desired phase and tune the magnetic properties. In $\text{Mn}_{1+\delta}\text{As}_{1-x}\text{Sb}_x$ alloys, annealing at 800°C sharpened the magnetic transition and increased the magnetocaloric response [76].

2.6.3 External pressure

External pressure can be used to modify the interatomic distance, exchange interactions and structural parameters. Several studies have been performed to study the effect of hydrostatic pressure on the magnetic properties of materials, e.g., magnetovolume effect, volume stability, magnetocaloric effect etc. An interesting study by Caron *et al*, investigated the similarity between Cr content and hydrostatic pressure on the magnetocaloric effect in $\text{Mn}_{0.93}\text{Cr}_{0.07}\text{CoGe}$ alloys [77]. Both hydrostatic pressure as well as Cr content shifted the T_c towards lower temperatures and also exhibited a similar type of crystallographic coupling. Gaztanaga *et al* showed tuning of relative cooling power in LaNdCaMnO_3 compounds with increasing hydrostatic pressure and obtained table like

MCE, which is suitable for Ericsson like cycles [78]. Although, hydrostatic pressure can tune the Curie temperature in a desired range and the MCE response in a controlled manner, practical implementation of hydrostatic pressure in MCE device is still a challenge.

2.7 Fe-Al alloys: prospective MCMs

Iron is one of the most popular elements and is extensively used. Favorable characteristics of Fe include high abundance, easy processing and good mechanical properties, good magnetic properties, low-cost etc. However, Fe has some limitations as a MCM. Its Curie temperature (768° C) is too high to be used in MCE systems, it has a tendency to corrode etc. With the addition of other metals like Al, Cr, and Si, the mechanical properties of Fe can be improved and magneto-structural properties can also be varied [79]. Alloying with Al and Cr also provides corrosion resistance. FeAl alloys are well studied and exhibit low-cost, corrosion resistance, low density, excellent oxidation resistance, high tensile strength and soft magnetic properties [80-82]. The FeAl alloy system displays a change in magnetic properties when a change in the structure or composition of FeAl occurs [83]. These properties make Fe-Al an exciting system to study for magnetocaloric properties. It can undergo order-disorder transitions by small change in the FeAl composition ratio. Figure 2.4 shows that among the various phases present in FeAl alloys, the A2 phase is the disordered whereas B2 and D03 are ordered phases. The A2 phase possess a bcc structure (Im3m space group), Fe and Al atoms are randomly distributed at the crystallographic sites. The B2 is the stoichiometric CsCl type structure (Pm3m space group), Fe atoms occupy the corners and Al atoms occupy the center. The D03 structure is of the Fe₃Al type (Fm3m space group) and made up of four interpenetrating face centered cubic cells.

Figure 2.4 Crystal structures of Fe-Al alloys. Black balls represent Fe atoms, red balls represent Al atoms and green balls represent the Cr or Mn atoms [57].

Figure 2.5 Fe-Al phase diagram [84].

Fe_3Al ($\text{Fe}_{75}\text{Al}_{25}$) is the most exciting phase in this alloy system. Its magnetic properties closely depend on the extent of chemical order and the local atomic environment. From the phase diagram (figure 2.5) at the composition $\text{Fe}_{77}\text{Al}_{23}$, this alloy shows a tricritical point (T_{tc}) at which a second order magnetic transition changes to a first order transition. This T_{tc} is observed at a high temperature of 885K. Although the magnetization is quite high for $\text{Fe}_{75}\text{Al}_{25}$, the transition temperature is also high ($\sim 710\text{K}$), which is not suitable for room temperature MCE applications. Substitution of antiferromagnetic Cr or Mn in ferromagnetic Fe_3Al results in useful magnetic properties, i.e., room temperature ferromagnetism and soft ferromagnetic behavior [85]. Similar Curie temperature engineering was reported in high entropy alloys for MCE applications [86]. Depending on the processing conditions and composition the ordered D03 structure may transform to a L_{21} or B2 structure, by addition of Cr or Mn [87, 88]. The L_{21} structure of Heusler type Fe_2MAl ($\text{M} = \text{Mn}, \text{Cr}$) alloys is shown in figure 2.6 [89]. The A sites (blue balls) and B sites (yellow balls) are occupied by Fe atoms. These Fe atoms are different from each other

in their nearest neighboring atoms. Fe atoms at A sites are surrounded each by 4 Cr atoms (C sites, red balls) whereas Fe atoms at B sites are surrounded by 4 Al atoms (D sites) [90]. The order-disorder transitions, magnetic properties as well as Curie temperature in Fe_3Al alloys can be tuned by the addition of suitable 3d transition metals.

Figure 2.6 Crystal structure of $L2_1$ phase of $\text{Fe}_{50}\text{M}_{25}\text{Al}_{25}$ ($M = \text{Cr}, \text{Mn}$) alloys. Blue balls represent Fe atoms, red balls represent Cr or Mn atoms and green atoms represent Al atoms.

2.8 Modelling of the MCE

Approaches to model the MCE are introduced in this section.

2.8.1 First principles modelling

First principle calculations are usually used to study the magnetic and electronic properties of those magnetic materials which show coupled magneto-structural transitions [91]. The experimentally determined values of magnetic moments are used as input values for first principle calculations and subsequently used in thermodynamic models such as Bean

Rodbell model, Heisenberg model etc. to extract the MCE properties and transition temperature [92]. Detailed information about the material is required.

2.8.2 Thermodynamic modelling

In the thermodynamic models, macroscopic variables are used to describe a system. These variables are obtained by fitting the experimental results. We describe the thermodynamic modelling approach for SOPT materials. For SOPT materials, the thermodynamic models follow the Landau formalism and hence consider either the mean field interaction model or an equation of state (EOS) e.g., the Arrott-Noakes EOS [93, 94].

$$H^{\frac{1}{\gamma}} = a(T - T_c)M^{\frac{1}{\gamma}} + bM^{\frac{1}{\gamma} + \frac{1}{\beta}} \quad (2.20)$$

Where β and γ are critical exponents, T_c is the Curie temperature; a , b are the constants which are specific to the material. By using the Arrott-Noakes equation, the change in entropy can be calculated as

$$-\Delta S_M = \int_{M_s}^{M_{max}} \left[a\gamma M(a(T - T_c)) + bM^{\frac{1}{\beta}} \right]^{\gamma-1} dM \quad (2.21)$$

The behavior of a SOPT magnetic material which undergoes a phase transition from the paramagnetic to the ferromagnetic state can be characterized by a set of values called as critical exponents. If we can determine the critical exponents using methods such as the Kouvel-Fisher method [95], then, by fitting the magnetization data in the Arrott-Noakes equation of state the value of a and b can be calculated and the entropy curve can be determined. Figure 2.7 shows the experimental values of ΔS_M at a field change of 1.5T for Fe-Cr-B amorphous alloys, red crosses represent theoretical values.

Figure 2.7 MCE of Fe-Cr-B alloys for a field change of 1.5T. Red crosses represent experimental results while the blue curve is the theoretically predicted fit of the Arrott-Noakes equation [96].

Critical exponents near the transition temperature can help to determine the nature of the phase transitions, magnetocaloric properties and the nature of ordering in the material [97]. These critical exponents are γ , δ , β , and η , where γ corresponds to the inverse initial magnetic susceptibility, δ corresponds to the critical magnetization at T_c , β corresponds to the saturation magnetization and η corresponds to the field dependent change in entropy. The relationships are [97]:

$$M = DH^{\frac{1}{\delta}}, \varepsilon = 0, T = T_c \quad (2.22)$$

$$M_S(T) = M_o([-\theta])^\beta, \theta < 0, T < T_c \quad (2.23)$$

$$\chi_o^{-1}(T) = \left(\frac{h_o}{M_o}\right) \theta^\gamma, \theta > 0, T > T_c \quad (2.24)$$

where, $\theta = (T - T_c)/T_c$ is the reduced temperature, D and h_o/M_o are critical amplitudes.

The slope of the M^2 vs H/M curves (Arrott plots) around the transition temperature yields information about the order of the phase transitions [98]. Positive slopes correspond to second order phase transitions while negative slopes correspond to a first order magnetic phase transition.

These critical exponents can be used to evaluate the MCE using the following relationship [99],

$$\Delta S_m = \frac{-a\beta\gamma}{b^{\frac{\beta+\gamma}{\beta}}(2\beta+\gamma-1)} H^{\frac{\beta-1}{\beta+\gamma}+1} = AH^n \quad (2.25)$$

Where, a and b are constants, H is the magnetic field, β and γ are critical exponents, and n can be expressed as, $n = \frac{\beta-1}{\beta+\gamma} + 1$. Similarly, RCP can also be deduced using the critical exponents when the RCP is expressed in a power law form as,

$$RCP \propto H^{1+\frac{1}{\delta}} \quad (2.26)$$

Equation (2.25) and (2.26) show that MCE values can be deduced from the critical exponents even for high magnetic field strength values, which is rather difficult to achieve in some laboratories.

2.9 Thermomagnetic fluid

There have been rapid developments in the field of electronic and mechanical devices. Hence there is a demand for reliable thermal management systems to efficiently remove the waste heat from these devices. Removing waste heat during use increases service life and boosts efficiency. Various active and passive methods of heat transfer have been studied and implemented for cooling applications. Active methods suffer from limitations like mechanical vibration, noise, high maintenance requirement, and requirement for external energy input for their operation. On the other hand, passive cooling methods can operate with low or no energy input just by utilizing the thermo-responsive properties of the fluid to pump it through the channel. A magnetic nanofluid based heat pump can be a passive method of cooling.

A magnetic nanofluid, also known as a ferrofluid, is a colloidal suspension of magnetic nanoparticles, in subdomain range, in a suitable carrier fluid [100]. This unique class of fluid has the exceptional feature of being magnetic in nature apart from possessing fluidic properties. Hence the flow behavior can be tuned by applying external magnetic fields of different orientation and strength. Due to these unique features, ferrofluids have been extensively used in diverse areas such as biomedical engineering, thermal engineering, medical sciences, energy harvesting etc [101, 102]. One application is the use of a magnetofluidic pump for cooling [103-105].

The use of ferrofluids to transport heat using a combined magnetic field gradient and a temperature gradient is known as thermomagnetic convection. In thermomagnetic ferrofluidic pumps, the pressure gradient is created by the temperature dependent magnetization of the ferrofluid. When the differentially heated ferrofluid is subjected to an external magnetic field, it results in a non-uniform magnetic body force due to the temperature dependent magnetization [106]. These pumps autonomously regulate the thermomagnetic pumping capacity depending on the heat load temperature because of the occurrence of non-equilibrium state in the magnetization. Hence they are self-pumping in nature [107]. As there are no mechanical moving parts maintenance issues are minimized.

Utilizing a ferrofluid to remove waste heat by thermomagnetic convection has been studied [108]. Xuan and Lian designed an automatic energy transport device utilizing a rare earth permanent magnet and waste heat to pump the fluid and investigated the self-regulating nature by varying the heat load condition [104]. Goharkhah *et al* studied the effect of an alternating non-uniform magnetic field on the forced convective heat transfer process [109]. They showed an enhancement in the heat transfer by 13.9% with an increase in Reynolds number. Ganguly *et al.* [9] investigated the performance of a thermomagnetic pump for microfluidics by using a 2mm diameter glass capillary tube to drive the ferrite ferrofluid across the heat load region. They also examined the effect of head distance, input heat load power and field current variation on the discharge profile [110]. Sundar *et al* evaluated the effect of turbulent convective heat transfer on the heat transfer coefficient and obtained an enhancement of 30.96% at 0.6% Fe_3O_4 nanoparticle volume fraction [111]. Thermomagnetic convection is more efficient due to a notable enhancement in thermal conductivity of the ferrofluid under the influence of an external magnetic field [112]. Parekh *et al* observed an enhancement in thermal conductivity of almost 30% for a magnetite nanoparticle volume fraction of 4.7% by applying a transverse magnetic field [113]. Philip *et al* observed a dramatic 300% increase in thermal conductivity for a magnetite particle loading of 6.3 vol % and attributed the effect to the formation of chainlike structures within the nanofluid [112].

Most of the thermomagnetic pumping devices utilize ferrite based ferrofluids for cooling. The position and strength of the magnetic field, flow conditions and tube geometry have been varied to enhance the pumping performance. As the thermal conductivity of magnetic nanoparticles is an essential property, using highly thermal conductive metallic/alloy-based magnetic nanoparticles can enhance the cooling capacity by rapid heat transfer. However, due to the higher particle density of these nanoparticles compared to ferrite-based nanoparticles, the metallic nanoparticles do sediment over time. Therefore, it is difficult to get a stable colloidal dispersion. Chaudhary *et al* prepared alloy-based ferrofluids from ball milled Fe-Ni-Cr nanoparticles by coating them with oleic acid and ammonium hydroxide and then dispersing them in oleic acid. They investigated the cooling performance of this alloy-based ferrofluid by exposing it to a thermal gradient and magnetic field gradient inside a circular polymeric tube [64].

2.10 Summary

It can be summarized that the magnetocaloric effect is an extensively studied phenomenon in solid-state physics. Among different materials, exploration of MCE in rare earth free iron-based materials offers several advantages such as low-cost, high RCP values, large working temperature span, and superior mechanical and thermal properties. The MCE properties of such alloys can be effectively tuned by varying the composition, processing techniques and application of external pressure. Various modelling approaches can be used to study the nature of the phase transitions and predict the MCE behavior. The thermomagnetic convection is an efficient way to transfer heat and demonstrate cooling effect. It offers several advantages such as no requirement of external energy input and moving parts, self-regulating behavior, application over a broad temperature range depending on the T_c of ferrofluid etc.

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Chapter 3

Experimental methodology

This chapter describes the experimental methods and characterization techniques used for material synthesis and property evaluation. The experimental plan is discussed using a flow chart, followed by the methods of sample preparation using arc melting, melt spinning and high energy ball milling. Bulk, ribbon and powder samples were used in this thesis work. X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM), hydrostatic pressure cell (M-cell), extended x-ray absorption fine structure (EXAFS) and physical property measurement system (PPMS) were used to characterize the samples for their structure, morphology and magnetic properties. The working principle of these techniques is also discussed followed by the methodology of property evaluation.

3.1 Overview of experimental plan

A flow chart of the experimental work flow is provided below. It starts with material synthesis, characterization, analysis, subsequently leading to the development of a prototype. Samples were synthesized using three processing techniques, i.e., arc melting, melt spinning and ball milling. For homogenization, vacuum annealing was employed. The ball milling time and speed of milling were optimized. Nanoparticles were synthesized using surfactant-assisted ball milling. Structural characterization of the samples was performed by XRD and EXAFS techniques. The morphological characterization was performed by SEM and TEM techniques. For magnetic property evaluation, a physical property measurement system (PPMS) and pressure assembly (M-cell) were used. Further analysis was performed using various software tools and theoretical models e.g., Rietveld refinement, Athena, Diamond, ImageJ, reaction rate model, critical exponent analysis, scaling and power laws.

Figure 3.1. Flow chart of the experimental plan

3.2 Rationale for selection

Vacuum arc melting is usually the first step in alloy preparation. For bulk materials, arc melting is a standard technique. Pure elements in the desired ratio are melted under an electric arc produced by an electrode. Several elements can be simultaneously alloyed

using the arc. To avoid oxidation during melting, zirconia or tantalum foil can be used, which works as an oxygen scavenger. Melt spinning was also used to prepare ribbons. Melt spinning is a popular technique to produce rapidly solidified materials. The fast cooling rates can give rise to amorphous alloys with a homogenous microstructure. One advantage of using melt spinning for crystalline alloys is that undesirable phases may be minimized.

The cooling rate and solidification rate strongly influence the microstructure, resulting in changes in the mechanical, physical and magnetic properties. Mechanical alloying is a processing method to produce micron sized or nano sized powders for a variety of applications. High energy ball milling is an effective mechanical alloying technique to produce nanoparticles of multi-elemental compositions. The type of milling bowls and balls, ball to powder ratio, rotation speed and effective milling time are factors which influence the morphology, particle distribution and properties of the milled alloy. Ball milling can also produce materials with the desired phase, e.g., amorphous or quasi-crystalline or crystalline, depending on the processing parameters.

3.2.1 Bulk alloy synthesis

Alloy ingots with nominal compositions of $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($19 \leq x \leq 25$) and $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ ($12.5 \leq x \leq 25$) were prepared using an arc melter (Edmund Buhler, MAM-1) under Ar gas atmosphere in a water-cooled copper hearth. The elemental constituents were iron pieces (3.2-6.4mm, Aldrich, 99.99%), chromium chip (~1mm thick, Aldrich, 99.995%), manganese chip (< 1.5mm thick, Aldrich, 99%), and aluminum sheet (0.3mm thick, 30mm width, Emsure). Melting was performed several times to homogenize the samples. Argon gas was used to minimize oxidation of samples. To further homogenize the alloys, as-prepared buttons were treated in a vacuum furnace (Carbolite STF) at 1273 K for 24 h at a ramp rate of 5°C/min and were left to cool down slowly to room temperature. An Isomet 4000 cutting tool with a diamond cutter wheel operating at a speed of 3000 rpm, was used to slice the sample. Arc melting works on the principle of heating the material above its melting point with an electric arc [1]. An arc is developed between the electrode and material and the temperature can reach up to 3500 °C. The chamber was evacuated to a

vacuum better than 10^{-4} Pa, followed by Ar gas flushing up to 30 kPa. This step was repeated 3 times before starting the melting to ensure minimal oxidation.

3.2.2 Preparation of melt-spun ribbons

Melt spinning works on the principle of rapid quenching of the molten alloy on a spinning wheel. It produces ribbons of thickness $< 50 \mu\text{m}$, the length can range from a few mm to a few cm. Figure 3.2 shows the melt spinning equipment, the enlarged area shows the relevant melt spinning related equipment.

The arc melted buttons were used to make ribbons using melt spinning equipment (Edmund Buhler). A crucible made of boron nitride (Achema) was used with a 14 mm inner diameter and a slit nozzle of $10 \times 0.4 \text{ mm}$. $\text{Fe}_{75-x}\text{M}_x\text{Al}_{25}$ ($\text{M} = \text{Cr}, \text{Mn}$ and $20 < x < 25$) buttons ($\sim 5\text{g}$) were used for melt-spun treatment. Prior to the melt spinning, the wheel was polished with an emery paper of grade 220 and metal polish. The molten alloy was ejected under Ar gas flow, melt-spun ribbons were prepared over a polished copper wheel rotating at a velocity of 35 ms^{-1} and power ($P \sim 55\%$). The thickness of the melt-spun ribbons was $20\sim 30 \mu\text{m}$.

Figure 3.2. Melt spinning equipment (Edmund Buhler). Enlarged area, showing the details of the melt spinning equipment.

3.2.3 Milled powder samples

The melt-spun ribbons and arc melted buttons of $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($x=21$) were cut, cleaned and crushed to powder using a mortar and pestle, and used for ball milling in Ar atmosphere. Zirconia balls (125 ml) and a bowl (15 mm diameter) were used for high

energy ball milling (Fritsch Planetary Micro Mill P7). To initiate the reaction and avoid cold welding, a few drops of ethanol were added before sealing the bowl. Sealing and opening of the bowl was always performed in a glove box. Milling was performed at a powder to ball ratio of 1:10 and milling speeds, ranging from 500 to 700 rpm, and milling times ranging from 15 min to 600 min. To avoid excessive heating and cold welding at higher speeds, milling was paused for 20 min after every run of 10 min.

For nanoparticle and magnetic fluid synthesis, high energy ball milling assisted by surfactant addition was performed on $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($x = 19, 23$ and 25) buttons. The buttons were ground to powder in a mortar pestle and then loaded in the bowl with a powder to ball ratio of 1:10. Ball milling was performed at 600 rpm/min under argon gas atmosphere. After every 60 min, oleic acid (1-2 drops) was added to the bowl. The powder was mixed thoroughly from the walls and sealed. To avoid oxidation, the bowls were only opened and sealed inside the glove box. Subsequently, these surfactant coated powders were ball milled at 500 rpm for 10 h to synthesize the corresponding magnetic fluids using oleic as the carrier fluid.

Figure 3.3. High energy ball milling equipment (Fritsch P7). Enlarged area shows the top view of the zirconia bowl containing the powder and zirconia balls. The anticlockwise arrow shows the rotation direction of the bowl and the clockwise arrow shows the direction of movement of the balls.

