Study of iron based magnetocaloric nanomaterials

Chaudhary, Varun

2016

Chaudhary, V. (2016). Study of iron based magnetocaloric nanomaterials. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/144047>

<https://doi.org/10.32657/10356/144047>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 10:12:40 SGT

NANYANG
TECHNOLOGICAL
UNIVERSITY

**STUDY OF IRON BASED MAGNETOCALORIC
NANOMATERIALS**

VARUN CHAUDHARY

**INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE@NTU (ERI@N)**

2016

STUDY OF IRON BASED MAGNETOCALORIC NANOMATERIALS

VARUN CHAUDHARY

**INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE@NTU (ERI@N)**

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

2016

Abstract

Magnetic materials experience a change in temperature when they are adiabatically magnetized and demagnetized, this phenomena is known as the magnetocaloric effect (MCE). The MCE can be employed in environmentally friendly, green and novel energy efficient cooling systems as this technique does not have hydrofluorocarbons or ozone depleting gases, unlike conventional gas compression cooling systems. The giant MCE in rare earth based materials has motivated magnetocaloric research in the last two decades. However, the systems studied so far, i.e., gadolinium based materials are very expensive, corrode easily and have limited availability. Developing a new, affordable, readily available and corrosion resistant material is desired for commercial use. Low relative cooling power (RCP) is often another challenge in developing a magnetic cooling system. Nanoparticles can increase the working temperature span, therefore we developed transition metal based magnetocaloric nanoparticles which are environmentally friendly, affordable and possess RCP higher than those of gadolinium nanoparticles.

The MCE of $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{A}_x$ nanocrystalline powders with $\text{A} = \text{B}, \text{Mn}$ and Cr produced by high energy ball milling has been investigated. Binary $\text{Fe}_{70}\text{Ni}_{30}$ nanoparticles show high magnetization and low coercivity but they are not useful for room temperature cooling applications because of their high Curie temperature ($T_C \sim 443 \text{ K}$). Boron, manganese and chromium, were individually used to tune the T_C closer to room temperature.

$(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles were found to exhibit very high RCP up to $640 \text{ J}\cdot\text{kg}^{-1}$ for a field change ΔH of 5 T with $T_C \sim 381 \text{ K}$. Broad operating temperature range along with moderate change in entropy and very high RCP make these nanoparticles potential candidates for magnetic cooling applications in low grade waste heat recovery. Critical analysis of the magnetic phase transition using the modified Arrott plot, Kouvel-Fisher method and critical isotherm plots yields critical exponents of $\beta = 0.364$, $\gamma = 1.319$, $\delta = 4.623$ and $\alpha = -0.055$, which are close to the theoretical exponents obtained from the 3D-Heisenberg model.

The MCE of $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mn}_x$ nanoparticles were measured before and after γ – phase stabilization. It was shown that fast quenching is required for γ –phase stabilization. The γ - $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ ($T_C \sim 338$ K) and γ -($\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ ($T_C \sim 317$ K) nanoparticles possess good relative cooling power (RCP) up to $470 \text{ J}\cdot\text{kg}^{-1}$ and $415 \text{ J}\cdot\text{kg}^{-1}$, respectively, for a field change of 5 T. Good agreement was found between the critical exponents of the γ -($\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ alloy nanoparticles determined by the modified Arrott plot and those obtained from the Kouvel-Fisher method. The Widom’s scaling relation showed good agreement with the critical exponents $\beta = 0.319$, $\gamma = 1.195$ and $\delta = 4.71$.

For further tune the T_C , the magnetic and magnetocaloric properties of transition metal based $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$ ($x = 1, 3, 5, 6$, and 7) nanoparticles were studied. Only 5 % of Cr alloying with Fe-Ni reduce the T_C from ~ 443 K to 258 K, the RCP value is $406 \text{ J}\cdot\text{kg}^{-1}$ higher than those of Gd nanoparticles ($400 \text{ J}\cdot\text{kg}^{-1}$) for $\Delta H = 5$ T. Our results demonstrate the feasibility of developing high RCP, low cost, rare earth free magnetocaloric nanoparticles for near room temperature applications.

A prototype of self-pumping magnetic cooling based on thermomagnetic effect has been constructed. $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Cr}_5$ nanoparticles were used as the ferrofluid. $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles, synthesized by hydrothermal method were also studied. A series of experiments have been conducted to examine the effect of heat load, magnetic fluid density, fluid volume and magnetic field on cooling. It was found that the performance of this system depends strongly on heat load, magnetic field, volume fraction of particles and density of ferrofluid. For the ferrite nanoparticles, cooling by ~ 27 °C has been achieved by application of 0.3 T magnetic field. These results matched well with our simulations. This technique has considerable potential for electronic cooling applications since there is no moving mechanical part and therefore no maintenance required. Our system is self-regulating; as the heat load increases the magnetization of the ferrofluid decreases and driving force rises, transferring the heat from heat source to heat sink more quickly.

Acknowledgements

I would first like to thank my supervisor *Prof. Raju V Ramanujan* for providing me the opportunity to carry out research under his able guidance. I am grateful to him for his patience, constant encouragement, excellent guidance and generosity. I really gained a lot of knowledge from the discussions I had with him. I would like to thank my co-supervisor *Prof. I. Sridhar* for his trust, encouragement and lesson of honesty. My special thanks to Prof Rajdeep Singh Rawat and Prof Pinaki Sengupta for serving on thesis advisory committee for their critique and constructive comments on this research time to time.

I would like to extend my sincere thanks to past and present group members of Prof Raju; Anansa, Ayan, Chen Xi, Harshida, Mahesh, Manivel, Suresh, Tan Xiao, Vijay, Vinay, Vitul, Xing Hua, Yaoying and Zhaomeng for the lively and cooperative environment in the lab during the work.

I express my sincere gratitude to my friends Apoorva, Crish, Gurudayal, Manoj, Prince, Vipin, Yogesh, who provide me joyful company and help during the stay here.

I thank Lily, Ellen, IGS team and MSE staff for their selfless help throughout this journey.

This work would not have been possible without the support of NTU-HUJ-BGU Nanomaterials for Energy and Water Management Programme under the Campus for Research Excellence and Technological Enterprise (CREATE), that is supported by the National Research Foundation, Prime Minister's office, Singapore.

I would like to thanks Interdisciplinary Graduate School (IGS), Energy Research Institute at NTU (ERI@N) and School of Materials Science and Engineering (MSE) who provided me scholarship and support to attend the scientific meeting locally and overseas. I thank to IEEE magnetics society for providing me the summer school scholarship at University of Minnesota, Minneapolis (USA), where I benefited greatly.

Really, the list of acknowledgment will not be complete if do not mention the support of my family members that was always a source of inspiration for me. It was their love and affection which keeps me going on the endless path of knowledge. I do not have words to express my feeling indebtedness to them. My sincere gratitude to my lovely wife for her continues support.

Finally, I would like to thank *Lord Hanuman*.

Table of Contents

Abstract	i-ii
Acknowledgements	iii
Table of Contents	v
Table Captions	xi
Figure Captions	xiii
Abbreviations	xxiii
 Chapter 1 Introduction.....	 1
1.1 Magnetocaloric effect and magnetic cooling	2
1.2 Motivation	3
1.3 Objective	7
1.4 Novelty	8
1.5 Materials selection	9
1.6 Organization of thesis	11
1.7 Significant finding and outcomes	12
References.....	13
 Chapter 2 Literature review	 17
2.1 The thermodynamics of MCE	18
2.1.1 Adiabatic change in temperature and isothermal change in entropy.....	20
2.2 Relative cooling power.....	22

2.3	First and second order magnetic phase transition materials	23
2.4	A survey of magnetocaloric materials	24
2.4.1	Re ₂ Fe ₁₇ alloy	25
2.4.2	Fe-B-Cr-R (R = 1 to 15 %) alloy	27
2.4.3	Rare earth free iron based alloy	28
2.4.4	Manganites	33
2.4.4	Other recent work on MCE.....	35
2.5	Critical exponent analysis	37
2.6	Magnetothermal fluid	40
2.6.1	Magnetothermal fluid self-pumping	40
	References.....	43
Chapter 3	Experimental procedures	51
3.1	Rationale for selection of Methods	52
3.1.1	Nanoparticles preparations – Ball milling	52
3.1.2	Type of mill and milling container	53
3.1.3	Milling speed and time.....	54
3.1.4	Ball to powder ratio	54
3.1.5	Atmosphere and temperature inside the mill	55
3.2	Bulk sample preparation – Arc melting	55
3.3	Ferrofluid preparation	56
3.4	Materials Characterization	56
3.4.1	X-ray diffraction	57
3.4.2	Transmission electron microscopy	58
3.4.3	Energy dispersive X-ray spectroscopy	58

3.4.4	Electron probe micro analyser (EPMA)	59
3.4.5	Physical properties measurement system	59
3.5	Property evaluation of magnetocaloric effect	61
3.5.1	Curie Temperature	61
3.5.2	Magnetic entropy change	63
3.5.3	Magnetic and thermal hysteresis.....	64
3.5.4	Relative cooling power	64
3.6	Self-pumping magnetic cooling prototype.....	64
3.7	Simulation	65
	References	66
 Chapter 4 Magnetocaloric effect and critical behavior of FeNiB nanoparticles		69
4.1	Introduction	70
4.2	Experimental details	72
4.3	Results and discussion	72
4.3.1	Phase analysis	72
4.3.2	Magnetocaloric effect	74
4.3.3	Critical behavior of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles	80
4.3.3.1	Arrott plots	80
4.3.3.2	Determination of critical exponents β , γ , δ and α	82
4.3.3.3	Field dependence of $\Delta S_M(n)$ and RCP (N)	84
4.4	Conclusions	86
	References	86

Chapter 5	Magnetocaloric effect of FeNiMn nanoparticles	91
5.1	Introduction	92
5.2	Experimental details	93
5.3	Results and discussion	93
5.3.1	<i>in-situ</i> XRD: (Fe ₇₀ Ni ₃₀) ₉₂ Mn ₈ nanoparticles	93
5.3.2	XRD: (Fe ₇₀ Ni ₃₀) ₉₅ Mn ₅ , (Fe ₇₀ Ni ₃₀) ₉₂ Mn ₈ and (Fe ₇₀ Ni ₃₀) ₈₉ Mn ₁₁ nanoparticles	94
5.3.3	Curie temperature, change in entropy, relative cooling power: (Fe ₇₀ Ni ₃₀) ₉₅ Mn ₅ nanoparticles	95
5.3.4	Curie temperature, change in entropy, relative cooling power: (Fe ₇₀ Ni ₃₀) ₉₂ Mn ₈ nanoparticles	100
5.3.5	Curie temperature, change in entropy, relative cooling power: (Fe ₇₀ Ni ₃₀) ₈₉ Mn ₁₁ nanoparticles	104
5.4	Critical behavior of (Fe ₇₀ Ni ₃₀) ₉₂ Mn ₈ nanoparticles	107
5.5	Conclusions	111
	References	111
Chapter 6	Magnetocaloric effect of FeNiCr nanoparticles	115
6.1	Introduction	116
6.2	Experimental details	117
6.3	Results and discussion	118
6.4	Conclusions	125
	References	125
Chapter 7	Magnetocaloric effect of bulk FeNiB alloy	129
7.1	Introduction	130

7.2	Experimental details	131
7.3	Results and discussion	131
7.3.1	Phase analysis	131
7.3.2	Magnetocaloric studies	134
7.4	Conclusions	139
	References	139

Chapter 8 Self-pumping magnetic cooling141

8.1	Introduction	142
8.2	Experimental details	143
8.3	Governing equations	145
8.4	Magnetic fluid equations	146
8.5	Experiments with $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles based ferrofluid.....	147
8.5.1	Effect of magnetic field	147
8.5.2	Effect of load temperature	149
8.5.3	Effect of fluid concentration	151
8.5.4	Switching ('0' and '1') of magnetic field	153
8.6	Experiments with $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Cr}_5$ nanoparticle based ferrofluid	154
8.7	Conclusions	156
	References	157

Chapter 9 Summary and future work.....159

9.1	Summary	160
8.1	Proposed future research	163

List of publications and conferences.....	165
---	------------

Table Captions

Table 1.1	List of international and national project worldwide	6
Table 1.2	Approach, novelty and a brief description of our work.	8
Table 2.1	Critical exponents of relevant materials	39
Table 4.1	Curie temperature (T_C), grain size, change in entropy (ΔS_M) and relative cooling power (RCP) for selected magnetocaloric nanomaterials	78
Table 4.2	Experimental values of the critical exponents of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$, results from theoretical models as well as critical exponents of other related ferromagnets.	84
Table 5.1	Curie temperature (T_C), particle size (d), the magnitude of change in magnetic entropy ($ \Delta S_m $) and relative cooling power (RCP) for selected magnetocaloric nanoparticles.....	107
Table 6.1	Curie temperature (TC), change in magnetic entropy (ΔS_M) and relative cooling power (RCP) for selected magnetocaloric materials	124
Table 7.1	Crystal structure, Space groups, weight fractions, unit cell parameters and Bragg R factor obtained from Rietveld refinement of X-ray diffraction patterns.	132
Table 7.2	Working temperature span (δT_{FWHM}), Relative cooling power (RCP), change in entropy ($-\Delta S_m$), transition temperature (T_C) and exponent (n) for different magnetocaloric materials including Multi-phase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$	137

Figure Captions

- Figure 1.1** Schematic representation of a) lattice and magnetic subsystems in a magnetocaloric material, and four stages of magnetic refrigeration cycles: (b) application of magnetic field under adiabatic condition (c) removing heat, d) adiabatic demagnetization, and (e) cooling of refrigerator contents.....2
- Figure 1.2** Publications on MCE using SCOPUS: “Magnetocaloric Effect” in the "Article title, Abstract and Keywords" fields, number of published article on MCE every year since 1950 to 2015 (the data were export at 22nd July 2015).3
- Figure 1.3** Energy consumption in data center.....5
- Figure 1.4** The Bethe-Slater curve (schematic) showing the dependence of the exchange interaction on the ratio of interatomic distance to the diameter of the 3d electron shell.10
- Figure 2.1** Schematic diagram for magnetization in terms of temperature and magnetic field for (a) first order magnetic phase transition and (b) second order magnetic phase transition materials24
- Figure 2.2** Temperature dependence of calculated $|\Delta S_M|$ values under the application of magnetic field $H = 1.5$ T for bulk and milled $\text{Nd}_2\text{Fe}_{17}$ samples. δT_{FWHM} is shown by the horizontal lines for each sample. The inset shows the magnetic field dependence of δT_{FWHM} for all the samples26
- Figure 2.3** Temperature dependence of magnetic entropy change under the application of magnetic field 1.1 T for (a) $\text{Fe}_{80-x}\text{B}_{12}\text{Cr}_8\text{La}_x$ (b) $\text{Fe}_{80-x}\text{B}_{12}\text{Cr}_8\text{Ce}_x$ (c) $\text{Fe}_{80-x}\text{B}_{12}\text{Cr}_8\text{Gd}_x$ melt spin ribbons27

Figure 2.4 Magnetic entropy change as a function of temperature under magnetic field of 0.4 T for (a) $\text{Fe}_{90-x}\text{Zr}_{10}\text{B}_x$ ($x = 3$ to 9) and (b) $\text{Fe}_{93-x}\text{Zr}_7\text{B}_x$ ($x = 0$ to 13)	31
Figure 2.5 Relative cooling power (below yellow) with applied magnetic field of 1.5 T and Curie temperature (upper blue line) for reported iron based magnetocaloric materials	33
Figure 2.6 Schematic diagram of magnetothermal self-pumping principle	41
Figure 3.1 Schematic of high energy ball milling synthesis mechanism for Fe-Ni-B/Mn/Cr alloy nanoparticles (a) Rotating reaction chamber (vial) with milling balls and a mixture of starting elements. (b) Repeated welding fracture provides the final alloyed powder.	53
Figure 3.2 Schematic of X-ray diffractometer	57
Figure 3.3 Working principle for VSM.....	60
Figure 3.4 Fe–Ni phase diagram and dashed red line is extrapolation in γ -phase region showing T_C for corresponding composition in iron rich region.	62
Figure 3.5 Left axis show the temperature dependence of magnetization $M(T)$ for γ -($\text{Fe}_{70}\text{Ni}_{30}$) nanoparticles while the right axis shows corresponding derivative with respect to temperature (dM/dT).	63
Figure 3.6 Magnetic cooling prototype	65
Figure 4.1 (a) XRD patterns of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles after milling times 4, 5, 7, 8 and 10 h under Ar atmosphere. (b) Higher magnification of 110(bcc) and 111(fcc) diffraction peaks.	73

- Figure 4.2** Bright field TEM of γ -(Fe₇₀Ni₃₀)₈₉B₁₁ nanoparticles with magnified inset showing lattice spacing corresponding to 111 planes.74
- Figure 4.3** (a) $M(T)$ versus T of as milled and water quenched of (Fe₇₀Ni₃₀)₈₉B₁₁ nanoparticles for $\mu_0 H = 0.1$ T, the inset of (a) shows dM/dT versus T plot for the quenched sample. (b) M versus H at 10 K for the quenched sample.75
- Figure 4.4** The temperature dependence of magnetizations for water quenched (Fe₇₀Ni₃₀)₁B_{1-x} ($x=0, 0.11, 0.15, 0.18$) at applied magnetic field 0.1T.76
- Figure 4.5** Magnetization isotherms obtained from temperature 100 to 600 K for a maximum applied magnetic field 5 T, the temperature difference between two isotherm from 100 K to 300 K and from 500 K to 600 K was 10 K while from 300 K to 500 K it was 5 K.77
- Figure 4.6** (a) $-\Delta S_m$ versus T for quenched (Fe₇₀Ni₃₀)₈₉B₁₁ nanoparticles for ΔH ranging from 1 T to 5 T. (b) ΔS_M^{peak} (left scale) and RCP (right scale) as a function of ΔH78
- Figure 4.7** (a) $M(H)$ isotherms around T_C (b) Arrott plot (Mean-field model) (c) 3D-Ising model (d) 3D-Heisenberg model (e) Triclinic mean field model and (f) Relative slope (RS) as a function of temperature.81
- Figure 4.8** (a) Kouvel-Fisher (KF) plot for $M_s \cdot (dM_s/dT)^{-1}$ (left) and $\chi_0^{-1} \cdot (d\chi_0^{-1}/dT)^{-1}$ (right) versus T . (b) $M(H)$ at $T_C = 381$ K, inset shows $\ln M$ versus $\ln H$. (c) Scaling plots of $M(H)$ isotherms above and below T_C using β and γ from the KF equations. Inset of (c) shows the same plot in log-log scale.83
- Figure 4.9** Field dependence of change in entropy ΔS_M^{peak} (left scale) and relative cooling power RCP (right scale) in ln-ln scale85

Figure 5.1 X-ray diffraction patterns of $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ recorded at temperatures between room temperature and 973K during heating ($\uparrow$) and cooling ($\downarrow$). The star (*) is showing an impurity of spinel phase. (b) Selected diffraction peaks (bcc, 110 and fcc, 111) in “ 2θ ” range 40 to 45°94

Figure 5.2 XRD patterns of $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$, $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ and $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Mn}_{11}$ nanoparticles after annealing at 700 °C for 2 h and then quenching in water.95

Figure 5.3 (a) The temperature dependence of magnetization for as milled (black square) and after water quenching (red circle) of $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ nanoparticles at applied magnetic field 0.1 T. Inset a) shows dM/dT versus T plot for quenched sample, (b) Isothermal magnetization M at 300 K for as milled and quenched $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ nanoparticles. The inset of (b) is zoom portion for showing the hysteresis.97

Figure 5.4 (a) Magnetization isotherm curves obtained from temperature 10 K to 400 K for a maximum applied magnetic field 5 T, (b) Magnetic entropy changes for quenched $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ nanoparticles as a function of temperature for different field98

Figure 5.5 Variation of ΔS_M^{max} (left scale) and RCP (right scale) as a function of ΔH . Insets (a and b) depicts the same graphs in Log-Log scale, respectively.99

Figure 5.6 $M(H)$ magnetic isotherm at $T_C = 338$ K, inset shows $\ln(M)$ versus $\ln(H)$ with $H > 0.5$ T.100

Figure 5.7 (a) Magnetization as a function of temperature for as milled sample at magnetic field of 0.1T in the temperature range from RT to 973K in three modes;

during heating (black circle), cooling (red square) and again heating (blue triangle). The inset of (a) is dM/dT versus T plot during heating and cooling. (b) Magnetization as a function of temperature for water quenched sample at magnetic field of 0.1T in the temperature range from 10 K to 400 K. The inset of b is dM/dT versus T plot during heating and cooling.101

Figure 5.8 Magnetization isotherms $M(H)$ obtained for a maximum applied magnetic field of 5 T (a) from 10 to 570 K for the α – phase, (b) from 10 to 500 K for the γ - phase. Magnetic entropy change as a function of temperature for a range of magnetic field from 1 T to 5 T (c) for γ -FeNiMn and (d) α -FeNiMn nanoparticles.103