3.3 Characterization techniques

3.3.1 X-ray diffraction

The crystal structure and phase determination were performed using X-ray diffraction (XRD) which is a non-destructive analytical technique. The atoms in a crystal are arranged in regular patterns, i.e., periodic arrays, which can diffract light. Since the wavelength of X-rays is of the order of distance between atomic planes, the scattering of X-rays from atomic planes produces a diffraction pattern which provides information about atomic arrangement in the crystal structure. In a diffractometer optics, X-rays coming from the source pass through a combination of a filter, divergence slit and soller slit before interacting with the sample. The diffracted rays from the sample then pass through the anti-scatter slit and the soller slit before reaching the detector. The machine then records the intensity of the diffracted rays as a graph of count/intensity against detector angle generating the XRD profile of the sample. At the sample, the x-rays get diffracted by the lattice structure of the sample. The Bruker D8 advance diffractometer uses a Bragg-Brentano geometry wherein θ is the incident angle and 2θ is the diffraction angle. If the tube is fixed and sample moves, it is called $\theta:2\theta$ geometry. If the tube moves and sample is fixed, then it is called $\theta:\theta$ geometry.

XRD is an extremely powerful tool to study qualitative as well as quantitative features of a crystalline material. XRD analysis provides important information like crystal structure, unit cell dimensions, amorphous content, crystal size, residual stress in the sample, texture etc. A Bruker D8 Advance diffractometer operating at 40 kV, 40 mA, Cu K_{α} radiation ($1.5418\text{\AA}$) as the x-ray source was used to obtain the XRD patterns. The scan range was $2\theta = 20^{\circ}$ to 100° , the step size was 0.01 and the scan speed was $1^{\circ}/\text{min}$. The bulk samples were cut into flat slices, polished and loaded on a bulk XRD sample holder. The melt-spun ribbons were cut into small pieces and glued on a glass slide using a double-sided tape. Silicon low background sample holders were used for low mass samples.

3.3.2 Scanning electron microscopy

An electron beam can generate a variety of signals when it interacts with a specimen (figure 3.4). These signals can be captured and analyzed by a SEM. Figure 3.4 shows that the

interaction depth for back scattered electrons (BSE) is more than that of the secondary electrons (SE), resulting in lower resolution (1 μm) in BSE mode images compared to the resolution ($\sim 10\text{ nm}$) in SE mode images. The signals arising from the continuous X-rays are useful in quantitative determination of the chemical composition and to prepare elemental maps using electron diffraction X-ray spectroscopy (EDS). EDS is a useful analytical technique to find out the elemental composition. It is a spectroscopy-based technique of investigating a sample through interaction between matter and electromagnetic radiations. Since, each element has a unique atomic structure and energy levels, hence the emitted X-rays are also characteristic of that element. In principle, all elements with atomic no. more than 4 (i.e., Be) can be detected using EDS. For qualitative information, different spectral lines are identified whereas intensities of these lines give quantitative information. For microstructural characterization, a field emission scanning electron microscope (FE-SEM 6340F) with a cold cathode field emission electron gun, operating at 5 kV and 12 μA was used. The compositional analysis was performed using the X-ray spectroscopy accessory of a FE-SEM 6340F, equipped with Oxford INCA tower. The samples (bulk, ribbons or powder) were placed on a carbon tape and placed on a copper stub. Before imaging, the samples were coated with gold to minimize charging and improve the signal. Imaging was performed in secondary electron imaging (SEI) mode at a working distance of 8 mm.

Figure 3.4. Interaction volume of electrons interacting with a specimen [2].

3.3.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is a sophisticated microscopy technique in which a highly energetic beam of electrons is transmitted through a sample. The image is formed by interaction of these energetic electrons and specimen. Thickness of sample is crucial in TEM and it should be typically about 100 nm. TEM provides one of best resolution (up to 0.2 nm) among different types of imaging techniques. There are two standard modes of imaging in TEM i.e., Bright field mode and dark field mode. Sample region appears dark whereas region with no sample appears bright in a bright field TEM image. Crystallographic information can also be obtained in TEM by performing selected area electron diffraction (SAED) which gives diffraction spots. The spacing and orientation of these diffraction spots correspond to atomic plane spacing.

The morphological characterization to identify the particles and average size distribution, transmission electron microscopy (TEM) was performed on a TEM JEOL 2010 HR equipped with a LaB6 gun at an operating voltage of 200 kV and a point resolution of 2.3 Å. The samples were prepared by dispersing in hexane and ultrasonication for 1 h. Well dispersed particles were then dropped on holey carbon supported on a copper grid, and

subsequently dried in an oven for 3 days. Micrographs were collected in bright field imaging mode. Selected area electron diffraction (SAD) patterns were also collected.

3.3.4 Extended X-ray absorption fine spectrum (EXAFS)

X-ray absorption fine spectrum (XAFS) is a part of the spectrum observed in X-ray absorption spectroscopy (XAS). XAFS is a powerful characterization technique which can provide information about local structure, degree of order, electronic state etc. EXAFS is an element specific technique to investigate the chemical and physical properties at atomic level which uses X-rays having energies equal to or higher than the binding energy (BE) of the particular atomic level. To study the influence of high energy ball milling on the local structure, EXAFS (extended X-ray Absorption Fine Structure) characterization was performed at the XAFCA beamline of Singapore Synchrotron Light Source (SSLS), Singapore. The typical beamline layout is shown in figure 3.5. The X-rays are produced from a Helios 2 synchrotron and directed towards a collimating mirror. These rays then directed towards the monochromator which allows selected x-rays of specific energies to pass through. One more focusing mirror is placed after the monochromator to further focus the beam before reaching the end station where the sample is placed.

Figure 3.5 Schematic of the layout of the XAFCA beamline. (Adapted from <http://ssls.nus.edu.sg/facility/xafca.html>)

Measurements were performed at room temperature at both Fe-K (7.112 keV) and Cr-K (5.989 keV) edges. In a typical experiment ~100 mg of the sample was mixed and pressed into a BN pellet and mounted onto the sample holder for measurement using a transmission geometry. The absorption thickness ($\delta\mu_x$) of all powder samples was maintained at ~1, which is optimal for transmission EXAFS. Typical data collection times were 330 s per scan. A Si (111) crystal monochromator was used and data was collected in Quick EXAFS mode. The Athena program was used for data reduction, background subtraction and normalization. Curve fitting analysis of the normalized data was carried out using the Artemis program. All fits were performed in R-space. A k-range of 2.8–11.2 Å⁻¹ and an R-range of 1.1–2.5 Å was used for the Fourier transform and curve fitting, respectively. Amplitude reduction factors of 0.8 and 0.9 were used for Fe-K and Cr-K data analysis, respectively. These factors were obtained by fitting to the relevant reference EXAFS data. Coordination numbers, inter-atomic distances, and the Debye-Waller factors were generated by structural refinement of the first-shell EXAFS.

3.3.5 Physical property measurement system (PPMS)

The magnetic properties and its dependence on magnetic field and temperature were investigated using a Physical Property Measurement System (PPMS), (EverCool-II, Quantum Design, USA) equipped with a vibrating sample magnetometer (VSM).

PPMS is a property measurement equipment which is used to investigate a variety of physical properties like magnetic properties, electrical resistivity, heat capacity, AC transport etc. The focus of this PhD thesis is magnetic properties, hence the VSM feature of PPMS was used. For high temperature magnetization measurements, the VSM-oven option was used. The original work by Simon Foner demonstrates a detailed working of VSM [3].

A vibrating sample magnetometer (VSM) works on the principle of Faraday's law of induction which states that a change in the magnetic flux produces voltage in a pickup coil. The induced voltage is given as,

$$V_{coil} = \frac{d\phi}{dt} = \frac{d\phi}{dz} \times \frac{dz}{dt}$$

,where ϕ is magnetic flux and v is voltage induced in the coil, t is time and z is the vertical position of the sample w.r.t. pickup coil. The sample is driven to oscillate on a VSM rod inside a PPMS chamber and the resulting induced voltage is given by,

$$V_{coil} = 2\pi f K M A \sin 2\pi f t$$

,where f is the frequency of oscillation, K is the coupling constant, M is the magnetic moment of the sample and A is the amplitude of oscillation. This magnetic moment is recorded from the sinusoidal voltage response from the pickup coils. The principle of VSM in a PPMS is shown in figure 3.6. The sample is driven sinusoidally on the sample rod attached through the VSM motor. The oscillation occurs at the center of the pickup coil. The VSM motor module controls precise position and amplitude of the oscillation. The induced voltage in the pickup coil is then amplified and detected by the VSM detection module. This detection module uses a reference encoder signal for synchronous detection. The VSM motor module receives the raw encoder signal from the linear motor and processes it. The in-phase signals from the motor module and the pickup coils are then

detected by the VSM detection module. The controller area network (CAN) module then averages these signals and sends this information to a data acquisition and analysis system available on a linked computer. The *PPMS MultiVu* software was used to collect the data and operate the system after activating the VSM option.

Figure 3.6. Schematic of the operation of the VSM in a PPMS.

3.3.6 Hydrostatic pressure cell (M-cell)

To explore the effect of external hydrostatic pressure on the magnetic and MCE properties of Fe-Mn-Al alloys, a beryllium copper (BeCu) high pressure cell was used with an applied maximum pressure of up to 1.3 GPa. The typical length of the teflon tube holder is ~ 4-5 mm. It contains the daphne oil, which acts as the pressure transmitting media, and the sample. The sample should be prepared in such a way that it fits in the teflon holder without damaging it. The typical dimensions and mass of the sample was ~ 2-3 mm and ~1 mg. The different components of a pressure cell are shown in figure 3.7.

(A)

(B)

Figure 3.7. (A) Pressurization spanners and cell and (B) Pressure cell assembly and sample position.

Calibration of the beryllium copper (BeCu) cell was performed using a reference Pb wire (figure 3.8). The magnetization measurements were performed at ambient pressure after loading the sample in the cell assembly. Subsequent measurements were performed under finite pressure, applied using the pressure spanners. The applied pressure was determined by measuring the compression in the cell using a digital Vernier caliper. A specific value of compression corresponds to a specific value of applied pressure as deduced from the calibration curve. Although the maximum pressure is 1.3 GPa, this may damage the pressure cell and the cell pistons cannot be reused. Hence, we applied a maximum pressure of 1.15 GPa.

Figure 3.8. Calibration plot of pressure versus cell compression for a standard Pb wire at 7K.

3.4 Property evaluation

3.4.1 Structural analysis

The structural and phase analysis was performed using Match! and Topas software. Diamond software was used to generate a crystal structure. Match! was used to perform the initial phase identification from the diffraction data. Qualitative analysis was performed by comparing the diffraction data with the reference patterns found in the Inorganic Crystal Structure Database (ICSD) database. For quantitative evaluation of lattice parameters, cell volume, atomic site occupancy and space groups determination, Rietveld refinement was performed using a Total Pattern Analysis Solution (DIFFRACplus TOPAS) software. The difference between the experimentally observed diffraction data and the modelled crystal structure is minimized using the user defined parameters, crystallographic information (CIF) file and instrumental parameters. This method can provide information about the phases present in the sample. For a multiphase material, the relative amount of each phase can be determined. For a single-phase material (bulk or nano), the preferred orientation can be determined. Some important input parameters for refinement are related to the

background, zero shift, sample displacement, Lorentz and Polarization (LP) factor etc. To check the quality of profile fit and refinement, the main indicators are a good difference curve, smaller values of residual (R_{wp}) and R_{bragg} factors and small error index values [4]. Diamond software was used for visualization and construction of crystal structure. DEMETER (Athena, Artemis) software was used for the evaluation of structural parameters from EXAFS raw data.

3.4.2 Magnetic and MCE property evaluation

The magnetic properties were investigated by a PPMS unit equipped with a VSM head. Measurements were taken in standard mode in a temperature range from 10K to 400K. An oven (model P527) was attached to the VSM head for high temperature measurements. Three kinds of measurements were recorded to characterize the magnetic properties. To obtain temperature dependent magnetic properties, M v/s T measurements were performed for a temperature sweep of 10K to 400K. The applied magnetic field was 0.1T. To check for thermal hysteresis, samples were first cooled down from 400K to 10K, and then heated up from 10K to 400K. Overlap of heating and cooling M v/s T curves implies absence of thermal hysteresis. The Curie temperature was obtained from the value corresponding to the minima of the dM/dT v/s T curve, i.e., the maximum change in magnetization w.r.t. temperature. M v/s H curves were obtained at 300 K and 10 K, and field sweeps from -5 T to $+5$ T, respectively, to determine the field dependent magnetic properties such as saturation magnetization, coercivity, magnetic hysteresis etc. These M - H loops were obtained. The coercivity of samples investigated in this thesis were observed to be less than 100 Oe. For selected samples, zero field cooling (ZFC) and field cooling (FC) behavior was also recorded to check for the possibility of spin glass behavior i.e., for the bifurcation effect [5]. In ZFC, the sample is cooled below its blocking temperature in zero magnetic field. In FC, the sample is cooled below its blocking temperature in an applied field. In ZFC, the sample was initially cooled to the desired temperature without applying magnetic field. Data was collected while heating the sample at a small magnetic field of 100 Oe. For FC curves, the sample was cooled at zero magnetic field to the desired temperature. For data collection, two modes can be adapted, i.e. field cooled cooling (FCC) in which data is collected during cooling or field cooled warming (FCW) in which data is collected

during heating. The temperature at which the curves separate is called as spin freezing temperature. For theoretical investigation of the MCE using critical exponent analysis, isothermal M versus H curves were recorded around the Curie temperature with $\Delta T = 2\text{K}$.

To investigate the MCE properties, isothermal M vs H curves (with a temperature difference of $\sim 5\text{K}$) around the Curie temperature were recorded. The Maxwell's equation, i.e., $\Delta S_m = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH$ was used to yield the corrected isothermal entropy change ($-\Delta S_m$). To simplify calculation, the numerically integrated form of Maxwell's equation was used to find the change in magnetic entropy:

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

The milled sample can exhibit shape effects, which will result in a magnetic field which is different from the applied external field. Hence, the demagnetization factor should be included for accurate determination of the isothermal entropy change. The applied magnetic field is modified by the internal magnetic field (H_{int}) as, $H_{int} = H - N_{dm}M$, where H is the applied magnetic field, N_{dm} is the demagnetization factor and M is the magnetization of the material [6]. The milled samples were assumed to be spherical, hence N_{dm} was taken as $1/3$.

The RCP is an important figure of merit for magnetocaloric materials. It was determined as the product of the temperature span at full width of half maximum and the magnitude of maximum entropy change and, i.e. $RCP = |-\Delta S_{max}| \times \delta T_{FWHM}$ [7]. Large RCP also signifies a broader operating temperature range, i.e., greater δT_{FWHM} . A good magnetocaloric material must possess large RCP for practical applications [8].

Analysis of the MCE and the nature of the phase transition were performed using master entropy curves and local exponent analysis [9]. The second order phase transitions can be

justified if the normalized entropy versus rescaled temperatures at different applied fields collapse in a single master curve. The rescaled temperature (R_T) is given by,

$$R_T = (T - T_P)/(T_r - T_P),$$

where T_r is a reference temperature which corresponds to $(-\Delta S_m) = 0.5 \times (\Delta S_m)^{max}$ and T_P is the temperature where maximum entropy change is observed [10]. The normalized entropy is given by $\frac{\Delta S_m}{\Delta S_m^{max}}$. This scaling analysis removes the field and temperature dependence of a set of ΔS_m versus T curves for fixed ΔH . The local exponent n , derived from the power law expression, $\Delta S_m \propto H^n$, can be used to explain the magnetic state of the sample, transition temperature etc [11]. The relationship between local exponent n and temperature can be given using the relationship $n = \frac{d \ln |\Delta S_m|}{d \ln H}$.

3.5 Design and Modelling of a prototype

A $15 \times 15 \text{ cm}^2$ borosilicate glass tube with a wall thickness of 1 mm, an internal diameter (ID) of 5 mm and a circular cross-section was used for the flow of MF and for demonstrating magnetic cooling. A heat load of 50 mm in length, was prepared by coiling kanthal wires with resistivity of $15 \Omega/\text{m}$ on the top of an aluminum foil, which was wrapped around the glass. Ceramic wool was used to insulate the heat load region. Cold water at 18°C was used as the coolant in the heat sink region. An Nd-Fe-B permanent magnet of field strength 0.3T was placed at distance of 5 mm from the tube to provide a gradient magnetic field near the heat load region. A thermocouple was placed at the outer wall of the tube to read the heat load temperature. The other end of the thermocouple was connected to a temperature logger (Lutron TM-947SD Thermometer) to record the temperature change with time. Figure 3.9 shows the geometry of the prototype, the position of the heat sink, heat load, and the permanent magnet. It provides an overview of temperature distribution profile as well as the magnetization profile of the magnetic fluid along the tube, which is a key aspect for thermomagnetic convection.

Figure 3.9 (a) The prototype (b) Keithley 2200-30-5 external supply system.

Table 3.1: A comparison between Fe-Cr-Al magnetic fluid and commercial ferrofluid (Ferrotec APG1100 series).

Property	Fe-Cr-Al MF	Commercial FF
Composition	$\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($19 \leq x \leq 25$)	Fe_3O_4
Density of particles ρ	(~8 g/cm ³)	5.25 g/cm ³
Average particle size	25 nm	10 nm
Carrier fluid	Oleic acid	Organic ester oil
Dynamic viscosity μ	0.0274 Pa.s	0.08 Pa.s
Specific heat C_p	1800 J.kg ⁻¹ K ⁻¹	1614 J.kg ⁻¹ K ⁻¹
Thermal conductivity k	0.14 Wm ⁻¹ K ⁻¹	0.18 Wm ⁻¹ K ⁻¹
Concentration (v/v)	0.2-0.8%	3% to 12 %
Stability	Few days	Few months

Data for commercial ferrofluid collected from:

<http://www.ferrotec.com.sg/ferrofluid.ferrotec/ferrofluid-home.html>

To model magnetic cooling, a two-dimensional model was used using COMSOL Multiphysics software. The software works on the finite element method for solving coupled partial differential equations [12]. In this model, coupling between three fundamental phenomena viz. magnetic, thermal and fluid dynamics features were included. Certain assumptions were considered while numerically solving the model. The magnetic fluid (MF) was assumed to be electrically non-conductive, incompressible Newtonian fluid, single-phase, and its properties were taken as constants (Table 3.1) except for the magnetization values. The temperature dependent magnetization behavior at 1kOe from 400 K to 10 K was used as an experimental input. Table 3.1 shows a comparison of different properties of a commercial ferrofluid and the Fe-Cr-Al based MF. No-slip boundary condition was applied at the duct walls. For the thermal boundary conditions, constant temperature (18°C) was applied at the heat sink. The effect of gravity was neglected for the force calculations.

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Chapter 4

Fe_{75-x}Mn_xAl₂₅ Magnetocaloric Alloys*

This chapter contains the results of the synthesis, characterization and property evaluation of Fe-Mn-Al alloys. The MCE properties of low-cost, high relative cooling power Fe_{75-x}Mn_xAl₂₅ ($12.5 \leq x \leq 25$) alloys are discussed in the first part. Fe₆₀Mn₁₅Al₂₅ and Fe_{57.5}Mn_{17.5}Al₂₅ buttons exhibited large values of RCP, i.e., 395 Jkg⁻¹ and 430 Jkg⁻¹, respectively and T_c near room temperature, making such alloys technologically attractive. Theoretical analysis (local exponent and scaling behavior) of MCE data was performed to study the phase transitions. The influence of annealing duration and external hydrostatic pressure on the structural, magnetic and MCE properties of Fe₅₆Mn₁₉Al₂₅ melt-spun ribbons were also investigated. Optimal annealing conditions resulted in an enhancement in MCE parameters, i.e., ΔS_m and RCP. With increasing pressure from 0 kbar to 11.5 kbar, T_c shifted towards lower values at a rate of $dT_c/dP \sim 1.8$ K/kbar. The saturation magnetization (M_s) at 300 K also decreased at the rate of -0.8 emu/g/kbar. The isothermal magnetic entropy change decreased with increasing pressure.

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4.1 Introduction

As a result of climate change, global warming, and the impact of ozone layer depletion, it becomes necessary to replace conventional gas compression-based cooling technology with efficient, green and commercially feasible alternatives. Magnetic cooling is more energy efficient and environmental friendly [1]. Recently Haier, BASF, Astronautics Corporation of America constructed a wine cooler and showed that the efficiency for this magnetic cooling based system can be 35 % higher than that of a vapor compressor cooling system, with additional benefits of less vibrations and reduced wear and tear [2, 3].