Figure 5.9 (a) Magnetization isotherms $M(H)$ obtained for a maximum applied magnetic field of 5 T from 100 to 400 K for the quenched γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles (b) Magnetic entropy change as a function of temperature for a range of magnetic field from 1 T to 5 T for quenched γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles.103

Figure 5.10 (a) The temperature dependence of magnetization for quenching (Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles at applied magnetic field 0.1 T. Inset a) shows dM/dT versus T plot, the T_C for this sample is 220 K (b) Isothermal magnetization M at 10 K.105

Figure 5.11 (a) Magnetization isotherms $M(H)$ obtained for a maximum applied magnetic field of 5 T from 10 K to 400 K for the quenched (Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles (b) Magnetic entropy change as a function of temperature for a range of magnetic field from 1 T to 5 T for quenched (Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles.105

Figure 5.12 Magnetic entropy change as a function of temperature at applied magnetic field of 5 T for $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ (quenched), $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ (as milled), $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ (vacuum annealed), $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ (quenched), $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Mn}_{11}$ (quenched) nanoparticles106

Figure 5.13 (a) $M(H)$ isotherm around T_C , (b) Arrott plot (mean field model), M^2 versus H/M and (c) 3D-Heisenberg model.108

Figure 5.14 (a) Kouvel-Fisher (KF) plot for $\mathbf{M}_s \cdot (d\mathbf{M}_s/dT)^{-1}$ (left) and $\chi_0^{-1} \cdot (d\chi_0^{-1}/dT)^{-1}$ (right) v/s T . (b) $\ln(M)$ v/s $\ln(H)$ for $H > 3000$ Oe at $T_C = 340$ K. (c) Scaling plots of $M(H)$ isotherms above and below T_C using β and γ from the KF equations, inset shows the same plot in log-log scale.110

Figure 6.1 Bright field TEM of (a) Cr3 and (b) Cr5 nanoparticles with magnified insets showing lattice spacing corresponding to 111 planes.118

Figure 6.2 Left axis show the temperature dependence of magnetization $M(T)$ for (a) Cr0, (b) Cr1, (c) Cr3, Cr5, Cr6 and Cr7 while the right axis shows corresponding derivative with respect to temperature (dM/dT) . The Curie temperature for Cr0, Cr1, Cr3, Cr5, Cr6 and Cr7 is 438 K, 398K, 323K, 258K, 245K and 215K, respectively.119

Figure 6.3 Phase diagram for ternary system $(\text{Fe}_{70}\text{Ni}_{30})_{1-x}\text{Cr}_x$ with $x = 0$ to 8. Solid line represents the theoretical values predicted from FeNi phase diagram and empirical equation $T_C = T_C^I + (T_C/dc) c$, while points (red square) are experimental results.120

Figure 6.4 Phase diagram for ternary system $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mn}_x$ with $x = 0$ to 11. Solid line represents the theoretical values predicted from FeNi phase diagram and empirical equation $T_C = T_C^I + (T_C/dc) c$, while points (red square) are experimental results.121

Figure 6.5 Temperature dependence of the magnetic entropy change ($-\Delta S_M$) under magnetic field ranging from 0.5 T to 5 T for (a) Cr1, (b) Cr3, (c) Cr5, (d) Cr6 and (e) Cr7 alloy. (f) Dependence of $-\Delta S_M$ (left axis, black square) and RCP (right axis, blue circle) on Chromium percentage in $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$ nanoparticles at applied magnetic field 5 T.122

Figure 6.6 (a) Field dependence of working temperature span (δT_{FWHM}) for Cr1, Cr3, Cr5 Cr6 and Cr7 alloys. (b) Maximum change in entropy ($-\Delta S_M^{\max}$) as a function of applied field and (c) Variation in relative cooling power (RCP)). The plots (b) and (c) are in log-scale.123

Figure 7.1 Room temperature X-ray diffraction pattern of arc melted FeNiB. Blue line, red line and bottom black line are observed, calculated and differences, respectively. The Rietveld refinement of the diffraction pattern shows that the sample exhibits a mixture of a face centered cubic ($Fm-3m$, 71.75 %) phase, a body centered cubic ($Im-3m$, 20.95 %) phase and a spinel ($Fd-3ms$, 7.30 %) phase ...132

Figure 7.2 (a) Temperature dependence of magnetization in cooling (filled symbols) and heating (open symbols) mode for $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy at applied magnetic fields of 0.05 T, 0.1 T, 0.5 T and 1 T, the hysteresis is negligible. (b) The corresponding dM/dT versus T curves, showing the Curie temperature for the γ - and α - phase. Inset of (b) shows changes in transition temperature (T_C^γ and T_C^α) with applied magnetic fields.133

Figure 7.3 (a) Magnetization isotherms obtained from temperature 10 K to 950 K for a maximum applied magnetic field 5 T, showing almost zero magnetic hysteresis in magnetic field sweep cycles. (b) Magnetic entropy changes for $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy as a function of temperature for ΔH ranging from 1 T to 5 T, resulting two peak values at transition temperature of γ - and α - phase.135

Figure 7.4 (a) Field dependence of working temperature span (δT_{FWHM}) for multiphase bulk alloy $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ and γ - $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles (b) RCP as a function of change in applied magnetic field.136

Figure 7.5 Temperature dependence of the exponent “ n ” for single and multiphase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloys calculated by linear fitting of change in entropy versus applied magnetic field for $\Delta H = 5$ T. The exponent “ n ” for multiphase is higher than that of single phase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$138

Figure 8.1 Bright field TEM of MnZn Ferrite nanoparticles with the histogram of particle size distributions.144

Figure 8.2 Schematic layout of automatic magnetic cooling system145

Figure 8.3 Schematic of 2D model showing the temperature distribution (a) without magnetic field (b) with magnetic field.147

Figure 8.4 Effect of magnetic field in the cooling of heat load.148

Figure 8.5 Temperature difference of the heat load with and without magnetic field for both experiment (black square) and simulated data (red circle)149

Figure 8.6 Temperature v/s time for initial temperature of heat load of (a) 64°C , (b) 74°C and (c) 87°C , respectively, without and with magnetic field of 0.3 T.150

Figure 8.7 Temperature difference of the heat load with and without magnetic field for different initial temperature. The experiment and simulated data were shown by symbol of black square and red circle, respectively.....151

Figure 8.8 Effect of volume fraction of magnetic nanoparticles on the cooling of heat load.	152
Figure 8.9 Temperature difference of the heat load with different volume fraction of magnetic nanoparticles.....	152
Figure 8.10 The effect of application and removal of magnetic field of 0.3 T on the temperature profile for initial temperature of heat load of (a) 87° C, (b) 74° C and (c) 64° C, respectively. The temperature drop (cooling) in (a), (b) and (c) was ~ 20 ° C, ~ 24 ° C and 28 ° C, respectively	153
Figure 8.11 Temperature v/s time for initial temperature of heat load of (a) 64.4° C, (b) 53.4° C and (c) 47.4° C, respectively, without and with magnetic field of 0.25 T	154
Figure 8.12 Simulated temperature profiles for initial temperature of heat load of (a) 64.4° C, (b) 53.4° C and (c) 47.4° C, respectively, without and with magnetic field of 0.25 T	155
Figure 8.13 Temperature difference of the heat load with and without magnetic field for different initial temperatures. The experiment and simulated data were shown by symbol of black square and red circle, respectively	156
Figure 9.1 The relative cooling power of our iron based nanoparticles and gadolinium nanoparticles.	162

Abbreviations

EDS	Energy Dispersive X-ray Spectroscopy
EPMA	Electron Probe Microanalysis
PXRD	Powder X-ray Diffraction
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
MCE	Magnetocaloric Effect
MCM	Magnetocaloric Materials
FOTM	First order Magnetic Transition Materials
SOTM	Second order Magnetic Transition Materials
RCP	Relative Cooling Power
ECE	Electrocaloric effect

Chapter 1

Introduction

The energy resources of the world are very limited, which makes it vital to search for new energy sources and reduce energy consumption. Environmental policies throughout the world demand the mitigation of global warming. Magnetic materials can contribute to saving energy as well as reducing toxic emissions and greenhouse gases. Magnetic cooling offers several advantages over the conventional gas compression cooling technique. The cooling efficiency of magnetic cooling technology can be much higher than conventional gas based cooling methods without any use of hazardous gases such as chlorofluorocarbons and hydro chlorofluorocarbons that are harmful to the ozone layer. Hence, this technology is 'green' and very environmentally friendly compared to conventional gas compression cooling. This chapter provides an overview of the historical development, motivation, objectives, novelty and scope of the thesis.

1.1. Magnetocaloric effect and magnetic cooling

In recent years, magnetic cooling based on the magnetocaloric effect (MCE) has attracted considerable interest as a technology for minimizing global warming¹⁻⁸. In 1918, a reversible change in temperature of 0.7 K in nickel by applied magnetic field of 1.5 T was observed near the Curie temperature (T_C) by Weiss and Piccard⁹. Therefore, they identified the main features of MCE: that it is reversible and is largest in the vicinity of the T_C . Debye in 1926 and Giauque in 1927 independently explained the origin of the MCE.^{10,11} The nature of MCE in a solid is the result of the entropy change due to the coupling of the magnetic spins with the magnetic field⁷. Magnetic cooling has significant advantages compared with conventional gas-compression cooling technique, e.g., no greenhouse gases as well as high energy efficiency^{1-7,12-15}. The magnetic refrigeration cycle can be explained in terms of the magnetic moments and lattice vibrations of magnetocaloric materials (Fig. 1.1).

Fig. 1.1 Schematic representation of a) lattice and magnetic subsystems in a magnetocaloric material, and four stages of magnetic refrigeration cycles: (b) application of magnetic field under adiabatic condition (c) removing heat, d) adiabatic demagnetization, and (e) cooling of load contents³.

The lattice vibrations and fluctuation of magnetic moments depends on the magnitude of the applied magnetic field and the temperature of the material. When

a magnetic field is applied adiabatically, the lattice vibrations increase and magnetic moments align parallel to the field. Therefore, magnetic entropy decreases and lattice entropy increases, but the total entropy of the system does not change. The temperature of the system increases because of increased lattice vibrations (Fig. 1.1b). By using a suitable heat transfer fluid, the system temperature can be reduced back to its initial value (Fig. 1.1c). Importantly, when the magnetic field is removed adiabatically, the magnetic entropy of the sample goes up and therefore its lattice entropy and temperature drops (Fig. 1.1d). Now the magnetocaloric material is cool, therefore it can absorb heat from the heat load (Fig. 1.1e). By performing these steps, a magnetic refrigeration cycle can be constructed.