Despite high ΔS_m values exhibited by rare earth (RE) alloys near room temperature, strategic limitations, poor corrosion and oxidation resistance, less availability and high processing cost make such materials unsuitable for commercial applications [4]. Several MCM are low-cost and exhibit a “giant” magnetocaloric response, but they might suffer from high magnetic and thermal hysteresis along with a narrow operating temperature range, which decreases the device performance [5]. Iron-based alloys with transition metal content are low-cost, readily available, show less hysteresis. Their T_c can be easily tuned in a wide range [6]. Reasonable MCE properties in Fe_xCu_{100-x} binary alloys were reported by Repaka *et al.* These alloys offer advantages of ready availability of the relevant elements, i.e., Fe and Cu and high thermal conductivity [7]. Corrosion resistance is required in practical cooling devices [8].

Fe-Al alloys are of commercial significance. They are less expensive, corrosion and oxidation resistance, easily available, high in tensile strength, low in density, have established manufacturing techniques and possess superior mechanical properties [9, 10]. The Fe_3Al phase shows good magnetic properties. At room temperature it exists in a DO_{19} crystal structure. The T_c of Fe_3Al is nearly 700 K, which is too high for a magnetic cooling system. Manganese replaces iron atoms in the stoichiometric Fe_3Al structure. The Fe-Mn-Al alloys may exhibit a $L2_1$ structure accompanied by reduction in T_c [11]. This is due to the contribution of the antiferromagnetic Mn atoms.

Alloying, magnetic field strength variation and external pressure are among the methods by which the magnetocaloric properties can be tuned. While alloying is the most popular way to modify the magnetocaloric response, it suffers from some disadvantages, e.g., purity of the sample may not be maintained, composition may not be uniform etc. [12]. Application of a magnetic field is directly related to the magnetic entropy change through the Maxwell relationship, $\Delta S_M = \int_0^{H_m} (\partial M / \partial T)_H dH$, but practical limitations in applying high magnetic fields limits the magnitude of MCE [13]. On the other hand, external pressure is a method which can tune magnetic and magnetocaloric properties by modifying the atomic environment, exchange interactions and phase transitions [14]. The structural parameters and magnetic phase transitions in a material are influenced by application of external pressure. Hydrostatic pressure can tune the magnetocaloric properties in a variety of ways, e.g., alter the entropy change, vary the transition temperature, increase or decrease the δT_{FWHM} etc. Most studies of the influence of external pressure on MCE properties have focused on materials exhibiting first order phase transitions or magneto-structural transitions. Recently, Hao et al. reported the influence of hydrostatic pressure on spin reorientation and MCE in PrGa compound, in which first order phase transitions get strengthened by application of pressure, resulting in a broadening of the ΔS_m curve [15]. Abuin *et al* studied the pressure dependence of phase transitions in Fe phase of an Nd-Fe-B magnet [16]. Very few studies have explored the effect of hydrostatic pressure on systems with second order magnetic phase transitions. Leary et al explored the effect of pressure on phase stability in $Fe_{89}Zr_7B_4$ alloys [17]. Since Fe_3Al alloys are sensitive to the order-disorder transitions and local atomic environments [18, 19], hydrostatic pressure can modify structural ordering, resulting in a change in magnetic and MCE properties. In $Fe_{3-x}Mn_xAl$ alloys, the Mn-Mn distance strongly affects the Mn-Mn exchange interactions, giving rise to a change in magnetic properties. These Mn-Mn distances can be modified by hydrostatic pressure [20].

Annealing has been used as an important post-synthesis processing technique to optimize phase stability, structural ordering, magnetic transitions and magnetocaloric properties [21]. Annealing can be optimized by either changing the temperature or annealing duration. Zhang *et al.* studied the influence of annealing time on the magnetic properties of Ni-Mn-

Sn alloys and observed an enhancement of 125 % in ΔS_m and 75 % in the refrigeration capacity [22].

The MCE properties of arc melted $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ alloys is reported for the first time. The effect of Mn addition on the structure and magnetic properties were investigated in detail. The MCE properties of $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ buttons, which exhibited near room temperature T_c were studied in detail. Local exponent and scaling analysis were performed to explore the role of impurities and the nature of the phase transitions in these alloys. We selected an annealing temperature of 1000 °C and varied the annealing time, to optimize the MCE properties of $\text{Fe}_{3-x}\text{Mn}_x\text{Al}$ melt-spun ribbons. Finally, the role of external pressure on the MCE and magnetic properties of $\text{Fe}_{56}\text{Mn}_{19}\text{Al}_{25}$ melt-spun ribbons was explored. Sample synthesis details have been provided in section 3.2.1.

4.2 Results and discussion

4.2.1 $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ bulk alloys

4.2.1.1 Structural analysis

The International Centre for Diffraction Data (ICDD) PDF database (PDF-4+2019 RDB) was used to index the XRD patterns of $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ alloys which corresponded to PDF card no. #04-003-7905. The Rietveld refined X-ray diffraction patterns and the plot of variation of lattice parameter with T_c of $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ ($x = 12.5, 15, 17.5$ and 25) alloys are shown in figure. 4.1 (a and b). All buttons showed a cubic crystal structure. The $L2_1$ structure of this composition was confirmed by the presence of (200) and (111) peaks in the XRD data of $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$. For $\text{Fe}_{62.5}\text{Mn}_{12.5}\text{Al}_{25}$, both these superlattice peaks were negligible in intensity w.r.t. the most intense peak (220), confirming a bcc (A2 type) structure. A B2 crystal structure [8, 23] was found in $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ and $\text{Fe}_{50}\text{Mn}_{25}\text{Al}_{25}$. This was confirmed by the presence of the (111) superlattice peak. The extra peaks observed around 35° (shown by arrows) were due to minor impurities (*fct* type) [12]. The EDS plots confirmed the composition of $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ and $\text{Fe}_{50}\text{Mn}_{25}\text{Al}_{25}$ bulk samples (Figure 4.1 (c)).

Figure 4.1 (A) Rietveld refined XRD patterns for $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ ($12.5 \leq x \leq 25$) bulk samples. Arrows point towards minority phase, (B) The dependence of T_c and lattice parameter on Mn wt %. (C) EDS spectrum for $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ ($x = 15$ and 17.5) bulk alloys.

4.2.1.2 Magnetic and MCE properties

Figure 4.2(a) shows magnetization versus applied magnetic field plots measured at 300 K, from -5 T to +5 T. Coercivity (H_c) was found to be < 50 Oe (inset figure 4.2(a)), indicating soft ferromagnetic behavior. The temperature dependent magnetic properties were measured at 0.1 T for both cooling and warming sweeps from 400 K to 10 K (Figure 4.2(b)). It was observed that the cooling and warming M-T curves were exactly similar, suggesting the absence of temperature dependent hysteresis. The M-T behavior was broad and transition from PM to FM state was smooth representing the presence of SOPT. By taking the temperature at minima of the dM/dT v/s T curves, the Curie temperature (T_c) was determined. For $x = 12.5, 15, 17.5$ and 25 , the T_c values were found to be > 400 K, 290 K, 250 K and 58 K, respectively. The antiferromagnetic nature of Mn atoms provides negative exchange parameters in the Fe_3Al system. This results in a lowering in net exchange parameters, thereby decreasing Curie temperatures [6]. Since $Fe_{60}Mn_{15}Al_{25}$ and $Fe_{57.5}Mn_{17.5}Al_{25}$ samples exhibited near room temperature T_c , i.e., 290 K and 250 K, respectively, further investigations were carried out only on these samples.

Figure 4.2. (a) Magnetization v/s applied field curves for $Fe_{75-x}Mn_xAl_{25}$ ($12.5 \leq x \leq 25$) samples. Inset shows the variation of H_c with Mn wt % (b) Magnetization v/s temperature plot for $Fe_{75-x}Mn_xAl_{25}$ ($12.5 \leq x \leq 25$) samples from 10 K to 400 K under 0.1 T magnetic field.

Isothermal magnetization curves at varied magnetic fields were measured from 10 K to 400 K with interval of 5 K, from 0 T to 5 T in order to evaluate the MCE property.

The ΔS_m was determined from Maxwell's equation in the form,

$$\Delta S_m = \sum_i \frac{M_i(T_{j+1}, H_i) - M_i(T_j, H_i)}{T_{j+1} - T_j} \Delta H_i$$

where $M_i(T_{j+1}, H_i)$ and $M_i(T_j, H_i)$ are magnetization values at temperatures T_{j+1} and T_j respectively, at an applied field H_i . The temperature dependent variation of $-\Delta S_m$ for $x = 15$ and 17.5 are shown in figure 4.3. The magnitude of ΔS_m was maximum near the transition temperature and exhibited an increase upon increasing the magnetic field. The ΔS_m versus T curves were wide, exhibiting high values of δT_{FWHM} . The δT_{FWHM} value denotes the difference in temperatures between the cold end and the hot end in a cooling cycle. The widening of the ΔS_m versus T curves can be attributed to the broadening of magnetic transition. The asymmetric exchange interactions often caused due to fluctuations in atomic spacing and increased defect concentration lead to broadening in magnetic transitions. The broadening of magnetic transition results in a broad entropy response and hence an increase in refrigeration capacity [24, 25]. The magnitude of ΔS_m at 5 T field was $0.95 \text{ Jkg}^{-1}\text{K}^{-1}$ and $1.07 \text{ Jkg}^{-1}\text{K}^{-1}$, for $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ respectively.

Figure 4.3. The temperature dependence of ΔS_m for (a) $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and (b) $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ alloys, at magnetic fields upto 5T, from 100 K to 400 K.

For commercialization, the magnetocaloric material must exhibit high ΔS_m and RCP values. The graphs of RCP and $-\Delta S_{max}$ of $x = 15$ and 17.5 samples, respectively, from 1 T to 5 T applied fields are shown in figure 4.4 (A, B). The plot of $-\Delta S_m$ versus H showed a linear change in $-\Delta S_{max}$ values for both $x = 15$ and 17.5 samples, with higher values for the $x = 17.5$ samples (figure 4.4(B)). RCP of 395 Jkg^{-1} and 430 Jkg^{-1} were observed for $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ at 5 T, respectively (figure 4(A)). The RCP showed a linear increase with increasing magnetic field. The RCP at 5 T for $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ was found to be $\sim 10\%$ larger than RCP of $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$. The larger Mn content lead to more asymmetrical distribution in exchange interactions [24]. The $-\Delta S_m$ and RCP of FeMnAl alloys are considerably better than the MCE values of $\text{Co}_{71}\text{Mo}_9\text{P}_{14}\text{B}_6$ metallic glasses, which exhibited a $-\Delta S_m$ value of $0.96 \text{ Jkg}^{-1}\text{K}^{-1}$ and a RCP value of 70.5 Jkg^{-1} as well as HEAs like $\text{NiFeCoCrPd}_{0.25}$, which exhibited $-\Delta S_m$ of $0.9 \text{ Jkg}^{-1}\text{K}^{-1}$ and RCP of 215 Jkg^{-1} at 5 T [26, 27].

The cost of the magnetocaloric material is one of the important prerequisites for developing a magnetic cooling system. Zimm *et al* presented a detailed analysis of the major costs involved in the building a magnetic cooling device which included the cost of MCM and permanent magnet [28]. A summary of the MCE properties along with the cost of our materials and other recently developed iron-based magnetocaloric materials is shown in the Table 4.1. Including rare earth elements and compounds increases the magnetocaloric material cost drastically, e.g., the cost of 1 kg of $\text{Fe}_{62}\text{Cr}_6\text{Tb}_5\text{B}_{23}\text{Nb}_4$ is ~ 107 times more than the cost of a $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ alloy (Table 4.1). The cost of $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ alloy was less than 5 % of the cost of $(\text{Fe}_{0.7}\text{Mn}_{0.3})_2\text{Y}$ alloys. The RCP of $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ alloy was $\sim 370\%$ larger than a RCP value of 90 Jkg^{-1} for $(\text{Fe}_{0.7}\text{Mn}_{0.3})_2\text{Y}$ alloy (Table 1). The cost of $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ ($x = 17.5$) is nearly 2 % of the cost of the materials exhibiting “giant” MCE response, e.g., $\text{Gd}_5\text{Si}_2\text{Ge}_2$ alloys and 1.9 % of the cost of, $\text{Gd}_5\text{Ge}_{1.9}\text{Si}_2\text{Fe}_{0.1}$ alloy.

Table 4.1 Isothermal entropy change ($-\Delta S_m$), RCP values, Curie temperature (T_c) and cost of alloy per kg for our material and other promising iron-based magnetocaloric materials.

Sample	ΔH (T)	$(\Delta S_m)^{\max}$ (Jkg ⁻¹ K ⁻¹)	RCP (Jkg ⁻¹)	T_c (K)	Cost USD/ kg	Ref.
Fe ₆₀ Mn ₁₅ Al ₂₅	5	0.95	395	290	78	This work
Fe _{57.5} Mn _{17.5} Al ₂₅	5 (2)	1.07 (0.51)	430 (150)	250	77	This work
Fe ₃₃ Cu ₆₇	5	0.83	208	313	90	[7]
Fe ₆₂ Cr ₆ Tb ₅ B ₂₃ Nb ₄	2	0.56	54	320	8330	[29]
Fe _{40.2} Co _{20.1} Ni _{6.7} B _{22.7} Si _{5.3} Nb ₅	2	0.66	78	505	696	[30]
(Fe _{0.7} Mn _{0.3}) ₂ Y	5	1.65	90	320	1945	[31]
Fe _{2.5} Mn _{2.5} Sn ₃	2	0.93	43	347	159	[32]

Cost of pure element per 100 g was taken from <https://www.chemicool.com/>

Figure.4.4 The dependence of (A) relative cooling power (RCP) and (B) magnetic entropy change ($-\Delta S_m$) on the applied magnetic field for $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and $\text{Fe}_{60}\text{Mn}_{17.5}\text{Al}_{25}$ alloy

The normalized magnetic entropy change v/s rescaled temperature plots for $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$, from 1 T to 5 T are shown in figure 4.5. For materials with SOPT, the magnetic entropy change curves, measured at varied applied fields must meet in a single curve [22, 23]. The rescaled temperature is $\theta = (T - T_P) / (T_r - T_P)$, where T_r is a reference temperature which corresponds to $(-\Delta S_m) = 0.5 \times (-\Delta S_m)^{\max}$ and T_P is the temperature which corresponds to the maximum value of entropy change. At lower temperatures these curves start to split. This could be due to minority phases and magnetic inhomogeneity [33]. The normalized entropy curves did not collapse in a single curve, implying the presence of impurity phases and magnetic inhomogeneity. Miller *et al.* explained the presence of inhomogeneities in $\text{NiFeCoCr}_1\text{Pd}_x$ HEAs by similar splitting behavior at low temperatures. A large distribution of exchange parameters results in higher inhomogeneity, causing the rescaled curves to split at low temperatures.

Figure 4.5. Entropy change $\Delta S_m/\Delta S_m^{max}$ v/s rescaled temperature Θ from 1 T to 5 T, for (a) $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and (b) $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ samples.

Based on the mean field theory (MFT), a simple relationship between the entropy change near the Curie temperature T_c and the applied field (H) can be given as $-\Delta S_m \propto H^n$, where n denotes the local exponent. The value of n is 0.66 if the MFT assumptions are fulfilled [34]. This value of n directly depends upon the magnetic state of the material. A change in n with T (figure 4.6) was extracted by experimentally fitting the values of $-\Delta S_m$ v/s H for $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ samples. In the ferromagnetic region, i.e., $T < T_c$, the value of n reached ~ 1 , because magnetization (M) is not dependent on the variation in magnetic field. In the paramagnetic region, n reached values larger than 1. If the assumptions of the Curie-Weiss law are satisfied, the value of n should reach to a value close to 2 [35]. In our case, the values of n at the minima were found to be 0.756 and 0.792 for $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$. These values are larger than the value of 0.66 predicted from MFT. However, these values of n are comparable to the value 0.75 observed for $\sigma\text{-Fe}_{60}\text{V}_{40}$ alloys [36]. These values of n are higher and indicate the presence of inhomogeneities in the material, resulting in broader T_c change and higher values of RCP [35].

Figure 4.6. Local exponent n versus Temperature (T) in the range of 0-5 T for $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$ alloys. The minima denote the T_c of the sample.

4.2.2 Influence of annealing

4.2.2.1 Structural analysis

Four samples were taken into consideration for this study. As-quenched samples were heat treated at 1000 °C for 6 h to give sample A1. Sample A1 was further annealed for 6 h and named as sample A2. One set of as-quenched sample was annealed for 12 h to give sample A3. All the samples crystallized in the B2 crystal structure, although the intensity of (200) superlattice peak signifying the ordering in Fe-Cr sublattice was different for each sample (figure 4.7) [37]. Due to the high cooling rate in melt spinning process, substantial disorder was present in the as-quenched ribbon. The degree of structural order (DSO) was estimated by the ratio of the intensity of (200) superlattice reflection and the intensity of the most intense peak [22]. For long annealing duration, the (200) superlattice peak intensity was observed to be the highest, suggesting an increase in order in the Fe-Cr sublattice [38]. The highest DSO was observed to be 0.82 for sample A3, followed by 0.645 for sample A1,

0.55 for sample A2 and 0.52 for as-quenched ribbons. Li *et al* also observed an increase in the degree of order in CoMnSb alloy upon long term annealing [39].

Figure 4.7. X-ray diffraction data for as-quenched ribbon samples and annealed samples (A1, A2 and A3). The intensity of the (200) peak was used to determine the degree of structural order.

4.2.2.2 Magnetic and MCE properties

The temperature dependent magnetization (M-T) plots are shown in figure 4.8. The M-T curves were measured by applying a magnetic field of 0.1 T, from 400 K to 10 K (cooling) and 10 K to 400 K (warming). Both the cooling and warming sweeps overlapped, suggesting an absence of temperature related hysteresis. The shape of the M-T curve was similar for all samples, although sample A1 shows a comparatively broader transition from the PM state to the FM state.

Figure 4.8. Temperature dependent magnetization data for as-quenched ribbon samples and annealed samples (A1, A2 and A3), at 0.1 T applied field.

The T_c was deduced from the minima of the dM/dT curves (figure 4.9). As-quenched ribbons possessed a T_c of 195 K. Annealing treatment resulted in a large increase in T_c , i.e. 290 K for sample A1, 265 K for sample A2 and 277 K for sample A3. These values of T_c are technologically attractive and highly desirable for room temperature cooling applications. This enhancement in T_c upon annealing for longer duration could be attributed to higher degree of structural order. Similar increase of T_c with annealing duration was observed in Ni-Mn-Ga and Ni-Mn-In ribbons [40, 41].

Figure 4.9. dM/dT versus T for as-quenched ribbon samples and annealed samples (A1, A2 and A3).

The field dependent magnetization data was recorded at room temperature and field sweeps ranging from -5 T to $+5$ T (figure 4.10). The saturation magnetization increased after annealing from 28 emu/g for as-quenched ribbons to 48 emu/g for sample A3. This enhancement in saturation magnetization was due to a variation in magnetic correlations with annealing duration. As a result of annealing, the ordering of Mn atoms increased, resulting in increased exchange interactions between Mn and Fe atoms, causing a rise in saturation magnetization [22]. The coercivity remained unaffected by annealing and was found to be less than 50 Oe for all the samples.

Figure 4.10 Field dependent magnetization plots for as-quenched ribbon samples and annealed samples (A1, A2 and A3). H_c denotes the Coercivity.

To evaluate the MCE properties of as-quenched and annealed samples, isothermal M-H curves near the T_c were measured with $\Delta T = 5$ K. From the Maxwell thermodynamic relation, $\Delta S_M = \int_0^{H_m} (\partial M / \partial T)_H dH$, the isothermal entropy change with respect to temperature (ΔS_M vs T) was determined from 0 T to 2 T as well as 0 T to 5 T applied field (figure 4.11). As-quenched ribbons exhibited a ΔS_M value of $0.98 \text{ J kg}^{-1} \text{ K}^{-1}$ at 5 T applied field, which increased for annealed samples. A maximum ΔS_M was observed for sample A3, which exhibited ΔS_M of $1.2 \text{ J kg}^{-1} \text{ K}^{-1}$. For magnetocaloric materials, relative cooling power (RCP) should be high as possible, since it is a measure of amount of heat that can be transferred from the hot end to the cold end in a cooling cycle [42]. The RCP for as-quenched ribbon was found to be 290 J kg^{-1} . After annealing the RCP was found to be higher, showing values of 388 J kg^{-1} , 405 J kg^{-1} and 395 J kg^{-1} for sample A1, sample A2 and sample A3, respectively. This enhancement in ΔS_M and RCP with heat treatment could be the result of an increase in the degree of structural order in annealed samples. Slight differences in the RCP values of samples A1, A2 and A3 are due to the differences in the Curie temperature distribution, which affects the δT_{FWHM} value. Zhang *et al* also observed

a similar effect of atomic ordering on MCE properties in Ni-Mn-Sn ribbons by varying the annealing durations [22].

Figure 4.11. Temperature dependent magnetic entropy change (ΔS_m) plots. Open symbols represent the ΔS_m values for 2 T magnetic field. Closed symbols represent the ΔS_m values for 5 T magnetic field.

4.2.3 Influence of hydrostatic pressure

The effect of external pressure on the magnetic and MCE properties of $\text{Fe}_{56}\text{Mn}_{19}\text{Al}_{25}$ ribbons sample was explored. Figure 4.12 shows the temperature dependent magnetization curves, at an applied field of 0.1 T, for hydrostatic pressures ranging from 0 kbar to 11.5 kbar, with temperature sweeps in a range from 380 K to 10 K. The hydrostatic pressure retained the second order transition, with no thermal hysteresis. The M-T curves changed in a similar fashion as that observed with an increase in Mn content in the alloy [43]. However, this shifting of the M-T curves with hydrostatic pressure towards lower temperatures takes place in a controlled and uniform manner (inset figure 4.12).

Figure 4.12. Temperature dependent magnetization plots for different applied pressure at 0.1 T magnetic field. Inset shows the zoom-in part at FM to PM transition.

The Curie temperature (T_c) was determined from the minima of dM/dT versus T curves (figure 4.13). With application of hydrostatic pressure, the Mn-Mn interatomic distance decreases, which favors antiferromagnetic coupling, resulting in a decrease in T_c . The T_c decreased with applied pressure at a rate of $dT_c/dP \sim 1.39$ K/kbar. At 11.5 kbar, a technologically attractive value of T_c was obtained, i.e. 273 K (0 °C).

Figure 4.13. dM/dT versus temperature plots at different applied pressures. The minima correspond to the Curie temperature.

The field dependent magnetization behavior under hydrostatic pressure is shown in figure 4.14. The data was recorded at 300 K and 10 K (inset figure 4.14). Except for small differences in magnetization values, the behavior of M-H curves were similar at ambient and high pressures. No significant effect of pressure on the magnetic hysteresis and coercivity values was observed.

Figure 4.14. Field dependent magnetization (M-H) curves for at 300K and 10 K (inset), for ambient and higher applied pressure.

The magnetic entropy change at different pressures, as a function of temperature, is shown in figure 4.15. The ΔS_m was calculated by numerically integrating the isothermal M-H curves obtained with a temperature difference of 5 K around the T_c . The application of pressure decreased the ΔS_m value from $1.19 \text{ J kg}^{-1} \text{ K}^{-1}$ ($P = 0 \text{ kbar}$) to $1.08 \text{ J kg}^{-1} \text{ K}^{-1}$ ($P = 10 \text{ kbar}$) for $\text{Fe}_{56}\text{Mn}_{19}\text{Al}_{25}$ ribbons. The peak temperature (temperature corresponding to the maximum value of ΔS_m) also exhibited a uniform shift towards lower temperatures with applied pressure. Hence, it is possible to tune the peak temperature of ΔS_m in Fe-Mn-Al alloys by the application of pressure. Various researchers have observed a drastic decrease in ΔS_m values with increasing pressure. Liang *et al* reported a decrease of ΔS_m in $\text{MnCoGe}_{0.99}\text{In}_{0.01}$ compounds from a value of $18 \text{ J kg}^{-1} \text{ K}^{-1}$ at 0 kbar to a value of $3 \text{ J kg}^{-1} \text{ K}^{-1}$ at 8.7 kbar, due to the splitting of magnetic and structural transitions [44]. Similar observations were reported for PrGa [15] and Ni-Co-Mn-Sn alloys [45]. A few studies have shown an enhancement in MCE with applied pressure, e.g., in phase separated manganites $\text{La}_{0.35}\text{Pr}_{0.35}\text{Ca}_{0.3}\text{MnO}_3$, a $\sim 10\%$ increment in ΔS_m was observed [46]. Hence, it

can be concluded that depending on the type of interatomic interactions, degree of structural ordering and nature of phase transitions, hydrostatic pressure can modify the MCE behavior.

Figure 4.15. Temperature dependent magnetic entropy change (ΔS_m) plots at ambient, 5 kbar and 10 kbar, from 1 T to 5 T applied field.

Figure 4.16 shows the behavior of spontaneous magnetization ($M_{\text{spont.}}$), Curie temperature (T_c), ΔS_m and ΔS_m versus H , with applied pressure. Both $M_{\text{spont.}}$ and T_c displayed a linear decrease with applied pressure. From the plot of ΔS_m vs P , it was observed that ΔS_m^{max} increases with applied field H . However, no appreciable change in ΔS_m^{max} was observed with increase in hydrostatic pressure.

Figure 4.16 (a) Spontaneous magnetization ($M_{\text{spont.}}$) at 10 K as a function of pressure, (b) Curie temperature as a function of pressure, (c) maximum entropy change (ΔS_m^{max}) as a function of pressure and (d) maximum entropy change (ΔS_m^{max}) as a function of magnetic field at different pressures.

4.3 Conclusions

For the first time, the MCE properties of rare earth free, low-cost, $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ ($x = 12.5, 15, 17.5$ and 25) bulk alloys were studied. High values of RCP, i.e., 430 Jkg^{-1} and 395 Jkg^{-1} as well as T_c near room temperature, i.e., 290 K and 250 K, were found $\text{Fe}_{60}\text{Mn}_{15}\text{Al}_{25}$ and $\text{Fe}_{57.5}\text{Mn}_{17.5}\text{Al}_{25}$. The low-cost of $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ alloys in comparison to rare earth-based and other transition metal based MCM provides a significant advantage. The failure of normalized entropy curves to meet in a single curve was due to impurity and inhomogeneity. The theoretical analysis using local exponent n supported the observation of broad distribution of Curie temperatures. Annealing treatment at 1000°C and optimum duration was found to enhance structural order in the $\text{Fe}_{56}\text{Mn}_{19}\text{Al}_{25}$ ribbons, which in turn, enhanced the magnetic and magnetocaloric properties. Interestingly, the Curie temperature

was tuned to the room temperature range. While an applied pressure of 11.5 kbar fine can be used to tune the transition temperature and other magnetic properties, the magnitude is insufficient to display any metamagnetism or a magneto-structural transition. Superior mechanical properties, well established manufacturing technology, good corrosion resistance are additional advantages of Fe-Mn-Al alloys.

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Chapter 5

$\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ Magnetocaloric alloys*

This chapter contains the results of the synthesis, characterization and property evaluation of Fe-Cr-Al alloys. We studied the structure, magnetic and MCE properties of RE free $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($19 \leq x \leq 25$) arc melted alloys. The T_c was tuned from 220 K up to room temperature by Cr alloying. The RCP/\$ of Fe-Cr-Al alloys was found to be superior to the corresponding values of RCP/\$ of other MCM exhibiting T_c near RT. A crystal structure change from $L2_1$ phase to B2 phase in $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ buttons accompanied by an enhancement of 33% in ΔS_m and 25% increase in RCP was observed for ribbons compared to the buttons. The effect of short duration ball milling on the structure, magnetic and MCE properties was investigated. The degree of structural order in the Fe-Cr sublattice was found to vary with milling time in a cyclic fashion at a milling speed of 600 rpm. Interestingly, the 15 min. milled sample exhibited ~50 % higher M_s and 22 % higher RCP compared to the value before milling.

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5.1 Introduction

More than 15% of the total energy utilization in the world is for thermal management of residential, commercial and industrial structures [1]. Magnetic cooling is more energy efficient and environmentally friendly [2, 3]. Materials exhibiting first order phase transitions (FOPT) e.g., $\text{MnFeP}_{0.45}\text{As}_{0.55}$ [4], $\text{MnAs}_{1-x}\text{Sb}_x$ [5], $\text{Gd}_5\text{Si}_2\text{Ge}_2$ [6] etc. exhibit excellent MCE properties but they suffer from hysteresis losses, which can drastically reduce the efficiency of a cyclic process. On the other hand, interest in TM-based, RE free, MCM has risen due to their superior mechanical properties, high abundance, and less expensive precursors, e.g., Fe-Cu [7], Fe-Cr-Si-B [8], Fe-Ni-Mn [9] and $(\text{Fe}, \text{Cr})_3\text{Al}$ [10] alloys. Various research groups have focused on economic aspects of soft alloys and suggested alloy substitutions for cost reduction in soft magnetic materials [11, 12].

Iron aluminides exhibit attractive thermo-physical and mechanical properties [13-15]. Adding Cr in Fe_3Al alloy brings down the Curie temperature, from $\sim 700\text{K}$ to the near RT values due to the AFM nature of Cr [10]. The addition of Cr can also result in a change in crystal structure from the DO_3 structure to the L_{21} or B2 structure, depending on the composition and processing conditions [16]. Critical analysis around the Curie temperature has been shown to be a powerful tool to understand the underlying behavior of the magnetic transition, degree of order and MCE properties [17-19].

Mechanical alloying (MA) can be used to tune the microstructure, magnetic transition temperature and MCE properties of magnetocaloric materials. MA is a solid-state processing technology which uses conventional or high energy ball milling (HBM) to produce powder particles, nanostructured grains, amorphous structures, metastable crystalline phases and quasicrystals [20]. Chevalier *et al.* obtained amorphous GdNiAl alloys with interesting MCE properties by HBM [21]. Fe-based materials can also be produced by MA. Fe-10% Ni nanocrystalline magnetic alloys produced by HBM after milling for long duration (96 h), showed larger lattice parameter, high saturation magnetization and low coercivity [22]. On the other hand, Fe-50%Al alloys exhibited increased coercivity and lower magnetization values after ball milling for 5 h [23]. Unusual cyclic behavior in the properties of materials has also been observed after MA. Zhang *et al*

reported cyclic changes in the hardness of nanocrystalline Zn upon cryomilling[24]. El-Eskandarany *et al.* observed cyclic crystalline-amorphous transformations in $\text{Co}_{75}\text{Ti}_{25}$ alloys on ball milling[25]. The properties of these alloys can be highly sensitive to their crystal structure and degree of order [26] ; order-disorder and amorphous-crystalline transitions have been observed in these alloys. Ball milling usually creates defects and disorder in materials [27]. Thus, the structure and properties of Fe-Al based alloys is expected to be significantly altered by ball milling. Mukhopadhyay *et al.* reported a fully amorphous state in Fe_3Al after 50 h of ball milling [28]. Similarly, Dong et al reported that an amorphous state was obtained in Fe-20 at% Al after mechanical alloying for even longer duration (180 h) [29]. Unlike these earlier studies, we hypothesize that, in alloys and intermetallics, e.g. Fe-Al based alloys, where the degree of order can significantly affect the magnetic properties, even *short duration* high energy ball milling will be sufficient to significantly influence the local structure, magnetic and magnetocaloric properties. Only a few reports are available on the correlation between MCE and the degree of order or crystal structure [30].

The structure, magnetic and magnetocaloric properties of $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($19 \leq x \leq 25$) arc melted bulk samples are reported in the first part of this chapter. Subsequently, we prepared the ribbons of $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ buttons by melt spinning technique and studied for the first time their magnetocaloric properties. An enhanced MCE in melt-spun ribbons compared to arc melted buttons was observed. To investigate the nature of structural ordering near the critical temperature the critical behavior of $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ melt-spun ribbons was also studied. In the last part of this chapter, the effect of short duration high energy ball milling on the local structure, magnetic and magnetocaloric properties of Fe-Al-Cr alloys was studied. We determined the local structure, magnetic and magnetocaloric properties of $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ alloy samples before milling and after milling. An interesting unusual cyclic behavior of structural order was observed in these milled $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ alloys. Cr-19, Cr-21, Cr-23 and Cr-25 were the nomenclature for $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($x = 19, 21, 23$ and 25), respectively.

5.2 Results and discussion

5.2.1 $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ bulk samples

5.2.1.1 Structural analysis

The refined XRD patterns of $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($19 \leq x \leq 25$) bulk samples are shown in figure 5.1 (i). All the bulk samples were found to be single phase and possessed a L2_1 structure and $\text{Fm}\bar{3}\text{m}$ space group. The (200) and (111) superlattice reflections should be present in an L2_1 structure, which signifies the structural order in the Fe-Cr sublattice and Al-Cr sublattice, respectively [31]. The lattice parameters were deduced from the refined data. The value of lattice parameter exhibited a decrease, from 5.83 Å to 5.79 Å for Cr-19 and Cr-25, respectively. The cell volume and lattice parameter both decreased with increasing Cr wt %. This behavior could be a result of compression of the lattice in the x -y direction[32]. Figure 5.1 (ii, iii and iv) shows the EDS data of bulk samples confirming the nominal composition.

Figure 5.1. (i) Refined XRD data for $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ (a) $x = 25$, (b) $x = 23$, (c) $x = 21$ and (d) $x = 19$ bulk samples. Red line represents calculated values, black line shows experimental data points and

the blue line shows the difference in calculated and experimental points. (ii, iii and iv) represents the EDS spectrum on whole screen for $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ bulk alloys.

5.2.1.1 Magnetic and MCE properties

The magnetization as a function of temperature (M-T) is shown in figure 5.2. The M-T plots were taken at 0.1 T and temperature cycle (cooling and warming) from 400 K to 10 K and vice versa. Both cooling and warming sweeps overlapped denying any temperature hysteresis. The values of T_c found from dM/dT curve were 220 K, 235 K, 282 K and 300 K respectively for $x = 25, 23, 21$ and 19, respectively (inset figure 5.2). The antiferromagnetic Cr atoms contribute opposite exchange parameters to the FM Fe-Al composition and decreases the T_c [33].

These T_c values, i.e., 282 K and 300 K are technologically good for near RT cooling applications. All buttons showed a broad transition from PM to FM state.

Figure 5.2. Magnetization as a function of temperature (M-T) curves for $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($19 \leq x \leq 25$) buttons. The plot of T_c v/s Cr wt % is shown in inset.

The magnetization versus applied magnetic field curves (M - H) were measured at 300 K and applied field from +5 T to -5 T (figure 5.3). All bulk samples possessed low coercivity values, i.e., 32 Oe, 53 Oe, 31 Oe and 52 Oe for Cr-19, Cr-21, Cr-23 and Cr-25 alloys, respectively. Low values of coercivity are desirable for practical magnetic cooling applications. The increase in M_s with decreasing Cr content could be explained on the basis of the mean field theory and Bethe-Slater curve [34]. The lattice parameter increased with decreasing Cr content, hence the effective net exchange interaction increased, yielding larger values of M_s .

Figure 5.3. Magnetization as a function of field (M - H) for $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($19 \leq x \leq 25$) buttons from +5 T to -5 T at 300 K. The behavior of Bohr magneton per formula unit ($\mu_{f.u.}$) v/s Cr wt % is shown in the inset.

To study the MCE properties, the M - H isotherms were recorded from a temperature range of 100 K to 400 K with $\Delta T = 10$ K and an applied field of 5 T (M - H isotherms not shown here). The isothermal entropy change ($-\Delta S_m$) was calculated using the Maxwell relation,

$\Delta S_m = \int_0^H (\partial M / \partial T)_H dH$ for a range of magnetic field strengths ($\Delta H = 1$ to 5 T). (Figure 5.4). The magnitude of ΔS_m should be highest around the T_c [35]. With an increase in the applied field, the magnitude of ΔS_m increased due to an increase in FM interactions. Decreasing Cr content shifted the peak of ΔS_m curve towards higher temperature. This behavior was similar to the trend in T_c . The increase in T_c was accompanied by $\sim 19\%$ enhancement in the ΔS_m value of Cr-19.

The width of the curve, i.e., δT_{fwhm} is also an important parameter for comparing different MCM. For Cr-19, both δT_{fwhm} and RCP are highest, the values decrease with further addition of Cr. Our alloys exhibit RCP values which better than those of other promising materials such as, NiFeCoCrPd_x HEAs [36], (Fe_{1-x}Mn_x)₂Y [37] and Pr_{0.4}Re_{0.1}Sr_{0.5-y}Ba_yMnO₃ [38].

Figure 5.4. $-\Delta S_m$ versus T curves for Fe_{75-x}Cr_xAl₂₅ ($x = 19, 21, 23$ and 25) buttons. Open symbols represent values at 2T and closed symbols represents values at 5T.

The scaling behavior was investigated using entropy change (normalized) v/s rescaled temperature curves, for $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($x = 19, 21, 23$ and 25) buttons, at different applied fields, are shown in figure 5.5. This analysis, known as the master entropy curve analysis, is used to deduce the nature of the phase transition from ΔS_m versus T curves [39]. This scaling analysis removes the field and temperature dependence of a set of ΔS_m versus T curves for a fixed ΔH value. The rescaled temperature is given by $R_T = (T - T_P)/(T_r - T_P)$, where T_r corresponds to $(-\Delta S_m) = 0.5 \times (-\Delta S_m)^{max}$ and T_P corresponds to maximum entropy change. The $\Delta S_m/\Delta S_m^{max}$ versus rescaled temperature R_T curves, at different applied fields collapsed in a single curve confirming the SOPT in our material. At lower temperatures ($R_T < 0$), the curves tend to split, signifying the presence of magnetic inhomogeneities [40].

Figure 5.5. Master curves ($\Delta S_m/\Delta S_m^{max}$ v/s R_T) from 1 T to 5 T for $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($x = 19, 21, 23$ and 25) buttons.

The cost of a magnetocaloric material is critical factor to consider to developing an industrial system [41]. Ucar et al presented a comprehensive review on cost analysis of various magnetocaloric materials with Curie temperature near room temperature [42]. An analysis of RCP_{fwhm} in terms of the material cost was carried out (Figure 5.6). Various

materials which show promising RCP values with T_c near room temperature, e.g., iron-based alloys, Gd-based alloys and HEAs were used for this cost analysis. Gd exhibits good RCP but its production cost is very high. Hence, the performance of Gd in terms of cost i.e. RCP/US \$ is quite low compared to $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($x = 19, 21, 23$ and 25) buttons. $\text{Ce}_{11}\text{Fe}_{79}\text{B}_6$ shows a value of 420 Jkg^{-1} at 5 T [43], which is larger than the RCP (300 Jkg^{-1}) of $\text{Fe}_{56}\text{Cr}_{19}\text{Al}_{25}$. However, the performance of $\text{Fe}_{56}\text{Cr}_{19}\text{Al}_{25}$ in RCP / US \$ is 400 % more than corresponding value for $\text{Ce}_{11}\text{Fe}_{79}\text{B}_6$. The RCP/\$ performance for Fe-Cr-Al buttons was ~15 times more than that of $\text{Gd}_2\text{Si}_2\text{Ge}_2$ and ~24 times more than the RCP/\$ of “benchmark” Gd.

Figure 5.6. (a) Cost of various promising MCM [The element cost in US \$ taken from <https://www.chemicool.com/>] (b) RCP/US\$ for the MCM corresponding to (a).

The variation of structural, magnetic and MCE parameters with Cr content is summarized in figure 5.7. With an increase in Cr content from 19 wt. % to 25 wt. %, the saturation magnetization M_s at 300 K, decreased almost linearly from a value of 40 emu/g to 21 emu/g, with similar trends observed in T_c ; T_c values dropped varied from 300 K to 220 K.

Figure 5.7. Compositional dependence of (a) lattice parameter and saturation magnetization at 300 K, (b) δT_{fwhm} and RCP (c) ΔS_m and T_c

5.2.2 Fe_{75-x}Cr_xAl₂₅ bulk and ribbon samples

5.2.2.1 Structural analysis

Figure 5.8 (a, and b) shows the ball and stick model of the B2 and L2₁ crystal structure. In the B2 phase, Fe atoms are represented by blue balls; Cr and Al atoms can randomly occupy any positions represented by red balls. In L2₁ phase, Cr and Al atoms can occupy only specific positions represented by the green and red balls, respectively [26]. Both (111) and (200) superlattice reflections are present in the XRD patterns of the L2₁ crystal structure, whereas the absence of one of these reflections indicates the B2 crystal structure; absence of both of these reflections signifies the presence of an A2 (bcc) type structure [44].