1.2. Motivation

Today's research is focused to find new magnetocaloric materials and an optimal design of magnetic refrigerator for near room temperature applications^{3,16}. The data for Fig. 1.2 were exported from the Scopus by using the words "magnetocaloric effect" in "Article title, Abstract and Keywords" fields.

Fig 1.2 Publications on MCE using SCOPUS: "Magnetocaloric Effect" in the "Article title, Abstract and Keywords" fields Number of published article on MCE every year since 1950 to 2015 (the data were exported on July 2015).

It is apparent from Fig.1.2 that the search of new materials with large MCE has gained large momentum in the last decade. Scientists and researchers

throughout the world have devoted much attention to search for new magnetocaloric materials. The world is warming because of air conditioners and refrigeration, and we are trying to stay cool in the warm world by using air conditioners! Nowadays, the target to control global warming to below 2 °C is the main focus of the international climate debate^{17, 18}.

In July 2012,¹⁹ Stan Cox reported that the United State (US) has more energy consumption in air conditioning than the rest of the world. The US also uses more electricity for cooling than the electricity consumption of entire Africa. During 1993 to 2005, the energy consumed by residential air conditioning in the US has doubled because of larger homes and hotter summers, and further jumped another 20 % by 2010. The climate impact of air conditioners is about half of billion metric tonnes of CO₂ per year. China is also one of the biggest users of electricity for air conditioning and may overtake the US by 2020. In another survey in India, about 40% of electricity of Mumbai city was consumed in air conditioning²⁰. Companies are making more than 180 Million cooling device every year by using 10 K tonnes of environmentally harmful hydrofluorocarbons (HCFCs) which may be equivalent to 28 – 45 % of CO₂ emission in 2050.^{21, 22} Magnetic cooling, which is an environmentally friendly and energy efficient technology, may be a good alternative for making an improvement, as it is more energetically efficient than the current conventional cooling techniques. Magnetic cooling can achieve 60% of Carnot (ideal) efficiency in the laboratory, while the best gas compression cycle can reach only 40%.^{22, 3} In addition, compressors are noisy and vibrate a lot, whereas magnetic cooling devices can be silent and vibration free^{22, 23}.

Applications of magnetic cooling can be (a) magnetic home refrigeration (b) magnetic air-conditioning in building (c) magnetic refrigeration in medicine (d) magnetic cooling in food industry (e) magnetic cooling of electronic devices (f) magnetic cooling in transportation (g) Magnetic cooling of solar cell panels, etc. Nowadays a lot of money is spent for cooling of huge data servers, as about 50% of total energy consumed to cool them. Fig 1.3 shows the flow chart for the power consumptions in data center²⁴.

Fig.1.3 Energy consumption in data center²⁴

The uses of MCE based technology can be extended for other applications. By dispersing the magnetic nanoparticles in suitable fluid, this technology is also very useful for the applications to cool electronic microchips and other small devices³. If one is able to cool electronic devices, computer processors etc. they would definitely be much more efficient.

In 2013, Whirlpool, Camfridge, TCS Micropump, PSU Tec, Cemafrroid, and International Institute of Refrigeration (IIR) developed a European Union project ELICiT (Environmentally Low Impact Cooling Technology). The main goal of ELICiT is to replace the domestic refrigerator with a solid state magnetic refrigerator and thus reduce energy consumption. General Electric (GE), Toshiba, and BASF are also developing magnetic cooling systems. Astronautics Corporation of America and BASF has introduced a commercial wine cooler, refrigerated by a magnetocaloric pump at the International Consumer Electronics Show (CES) in Las Vegas. They have used Fe-Mn based material developed in collaboration of Delft University of Technology. GE has also fixed the aim of bringing a magnetic refrigerator into the market by 2020. The ongoing project on MCE worldwide are listed in the following table 1.1.

Table 1.1 List of international and national project worldwide²⁵

Project Name	Duration for project
Novel magnetocaloric air conditioner, U.S. Department of Energy	2015-
Magnetocaloric Refrigeration, US DOE – CRADA PROJECT (ORNL + GE)	2013-2016
Air Conditioning With Magnetic Refrigeration, Program: BEETIT, ARPA-E AWARD	2010-2014
ELICiT- Environmentally Low Impact Cooling Technology	2013-2016
DRREAM- Drastically Reduced Use of Rare Earths in Applications of Magnetocaloric	2013-2016
ICE Magnetocaloric Refrigeration for Efficient Electric Air Conditioning	2010-2014
FRIMAG- Demonstrator of drinks cooler running by means of magnetic refrigeration, France and Switzerland	-
ENOVHEAT project, Danish Council for Strategic Research within the Programme Commission on Sustainable Energy and Environment, Denmark	2013–2017
SPP 1599 “Ferroic Cooling” Caloric Effects in Ferroic Materials: New Concepts for Cooling, Germany	2012-
MagCool: “New giant magnetocaloric materials round room temperature and applications to magnetic refrigeration, France	2011-2015

Now the question is if the magnetocaloric based cooling technique has huge advantages than why is this technique not yet widely commercialized? The most challenging reason is to find a suitable magnetocaloric material. The rare earth based materials exhibit high change in entropy and therefore, in last decade, considerable research has been aimed at rare earth based magnetocaloric materials. However, there are many complicated issues around rare earth materials because of international politics, economics, cost and availability. China has been the dominant supplier for rare earth materials for the past several decades (over 90% of world production in 2013). However, in early 2015, China has eliminated the share system for rare-earths. Other issue is that the high performance magnetocaloric materials exhibit magnetic and thermal hysteresis, which reduces their final efficiency. Therefore, developing a magnetocaloric material without rare

earth's content and with no or negligible magnetic and thermal hysteresis is essential to bring this technique in market.

The electrocaloric effect (ECE) is analogous to magnetocaloric energy conversion; however, different external influences are needed. The ECE is a physical phenomenon that occurs in some dielectric materials under the influence of a varying electric field. It is expressed as the adiabatic temperature or isothermal entropy change of the material. The ECE possesses possible advantages as well as some disadvantages in comparison with MCE. However, electrocaloric solid state energy conversion is at an early stage of development, it is not yet reasonable to compare this with magnetocaloric energy conversion. An important milestone came in 2006 in giant electrocaloric effect $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ (PZT) ceramic thin films³⁶. Using indirect measurements, this material undergoes an adiabatic temperature change of 12 K for an electric field change of 48 MV/m. After 2006 many researchers reported the discovery of new electrocaloric materials, including several ceramics and some polymers³⁷.

One serious disadvantage of lead oxides is difficulties in production of free-crack ceramic. There are large number of cracks due to change of sample volume during cooling below the Curie temperature (T_C). In addition, lead is very toxic. On the other hand, limited temperature change in one cooling cycle for low fields is one of the main disadvantage in MCE.

1.3.Objective

Based on the motivation discussed earlier, the main aim of this thesis is to develop a rare earth free, affordable, and readily available magnetocaloric nanomaterials with tunable Curie temperature (T_C) for near room temperature thermal management applications. The materials must have negligible magnetic and thermal hysteresis. We have chosen Fe-Ni as the host material and a suitable third element was added to tune the T_C while retaining attracting magnetocaloric properties. The objective can be divided in the following points

1. Synthesis of $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{A}_x$ alloy nanoparticles with $\text{A} = \text{B}, \text{Mn}$ and Cr
2. The effect of composition and synthesis conditions on the structure

3. The magnetic properties of these synthesized materials to determine the Curie temperature, magnetic and thermal hysteresis, the change in entropy, working temperature span and relative cooling power.
4. Critical behaviour analysis in order to understand the magnetocaloric effect near the magnetic phase transition temperature.
5. To synthesize the ferrofluid and its use in a self-pumping magnetic cooling prototype. Study the effect of temperature/heat load, magnetic field and tube diameter on the cooling experimentally and with modeling.

1.4. Novelty

Considerable literature is available for pure lanthanide (rare earth) based materials and mixtures of rare earth and 3d transition MCE materials. On the other hand, we wish to study 3d transition MCE alloys which are much cheaper and readily available. Our materials exhibit second order magnetic transition with negligible magnetic and thermal hysteresis. The novelty, along with a brief description for this work is provided in Table 1.2.

Table 1.2 Approach, novelty and a brief description of our work^{4, 26-30, 32-35}.

Related Previous work	Our work	Novelty	Summary
Fe-Ni-Zr-B (2011)	Fe-Ni-B Nanoparticles series	No previous report of the MCE of these nanoparticles for any of the composition No critical analysis has been reported for these nanoparticles	(Fe ₇₀ Ni ₃₀) ₈₉ B ₁₁ nanoparticles are having promising MCE for low grade waste heat recovery ($T_C = 381$ K) Relative cooling power (RCP) for (Fe ₇₀ Ni ₃₀) ₈₉ B ₁₁ nanoparticles is very high (640 J/kg for $\Delta H = 5$ T), highest for rare earth free transition materials Critical exponents $\alpha = -0.055$, $\beta = 0.364$, $\gamma = 1.319$ and $\delta = 4.623$ are close to the value obtained from 3D-Heisenberg model

Fe-Ni (2013) Fe-Ni-Mo (2014)	Fe-Ni-Mn Nanoparticles series	No previous report of the MCE for these alloy nanoparticles No critical analysis has been reported for these nanoparticles	The γ -phase stabilization was confirmed by in-situ XRD and magnetometry. γ -phase of $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_8$ and $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ nanoparticles have promising MCE for near room temperature application while α -phase of $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_8$ is useful for low grade heat recovery Field dependence of RCP was measured experimentally ($\text{RCP} \propto H^{1.21}$) and modeled theoretically (3D Heisenberg model) Critical exponent of γ -phase of $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_8$: $\beta = 0.319$, $\gamma = 1.195$ and $\delta = 4.71$
Cr was used to tune T_C in other alloys : Fe-B-Cr (2011)	Fe-Ni-Cr Nanoparticles series	No previous report of the MCE for these alloy nanoparticles	Only 7 % of Cr alloying with Fe-Ni is able to tune the T_C from ~ 438 K to 215 K. The influence of Cr alloying with FeNi on Curie temperature were assured by the empirical relation $T_C = T_{C1} + (dT_C/dc) c$. High working temperature span which is useful to enhance an important figure of merit, relative cooling power
Rosensweig and Love et al., (2004)	Self-pumping magnetic cooling	There are few reports available but still many parameters are unclear Pumping and cooling with no moving mechanical part	Self-pumping magnetic cooling prototype was build Mn-Zn Ferrite nanoparticles with average size of 10 nm were synthesized and used to make the water based ferrofluid. The effects of magnetic field, particles density, initial temperature, tube diameter have been studied experimentally and theoretically

1.5 Materials selections

It is clear that developing a high performance rare earth free MCM is one of the most critical issues to make magnetic cooling based devices widely available on a commercial bases. Binary Fe-Ni alloys can show high magnetization and low coercivity, which are the initial requirements for a good MCM. However, the T_C for these alloys is quite high. Our interest in MCE studies focus the commercially important on near room temperature (RT) applications. Our hypothesis was that B (glass forming), Mn or Cr (antiferromagnetic) alloying addition can reduce T_C . The Bethe-Slater curve qualitatively describes the variations in strength of the direct exchange as a function of the ratio of the interatomic distance to radius of atomic distance $(r_a/r_{3d})^{31}$.

Fig. 1.4 The Bethe-Slater curve (schematic) showing the dependence of the exchange interaction on the ratio of interatomic distance to the diameter of the 3d electron shell.

Hence, with the aim of tuning the T_C closer to room temperature, the influence of B, Mn and Cr additions on the MCE of Fe-Ni alloys was studied. It was found that addition of 11 wt% B, 8 wt% Mn and 5 wt% Cr in Fe-Ni reduces the T_C from 443°C to 381, 340 and 267°C, respectively, while retaining attractive magnetocaloric properties.

Another hypothesis is that we have focused on nanoparticles because reduction in particle size can result in broad a ferromagnetic to paramagnetic transition i.e., distribution of T_C . This distribution in T_C is associated with a large relative cooling power (RCP). To synthesize ternary alloy nanoparticles by chemical method is difficult because each element has its own reducing potential and solubility. Instead, we used a high speed ball milling technique. After parameter optimization, this technique is scalable and easy to handle.

Furthermore, the magnetocaloric properties and T_C of the materials can be explained in terms of positive and negative exchange interaction between the

ions/atoms. 3D Heisenberg, 3D Ising and triclinic models were used for the critical analysis near T_C .

1.6 Organization of thesis

The present study aims to develop novel rare earth free iron based magnetocaloric materials. The thesis comprises nine chapters, as follows:

Chapter 1: General introduction to MCE and cooling, motivation with the problem statements are outlined. The objectives, scope and hypothesis of the project are introduced along with the significance and novelty of this work.

Chapter 2: The thermodynamics of MCE, in terms of Gibbs free energy, change in magnetic entropy, critical exponents etc. are described. A literature survey of promising MCM was also listed.

Chapter 3: The experimental methods, including synthesis procedure and characterization techniques to determine the structural and magnetic properties of the materials are introduced. The working principle of the techniques and parameters used in the characterization are explained.

Chapter 4: The experimental results for the $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{B}_x$ are presented with detailed discussion. A critical analysis of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ was performed. We compared our results with other promising MCM available in the literature.

Chapter 5: The magnetocaloric properties for $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mn}_x$ with detailed discussion are presented. The *in-situ* XRD was used to check the structural transition from the α - to the γ -phase. The critical analysis of γ - $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ is also presented.

Chapter 6: The results for $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$ nanoparticles with discussion on tuning of T_C , are presented.

Chapter 7: In this chapter, MCE of bulk $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy was explained.

Chapter 8: The experimental and simulation results for self-pumping magnetic cooling are described.

Chapter 9: The summary, conclusion and future work are presented.

1.7 Significant Findings and outcomes

Magnetic cooling technique are economically and environmentally superior compared to commercial vapour cooling systems. Our MCE nanomaterials have been developed through structural control and process optimization. Developing a low cost, readily available MCM can create the right conditions for commercially feasible magnetic cooling technology for a variety of advanced technological applications. The research led to several novel outcomes:

1. A very high RCP in a study of the MCE in $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles was demonstrated³². RCP was found to be $640 \text{ J}\cdot\text{kg}^{-1}$ for a field change of 5 T, this value is the largest for rare earth free iron based magnetocaloric nanomaterials. Detailed analysis of the magnetic phase transition using the modified Arrott plot, Kouvel-Fisher method and critical isotherm plots yields critical exponents of $\beta = 0.364$, $\gamma = 1.319$, $\delta = 4.623$ and $\alpha = -0.055$, which are close to the theoretical exponents obtained from the 3D-Heisenberg model. Our results indicate that these $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles are potential candidates for magnetocaloric fluid based heat pumps and low grade waste heat recovery.
2. The inadequate temperature span is often a challenge in developing magnetic cooling system. To enhance the working temperature span (δT_{FWHM}) of the magnetic entropy change and the relative cooling power, a multiphase Fe-Ni-B bulk alloy is proposed³³. The coexistence of bcc, fcc and spinel phases results in large working temperature spans of 322.3 K and 439.0 K for magnetic field change of 1 T and 5 T, respectively. δT_{FWHM} for this multiphase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy is about 86 % higher than the corresponding value for single phase γ - $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy for $\Delta H = 1 \text{ T}$.
3. We investigated the magnetocaloric properties of $(\text{Fe}_{70}\text{Ni}_{30})_{1-x}\text{Mn}_x$ alloy nanoparticles^{34,35}. Near room temperature magnetocaloric effect, with high relative cooling power (RCP), was obtained by alloying FeNi with Mn and fcc (γ) phase stabilization. Critical exponents values for γ - $(\text{Fe}_{70}\text{Ni}_{30})_{1-x}\text{Mn}_x$ alloy nanoparticles were found to be $\delta = 4.71$, $\beta = 0.319$ and $\gamma = 1.195$, close to those obtained from the short range order 3D-Heisenberg model.

4. The influence of Cr alloying with FeNi on the Curie temperature was studied. Only 7 % of Cr alloying with Fe₇₀Ni₃₀ lowered T_C from ~ 443 K to 215 K. The entropy change and relative cooling power of (Fe₇₀Ni₃₀)_{100-x}Cr_x ($x = 1, 3, 5, 6$, and 7) alloy nanoparticles for below room temperature applications were studied.
5. A series of experiments were conducted to examine the effect of heat load/temperature, magnetic field and tube diameter on cooling. It was found that the performance of the cooling device strongly depends on heat load, magnetic field and volume of ferrofluid. Cooling of 16 °C and 27 °C has been achieved at 0.3 T magnetic field when mass fraction of magnetic particles was 5 % and 10 % respectively. These results matched well with simulation performed with COMSOL Multiphysics. Our system is self-regulating since as heat load increases, magnetization of the ferrofluid decreases and the driving force rises. Therefore, heat is transferred more quickly from heat source to heat sink.

References

- ¹ K. A. Gschneidner and V. K. Pecharsky, Annual Review of Materials Science **30**, 387 (2000).
- ² M.H. Phan and S.C. Yu, Journal of Magnetism and Magnetic Materials **308**, 325 (2007).
- ³ V. Franco, J. S. Blázquez, B. Ingale, and A. Conde, Annual Review of Materials Research **42**, 305 (2012).
- ⁴ H. Ucar, J. J. Ipus, M. E. McHenry, and D. E. Laughlin, Journal of Metals **64**, 782 (2012).
- ⁵ M. Balli, S. Jandl, P. Fournier, and M. M. Gospodinov, Applied Physics Letters **104**, 232402 (2014).
- ⁶ J. R. Gómez, R. F. Garcia, A. D. Catoira, and M. R. Gómez, Renewable and Sustainable Energy Reviews **17**, 74 (2013).
- ⁷ K. A. Gschneidner Jr, V. K. Pecharsky, and A. O. Tsokol, Reports on Progress in Physics **68**, 1479 (2005).

- ⁸ A. Smith, C. R. H. Bahl, R. Bjørk, K. Engelbrecht, K. K. Nielsen, and N. Pryds, *Advanced Energy Materials* **2**, 1288 (2012).
- ⁹ A. Piccard, *P. Weiss Comptes Rendus* 352 (1918).
- ¹⁰ P. Debye, *Ann. Phys* **81**, 1154 (1926).
- ¹¹ W. F. Giauque, *J. Amer. Chem. Soc* **49**, 1864 (1927).
- ¹² D. Fatnassi, K. Sbissi, E. K. Hlil, M. Ellouze, J. L. Rehspringer, and F. Elhalouani, *Journal of Nanostructure in Chemistry*, 1 (2015).
- ¹³ J. W. Lai, Z. G. Zheng, X. C. Zhong, V. Franco, R. Montemayor, Z. W. Liu, and D. C. Zeng, *Journal of Magnetism and Magnetic Materials* **390**, 87 (2015).
- ¹⁴ L. Li, Y. Yuan, Y. Zhang, R. Pöttgen, and S. Zhou, *Journal of Alloys and Compounds* **643**, 147 (2015).
- ¹⁵ J. K. Murthy, K. D. Chandrasekhar, M. Sudipta, D. Topwal, and A. Venimadhav, *Journal of Physics D: Applied Physics* **48**, 355001 (2015).
- ¹⁶ O. Tegus, E. Bruck, K. H. J. Buschow, and F. R. de Boer, *Nature* **415**, 150 (2002).
- ¹⁷ S. Randalls, *Wiley Interdisciplinary Reviews: Climate Change* **1**, 598 (2010).
- ¹⁸ J. Rogelj, D. L. McCollum, A. Reisinger, M. Meinshausen, and K. Riahi, *Nature* **493**, 79 (2013).
- ¹⁹ S. Cox, *Yale Environment* 360 (2012).
- ²⁰ *The Times of India* (India 2009) <http://archive.is/2oErp>
- ²¹ G. J. M. Velders, D. W. Fahey, J. S. Daniel, M. McFarland, and S. O. Andersen, *Proceedings of the National Academy of Sciences* **106**, 10949 (2009).
- ²² <http://www.prizz.fi/sites/default/files/tiedostot/linkki2ID917.pdf>
- ²³ B. Ekkes, *Journal of Physics D: Applied Physics* **38**, R381 (2005).
- ²⁴ www.infotech.com/download/32455
- ²⁵ U. T. J. Tušek, A. Kitanovski, U. Plaznik, M. Ožbolt and A. Poredoš, *Magnetocaloric Energy Conversion* (Springer International Publishing Switzerland, 2015).
- ²⁶ K. L. McNerny, Y. Kim, D. E. Laughlin, and M. E. McHenry, *Journal of Applied Physics* **107**, 09A312 (2010).