Figure 5.8. (a) B2 crystal structure; Blue balls indicate Fe atoms, Red balls indicate Cr or Al atoms, (b) L2₁ crystal structure; Blue, Red and Green balls indicate Fe, Al and Cr atoms, respectively.

Figure 5.9 shows the XRD patterns for the bulk and the ribbons and the corresponding Rietveld refinement. The (Fe_{0.72}Cr_{0.28})₃Al bulk sample possessed an L2₁ face centered cubic structure with space group of Fm3m [45] (Fig. 5.9 (a)). No additional peaks were observed, showing that the structure is single phase. The XRD pattern of melt-spun ribbons differs from that of the bulk alloy. All the diffraction peaks for the ribbon samples could be indexed by the B2 crystal structure (Im3m space group), on the other hand the bulk sample displayed the L2₁ crystal structure. It was found that the lattice parameter of the

ribbons is smaller than that of the bulk, which may be due to compression of the lattice in the x - y plane.

Figure 5.9 X-ray diffraction data and Rietveld plots for $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ alloys (a) bulk and (b) ribbon samples.

Figure 5.10 (a) and (b) show scanning electron microscope micrographs for bulk alloys and ribbons, respectively. It was observed from the micrographs of the bulk alloy that its surface was smooth. However, grain boundaries can be clearly observed on the ribbon surface (figure 5.10(b)). This change in morphology could be due to the moderate nucleation rate and rapid solidification at the melt-wheel interface [46]. The grains were homogenous and equiaxed with an average size of 5-8 μm . Melt spinning provides a high cooling rate which could be the reason for observation of a homogenous and uniformly granular microstructure [47]. In both cases, a single-phase morphology was observed (confirmed from the backscattered electron image), consistent with the XRD findings.

Figure 5.10. Scanning electron microscope (SEM) secondary electron images (SEI) of $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ (a) bulk, and (b) ribbons

5.2.2.2 Magnetic and MCE properties

The temperature dependent magnetic properties of bulk and ribbons of $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ are shown in Figure. 5.11 (a). The inset of the figure shows the Curie temperature (T_c) of the bulk (black square) and ribbon samples (red circle). It can be observed that the T_c of the ribbons is larger than that of the bulk alloy. The samples did not show temperature dependent hysteresis. The M - T curves were smooth and showed a broad transition from the PM to the FM phase, indicative of a second order phase transition. Figure 5.11 (b) shows the M - H curves measured at room temperature. It is worth noting that the saturation magnetization (M_s) for $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ ribbons (43 emu/g) is higher than that of the bulk alloy (33 emu/g). Both the samples are soft ferromagnets at room temperature, with small field hysteresis (coercivity < 50 Oe), which is advantageous for efficient magnetic cooling [48].

Figure 5.11 (a) $M(T)$ vs. T curve for $\text{Fe}_{54}\text{Cr}_{21}\text{Al}_{25}$ bulk and ribbon on cooling from 400 to 10 K under a field $\mu_0 H = 0.1\text{ T}$. Inset shows the dM/dT vs T plot with minima at the Curie temperature (T_C). (b) M vs. $\mu_0 H$ curve for $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ bulk and ribbons at 300 K.

The M - H isotherms around the Curie temperature at temperature intervals $\Delta T = 5\text{ K}$ and applied field of 5 T are shown in the inset of figure 5.12 (a) and (b). Figure 5.12 (a) and (b) shows the $-\Delta S_m$ versus T curves obtained for $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ bulk and melt-spun ribbons, respectively. Interestingly, the positive peaks in the $-\Delta S_m$ curves occurred near room

temperature. The entropy change curves were broad, which is favorable for Ericsson-cycle magnetic regenerator applications [49]. The melt-spun ribbons exhibited a ΔS_m value of $1.16 \text{ J kg}^{-1} \text{ K}^{-1}$, which is 33% more than the $-\Delta S_m$ of the bulk alloy ($0.87 \text{ J kg}^{-1} \text{ K}^{-1}$).

The refrigeration capacity can be determined by two parameters, i.e. relative cooling power (RCP), which is the product of maximum entropy change and the temperature span at full width of half maximum, i.e. $RCP = |-\Delta S_{max}| \times \delta T_{FWHM}$ and refrigeration capacity (RC_{AREA}), which is calculated by numerically integrating the area under $-\Delta S_m$ vs T curve at half maximum of the peak taken as the integration limits, i.e. $RC_{area} = \int_{T_1}^{T_2} -\Delta S_m(T) dT$. The value of RCP or RC_{AREA} should be high for practical applications. The RCP for the ribbons was $\sim 305 \text{ J kg}^{-1}$ at 5 T, which is 25% higher than that of the bulk (240 J kg^{-1} at 5 T).

Based on the degree of structural disorder, the enhancement in magnetic and magnetocaloric properties of ribbons can be explained. Luo *et al.* modeled the effect of structural disorder on the magnetic properties of melt-spun ribbons of Fe_2CrAl using electronic-structure calculations. He predicted that the ribbons would exhibit enhanced magnetic properties as compared to the bulk alloys [50]. This increase was related to the atomic site disorder in the B2 structure compared to the $L2_1$ structure. The reason for increased MCE values in ribbons can be attributed to the high cooling rate during melt spinning which results in a homogenous granular microstructure. A similar increment in MCE properties was observed in $\text{LaFe}_{11.8-x}\text{Co}_x\text{Si}_{1.2}$ melt-spun ribbons [47]. Chen *et al.* also found that high $-\Delta S_m$ in $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$ ribbons occurred due to the high cooling rate during melt spinning processing [51]. Law *et al.* reported higher $-\Delta S_m$ values in Gd-based melt-spun ribbons compared to the crystalline counterparts [52]. Various groups have reported the effect of an increase in RCP values due to structural disorder. Qin *et al.* observed superior MCE properties in melt extracted Gd-based alloys compared to the bulk counterparts [53]. Lui *et al.* reported that structural disorder in amorphous alloys leads to fluctuation of exchange integrals, which results in broadening of the magnetic transition and enhancement in RCP [54].

The values of $-\Delta S_m$ and RCP of our samples are higher than the recently reported MCE values in RE free high entropy NiFeCoCrPd_x alloys [55]. Recently, Qiang *et al.* reported size dependent MCE properties of Fe-based glass forming alloys and found that the highest value of $-\Delta S_m$ at 5 T was 0.89 Jkg⁻¹K⁻¹ [56]. Comparison of the MCE results of our samples with selected results of RE free, second order phase transition materials is shown in Table 5.1. We found that the $-\Delta S_m$ and RCP values of our material are comparable to those other Fe-based materials for near RT cooling applications. Our alloy is corrosion resistant because of the presence of Cr [57].

Figure 5.12 The behavior of ΔS_m with temperature ($\text{Fe}_{0.72}\text{Cr}_{0.28}$)₃Al from 1 T to 5 T for (a) bulk and (b) ribbon. The insets show the corresponding magnetic isotherms from 10 to 400 K with a temperature difference of 10 K.

Table 5.1. Curie temperature (T_c), isothermal entropy change ($-\Delta S_m$), RCP_{FWHM} and RC_{AREA} values for our material and some recent iron-based magnetocaloric materials.

Nominal composition	T_c (K)	$-\Delta S_m$ at 5T (Jkg ⁻¹ K ⁻¹)	RCP_{FWHM} at 5T (Jkg ⁻¹)	RC_{AREA} at 5T (Jkg ⁻¹)	Reference
(Fe _{0.72} Cr _{0.28}) ₃ Al Ribbons	330	1.16	305	214	This work
(Fe _{0.72} Cr _{0.28}) ₃ Al Bulk	285	0.87	240	177	This work
Fe _{66.3} V _{13.7} Si ₈ B ₁₂	335	1.7	100	-	[58]
γ -Fe ₄₉ Ni ₂₉ Cr ₂₂	125	1.8	-	-	[59]
Fe ₇₅ Ta ₅ B ₁₀ Zr ₉ Cu ₁	313	2.03	241	-	[60]
Fe ₃₃ Cu ₆₇	312	0.83	208	148.5	[61]
NiFeCoCrPd _{0.25}	225	0.9	215	150	[55]
FeCrMnMoWBCSi	16.3	0.89	66	52	[56]
(Fe _{0.86} Cr _{0.14}) ₈₀ Si ₆ B ₁₄	291	1.8	347	260	[62]
(Fe ₇₀ Ni ₃₀) ₉₃ Cr ₇	215	1.11	306	216	[63]

5.2.2.3 Critical behavior

Arrott plots

To study the magnetic phase transition near the Curie temperature, the nature of the ordering and the MCE behavior of (Fe_{0.72}Cr_{0.28})₃Al ribbons, we calculated the critical exponents i.e, β, γ, δ and η , where β corresponds to the saturation magnetization $M_s(T)$, γ corresponds to the inverse initial magnetic susceptibility χ_0^{-1} , δ corresponds to the critical magnetization at T_c and η corresponds to the field dependent change in entropy [64],[65].

The critical exponents can be defined as:

$$M_s(T) = M_0(-\varepsilon)^\beta, \varepsilon < 0, T < T_c \quad (5.1)$$

$$\chi_0^{-1}(T) = \left(\frac{h_0}{M_0}\right) \varepsilon^\gamma, \varepsilon > 0, T > T_c \quad (5.2)$$

$$M = KH^{\frac{1}{\delta}}, \varepsilon = 0, T = T_C \quad (5.3)$$

where $\varepsilon = (T - T_C)/T_C$ is the reduced temperature, h_o/M_o and K are the critical amplitudes.

Figure 5.13 (a) shows the $M(H)$ isotherms for $\text{Fe}_{54}\text{Cr}_{21}\text{Al}_{25}$ ribbons from 304 to 352 K with a temperature difference of 2 K. Figure 5.13 (b) shows the Arrott plots i.e, M^2 v/s H/M , in the vicinity of the Curie temperature. According to the Banerjee criterion, the slope of the Arrott plots provides information on the order of the phase transition in a material [66]. For $\text{Fe}_{54}\text{Cr}_{21}\text{Al}_{25}$ ribbons, the slopes of the Arrott plots were positive, confirming a second order phase transition. Additionally, even at high magnetic fields, the Arrott plot curves are not parallel to each other, indicating the absence of long range order mean field interactions[67]. Hence, modified Arrott plots (MAP) were used to determine the critical behavior and the nature of the transition, as proposed by the Noakes equation i.e, $(H/M)^{\frac{1}{\gamma}} = \frac{(T - T_C)}{T_C} + (M/M_1)^{\frac{1}{\beta}}$, where M_1 is the material constant[68]. Figure 6 (c, d and e) shows the modified Arrott plots using theoretical models: 3D-Heisenberg ($\beta = 0.365$, $\gamma = 1.386$), 3D-Ising ($\beta = 0.325$, $\gamma = 1.24$) and tricritical mean field ($\beta = 0.25$, $\gamma = 1$) model, respectively. Among these models, the best fit model was found by plotting the relative slopes ($RS = S(T)/S(T_c)$) versus temperature, where $S(T)$ is the slope of the straight line in the high field region at T . Figure 5.13 (f) shows the graphs of RS versus T . The 3D-Heisenberg model shows a value of RS with a close fit to a value of unity, whereas the tricritical mean field model and 3D-Ising model show more deviation from a value of unity [69]. Hence, the critical exponents were calculated using the 3D-Heisenberg model.

Figure 5.13 (a) $M(H)$ isotherms around T_c with 2K temperature difference from 304 K to 352 K, (b) Arrott plot (M^2 versus H/M), (c) 3D-Heisenberg model, (d) 3D-Ising, (e) Tri-critical mean field model, and (f) relative slope (RS) as a function of temperature.

Kouvel-Fisher (K-F) plots

The K-F plots were used to calculate the critical exponents and the Curie temperature [70].

The governing equations are:

$$\frac{M_s(T)}{(dM_s(T)/dT)} = \frac{T-T_C}{\beta} \quad (5.4)$$

$$\frac{\chi_0^{-1}(T)}{d\chi_0^{-1}(T)/dT} = \frac{T-T_C}{\gamma} \quad (5.5)$$

From figure 5.13 (c), at temperatures lower than the Curie temperature ($T < T_c$), the linear extrapolation of the modified Arrott plot from high fields to the intercept on the y-axis ($M^{1/\beta}$) at $M^{1/\beta} = 0$ yields the inverse magnetic susceptibility ($\chi^{-1}(T, 0)$). Similarly, at

temperatures higher than the Curie temperature ($T > T_c$), the linear extrapolation of the modified Arrott plot from high fields to the intercept on the x -axis ($(H/M)^{1/\gamma}$) at $(H/M)^{1/\gamma} = 0$ yields the spontaneous magnetization ($M_s(T, 0)$). According to equations (5.4 and 5.5), the slope of the graphs of $M_s (dM_s/dT)^{-1}$ v/s T and $\chi_0^{-1} (d\chi_0^{-1}/dT)^{-1}$ v/s T provide the critical exponents $1/\beta$ and $1/\gamma$ respectively. The intercept of these lines on the T axis provides the Curie temperature (T_c). Using the K-F plots for $\text{Fe}_{54}\text{Cr}_{21}\text{Al}_{25}$ ribbons (Figure 5.15 (a)), we obtained the critical exponents $\beta = 0.345$ with $T_c = 330.82$ K and $\gamma = 1.316$ with $T_c = 331.32$ K. These experimentally obtained values of β and γ agree well with the theoretical exponents of the 3D-Heisenberg model.

Critical isotherm plots

Using the scaling equation 5.3, the third critical exponent δ can be deduced from the slope of the M vs H plot. Figure 5.14 (b) shows the M vs. H isotherm at the Curie temperature (T_c). The inset of Figure 5.14 (b) shows a graph of $\ln(M)$ vs. $\ln(H)$, with the black circles as the experimental data and the red line as the fitted data. The slope ($1/\delta$) of this plot shows that the critical exponent δ has a value of 4.63.

Based on statistical theory, the critical exponents are related to each other by Widom's scaling relationship (WSR) : $\delta = 1 + (\gamma/\beta)$ [71]. We found $\delta = 4.81$ from this scaling relationship, which is in close agreement with the value obtained from the experimental results, as well as from the theoretical 3D-Heisenberg model. Additionally, using the scaling equations 5.1 and 5.2, the experimental values of spontaneous magnetization $M_s(T)$ and inverse magnetic susceptibility $\chi_0^{-1}(T)$ were plotted versus reduced temperature ($\varepsilon = T - T_c/T_c$) to yield the critical exponents $\beta = 0.31$ and $\gamma = 1.4$, respectively (Figure 5.14 (a) inset).

Table 5.2 shows the critical exponents determined experimentally and a comparison with the values obtained for other selected Fe based magnetic alloys. It was observed that the experimentally determined critical exponents are close to the 3D-Heisenberg model, indicating the presence of short-range interactions [72].

Figure 5.14 (a) Kouvel- Fisher (K-F) plots of spontaneous magnetization $M_s(T)$ (left axis) and inverse initial susceptibility χ_0^{-1} (right axis). Inset shows the $\ln(M_s)$ and $\ln(\chi_0^{-1})$ vs. $\ln(T-T_c/T_c)$ from scaling equations. (b) $M(H)$ recorded at T_c . Inset shows the same plot on the $\ln$ - $\ln$ scale, where the red line is the linear fit to the equation $M = KH^{1/\delta}$

Table 5.2. Experimentally deduced critical exponents for $(Fe_{0.72}Cr_{0.28})_3Al$ ribbons from different techniques compared with theoretical models and other recent literature. (Abbreviations: WSR= Widom's scaling relation, K-F = Kouvel-Fisher, CIA = critical isotherm analysis, RCP = relative cooling power)

Material/model	Technique	B	γ	δ	n	Ref.
Mean field	Theory	0.5	1	3		[73]
3D Heisenberg	Theory	0.365	1.336	4.8		[73]
3D Ising	Theory	0.325	1.242	4.82		[73]
Tricritical mean field	Theory	0.25	1	5		[74]
Fe		0.389	1.333	4.35		[73]
$(Fe_{70}Ni_{30})_{89}B_{11}$	K-F, WSR	0.364	1.319	4.623	0.875	[75]
$Fe_{85}Ni_5Zr_{10}$	K-F	0.425	1.323	4.11		[76]
$Fe_{54}Cr_{21}Al_{25}$ ribbons	K-F	0.345	1.316	-		This work
	Scaling law	0.31	1.4			-
	CIA	-	-	4.63		-
	WSR			4.81		-
	$RCP \propto H^{1+1/\delta}$			4.90		-
	$-\Delta S_m \propto H^n$				0.7575	-

5.2.2.4 Field dependent magnetocaloric behavior

The inset of figure 5.15 (a-b) are plots of RCP v/s magnetic field and $-\Delta S_m$ v/s magnetic field, respectively. Both RCP and $-\Delta S_m$ followed a linear trend with an increase in applied field. The values of RCP and $-\Delta S_m$ are significantly greater for the ribbons compared to the bulk alloy. The magnetic field dependence of $-\Delta S_m$ and RCP plots provide a more accurate method to determine the local exponent n and critical exponent δ . In magnetic materials with second order phase transition (SOPT), the field dependent $-\Delta S_m$ and RCP can be expressed in the form of power laws [77] :

$$\Delta S_m^{peak} \propto H^n \quad (5.6)$$

$$RCP \propto H^{1+1/\delta} \quad (5.7)$$

Figure 5.15 (a,b) shows a plot, on the $\ln-\ln$ scale, of RCP and $-\Delta S_m^{peak}$, at different fields, of bulk and ribbons, respectively. The critical exponent δ for ribbons, obtained from the slope of figure 5.15 (a), is 4.90. This value is close to the value obtained from the WSR ($\delta = 4.81$). The local exponent $n = 0.7575$ for $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ ribbons obtained from the slope of figure 5.15 (b), is greater than the value of 0.66 corresponding to mean field theory [78]. This deviation could be due to local inhomogeneities, which lead to a wider distribution of Curie temperature, which, in turn, increases RCP. The structural inhomogeneity could be a consequence of short-range chemical order in the ribbons, consistent with the facts that our critical exponents followed the 3D-Heisenberg model and that the x-ray diffraction pattern for $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ ribbons exhibited the B2 crystal structure [72].

Figure 5.15 (a) Field dependence of $\ln(RCP)$ and RCP (inset) for $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ bulk and

ribbons, (b) field dependence of $\ln(-\Delta S_m^{peak})$ and $-\Delta S_m$ (inset) for $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ bulk and ribbons.

5.2.3 $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ milled samples

5.2.3.1 *Evolution of structural order with milling time*

The evolution of structural order with milling time at different milling speeds was studied using x-ray diffraction (Figure 5.16). No change in the intensities of the superlattice peaks was observed in the x-ray diffraction patterns of the samples milled at 500 rpm (Figure 5.16 (c)). For the samples milled at highest milling speed, i.e., 700 rpm, ZrO_2 contamination was observed in the x-ray patterns of all the samples (Figure 5.16 (a)). A cubic crystal structure was observed for all the samples milled at 600 rpm with negligible ZrO_2 contamination for up to 120 min milling time. As observed in the inset of figure 5.17, the (111) and (200) superlattice reflections were only present in the 15 min milled sample (HBM 15) suggesting a L2_1 phase formed only in the HBM 15 sample. In the other samples, including the bulk sample, a B2 structure was observed. The table in figure 5.17 summarizes the relative intensities of the (200) superlattice reflection and (220) fundamental peak, as observed in the XRD patterns.

Figure 5.16 X-ray diffraction patterns of the Fe_{2.1}Cr_{0.9}Al alloys milled at (a) 700 rpm (b) 600 rpm and (c) 500 rpm, for upto 120 min. The asterisk (*) represents the peaks corresponding to zirconium oxide impurities.

Figure 5.17. X-ray diffraction pattern of bulk and milled samples, milled for up to 150 min at 600 rpm. Inset shows the enlarged XRD pattern for 2θ values from 25 to 35°, highlighting the (111) and (200) superlattice reflections. The asterisk (*) in the inset represents a minor impurity peak corresponding to zirconium oxide. The table summarizes the relative intensity I_{200}/I_{220} in different samples. (“—” stands for absence and “+” stands for presence).