- ²⁷ J. J. Ipus, H. Ucar, and M. E. McHenry, IEEE Transactions on Magnetics **47**, 2494 (2011).
- ²⁸ J. Popplewell, R. E. Rosensweig, and R. J. Johnston, Magnetics, IEEE Transactions on **26**, 1852 (1990).
- ²⁹ R. E. Rosensweig, International Journal of Refrigeration **29**, 1250 (2006).
- ³⁰ R. E. Rosenweig, *Ferrohydrodynamics* (Cambridge University Press, 1985).
- ³¹ C. W. Chen, *Magnetism and Metallurgy of Soft Magnetic materials* (North Holland Publishing Company, 1977).
- ³² V. Chaudhary, D. V. Maheswar Repaka, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, Journal of Applied Physics **116**, 163918 (2014).
- ³³ V. Chaudhary and R. V. Ramanujan, Magnetics Letters, IEEE **6**, 6700104(4) (2015).
- ³⁴ V. Chaudhary, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, IEEE Magnetics Letters **5**, 6800104 (2014).
- ³⁵ V. Chaudhary and R. V. Ramanujan, Journal of Physics D: Applied Physics **48**, 305003(2015)
- ³⁶ A. S. Mischenko, Q. Zhang, J. F. Scott, R. W. Whatmore, Science, **311**, 1270 (2006).
- ³⁷ J. F. Scott, Annu. Rev. Mater. Res., 41, 229 (2011)

Chapter 2

Literature review

The magnetocaloric effect (MCE) is an intrinsic property of the magnetic materials, it arises from the change in the degree of freedom of magnetic sublattices with an applied magnetic field. In this chapter we will discuss the theoretical aspects of the MCE and relevant literature of iron based magnetocaloric materials. In addition, the physics of critical behaviour and magnetothermal self-pumping will be discussed

2.1 The thermodynamics of MCE

The general thermodynamics of MCE materials can be understood by thermodynamic functions: internal energy (U), the Gibbs free energy (G) and the free energy (F).

The internal energy (U) of any system is a function of entropy (S), volume (V), and the magnetic moment (M).¹⁻³ The total differential of $U(S, V, M)$, when the system has pressure (p), magnetic field (H) and absolute temperature (T) has the form

$$dU = TdS - pdV - HdM \quad (2.1)$$

where, T , S , p , V , H and M are temperature, entropy, pressure, volume, magnetic field and magnetic moment, respectively.

For a system under constant pressure (p), the $G(T, p, H)$ can be described as

$$G = U - TS + pV - MH \quad (2.2a)$$

where, U , T , S , p , V , M and H are internal energy, temperature, entropy, pressure, volume, magnetic moment and magnetic field, respectively.

Correspondingly, the total differential of Gibbs free energy (G) can have the form

$$dG = Vdp - SdT - MdH \quad (2.2b)$$

where, V , p , S , T , M and H are volume, pressure, entropy, temperature, magnetic moment and magnetic field, respectively.

The internal parameters; entropy (S), magnetic moment (M) and pressure (p) in terms of the Gibbs free energy (G) can be described by the following equations^{1,2}.

$$S(T, H, p) = - \left(\frac{\partial G}{\partial T} \right)_{H, p} \quad (2.3a)$$

$$M(T, H, p) = - \left(\frac{\partial G}{\partial H} \right)_{T, p} \quad (2.3b)$$

$$V(T, H, p) = \left(\frac{\partial G}{\partial p} \right)_{T, H} \quad (2.3c)$$

If the magnetic moment M is an external parameter in place of the magnetic field H , then

$$H(M, T, p) = - \left(\frac{\partial G}{\partial M} \right)_{T, p} \quad (2.3d)$$

The specific heat at constant pressure of the materials can be described as the second derivative of the Gibbs free energy with respect to temperature⁴

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p \quad (2.4)$$

By definition, if the first derivative of the Gibbs free energy has a discontinuous value at the phase transition, the transition is first order. On the other hand, if the first and second derivatives of the Gibbs free energy at the phase transition have continuous and discontinuous values, respectively, then the transition is second order.

The Maxwell equations which will be used for describing MCE can be obtained from equations 2.3a, 2.3b, 2.3c and 2.3d.¹

$$\left(\frac{\partial S}{\partial H} \right)_{T, p} = \left(\frac{\partial M}{\partial T} \right)_{H, p} \quad (2.5a)$$

$$\left(\frac{\partial S}{\partial p} \right)_{T, H} = - \left(\frac{\partial V}{\partial T} \right)_{H, p} \quad (2.5b)$$

$$\left(\frac{\partial S}{\partial M} \right)_{T, p} = - \left(\frac{\partial H}{\partial T} \right)_{M, p} \quad (2.5c)$$

The total entropy of a magnetic solid (S) at constant pressure is a function of both magnetic field H and temperature T . It is the sum of magnetic (S_m), lattice (S_{Lat}), and electronic (S_{el}) entropies⁵

$$S(T, H) = S_m(T, H) + S_{Lat}(T) + S_{el}(T) \quad (2.6a)$$

The full differential of the total entropy of the closed magnetic system can be written as

$$dS = \left(\frac{\partial S}{\partial T} \right)_{H, p} dT + \left(\frac{\partial S}{\partial H} \right)_{T, p} dH + \left(\frac{\partial S}{\partial p} \right)_{T, H} dp \quad (2.6b)$$

Among these three types of entropies, the magnetic entropy is strongly field dependent while the other two, electron and lattice entropies, are less field dependent.

Under the isobaric ($dp = 0$), equation 2.6b can be written as

$$dS = \left(\frac{\partial S}{\partial T} \right)_{H,p} dT + \left(\frac{\partial S}{\partial H} \right)_{T,p} dH \quad (2.6c)$$

According to the second law of thermodynamics

$$C_H = T \left(\frac{\partial S}{\partial T} \right)_H \quad (2.7)$$

Equation 2.6c under the isobaric condition can be rewritten, substituting the values from equation 2.5a and 2.7 as:

$$dS = \frac{C_H}{T} dT + \left(\frac{\partial M}{\partial T} \right)_H dH = 0 \quad (2.8a)$$

Or

$$dT = - \frac{T}{C_H} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (2.8b)$$

Hence, the adiabatic temperature rise is directly proportional to the absolute temperature, to the derivative of magnetization with respect to temperature at constant field and to the magnetic field change. Also, indirectly proportional to the heat capacity.

2.1.1 Adiabatic change in temperature and isothermal change in magnetic entropy

The magnetic field usually changes from $H = 0$ to H . If the value of field is change from $H_i (H_1)$ to $H_f (H_2)$ these values can be used as the integration limit. If the change in applied magnetic field is represented by ΔH then the adiabatic change in temperature can be defined as¹

$$\Delta T_{ad} = \int_0^H - \frac{T}{C_H} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (2.9)$$

Integration yields Maxwell equation (2.5a)

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH \quad (2.10)$$

This equation indicates that the magnetic entropy change is proportional to the derivative of magnetization with respect temperature at constant field and to the magnetic field.

On the other hand, according to the second law of thermodynamics, the infinitesimal change of magnetic entropy can be described as

$$dS_M = \frac{C_H}{T} dT \quad (2.11)$$

Using the third law of thermodynamics *i.e.* the entropy of a system is assumed to be zero at temperature $T = 0$ and integration of equation 2.11, the entropy change in response to a magnetic field change can be expressed as²

$$\Delta S_M(T) = \Delta S(T) = \int_0^T \frac{[C_H(H_f, T) - C_H(H_i, T)]}{T} dT \quad (2.12)$$

Where $C_H(H_f, T)$ and $C_H(H_i, T)$ represent, at constant pressure p , the specific heat at final and initial magnetic field, respectively.

Researchers have used Eq. 2.9 and 2.10 to understand the behaviour of the MCE in materials and to search for new materials with a large MCE. Interpretation of ΔT_{ad} values for a magnetocaloric material is more straightforward than ΔS_M values but more difficult to determine experimentally. This is because the equation for ΔT_{ad} contains a term C_H ; some laboratories do not have the facility to measure C_H .

It is easy to see that a material should have large MCE when the value of the temperature derivative of magnetization at constant field $(\partial M / \partial T)_H$ is large and heat capacity C_H is small at the same temperature.⁶⁻⁸ Actual comparison between magnetocaloric materials can only be realized by making the comparison between both ΔT_{ad} and ΔS_M , this is because the magnitude of heat capacity may be different from one magnetocaloric material to another, e.g., manganite type materials have much greater heat capacity compared to Gd based systems.^{6,9} By the use of Eq 9 and 10, the following information about the MCE of materials can be developed: In both paramagnets and ferromagnets, the magnetization at constant field

decreases with increasing temperature i.e., $(\partial M / \partial T)_H < 0$. Hence $\Delta S_m(T)$ should be negative and $\Delta T_{ad}(T)$ should be positive for positive field changes ($\Delta H > 0$). In ferromagnets, the value of $|(\partial M / \partial T)_H|$ is largest at T_C , and therefore $|\Delta S_M(T, \Delta H)|$ should maximum at $T = T_C$. By using Eq. 2.8b and 2.9. Tishin *et al.* have reported that, in the limit of ΔH tending to zero, ΔT_{ad} shows a peak near T_C for ferromagnets¹⁰. The behavior of ΔT_{ad} and $|\Delta S_M(T)|$ should be similar, i.e., it will be gradually reduced on both sides of T_C . For the same $|\Delta S_M(T)|$ value, the value of ΔT_{ad} will be larger at higher absolute temperature T and lower heat capacity. Paramagnets display significant value of $\Delta T_{ad}(T, \Delta H)$ only at temperature close to absolute zero, where the limited value of $|(\partial M / \partial T)_H|$ is easily compensated by very small value of heat capacity. Furthermore, significant adiabatic temperature change (cooling or heating) is expected only if the solid orders spontaneously (i.e., significant value of $|(\partial M / \partial T)_H|$).

2.2 Relative cooling power (RCP)

Refrigeration capacity or relative cooling power (*RCP*) is a measure of heat transfer between the hot and cold reservoirs in one refrigeration cycle. For promising MCE materials, besides isothermal magnetic entropy change (ΔS_M) and adiabatic temperature change (ΔT_{ad}), a high *RCP* is also needed. This is an important parameter by which one can make a numerical comparison between the MCE of materials. A large *RCP* for magnetocaloric materials at a particular magnetic field implies a superior MCE material.^{1,6} Wood and Potter defined the *RCP* as³⁴

$$RCP = |\Delta S_M| (T_{hot} - T_{cold}) \quad (2.13a)$$

where $|\Delta S_M|$ is the change in the magnetic entropy, at the hot (T_{hot}) and cold (T_{cold}) end of the reservoirs. Therefore, The *RCP* of magnetocaloric materials can be easily calculated by the plots of ΔS_M v/s T . The simple product of maximum entropy

change ΔS_M and the temperature at full width of half maximum δT_{FWHM} of the peak^{6,11-16} i.e.,

$$RCP(S) = \Delta S_M \times \delta T_{FWHM} \quad (2.13b)$$

Some researchers calculate the RCP by the numerical integration of the $\Delta S_M(T)$ under the full width at half maximum temperature limit¹.

$$RCP(S) = \int |\Delta S_M(\max)| dT \quad (2.13c)$$

RCP can also be calculated by the plot of adiabatic temperature change v/s temperature.

$$RCP(T) = -\Delta T(\max) \times \delta T_{FWHM} \quad (2.13d)$$

In this thesis, the RCP was calculated using equation 2.13b.

The following factors should be considered to select a material for near room temperature magnetic cooling:

1. High ΔS_M near room temperature
2. Large working temperature span
3. High relative cooling power
4. Cost effective and easy to find
5. Zero or negligible magnetic and thermal hysteresis
6. Large saturation magnetization
7. High thermal conductivity and low specific heat
8. Easy sample synthesis and good chemical stability

2.3 First and second order magnetic phase transition materials

Materials which exhibit a discontinuity in the first derivative of Gibbs free energy with respect to a thermodynamic variable during phase transition are known as first order magnetic phase transition (FOMT) materials i.e., the transition that involves a discontinuity. The specific heat (C_H) exhibits a divergence at the transition temperature. However, with the application of magnetic field either this divergence is smeared out or the C_H peak is shifted to other temperatures. Therefore, FOMT materials exhibit large spike in magnetic entropy change in a narrow temperature range.

Second-order magnetic phase transitions (SOMT) are the transitions with continuous first derivatives of Gibbs free energy but discontinuous second derivatives. The continuous nature of the phase change results in a finite value for dM/dT and dS/dT , reaching a maximum at the transition temperature. C_H shows a discontinuity at the transition temperature; however, with applied field, the discontinuity can be smeared out. Therefore, materials having a second order phase transition exhibit comparatively less magnetic entropy change with broad temperature span. These materials do not have magnetic and thermal hysteresis. Many iron-based alloys exhibit the second order magnetic transformation. These alloys have been studied in bulk, ribbons and nanoparticle form. The schematic diagram for magnetization behaviour with temperature of FOMT and SOMT materials is shown in fig.2.1.

Fig. 2.1 Schematic diagram for magnetization in terms of temperature and magnetic field for (a) first order magnetic phase transition and (b) second order magnetic phase transition materials

2.4. A survey of magnetocaloric materials

The MCE of rare earth metals and their alloys were intensively investigated because of the various magnetic structures and high magnetization of these materials. The different magnetic structures arise due to oscillations in indirect interactions between 4f localized magnetic moments via conduction electrons. By

alloying with rare earths, one can vary the magnetic transition temperature and the type of magnetic phases. Out of all the rare earth metals, the MCE of gadolinium has been studied in most detail^{2,17}. Gadolinium is treated as the standard of MCE and generally, new materials are compared with it. There are many articles available on magnetocaloric properties of rare earth based materials¹⁷⁻²⁰. Here we will much focus on iron based alloy which have no rare earth content.

2.4.1. R_2Fe_{17} Alloy

R_2Fe_{17} intermetallic compounds, where R is rare earths, have been show moderate magnetocaloric effect (MCE) near room temperature. Gorria et al. discussed the potential for Pr_2Fe_{17} nanostructured material as a room temperature MCM.²¹ They have highlighted the differences in the MCE of arc-melted bulk and mechanically alloyed nanoparticles. The maximum change in entropy was found to be less in mechanically ball milled powder while the working temperature span increased by a factor close to 2, resulting increased RCP compared to the bulk alloy.²¹ The increase in RCP is attributed mainly to the broadening in magnetic entropy in nanoparticles. The exchange interactions in a nanostructured material usually have a distribution of magnetic transitions which results in a broader magnetization change with temperature and therefore large working temperature span. Álvarez et al. have used a high energy ball mill to produce nanocrystalline Nd_2Fe_{17} powders.²² They observed that the nanocrystalline samples exhibit a distribution in T_C , lowering in the maximum value of ΔS_M and high working temperature span. This is because the magnetization versus temperature curve reveals a slower decrease than that of the bulk sample. The MCE difference between bulk and ball milled sample, increasing working temperature span with milling time is illustrated in fig. 2.2.

Fig. 2.2 Temperature dependence of calculated $|\Delta S_M|$ values under the application of magnetic field of 1.5 T for bulk and milled $\text{Nd}_2\text{Fe}_{17}$ samples. δT_{FWHM} is shown by the horizontal lines. The inset shows the magnetic field dependence of δT_{FWHM} for all the samples²²

In another study, the correlation between the broadening of ΔS_M and the T_C distribution in nanostructured $\text{Pr}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}$ powder synthesized by high-energy ball-mill was studied.²³ The local environment of Fe atoms and therefore the magnetic interactions, change with increasing milling time, result in greater T_C distribution in both cases.

$\text{Er}_2\text{Fe}_{17}$ exhibits both direct and inverse MCE with reasonable ΔS_M and adiabatic temperature (ΔT_{ad}) change²⁴. The effect of demagnetizing factor on ΔS_M and RCP in $\text{Er}_2\text{Fe}_{17}$ prepared by arc melting, was investigated²⁵. NdPrFe_{17} ribbons composed of nanocrystals enclosed by an intergranular amorphous phase shows two successive phase transitions, giving rise to working temperature span, with enhanced RCP.²⁶ The RCP values for NdPrFe_{17} ribbons were larger than those of $\text{Pr}_2\text{Fe}_{17}$ bulk crystals.

2.4.2 Fe-B-Cr-R (R = 1 to 15%) Alloy

Law et al. studied the MCE of $\text{Fe}_{80-x}\text{B}_{12}\text{Cr}_8\text{R}_x$ ($\text{R}=\text{La, Ce or Gd}$, $x = 1-15$ at. %) alloys²⁷⁻³⁰. The various R additions to Fe-B-Cr amorphous alloys alter T_C differently. Ce alloying to Fe-B-Cr amorphous alloys tunes the peak temperature of the ΔS_M (T^{pk}) to near RT, making them interesting for RT applications. On the other hand, Gd additions to Fe-B-Cr alloys shift T^{pk} to higher temperatures, making them useful for high temperature applications. The addition of R in Fe-B-Cr amorphous alloys increased the value of RC. The best MCE in this series was observed for a $\text{Fe}_{79}\text{B}_{12}\text{Cr}_8\text{Gd}_1$ alloy, which exhibit ~29% larger MCE than that of $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{Fe}_{0.1}$, with T^{pk} at around 350 K. The RCP of $\text{Fe}_{79}\text{B}_{12}\text{Cr}_8\text{La}_1$ and $\text{Fe}_{75}\text{B}_{12}\text{Cr}_8\text{La}_5$ alloys were ~17-27% larger than that of $\text{Gd}_5\text{Si}_2\text{Se}_2$, while those of $\text{Fe}_{78}\text{B}_{12}\text{Cr}_8\text{Ce}_2$ and $\text{Fe}_{75}\text{B}_{12}\text{Cr}_8\text{Ce}_5$ alloys displayed a ~ 6-20% improvement over $\text{Gd}_5\text{Si}_2\text{Ge}_2$. The temperature dependence of ΔS_M for this series is presented in fig. 2.3

Fig. 2.3 Temperature dependence of ΔS_M under the application of magnetic field 1.1 T for (a) $\text{Fe}_{80-x}\text{B}_{12}\text{Cr}_8\text{La}_x$ (b) $\text{Fe}_{80-x}\text{B}_{12}\text{Cr}_8\text{Ce}_x$ (c) $\text{Fe}_{80-x}\text{B}_{12}\text{Cr}_8\text{Gd}_x$ melt spun ribbons¹.

By addition of 5% Ce to $\text{Fe}_{80}\text{B}_{12}\text{Cr}_8$, T^k could be tuned near room temperature. The good RCP values coupled with soft magnetic behavior and tunable T_C make Fe-B-Cr-R amorphous alloys useful for multi-MCM regenerators near and above room temperature.

The table-like MCE was found in $\text{Fe}_{88-x}\text{Nd}_x\text{Cr}_8\text{B}_4$ ($x=5, 8, 10, 12$, and 15) alloys³¹. By changing the Nd content from 5 at% to 15 at%, the T_C ranged from 322 K to 350 K however ΔS_M remained almost constant, with applied magnetic field of 5 T. All the sample with various Nd contents were prepared by stocking the ribbons layer by layer³¹. The ΔS_M of the composite approached a nearly constant value of $\sim 3.2 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ in a magnetic field change of 0 – 5 T and RCP of $\sim 408 \text{ J}\cdot\text{kg}^{-1}$. The substitution of Ce for Fe in the amorphous ribbons of $\text{Fe}_{78-x}\text{Ce}_x\text{Si}_4\text{Nb}_5\text{B}_{12}\text{Cu}_1$ ($x=0, 1, 3, 5$ and 10) alloy result a large T_C range from 465 to 281 K³². The ΔS_M for a field change of 5 T decreased from 3.25 to $2.18 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for $x=0$ to 10, respectively. Two types of composite materials with varied Ce contents were obtained by assembling the ribbons layer by layer³². The ΔS_M of the composites approach a closely constant value of $\sim 2.0 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for a field change of 5 T in a temperature span $\sim 80 \text{ K}$, resulting in RCP values, $>370 \text{ J}\cdot\text{kg}^{-1}$.

2.4.3 Rare earth free iron based alloy

Various alloys based on transition metals have been investigated for MCE and magnetic cooling. Johnson and Shull³³ reported the MCE in $(\text{Fe}_x\text{Co}_y\text{Cr}_z)_{91}\text{Zr}_7\text{B}_2$ amorphous alloy with $x: y: z = 100:0:0, 90:15:5, 85:5:10$ and $75:15:10$, prepared by melt spinning. The T_C values varying from 200 to 450 K by changing the composition, making this material promising for multistage regenerators. Feng *at al.*, investigated the MCE of amorphous (Fe-Zr-B-M with $M = \text{Mn}, \text{Cr}$ and Co) ribbons. They found an enhanced MCE in $\text{Fe}_{90-x}\text{Zr}_{10}\text{B}_x$ ($x = 5, 10, 15$ and 20) ribbons by adding B.³⁴ The T_C of the specimens can be decreased to about room temperature with appropriate Mn and Cr substitutions. It was also found that the magnetic entropy change of the Co-substitution series of $\text{Fe}_{85-y}\text{Zr}_{10}\text{B}_5\text{Co}_y$ ribbons almost remains constant although the T_C is increased to $\sim$

400 K for $y=5$. Therefore, $\text{Fe}_{85-y}\text{Zr}_{10}\text{B}_5\text{Co}_y$ ribbons are preferred for above room temperature applications due to the constant MCE and the high refrigeration capacity of $\sim 90 \text{ J}\cdot\text{kg}^{-1}$ for a magnetic field change of 1 T. Recently, amorphous Fe-Zr-B-M ($M = \text{Ni}, \text{Co}, \text{Al}, \text{and Ti}$) ribbons have also been studied for MCE.³⁵ Both the ΔS_M and RCP of the base alloy $\text{Fe}_{88}\text{Zr}_8\text{B}_4$ were enhanced by micro-alloying addition. T_C increases by the addition of Co but decreases with the addition of Al and Ti. The alloy containing 1 at. % Co, whose T_C is 295 K and whose ΔS_M reaches $1.48 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for an applied magnetic field of 1.5 T, is suitable for room temperature applications. On the other hand, the alloy containing 1 at. % Ti with T_C of 270 K and RCP of $183.5 \text{ J}\cdot\text{kg}^{-1}$ can be used for below room temperature applications.