The I_{200}/I_{220} value, signifying the structural order in the Fe-Cr sublattice was calculated by the ratio of the relative intensity of the (200) superlattice peak to the (220) fundamental peak [31]. A higher value of I_{200}/I_{220} corresponds to a higher degree of structural order in Fe-Cr sublattice. The normalized values of the relative intensities, i.e., I_{200}/I_{220} , were plotted on y-axis with the milling time on x-axis. Interestingly, a cyclic pattern in the magnitude of the I_{200}/I_{220} values was observed over a milling time of 150 min (figure 5.18 (a)). On further milling beyond 150 min., ZrO_2 contamination from the bowl walls and the zirconia balls was observed, hence the milling time was restricted to 150 min. We adopted the reaction rate model of Sluiter and Kawazoe [79], and used our experimental data to find the reaction rate model parameters. Sluiter and Kawazoe assumed that the stored energy during ball milling is proportional to the defect concentration. The larger the defect concentration, the greater is the stored energy, hence the probability of cyclic transformations increases. Here, we assumed that the number of defects created during high energy ball milling is larger than the number of defects which were annihilated. These

defects are a major contribution to the total stored energy (E_{stored}). From the model parameters, the value of stored energy during high energy ball milling was calculated. It was observed that E_{stored} versus milling time follows a cyclic pattern, the highest amount of stored energy being ~ 19 kJ/mol. In brief, according to this reaction rate model, let x correspond to the degree of chemical order, i.e. the I_{200}/I_{220} value, we start with a bulk sample with a value of I_{200}/I_{220} equal to zero at $t = 0$, i.e., $x = 0$ at $t = 0$. At $t > 0$, the rate of change of x with time is given by

$$\frac{dx}{dt} = -x(t)r \quad (5.8)$$

The reaction rate r for the transformation of the higher defect density structure to the lower defect density structure is given by,

$$r = ke^{-\beta(A-E_{stored})} \quad (5.9)$$

Where, k is the reaction rate parameter, A is the activation energy and E_{stored} is the energy stored during ball milling. The value of E_{stored} is dependent on the milling conditions. At $t = 0$, $E_{stored} = 0$ and at $t > 0$, $E_{stored} > 0$. If the number of defects created during milling is greater than the number of annihilated defects, the stored energy increases. This stored energy must be evaluated using the rate of defect creation and the rate of defect annihilation. Hence, the expression for the change in stored energy is given as,

$$\frac{dE_{stored}(t)}{dt} = B - fE_{stored}(t) \quad (5.10)$$

where, B is the rate of defect creation, f is the rate of defect annihilation. Hence, (B/f) is the maximum amount of stored energy. Solving equation (5.10) gives,

$$E_{stored} = \frac{B}{f} (1 - e^{-ft}) \quad (5.11)$$

Substitution of equation (5.11) in equation (5.9) and then in equation (5.8) gives an expression for the rate of change of x with time. Introducing the dimensionless variables P , Q and time $s = ft$, we obtain [24]

$$\frac{dx}{dt} = -x(s)Pe^{Q(1-e^{-s})} + x(s)P \quad (5.12)$$

where $P = \frac{k}{f}e^{-\beta A}$, $Q = \beta E_{stored}$, where $\beta = \frac{1}{k_B T}$ and f^{-1} yields the time at which maximum energy is achieved.

As mentioned previously, a higher value of I_{200}/I_{220} corresponds to greater order. The parameter Q corresponds to the total amount of stored energy during milling. The value of

k and P can be obtained from the experimental data. Lower values of E_{stored} are relevant for a change in the degree of order compared to the high values of E_{stored} reported for a cyclic change in the crystal structure [79]. To predict the values of stored energy E_{stored} with milling time, certain assumptions were made, as described later, and the value of P was obtained as 5.652×10^{-8} .

As shown in figure 5.18 (a), the bulk sample showed the least structural order, the normalized value of I_{200}/I_{220} is zero. Upon milling for 15 min, the I_{200}/I_{220} increased to a value of 0.75, signifying more structural order in the Fe-Cr sublattice. On further milling, the value of I_{200}/I_{220} varied cyclically with time. Using the above reaction rate model and the input parameters i.e., k , β , f^{-1} , P and A (Table 5.3), the total amount of stored energy (E_{stored}) was calculated from our experimental values i.e. $x(t)$, dx/dt and t , using equation 5.12. It was observed that E_{stored} also followed a cyclic pattern with milling time and saturated at a value of ~ 19 kJ/mol after 120 min.

Figure 5.18. Cyclic behavior of change in (a) normalized value of I_{200}/I_{220} versus milling time and (b) Stored energy E_{stored} versus milling time.

Table 5.3. Input parameters for calculation of E_{stored} during ball milling.

Reaction rate parameter k (s^{-1})	β (kJ/mol)	Time constant f^{-1} (s)	Dimensionless parameter P
10^7	0.38	$1.8 \times 10^3 \text{ s}$	5.652×10^{-8}

The following assumptions were used to calculate the parameters in table 1 in the reaction rate model:

1. Since no creation or annihilation of defects occurs at $t = 0$ s, stored energy is zero at $t = 0$ s.

2. Since the activation energy for vacancy formation and for diffusion in intermetallic compounds and transition metals is ~ 100 kJ/mol, we assume that the activation energy for diffusion and vacancy formation for our sample is 100 kJ/mol [79].
3. The temperature during ball milling was assumed to be ~ 320 K [25].

Further experiments to explore the detailed structural, magnetic and magnetocaloric properties were performed on bulk and 15 min milled (referred to as HBM 15) samples. These samples were selected because (a) the bulk sample showed a B2 structure whereas HBM 15 showed an $L2_1$ structure, hence it is appropriate to compare these samples and, (b) only bulk and HBM 15 samples showed T_c below 300 K while all other samples exhibited T_c higher than 400 K, which is not relevant for many MCE applications, e.g., refrigeration, which require T_c near room temperature.

5.2.3.2 Structural analysis

To identify the crystal structure and phases in the bulk and HBM 15 samples, the results of XRD are shown in greater detail in figure 5.19. The B2 crystal structure was observed for the bulk sample, with disorder in the Cr-Al sub-lattice and the Fe sublattice [44]. After 15 min. of ball milling, the (111) superlattice reflection peak was observed (inset of figure 5.19), due to the increased degree of order in the Cr-Al sublattice. The intensity of the (200) superlattice reflection also increased, implying a higher degree of order in the Fe sublattice [80]. Similar studies were performed on Fe-Al alloys, amorphization was observed after 70 min when ball milling was performed at a high intensity of 150 g, where g is the gravitational acceleration [81]. The crystal parameters obtained from Rietveld refinement (not shown here) showed that the lattice parameter a was 5.809 Å for the bulk sample, which decreased to a value of 5.796 Å after 15 min of ball milling and subsequently increased to 5.81 Å after 30 min of milling. A similar change was also reflected in the cell volume. The crystallite size increased from 38 nm to 48 nm after 15 min of milling. This could be due to stored energy during high energy ball milling which favors larger crystallite size and an increase in short-range order. Upon milling to 30 min, the ordered phase starts transforming into a relatively less ordered phase. On milling of $Co_{75}Ti_{25}$ alloys, El-Eskandarany et al obtained an amorphous phase followed by a crystalline phase and subsequently again obtained an amorphous phase. They suggested that point defects and

other lattice defects are responsible for such cyclic transformations [25]. Our experimental results also show an initially less ordered phase transforming to a more ordered phase upon milling for 15 min. Further milling transforms the more ordered phase back to a less ordered phase. Such “*less ordered* $\rightarrow$ *more ordered* $\rightarrow$ *less ordered*” transitions could be a result of large amount of the stored energy which also followed a cyclic pattern, although the maxima and minima of the stored energy curve do not match with the maxima and minima of the I_{200}/I_{220} curve.

Figure 5.19 X-ray diffraction pattern of bulk and HBM 15 samples. Inset shows the enlarged XRD pattern for 2θ values from 25 to 35°, highlighting (111) and (200) superlattice reflections.

Figure 5.20 shows the scanning electron micrographs of bulk and HBM 15 samples taken in SEI mode. The morphology of the bulk sample was smooth and featureless (figure 5.20 (a)). Ball milling for 15 min breaks down the bulk sample into pieces of average size of 100 μm which, at higher magnification, showed increased surface roughness (figure 5.20 (b and c)).

Figure 5.20 Scanning electron microscope (SEM) secondary electron images (SEI) of $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ (a) bulk (b) HBM 15 sample, and (c) HBM 15 sample enlarged image of the selected area.

5.2.3.3 Characterization of magnetic properties

The field dependent magnetization curves ($M-H$) of bulk and HBM15 samples, measured at 300 K, are shown in figure 5.21. The inset of figure 5.21 shows the $M-H$ curves at 10 K. All samples showed soft ferromagnetic behavior, with low hysteresis. After milling for 15 min, the saturation magnetization (M_s) increased from 25 emu/g of bulk to 38 emu/g for HBM15 sample, while the coercivity (H_c) remained small. Yang *et al* reported a decrease in saturation magnetization (M_s) values for $\text{Fe}_{50}\text{Cr}_{50}$ alloys with increasing milling time [82]. On the other hand, Hernando et al reported an increase in M_s as a function of milling time for FeAl powders [83]. This desirable increase in saturation magnetization, also observed in our work is encouraging, since it provides a method to increase magnetization by ball milling for short duration.

The temperature dependent magnetization ($M-T$) behavior is shown in figure 5.22. The samples showed negligible temperature dependent hysteresis. The $M-T$ graphs were found to be smooth. A broad transition from PM state to FM state was observed, indicating the presence of SOPT. The inset of figure 5.22 shows the zero-field cooled (ZFC) and field cooled (FC) curves for the two sample sets. Irreversibility was evident in the ZFC-FC curve for the HBM15 sample measured at 100 Oe magnetic field and temperature sweep from 400 K to 10 K. Chromium (Cr) can display antiferromagnetic (AFM) behavior. When both ferromagnetic and antiferromagnetic interactions coexist, the atomic spins get pinned in

various configurations at low fields due to antiferromagnetic anisotropy. This results in the splitting of the ZFC-FC curves. This irreversibility indicates pinning of intrinsic ferromagnetic domains by the antiferromagnetic environment [84]. The total magnetization is lower in the ZFC case compared to the FC case because preferred orientation was not present in ZFC. The bulk sample with B2 phase transformed to the L2₁ phase upon 15 min of milling with a concomitant increase in saturation magnetization. A similar effect of structural ordering on saturation magnetization was observed by Pandey *et al* in Co₂MnSi thin films. The saturation magnetic moment increased with structural order. Magnetization increased from the amorphous to the A2 to the B2 and finally to the L2₁, crystal structure [85].

Figure 5.21 M vs. $\mu_0 H$ curve for Fe_{2.1}Cr_{0.9}Al bulk and HBM 15 samples at 300 K. Inset shows the M-H curves at 10 K.

Figure 5.22 (a) $M(T)$ vs. T curve for $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ bulk and HBM15 samples on cooling from 400 to 10 K under $\mu_0 H = 0.1\text{T}$. Inset shows the zero-field cooled and field cooled (ZFC-FC) plots measured at an applied field of 100 Oe and temperature sweep from 400K to 10K.

The Curie temperature (T_c) was 256 K for the bulk sample whereas it decreased to 244 K for the HBM15 sample (figure 5.23). This lower T_c could be a consequence of short-range order, as is evident from the XRD and EXAFS results. The bulk sample showed a sharp T_c , resulting in a larger value of $-\Delta S_m$. Table 5.4 is a summary of the effect of ball milling on the magnetic and MCE properties, including our work and other similar reports. Most reports have suggested a decrease in saturation magnetization (M_s) and an increase in coercivity (H_c) as a function of milling time, however, our milled sample showed a 50 % increase in M_s at room temperature. The HBM15 sample showed an increase in coercivity by 23% but this increment was small compared to other reports of ball milled samples listed in table 5.4. While most materials show only a small change in T_c even after ball milling, another practical advantage of our alloy is the ability to tune the T_c by ball milling for just 15 min.

Table 5.4 Influence of milling time on the magnetic and MCE properties of selected alloys compared to their bulk counterpart. Notation: RCP = relative cooling power, n.a. = not available, H_c = coercivity, M_s = saturation magnetization, T_c = Curie temperature, $-\Delta S_m$ = isothermal magnetic entropy change. Note: Numbers within brackets provide the measured value.

Material	Milling time (min)	M_s (emu/g)	H_c (Oe)	T_c (K)	$-\Delta S_m$ (J/kg.K)	RCP (J/kg)	Ref.
HBM15	15	Increased 50%	Increased 23% (60 Oe)	Decreased 4.9 % (244K)	Decreased 12%	Increased 23% (300)	This work
Co ₂ MnSi	30	Decreased 13% (106 emu/g)	Increased 653% (98 Oe)	Increased 0.3% (1018K)	n.a.	n.a.	[86]
Gd ₅ Si _{1.3} Ge _{2.7}	150	n.a.	n.a.	Decreased 0.55 % (180 K)	Decreased 14% (0.38)	Decreased ~23%	[87]
Gd(Ni _{0.9} Fe _{0.1}) ₃	180	Decreased 1 % (5.97 uB/f.u.)	n.a.	Decreased 2.25% (260K)	Decreased 10%	Decreased 15%	[88]
Nd ₁₀ Fe ₈₅ B ₅	300	Decreased 27% (825KA/m)	Increased by 2000%	n.a.	n.a.	n.a.	[89]
Ho(Fe _{0.5} Co _{0.5}) ₃	420	Decreased 20.55%	Increased by 1870%	n.a.	n.a.	n.a.	[90]
Pr ₂ Fe ₁₇	600	n.a.	n.a.	Increase 2.5% (292K)	Decreased 35% (3.7)	n.a.	[91]
Tb(Ni _{0.95} Fe _{0.05}) ₃	1440	Decreased 58% (2.72 uB/f.u)	Increased 210% (3100 Oe)	No change (156 K)	Decreased 17.6% (2.75 at 7T)	n.a.	[92]

Figure 5.23. dM/dT vs T plot obtained from the $M(T)$ vs T curve for bulk and HBM 15 samples, with the minima at the Curie temperature (T_c).

5.2.3.4 Local structure analysis: EXAFS study

EXAFS studies were performed for both the bulk and HBM15 sample sets to further understand the effect of milling induced deformation on short-range order and to examine the effect of milling on the magnetic and magnetocaloric properties. Figure 5.24 (a) and (b) shows a comparison of Fe-K and Cr-K edge Fourier Transformed (FT) EXAFS data for bulk and HBM15 $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ samples, respectively. The intensity of the FT EXAFS peak is proportional to the degree of local atomic order, while the change in peak position indicates changes in interatomic distances resulting from local ordering. It is clear from figures 5.24 (a) and (b) that both position and intensity of the first shell co-ordination peak were significantly different, suggesting that the short-range order of the milled sample is different from that of the bulk sample.

For the Fe-K edge, the principal EXAFS peak of the bulk is asymmetric and has a relatively higher FWHM, indicating that the first shell EXAFS is a convolution of two individual sub-shells. This results in chemical disorder. However, after only 15 min. of ball milling, the first shell peak becomes symmetric, its FWHM is reduced and intensity is considerably increased. In addition, the position of the principal EXAFS peak shifts to a lower R value. Similar results were also obtained for Cr-K edge EXAFS analysis. Ball milling resulted in an increase in peak intensity, a reduction in FWHM, and a concomitant shift in peak position towards a lower R value. These changes in Fe-K and Cr-K edge EXAFS spectra caused by ball milling provide direct evidence of milling induced local atomic rearrangement and development of short-range order around Fe and Cr atoms in $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ alloys.

Figure 5.24 Real space Fourier transformed (a) Cr-edge EXAFS spectra for $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ bulk and HBM 15 samples and (b) Fe-edge EXAFS spectra for $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ bulk and HBM 15 samples.

To obtain quantitative data of the local order, we also performed curve fitting of the Fe-K and Cr-K edges from the Fourier transformed (FT) EXAFS data (figure 5.25 (a, and b)).

The crystallographic data of the ordered $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ alloy with a L2_1 structure was used to simulate the theoretical EXAFS spectra [45], which, in turn, was used as a model to fit the experimental EXAFS curves of the bulk and HBM15 samples.

Table 5.5 shows the EXAFS fitting parameters, i.e., coordination number (N), bond length (R), Debye-Waller factor (σ^2) and the edge energy difference. For both Fe-K and Cr-K edges, when EXAFS of the bulk alloy was fit using the L2_1 model structure described above, the edge energy difference resulting from these fits was found to exceed 15 eV (Cr-K edge: 20.8 eV, Fe-K edge: 16.1 eV). The results, consistent with the qualitative FT EXAFS analysis presented above, suggested that the local structure of the bulk sample is not chemically ordered and is significantly different from the “standard L2_1 ” structure. If the short-range chemical order of the bulk sample had been comparable to the L2_1 structure, their edge energies would also have been comparable and the edge energy difference obtained from the fits would not be as large as our experimental values.

However, in contrast, when the HBM15 sample was fit using a L2_1 model structure (figure 5.25 (a) and (b), respectively), the value of edge energy difference was found to be < 10 eV (Cr-K edge: 8.8 eV, Fe-K edge: 3.6 eV), which is significantly less than the respective edge energy difference obtained for the bulk sample. This confirms that milling induced deformation gives rise to considerable changes in atomic arrangement around Fe and Cr atoms in $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ alloys. While the structure of the bulk sample is chemically disordered, only 15 min. of ball milling is sufficient to develop a L2_1 -like local structure, which is more suitable for magnetocaloric properties.

Figure 5.25. Least square first shell fitting of EXAFS data of the $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ HBM 15 alloy (a) in Fe K edge (b) in Cr K edge R space. Red line denotes the fitted data.

Table 5.5. Bond length (R), Co-ordination number (N), disorder (Debye-Waller DW factor) and edge energy difference obtained by EXAFS fitting, for $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ bulk and HBM15 alloy, at Fe K edge and Cr K edge.

$\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$	N			R (Å)			DW factor (σ^2)			Edge energy difference (eV)		
	Cr-edge		Fe-edge	Cr-edge		Fe-edge	Cr-edge		Fe-edge	Cr-edge		Fe-edge
	Cr-Fe	Fe-Al	Fe-Cr	Cr-Fe	Fe-Al	Fe-Cr	Cr-Fe	Fe-Al	Fe-Cr	Cr-Fe	Fe-Al	Fe-Cr
Bulk	4.0	1.9	3.5	2.6	2.5	2.5	0.009	0.006	0.006	20.8	16.1	16.1
HBM 15	3.8	4.3	4.0	2.4	2.4	2.4	0.004	0.004	0.004	8.8	3.6	3.6

5.2.3.5 Magnetocaloric property analysis

Figure 5.26 (a, b) shows the ΔS_m versus T curves for bulk and HBM15 samples, respectively. These samples exhibited broad ($-\Delta S_m$) versus T curves. Some research groups include the demagnetization factor in the calculation of MCE properties [93]. The demagnetization factor can be included to account for shape effects which can affect the net magnetic field [94]. For the ball milled sample, assuming the powder particles to be spherical, the demagnetization factor N_{dm} was taken as 1/3 [95]. The applied magnetic field gets modified by the internal magnetic field (H_{int}) as, $H_{int} = H - N_{dm}M$, where H is the applied magnetic field, N_{dm} is the demagnetization factor and M is the magnetization of the material. As a result of the inclusion of the demagnetization factor, the isothermal entropy change ($-\Delta S_m$) gets modified and shows a slight decrease of $\sim 3\%$ around the Curie temperature (figure 5.27).

Figure 5.26 The temperature dependent magnetic entropy change ($-\Delta S_m$) at applied magnetic fields of 0 to 5 T for $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ (a) bulk and (b) HBM15 samples

The broadness of the $-\Delta S_m$ v/s T curves was even more pronounced in HBM15 sample (dotted lines in figure 5.26 (b)), due to the broad distribution of the Curie temperatures in this sample set. Hence, an improvement in RCP was observed for milled samples, although the $(-\Delta S_m)$ value decreased slightly from $0.9 \text{ Jkg}^{-1}\text{K}^{-1}$ for the bulk to $0.78 \text{ Jkg}^{-1}\text{K}^{-1}$ in HBM15 samples. Gorria *et al* reported an increase of 13% in RCP value upon 10 h ball milling of $\text{Pr}_2\text{Fe}_{17}$ alloys [96]. For $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ alloys, we observed an increase of 23% in RCP value after milling for only 15 min. Table 5.6 shows a comparison of the key parameters for bulk and HBM15 samples at different applied fields. The RCP value for the HBM15 sample was 300 Jkg^{-1} at 5 T, which is 23% higher than that of the bulk sample (244 Jkg^{-1} at 5 T).

Figure 5.27 The temperature dependent isothermal entropy change ($-\Delta S_m$) of the HBM15 sample set.

Table 5.6. Saturation magnetization (M_s) at 10 K and 300 K, Curie temperature (T_c), Coercivity (H_c), isothermal entropy change ($-\Delta S_m$), RCP_{FWHM} values at 5T applied field

Fe _{2.1} Cr _{0.9} Al	M_s (emu/g)		T_c (K)	H_c (Oe)	$-\Delta S_m$ (J/kgK)	RCP (J/kg)
	10K	300 K				
Bulk	52	25	256	< 50	0.9	244
HBM15	62	37.5	244	~ 60	0.78	300

Figure 5.28. (a) Field dependence of RCP for Fe_{2.1}Cr_{0.9}Al bulk sample and HBM 15 sample (b) field dependence of $\ln(-\Delta S_m^{peak})$ for Fe_{2.1}Cr_{0.9}Al bulk sample and HBM15 sample

Figure 5.28 (a, b) is a graph of RCP and $-\Delta S_m^{peak}$ of bulk and HBM 15 powders, respectively, from 1 T to 5 T. RCP for HBM15 increased at higher fields, the values are even higher than those of the bulk alloy. The value of local exponent (n) 0.7825 for HBM15, deduced from the slope of figure 5.28 (b), is greater than the value of 0.6835 for

the bulk sample obtained from mean field theory [78]. This increase in the value of n for HBM15 sample is a result of wider distribution of Curie temperatures compared to the bulk and hence an enhancement in RCP value. The short-range order in HBM 15 could result in an increased value of local exponent n .

Figure 5.29 The plot of n v/s T from 1 T to 5 T for $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ bulk sample and HBM 15 sample. The minima correspond to the T_c of the sample.

Based on the mean field theory, the value of entropy change near T_c can be calculated using the relationship, $-\Delta S_m = A(H)^n$, where n is the local exponent and take a value of 0.66 and A is proportionality constant [78]. For the FM region i.e., $T < T_c$, the local exponent is $n \sim 1$. At the FM-PM transition, i.e., T_c , the value of n is less than 1 (figure 5.29). The value of n decreased but did not reach the value of $2/3$ predicted by the mean field approach. The behavior of n was different in the bulk and the milled samples [78]. For the bulk sample the value of $n \sim 0.68$ is close to the mean field model but the value of $n \sim 0.78$ was considerably larger for the HBM15 sample. A large value of n implies a wider distribution of Curie temperatures, which in turn increases the RCP values of the milled samples [97].

5.3 Conclusions

The structure, magnetic and MCE properties of $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ bulk samples were explored for the first time. With an increase in Cr content, a compression in the x - y plane of the lattice was observed. The RCP/\$ for bulk samples with different Cr content was calculated. It was found to be superior to other promising MCM exhibiting near room temperature MCE. The RCP/\$ is an industrially relevant performance metric, hence RCP/\$ provides a critical advantage. Subsequently, the structural and MCE properties of buttons and ribbons of $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ alloys were also investigated. The bulk alloy possessed a L_{21} crystal structure. On the other hand, the melt-spun ribbons exhibit a B2 crystal structure. The critical exponents for $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ ribbons were determined using modified Arrott plots, the Kouvel-Fisher method, Critical isotherm analysis and field dependent MCE behavior. The exponents, deduced from different techniques, were close to each other and consistent with a short-range order 3D-Hesienberg model. The MCE properties of ribbons showed an enhancement of 33% in $-\Delta S_m$ and 25% in RCP values. The structural, magnetic and MCE properties of $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ alloys subjected to high energy ball milling were also studied. A cyclic behavior in degree of structural order in the Fe-Cr sublattice was observed at a milling speed of 600 rpm and, the cyclic order was related to the stored energy due to high energy ball milling. The bulk $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ alloy possessed a B2 crystal structure. High energy ball milling at 600 rpm for only 15 min transformed the sample to a more ordered L_{21} crystal structure. This structural ordering was confirmed by EXAFS studies. Ball milling for 15 min resulted in a local structure which yields higher saturation magnetization. The saturation magnetization (M_s) increased to ~50%. The relative cooling power (RCP) showed an increase of 23%. Thus, high energy ball milling of Fe-Cr-Al alloys can be a useful method to improve the magnetocaloric properties of these alloys for room temperature magnetic cooling applications. The bulk, ribbon and milled samples exhibited soft ferromagnetic nature, negligible hysteresis, broad $-\Delta S_m$ vs T and a Curie temperature near room temperature, which are highly desirable for magnetic cooling.

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Chapter 6

Magnetic cooling performance of Fe-Cr-Al based fluids*

As a proof of concept, magnetic fluids of Fe-Cr-Al alloy nanoparticles were synthesized and used in a thermomagnetic cooling device (TMCD). Systematic experiments were performed to investigate the effect of alloy composition, particle concentration and heat load on the cooling performance. Modelling of the results using COMSOL Multiphysics were found to be in good agreement with the experimental data. A temperature drop (ΔT) of 5.4°C was observed for $\text{Fe}_{50}\text{Cr}_{25}\text{Al}_{25}$ magnetic fluids. The results show the self-regulating and self-pumping nature of the device. These magnetic fluids, synthesized from ball milled powders of bulk alloys, can be useful for waste heat recovery applications.

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6.1 Introduction

Fluids employing magnetic materials find applications in many thermal management systems. Thermomagnetic pumps are one such example where a ferrofluid/magnetic fluid (MF) is used as the heat transfer medium [1, 2]. The cooling devices based on MF display a passive type of cooling because such devices operate with low or negligible input of energy as in the case of the heat pipes. It does not have limitations such as high maintenance cost, mechanical vibrations and noise [2]. MF is a colloidal suspension of subdomain magnetic nanoparticles dispersed in a carrier fluid [3]. MFs consists of colloidal suspensions of superparamagnetic iron oxide nanoparticles (SPION) which are suspended in a non-magnetic carrier fluid [4]. Due to the ability of SPIONs to exhibit heating on application of alternating magnetic field, they have been widely used in magnetic hyperthermia treatment and non-contact heating applications. The heat generation in SPIONs take place by relaxation mechanisms, i.e., Neel relaxation and Brownian relaxation. The size of nanoparticles, magnetic field strength and frequency directly influence the heating extent. Rosensweig theoretically established relationship between the specific absorption rate (SAR) of a MF, volume of SPIONs in MF and frequency of alternating magnetic field [5]. The heat dissipation is proportional to the frequency and square of the magnetic field strength. An optimal combination of particle size, field strength and frequency are required to achieve maximum heating of SPIONs in MF. MF possesses magnetic as well as fluidic properties, thereby making it possible to control the flow behavior by tuning the orientation and strength of the magnetic field. Due to these features, MF can be used in many research fields such as biomedical sciences, thermal devices, energy harvesting etc. [6, 7]. A magnetofluidic cooling pump is one of the areas where MF is used. These pumps are based on the principle of thermomagnetic (TM) convection. In TM convection, the MF feels a net drag force which is due to the non-uniform magnetic state of the MF. This non-uniform force field is developed by the synergistic effect of the applied magnetic field and temperature gradient [8-10]. Studies on MF are limited to ferrite-based MF synthesized by chemical synthesis methods [11, 12]. Despite higher thermal conductivity values of metallic alloys, only limited research has been done on metal alloy-based MF. This is due to limitations in the synthesis techniques,

resulting in particle agglomeration, broad particle size distribution and instability in suspensions [13].

The magnetic cooling performance of $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($19 \leq x \leq 25$) fluids prepared by surfactant-assisted ball milling is investigated in this chapter [14]. Surfactant-assisted ball milling avoids the problem of agglomeration by minimizing van der Waals interactions and magnetic dipole-dipole interactions. MF were prepared from these nanoparticles at different volume concentrations. These MF were then tested for cooling in a thermomagnetic cooling device (TMCD) under variable heat loads. A TMCD operates by the principle of thermomagnetic (TM) convection. The magnetic fluid (MF) experiences an effective driving force due to non-uniform magnetic state of the MF. This state is a result of the combined effect of an external magnetic field and the temperature difference between the heat load and the heat sink. In a closed TM convection loop, the MF persistently flows due to the magnetic field gradient and the temperature gradient.

6.2 Methodology

6.2.1 MF synthesis

For removal of waste heat from the heat load region MF based on Fe-Cr-Al alloy nanoparticles were employed as the working fluid. For magnetic fluid synthesis, high energy ball milling assisted by the addition of surfactant, i.e., oleic acid, was performed on the $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ ($x = 19, 23$ and 25) buttons. The buttons were ground to fine powder and subsequently placed in a zirconium bowl (125 ml) with zirconia balls (15 mm). The ratio of powder and balls was kept constant throughout the experiment, i.e., 1:10. Ball milling was operated at 600 rpm. Bowls were flushed with argon gas before starting the milling. Oleic acid (1-2 drops) was added after every 60 min. The bowls were opened and sealed only inside a glove box to prevent oxidation of coated alloy nanoparticles. The powder samples, coated with the surfactant, were further milled at 500 rpm for 24 h to prepare the corresponding magnetic fluids using oleic acid as dispersant. The synthesis strategy is summarized in figure 6.1.

Figure 6.1. Schematic of the synthesis. (A) Bulk alloy synthesis and (B) Surfactant-assisted ball milling synthesis of magnetic fluid.

A borosilicate glass tube ($15 \times 15 \text{ cm}^2$) with wall thickness of 1 mm was employed for fluid flow and demonstration of magnetic cooling (figure 6.2). The flow region was circular in cross-section with 5 mm internal diameter (ID). For uniform heat distribution, aluminum foil was encased around the tube. A kanthal wire was wrapped around the aluminum to prepare a heat load (50 mm). The heat load was thermally insulated using ceramic wool. Water at $\sim 18^\circ\text{C}$ was designated as heat sink placed opposite to the heat load. A permanent magnet (NdFeB) of dimensions $10 \text{ cm} \times 5 \text{ cm} \times 2 \text{ cm}$ was placed close to heat load to produce a magnetic field of 0.3 T. The heat load temperature was measured by a K-type thermocouple which was connected to a logging device on the other end to record temperature and time.

Figure 6.2. Schematic of magnetic cooling prototype.

6.2.2 Modelling

The basic principle of the TMCD is the establishment of a non-uniform Kelvin body force in the ferrofluid in the presence of an external magnetic field and thermal gradient, which leads to force imbalance. This induces stronger attractive force on the colder ferrofluid towards the higher magnetic field gradient region than the warmer ferrofluid. The phenomenon is called TM convection [15]. To investigate this effect of TM convection in TMCD, a two-dimensional (2 D) model was developed for the TMCD flow tube. The model used COMSOL Multiphysics simulation software, which is based on the finite element method, for solving coupled partial differential equations [16].

Governing equations

The governing equations for simulating the TM convection inside the TMCD is described in the following sections.

Magnetic field equations

Due to the presence of a static magnetic field, the Maxell-Ampere's law was used to define the magnetic field distribution [17],

$$\nabla \times \mathbf{H} = 0 \quad (6.1)$$

The displacement current vector ($\mathbf{J}$) was taken to be zero in the above equation by assuming the MF to be electrically non-conductive. Hence, the magnetic field can be derived using the relation,

$$\mathbf{H} = -\nabla V_m \quad (6.2)$$

Gauss's law of magnetism takes the form [17]

$$\nabla \cdot \mathbf{B} = 0 \quad (6.3)$$

The macroscopic magnetic property of the MF medium was described by the constitutive relation between the magnetic flux density ($\mathbf{B}$) and the magnetic field ($\mathbf{H}$)

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \quad (6.4)$$

However, magnetization ($\mathbf{M}$) is directly proportional to the applied magnetic field,

$$\mathbf{M} = \chi_m \mathbf{H} \quad (6.5)$$

Equation 6.4 can be rewritten using equation 6.5 as

$$\mathbf{B} = \mu_0(1 + \chi_m)\mathbf{H} = \mu_0\mu_r\mathbf{H} \quad (6.6)$$

where V_m is magnetic scalar potential, μ_0 and μ_r are magnetic permeability of free space and MF respectively, χ_m is the magnetic susceptibility of the MF.

MF flow and energy equation

Mass and energy transport in TM convection based TMCD is governed by the conservation of mass, momentum and energy. The governing equations take the form:

Continuity equation:

$$\rho \nabla \cdot \mathbf{V} = 0 \quad (6.7)$$

Momentum equation:

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla p + \nabla \cdot (\mu (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)) + \mathbf{F}_f \quad (6.8)$$

Energy equation:

$$\rho C_p \left(\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right) = \nabla \cdot (k \nabla T) \quad (6.9)$$

Here, $\mathbf{v}$ represents velocity of MF, T the absolute temperature, p the pressure while $\mathbf{F}_f$ denotes the volume force experienced by the MF. The MF properties are given by: ρ , the density; C_p , the specific heat; μ , the dynamic viscosity and k the thermal conductivity.

Volume force calculation

The volume force term ($\mathbf{F}_f$) used in the Navier-Stokes equation is the combination of magnetic volume force ($\mathbf{F}_m$) and gravitational volume force ($\mathbf{F}_g$)

$$\mathbf{F}_f = \mathbf{F}_m + \mathbf{F}_g \quad (6.10)$$

However, in the present study, the flow tube is perpendicular to the direction of gravity. Hence, $\mathbf{F}_g$ is neglected in this model.

The magnetic volume force experienced by MF is given by [4]

$$\mathbf{F}_m = \mu_0 M \nabla H + \mu_0 H \frac{\partial M}{\partial T} \nabla T \quad (6.11)$$

The first term on the right-hand side of equation 6.11 is known as the Kelvin magnetic body force term, while the second term is called the magnetocaloric force term. However, as the magnetic component of the fluid is made up of magnetocaloric Fe-Cr-Al nanoparticles exhibiting a broad second order transition, the pyromagnetic coefficient ($\partial M / \partial T$) is small. Hence the magnetocaloric force term is neglected in this model. Therefore, equation 6.10 can be rewritten as

$$\mathbf{F}_f = \mathbf{F}_m = \mu_0 M \nabla H \quad (6.12)$$

6.3 Results and discussion

6.3.1 Characterization of nanoparticles

The XRD pattern of the most intense peak i.e., (220) of Cr-19, Cr-23 and Cr-25 powders after ball milling are shown in Figure 6.3(a). The broad XRD peaks of each composition indicated that the crystal size is in the nm range. The crystal size calculated from Scherrer's formula [18] for Cr-19, Cr-23 and Cr-25 is 10 ± 1 nm, 12 ± 1 nm and 20 ± 1 nm respectively. The micrographs for Cr-25 samples are shown in figure 6.3(b). The particles displayed a broad size distribution and were equiaxed. The particles size varied in a range from 10 nm

to 60 nm with a mean size of ~ 25 nm. The inset of figure 6(b) shows a high resolution (HR) TEM micrograph of Cr-25 sample. The lattice spacing (a) value of ~ 0.208 nm was indexed to the (220) planes of $\text{Fe}_{50}\text{Cr}_{25}\text{Al}_{25}$. The selected area diffraction (SAD) pattern could be indexed to the $\text{Fe}_{50}\text{Cr}_{25}\text{Al}_{25}$ structure, possessing a Fm3m space group (Figure 6.3 (b): inset).

Figure 6.3. (a) Enlarged XRD pattern showing the fundamental peak of (220) plane for Cr-19, Cr-23 and Cr-25 samples, (b) Transmission electron micrograph (bright field mode) for Cr-25 ball milled powders. The HR-TEM micrograph is shown at lower left corner in inset of (b). The SAD pattern of the Cr-25 powder sample is also shown which is indexed to FCC crystal structure.

The magnetic fluid (MF) synthesized using surfactant-assisted high energy ball milling is shown in figure 6.4. The figure shows the Cr-25 MF without magnet and with magnet having a field strength of 0.3 T. As is evident from table 1, the density of particles in Fe-Cr-Al fluid is $\sim 52\%$ higher than that of the commercial ferrofluid, the resultant stability of the Fe-Cr-Al based fluid is significantly less than that of commercial ferrofluids. Long term stability of a ferrofluid is an important requirement for any ferrofluid based application. The synthesis routes for alloy-based ferrofluids are limited to methods like high energy ball milling, which often results in a non-uniform particle size distribution. To reduce magnetic agglomeration and achieve a stable suspension, the particle size must be less than $(144.k.T/\pi.\mu_0.M^2)^{1/3}$, where k , T and M , are Boltzman's constant, temperature and magnetization, respectively [19]. This condition is satisfied when the average particle size is ~ 10 nm. For our Fe-Cr-Al alloy-based fluids, the mean particle size is ~ 25 nm which is higher than the size required to achieve a stable suspension. The ball milling duration can

be increased to obtain size reduction. However due to the ductile behavior of Cr, the tendency for plastic deformation is high, and cold welding occurs after prolonged milling.

Figure 6.4. Cr-25 magnetic fluid (a) in the absence and, (b) presence of a magnet.

To further establish a relationship between experimental work and simulations table 6.1 shows the mesh details of prototype in COMSOL Multiphysics software. A free triangular meshing type was used for all the four objects.

Table 6.1 Mesh details of magnetic cooling prototype in COMSOL Multiphysics software.

Object	No. of mesh elements	Average mesh quality
Ferrofluid domain	83094	0.8771
Magnet domain	13138	0.9491
Tube wall	10882	0.9126
Air domain	166534	0.9018

MF of Fe-Cr-Al alloy nanoparticles were used as the coolant for removal of waste heat from the heat load in the TMCD. In the present study, the device under investigation is a

square loop containing MF and exposed to a non-uniform magnetic field. The field is created by placing an Nd-Fe-B permanent magnet close to the tube, near the heat load region. The thermomagnetic cooling performance of the TMCD was evaluated by recording the wall temperature as a function of time. Various parameters such as Cr % content, the input power and the volume concentration of the nanoparticles in the MF were systematically varied. The cooling performance was further studied by simulations using COMSOL Multiphysics software. Figure 6.5 shows the temperature distribution in the square tube, without and with application of magnetic field. It clearly shows that as the magnet is placed close to the heat load, the fluid starts moving towards the heat sink due to the thermomagnetic gradient.

Figure 6.5. A 2D Comsol model showing temperature distribution at different regions of the tube, (A) Without magnetic field and (B) with magnetic field. Arrows indicate the direction of the fluid flow.

To understand the flow behavior of magnetic fluid inside the tube, the simulated velocity vector profiles are presented in figure 6.6. Vorticity in the flow was observed near the point of higher thermal and magnetic field gradient. Thermal gradient is present near the heat load region. Magnetic field gradient is provided by a permanent magnet. During magneto-fluidic cooling, the magnet is placed closer to the heat load resulting in observed vortex formation. This vortex formation enhances local thermal transport. Hence, the enhanced cooling during MFC process is a combined effect of vortex formation and fluid flow due to thermo-magnetic convection.

Figure 6.6 (A) Simulated surface velocity vector plot of the magnetic fluid across the magnetic cooling prototype. Simulated surface velocity vector plot (A) near and, (B) far away from the magnet. (D) Full view of the heat load section velocity profile.

Figure 6.6. Observed variation of surface temperature of the heat load over time at zero magnetic field and with 0.3 T, at 4 W for (a) Cr-19, and (c) Cr-23 MFs. Modelled temperature profiles at zero magnetic field and with 0.3 T for (b) Cr-19, and (d) Cr-23 MF.

6.3.2 Effect of Cr content

Experiments were performed on Cr-19 MF, Cr-23 MF and Cr-25 MF samples at 4 W to evaluate the cooling performance. Figure. 6.6 (a, c and e) represents the heat load temperature at zero magnetic field and with 0.3 T, for Cr-25 MF, Cr-23 MF, Cr-19 MF. The modelled temperature is shown in figure. 6.6 (b, d and f). The simulation results were in agreement with the experimental values with error less than 4%. As the heat is transferred by the fluid, the temperature of heat load dropped upon application of magnetic field (figure 6.6). The experimental and simulation results suggest that the temperature drop is highest for Cr-19 MF compared to the values for other MF. This could be due to the higher M_s value of Cr19 MF [20]. This results in a greater magnetic attraction on the Cr19 MF compared to Cr-23 MF and Cr-25 MF, yielding larger temperature drop.

Figure 6.7. Effect of Cr25 magnetic nanoparticle concentration (Φ_p) of (a) 0.2%, (b) 0.4%, (c) 0.6%, and (d) 0.8% on temperature drop at 0.3 T and 4 W power.

6.3.3 Effect of volume concentration (Φ_p)

The effect of nanoparticle concentration in the oleic acid, on the performance was investigated using Cr-25 MF. The nanoparticle concentration (v/v %) in the oleic acid was varied (0.2 – 0.8 %). Cr-25 MF with varying concentration of nanoparticles was then used for cooling tests at constant power of 4 W, as shown in figure 6.7 (a-d). As expected, for higher particle concentration, higher cooling (ΔT) was observed. This higher temperature drop was due to an improvement in the magnetic volume force with increase in particle concentration [21].

Figure 6.8 The cooling performance with change in power of (a) 2 W, (b) 3 W, (c) 4 W, and (d) 5W, for 0.8% Cr₂₅-MF, at zero magnetic field and at 0.3 T.

6.3.4 Variation in applied power (P)

To study the effect of change in applied power on temperature drop, Cr-25 MF (0.8% v/v) was used. Figure 6.8 shows the cooling performance with change in power from 2 W to 5W at zero magnetic field and at 0.3 T. It was observed that the temperature drop, i.e., cooling, increased with increase in heat load (P). Higher heat load resulted in greater temperature gradient between the heat load and heat sink regions, resulting in a higher magnetic volume force experienced by the MF, thereby improving the cooling performance.

6.4 Conclusions

An average particle size of ~28 nm was observed for Fe₅₀Cr₂₅Al₂₅ milled powders. By suspending these nanoparticles in oleic acid, a magnetic fluid was prepared. A maximum cooling of ΔT of 5.4 °C was obtained for Fe₅₀Cr₂₅Al₂₅ magnetic fluids (0.8 % v/v) under 0.3 T applied magnetic field and an initial temperature of ~125 °C. These results show the

self-regulating and self-pumping nature of the TMCD. The device is self-regulating as the cooling performance improved automatically when the heat load power was increased. It is self-pumping as it did not require any mechanical pump to move the MF. The results indicate that these $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ alloys based magnetic fluids may be potentially useful for low-grade waste heat recovery applications.

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Chapter 7

Conclusions and future work

This chapter presents a brief summary of the significant results discussed in this thesis. The structural, magnetic and MCE properties of low-cost and rare earth free Mn doped Fe_3Al and Cr doped Fe_3Al alloys were experimentally studied for the first time and compared to the results of modelling of the phase transition and the magnetocaloric properties. As a proof-of-concept, the magnetic cooling performance was investigated for Fe-Cr-Al based magnetic fluids prepared by a surfactant-assisted ball milling method. Based on these results of the influence of processing routes on the magnetocaloric properties and the magnetic cooling performance, future work is discussed.

7.1 Summary

Investigation of the magnetocaloric properties of low-cost, easy to manufacture, rare earth free materials is of utmost importance. A detailed study of the magnetocaloric properties of Mn and Cr doped Fe₃Al alloys was performed in this thesis. The main objective was to develop low-cost, rare earth free iron-based magnetocaloric materials with T_c near room temperature. We have developed such low-cost materials using Fe₃Al alloyed with antiferromagnetic Mn and Cr. We also tuned the T_c as well as magnetocaloric properties in a wide range using different synthesis routes, as well as by annealing and hydrostatic pressure. The influence of synthesis routes, i.e. arc melting, melt spinning and ball milling on the structure, magnetic and magnetocaloric properties was investigated. Subsequently, Fe-Cr-Al based magnetic fluids were synthesized and used to test the thermomagnetic cooling performance. The results of cooling performance were compared to the simulation results. The good magnetocaloric properties, ready availability, established manufacturing techniques, low-cost, soft ferromagnetism, good corrosion resistance and thermal conductivity make these materials suitable for near room temperature thermal management. The major conclusions of the thesis are summarized as:

1. The structural, magnetic and magnetocaloric properties of Fe_{75-x}Mn_xAl₂₅ ($12.5 \leq x \leq 25$) alloys prepared by arc melting, were studied for the first time. Addition of Mn, in a range from 12.5 wt % to 25 wt %, decreased the Curie temperature in a linear manner, yielding near room temperature T_c values of ~ 290 K and 250 K for $x = 15$ and 17.5, respectively. Both the heating and cooling M-T curves overlapped, confirming the absence of thermal hysteresis. Coercivities of less than 50 Oe were observed in all the compositions, suggesting soft ferromagnetic behavior. Large values of RCP, i.e., 430 Jkg⁻¹ and 395 Jkg⁻¹ were obtained for Fe₆₀Mn₁₅Al₂₅ and Fe_{57.5}Mn_{17.5}Al₂₅ alloys. The entropy scaling curves provided information on the presence of magnetic inhomogeneities.
2. Different annealing treatment durations at 1000 °C and hydrostatic pressure, up to ~1.15 GPa were used to investigate the effect of post-synthesis processing, on the magnetic and magnetocaloric properties of Fe-Mn-Al melt-spun ribbons. Optimum annealing treatment enhanced the structural order and magnetic properties. The T_c was also tuned well in the near room temperature range, yielding values such as 265 K, 277 K and 290

- K. These ribbon sample with a T_c of 285 K was selected for hydrostatic pressure studies. With increasing pressure from 0 GPa to 1.15 GPa, the Curie temperature shifted towards lower values with a pressure derivative of T_c , i.e. $dT_c/dP \sim 1.8$ K/kbar, thus we could tune T_c by applying pressure. The saturation magnetization (M_s) at 300 K also exhibited a decrease at the rate dM/dP of ~ 0.85 emu/g/kbar. The isothermal magnetic entropy change decreased with increasing pressure. These results showed that external pressure can be used to tune the magnetic and MCE properties of these ribbons.
3. The effect of short duration high energy ball milling, with milling speed in the range of 500 rpm to 700 rpm, on the local structure, magnetic and magnetocaloric properties of $Fe_{2.1}Cr_{0.9}Al$ alloys was explored. An interesting unusual cyclic behavior of structural order was observed in $Fe_{2.1}Cr_{0.9}Al$ alloys milled at 600 rpm, up to 150 min. The reaction rate model was used to study the cyclic behavior and the stored energy was calculated. The arc melted sample possessed a B2 crystal structure. Upon 15 min. of milling at 600 rpm, the alloy exhibited a $L2_1$ crystal structure. The 15 min. milled sample showed a significant enhancement of 50 % and 23 %, in saturation magnetization and relative cooling power, respectively, compared to the bulk counterpart. This enhancement was due to the emergence of short-range order which was studied using extended x-ray absorption fine structure (EXAFS). Short duration high energy ball milling of Fe-Cr-Al alloys can serve as a useful technique to enhance the magnetic and magnetocaloric properties of these alloys for magnetic cooling applications
 4. To investigate the effect of synthesis route on the structural, magnetic and magnetocaloric properties, $Fe_{54}Cr_{21}Al_{25}$ arc melted buttons and melt-spun ribbons were compared. The bulk sample was found to possess an $L2_1$ structure with a Curie temperature of 285 K. Melt spinning resulted in a structural transition giving rise to a B2 crystal structure. A significant enhancement of 25% in RCP and 33 % increase in isothermal entropy change $-\Delta S_m$ was observed in ribbon samples which was attributed to the disordering of the Fe-Al and Fe-Cr sublattice, arising due to the high cooling rate observed during melt spinning. The nature of the magnetic transition, MCE behavior and degree of order around the Curie temperature was studied with the aid of critical exponents obtained using modified Arrott plots, critical isotherm analysis, the Kouvel-Fisher method and field dependent MCE behavior. The critical exponents were found

- to be $\beta = 0.345$, $\gamma = 1.316$ and $\delta = 4.63$, which corresponded to a short-range ordered 3-D Heisenberg model. These alloys possess promising performance attributes for near room temperature magnetic cooling applications.
5. The structure, magnetic and magnetocaloric properties of Cr alloyed Fe_3Al bulk alloys were studied. With Cr addition in the range from 19 % to 25 wt %, the T_c was tuned from room temperature to up to 220 K. All the samples were found to crystallize in an $L2_1$ structure and exhibited a linear decrease in lattice parameter with increase in Cr content, suggesting a lattice compression in the x - y plane. A cost analysis was performed to evaluate the magnetocaloric performance. The RCP/US\$ for the $\text{Fe}_{56}\text{Cr}_{19}\text{Al}_{25}$ alloy was found to be ~ 24 times higher than the RCP/US\$ of “benchmark” Gd and ~ 15 times higher than that of $\text{Gd}_2\text{Si}_2\text{Ge}_2$.
 6. Owing to good magnetic properties and tunable T_c of $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ bulk alloys, magnetic fluids of this material were prepared using surfactant-assisted high energy ball milling. TEM images revealed an average particle size of ~ 28 nm for $\text{Fe}_{50}\text{Cr}_{25}\text{Al}_{25}$ nanoparticles. Oleic acid was used as a surfactant as well as the carrier fluid. Various parameters were used to evaluate the magnetic cooling performance in a thermomagnetic cooling device (TMCD). With increase in Cr content from 19 wt. % to 25 wt. % in $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ fluids, the cooling (ΔT) decreased from 3.6°C to 2.2°C , when tested at 4 W and with 0.3 T magnetic field. Simulations performed on Comsol Multiphysics were in good agreement with experimental results. The effect of volume fraction, in a range from 0.2% v/v to 0.8 % v/v, on the cooling performance of $\text{Fe}_{50}\text{Cr}_{25}\text{Al}_{25}$ fluids was tested at an initial temperature of 125°C . A maximum cooling (ΔT) of 5.4°C was observed for 0.8% v/v fluids. The effect of different heat loads (2W, 3 W, 4W and 5 W) revealed the self-regulating nature of TMCD. The cooling performance improved automatically upon increasing the heat load. Thus, Fe-Cr-Al based magnetic fluids may be suitable for low-grade waste heat recovery applications.

Figure 7.1 represents a summary of the Curie temperatures and RCP values of different materials used in this thesis.

Figure 7.1 Summary of the T_c and RCP values of Mn and Cr alloyed Fe_3Al based magnetocaloric materials used in this thesis.

7.2 Future work

The main objective of this research work to develop low-cost iron-based magnetocaloric materials has been achieved. Possible future work can be stated as:

1. The effect of high energy ball milling on Fe-Cr-Al alloys was studied for a duration of 165 min. at different milling speeds. A cyclic behavior in the degree of structural order and stored energies was observed at a milling speed of 600 rpm. After 165 min, ZrO_2 contamination appears. However, experiments can be carried out to examine the effect of high energy ball milling for longer durations. This study will be interesting as it can shed light on the relationship between cyclic structural order and magnetic properties. It might be significant to study if the thermodynamic reaction rate model is valid for longer milling duration.

2. It is evident from the Fe-Al phase diagram that a tricritical point T_{tc} (change of first order phase transition to a second order phase transition) exists at $\sim 612^\circ\text{C}$. If this tricritical point can be observed around near room temperature, the resulting values of magnetic entropy change can drastically improve. Future work should focus on exploring the T_{tc} of Fe-Al alloys in the context of MCE. Different approaches can be used to tune T_{tc} of Fe-Al such as,
 - (a) Heat treatment such as vacuum annealing or water quenching can be used to tune the magneto-structural transitions. It has been observed that specific heat treatments induce order-disorder transitions in Fe-Al alloys due to change in lattice parameters, strain etc. Since we already observed an enhancement of 33 % in ΔS_M and 54% in RCP values in Fe-Al-Cr alloys, it is possible to achieve even further enhancement in MCE properties by coupling magnetic and structural transitions. Similar work on demonstrating an existence of tricritical point in lanthanum based manganites and investigation of magnetic properties around T_{tc} was recently reported by Phan et al [1].
 - (b) It is known that chemical pressure can be used to couple the magnetic and structural transitions and give rise to metamagnetism. Future work should focus on generating the internal pressure by chemical additions like Mn or Cr. According to Rhee et al [2], Fe_3Al system can exhibit metamagnetism at a pressure of 80 kbar. This pressure is quite high to be attained by chemical addition alone. Diamond anvil cell can be used to generate high pressure externally. Gas-membrane-driven diamond anvil cells were used by Stillwell et al to generate high pressures upto 100 kbar and investigated magnetic properties in LaCo_5 [3]. It will be required to customize the experiments by installing a diamond anvil cell within a PPMS and performing in-situ magnetic measurements. Hence by applying external hydrostatic pressure, pressure dependent metamagnetism in the Fe-Al system can be investigated.
3. Fe-Cr-Al based magnetic fluids were synthesized using surfactant-assisted ball milling as a part of this research work. Owing to various advantages of alloy-based fluids, e.g., high thermal conductivity and high magnetization, further studies may focus on developing novel synthesis routes for alloy-based ferrofluids. These routes may include chemical methods, microwave synthesis etc.

4. Magnetic cooling prototype using *thermal diodes*: The devices based on MCE are heat pumps, magnetic refrigerators and magnetic energy harvesting machines. A cooling mechanism based on MCE can be applied to such devices. Important aspects for commercialization of magnetic cooling devices are that they should perform better at small fields in a broad temperature range [4] and should work at high operating frequencies. One of the most serious obstacles that today's existing magnetic cooling prototypes face is the low operating frequency (number of thermodynamic cycles per unit time) which results in a low power density (cooling power per cost). If the heat transfer between the MCM and working fluid can be improved, the operating frequency can be drastically increased. As stated by Kitanovski [5], use of thermal diodes can result in high operating frequencies and increased power densities. One of the promising solutions to obtain higher frequencies can be the use of thermal diodes for fast heat transfer from or to the magnetocaloric material [6]. A thermal diode is a device which can control and manipulate the heat flow just like a p-n junction diode does in case of current flow. For our system we need such a diode which acts like a switch system i.e., when one thermal diode is operational, the other becomes inactive and the vice-versa. For this purpose, micro-Peltier diodes can be used and a thin layer of magnetocaloric material (MCM) will be sandwiched in between the two layered arrays of micro-Peltier diodes. Figure 7.2 shows a schematic of proposed solid-state magnetic cooling device. When the MCM is magnetized, it heats up and the micro-Peltier diode1 gets active and starts transferring heat from MCM to heat sink. Meanwhile, the micro-Peltier diode2 is inactive and acts like an insulator. In the next step the MCM is demagnetized, it cools down and the micro-Peltier diode2 gets operational and starts absorbing heat from the heat source. Meanwhile the micro-Peltier1 remains inactive. The dimensions of MCM can be chosen to be in millimeter range and in form of a thin film i.e., $100 \times 5 \times 0.5 \text{ mm}^3$. The diodes will be arranged in form of array on the both sides of MCM and cover the whole MCM area in order to provide maximum heat transfer. Water will be used as the working fluid on both the hot and cold ends.

Figure 7.2 Schematic of magnetocaloric device with thermal diodes [7].

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7.3 Publications and Conferences

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

1. **Sharma V.**, Pattanaik S., Parmar H., and Ramanujan, R.V. Magnetocaloric Properties and Magnetic Cooling Performance of Low-cost $\text{Fe}_{75-x}\text{Cr}_x\text{Al}_{25}$ Alloys, *MRS Communications*, pp 1-7, 2018; doi:10.1557/mrc.2018.122 **INVITED**
2. **Sharma V.**, Chaudhary, V. and Ramanujan R.V., “Near Room Temperature Magnetocaloric Properties of $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ Alloys”, *IEEE Transactions on Magnetics*, 54, 11, 2018.
3. **Sharma V.**, Repaka, D. M., Chaudhary, V. and Ramanujan, R.V. Enhanced magnetocaloric properties and critical behavior of $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$ alloys for near room temperature cooling. *Journal of Physics D: Applied Physics* 50, 145001, 2017
4. **Sharma V.**, Shukla S, Shibo X and Ramanujan R.V. “Cyclic structural ordering induced by high energy ball milling in a $\text{Fe}_{2.1}\text{Cr}_{0.9}\text{Al}$ magnetocaloric alloy”. *Journal of Magnetism and Magnetic Materials*, 474, 528-536, 2019
5. Repaka D.M., **Sharma V.**, Chanda A, Mahendiran R & Ramanujan R.V. “Pressure dependence of resistivity and magnetization in a $\text{Mn}_{1.9}\text{Cr}_{0.1}\text{Sb}$ alloy”; *AIP Advances* 7 (12), 125009, 2017, **Featured article**
6. Repaka, D. M., **Sharma V.** and Ramanujan, R.V. Near room temperature magnetocaloric properties and critical behavior of binary $\text{Fe}_x\text{Cu}_{100-x}$ Nanoparticles. *Journal of Alloys and Compounds* 690, 575-582, 2017
7. **Sharma V.** and Ramanujan R. V., Influence of annealing and hydrostatic pressure on the structure and magnetic properties of Fe-Mn-Al melt-spun ribbons, *manuscript under preparation*.

The following articles were published/under review as a part of collaborative projects:

1. Owuor P. S., Chaudhary V., Woellner C., **Sharma V.**, Ramanujan R.V., Stender A, Soto M, Ozden S., Barrera E., Vajtai R., Galvão D., Lou J., Tiwary C. S., Ajayan P. M., High stiffness polymer composite with tunable transparency, *Materials Today*, 2018
2. Magham, S.B.S., Sharma, M., Shannigrahi, S.R., Tan, H.R., **Sharma, V.**, Meng, Y.S., Idapalapati, S., Ramanujan, R.V. and Repaka, D.V.M., 2017. Development of Z-type

- hexaferrites for high frequency EMI shielding applications. *Journal of Magnetism and Magnetic Materials*, 2017
3. Panigrahi R, Zarek M, **Sharma V**, Cohn D. and Ramanujan R.V. "Bio Inspired Multiple Cycle Damage Sensing and Healing in Elastomer-Magnet Nanocomposites" *to be submitted*.
 4. Parekh K, Parmar H, **Sharma V** and Ramanujan R.V., Heating efficiency dependency on size and morphology of magnetite nanoparticles, *AIP conference proceedings*, 1942, 1, 2018.
 5. Chaudhary V. Zhong Y.Y., Parmar H., **Sharma V.**, Xiao T. and Ramanujan R.V., Mechanochemical synthesis of Fe, Co magnetic metal nanoparticles and Fe/Cao, Co/Cao nanocomposites, *Chemistry Open*, 2018, accepted

The work was presented at the following conferences/summer school,

1. "Magnetocaloric Behavior of $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ Alloys for Near Room Temperature Cooling", Vinay Sharma, R.V. Ramanujan, Intermag 2018, Singapore *Oral*
2. "Low-cost $\text{Fe}_{3-x}\text{M}_x\text{Al}$ ($\text{M} = \text{Cr, Mn}$) Magnetocaloric Alloys with High Relative Cooling Power", Vinay Sharma, R.V. Ramanujan, MRS Spring meetings, 2018, Phoenix, *Oral*
3. "Magnetocaloric properties of $(\text{Fe,Mn})_3\text{Al}$ based alloys under hydrostatic pressure", Vinay Sharma, R.V. Ramanujan, TMS 2018, Arizona, *Oral*
4. "Low-cost $(\text{Fe,Cr})_3\text{Al}$ Magnetocaloric Alloys with Tunable Curie Temperatures and Active Cooling Performance", Vinay Sharma, R.V. Ramanujan, IEEE Magnetics Symposium 2017, *Oral*.
5. "Low-cost $\text{Fe}_{75-x}\text{Mn}_x\text{Al}_{25}$ Alloys for Magnetic Cooling". Vinay Sharma, R. V. Ramanujan. ICMAT Singapore, 2017, *Oral*
6. "Low-cost $(\text{Fe,Mn})_3\text{Al}$ Magnetocaloric Alloys for Near Room temperature Magnetic Cooling Applications". Vinay Sharma, R. V. Ramanujan, Poster, IEEE Magnetics Summer School 2017, Santander, Spain, *Poster*
7. "Disorder-induced Enhanced Magnetic and Magnetocaloric Properties of $\text{Fe}_{54}\text{Cr}_{21}\text{Al}_{25}$ Melt-spun Ribbons". Vinay Sharma, DVM Repaka, Varun Chaudhary, R.V. Ramanujan. IEEE Magnetic Symposium 2016, *Oral*, **Best presentation award**