The effect of Co addition on the MCE of amorphous alloys with Nanoperm-type composition $\text{Fe}_{83}\text{Zr}_6\text{B}_{10}\text{Cu}_1$ and $\text{Fe}_{78}\text{Co}_5\text{Zr}_6\text{B}_{10}\text{Cu}_1$ have been studied for high temperature applications.³⁶ Co addition produces an increase in the ΔS_M and a shift to higher temperatures. The maximum RCP ($\sim 82 \text{ J}\cdot\text{kg}^{-1}$) was obtained for an applied magnetic field of 1.5 T. This value is 30% larger than that of a Mo-containing Finemet-type alloy measured under the same experimental conditions. The T_C of the as spun material $\text{Fe}_{88-2x}\text{Co}_x\text{Ni}_x\text{Zr}_7\text{B}_4\text{Cu}_1$ ($x = 0 - 22$) was found to increase with Co and Ni content from 346 K at $x = 0$ to 843 K at $x = 22$.³⁷ In this study, the MCE of this alloy was not examined. Ucar et al., have produced nanocrystalline powders of $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mo}_x$ ($x = 1$ to 4) by high energy mechanical alloying.³⁸ The T_C was lowered by Mo additions with a large working temperature span. This additional temperature span was attributed to increased positional disorder introduced by Mo additions into the γ -FeNi system. The $(\text{Fe}_{70}\text{Ni}_{30})_{96}\text{Mo}_4$ alloy was calculated to have RCP of $432 \text{ J}\cdot\text{kg}^{-1}$ at 5 T, comparable to other prominent MCM operating near room temperatures. The MCE with maximum entropy change of $1.8 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ at $\sim 125 \text{ K}$ for field change of 5T was observed in γ - $\text{Fe}_{49}\text{Ni}_{29}\text{Cr}_{22}$ alloy³⁹.

The partial substitution of Fe by Co and Ni in the series of $\text{Fe}_{88-2x}\text{Co}_x\text{Ni}_x\text{Zr}_7\text{B}_4\text{Cu}_1$ alloys results in an increase in T_C from 287 K for $x = 0$ to 626 K for $x=11$.⁴⁰ The maximum ΔS_M , for an applied magnetic field of 1.5 T, shows a value of $1.98 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$

$\text{K}^{-1}\text{kg}^{-1}$ for $x = 8.25$. The MCE in amorphous $\text{Fe}_{89-x}\text{B}_x\text{Zr}_{11}$ ($x = 0 - 10$) alloys prepared by melt spinning have been investigated.⁴¹ The T_C and saturation magnetization of this alloy increases almost linearly with B addition. High temperature thermomagnetic curves indicate an amorphous to crystalline transition above 800 K, corresponding to the precipitation of the α -Fe phase. ΔS_M showed enhancement from $1.3 \text{ J-K}^{-1}\text{kg}^{-1}$ for the $\text{Fe}_{89}\text{Zr}_{11}$ alloy to $1.73 \text{ J-K}^{-1}\text{kg}^{-1}$ for the $\text{Fe}_{79}\text{B}_{10}\text{Zr}_{11}$ alloy, for an applied magnetic field of 1.8 T. The ΔS_M and T_C of the $\text{Fe}_{92-x}\text{Cr}_8\text{B}_x$ amorphous alloys increases with increasing B content from 12 to 15.⁴² A larger ΔS_M was found in quenched $\text{Fe}_{81.6}\text{Mo}_{4.3}\text{Zr}_{3.3}\text{Nb}_{6.8}\text{B}_1\text{Cu}$ ribbons because of structural and stress relaxation during thermal treatment⁴³.

The effect of Zr and B on MCE for $\text{Fe}_{90-x}\text{Zr}_{10}\text{B}_x$ ($x = 3$ to 9) and $\text{Fe}_{93-x}\text{Zr}_7\text{B}_x$ ($x = 0$ to 13) amorphous alloys has been obtained.⁴⁴ The dependence of maximum ΔS_M on Zr+B total content was reported to be associated with average magnetic moment per Fe atom, which was also observed in the $\text{Fe}_{91-x}\text{Mo}_8\text{Cu}_1\text{B}_x$ ($x=15, 17, 20$) amorphous series^{44,45}. Fig. 2.3 shows the maximum ΔS_M as a function of temperature for both alloys under a magnetic field of 0.4 T. The T_C can be tuned from $\sim 225 \text{ K}$ to 350 K and from 250 K to 410 K for $\text{Fe}_{90-x}\text{Zr}_{10}\text{B}_x$ ($x = 3$ to 9) and $\text{Fe}_{93-x}\text{Zr}_7\text{B}_x$ ($x = 0$ to 13) amorphous alloys, respectively. Chromium addition to the $\text{Fe}_{81}\text{Nb}_7\text{B}_{12}$ alloy results in a decrease of the T_C from 363 to 279 K, making this series attractive for near room temperature applications⁴⁶. The ΔS_M of non-crystallized ribbons has been found to be $\sim 0.7 \text{ J kg}^{-1} \text{ K}^{-1}$, at an applied magnetic field of 0.7 T. The nanocrystallization of amorphous samples results in a more diffuse ferro-/paramagnetic transition, which causes a decrease of ΔS_M and increase in working temperature span. The $\text{Fe}_{80.5}\text{Nb}_7\text{B}_{12.5}$ melt-spun ribbons exhibit ΔS_M of $\sim 0.72 \text{ J-kg}^{-1}\text{K}^{-1}$ at T_C of 363 K, at an applied magnetic field of 0.7 T.⁴⁷

Fig 2.4 Magnetic entropy change as a function of temperature under magnetic field of 0.4 T for (a) $\text{Fe}_{90-x}\text{Zr}_{10}\text{B}_x$ ($x = 3$ to 9) and (b) $\text{Fe}_{93-x}\text{Zr}_7\text{B}_x$ ($x = 0$ to 13)⁴⁴

The partial substitution of Fe by Mn in amorphous $\text{Fe}_{80-x}\text{Mn}_x\text{B}_{20}$ ribbons results in a change in T_C of the alloys from 438 K for $x = 10$ to 162 K for $x = 24$.⁴⁸ The maximum ΔS_M passes from $1 \text{ J} \cdot \text{K}^{-1} \text{kg}^{-1}$ for $x = 10$ to $0.5 \text{ J} \cdot \text{K}^{-1} \text{kg}^{-1}$ for $x = 24$; the RCP changes from $117 \text{ J} \cdot \text{kg}^{-1}$ for $x = 10$ to $68 \text{ J} \cdot \text{kg}^{-1}$ for $x = 24$, for ΔH of 1.5 T. A linear relationship between maximum ΔS_M and average magnetic moment per transition metal atom $\langle \mu \rangle_{\text{Fe,Mn}}$ has been obtained.

Torrens-Serra et al. have reported changes in crystallization behaviour and MCE properties with variation of Nb content in $\text{Fe}_{79-x}\text{Nb}_{5+x}\text{B}_{15}\text{Cu}_1$ ($x = 0, 2, 4$) alloys.⁴⁹ The T_C and ΔS_M have been enhanced with reduction of Nb content. These samples exhibit soft magnetic behaviour with very low coercivity. $\text{Fe}_{90}\text{Sc}_{10}$ exhibits both positive and negative ΔS_M due to field-driven metamagnetic transition from spin-glass-like to ferromagnetic state by changing the temperature.⁵⁰ The T_C of $\text{Fe}_{90-x}\text{Mn}_x\text{Zr}_{10}$ amorphous alloys decreased from 210 K to 185 K with increasing Mn concentration, from $x = 8$ to $x = 10$.⁵¹ In addition, both alloys exhibit superparamagnetic behaviour above T_C where the mean magnetic moment of the superparamagnetic spin clusters decreased with increasing temperature. The maximum ΔS_M of $\text{Fe}_{82}\text{Mn}_8\text{Zr}_{10}$ was $2.87 \text{ J/kg} \cdot \text{K}$ at 210 K for an applied magnetic field of 5 T. In another study, the values of maximum ΔS_M of $\text{Fe}_{90-x}\text{Mn}_x\text{Zr}_{10}$ amorphous alloy were found to be 2.96, 2.51 and $2.29 \text{ J} \cdot \text{kg}^{-1} \text{K}^{-1}$ for $x = 0, 4$ and 6, respectively, in the vicinity of the respective Curie temperatures of 243, 228 and 218 K, respectively, for the same applied magnetic field of 5 T.⁵²

Changes in T_C and ΔS_M in $\text{Fe}_{80-x}\text{Mn}_x\text{P}_{10}\text{B}_7\text{C}_3$ metallic glasses have been achieved by changing Mn content in the range from $x = 13$ to 18.⁵³ The average magnetic moment per (Fe+Mn) atom correlates linearly with ΔS_M , which results in decreasing ΔS_M with increasing Mn. The $\text{Fe}_{65}\text{Mn}_{15}\text{P}_{10}\text{B}_7\text{C}_3$ alloy exhibits the maximum refrigeration capacity of $147.09 \text{ J}\cdot\text{kg}^{-1}$ and ΔS_M of $1.12 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for an applied magnetic field of 2 T. This family of low-cost Fe based alloys provides a MCM which can be used for near room-temperature applications.

Amorphous ribbons of two compositions, $\text{Fe}_{91}\text{Zr}_7\text{B}_2$ and $\text{Fe}_{88}\text{Zr}_8\text{B}_4$, with T_C values of 230 and 285 K, respectively, have been studied.⁵⁴ The maximum $\Delta S_M = 3 \text{ J}\cdot\text{K}^{-1}\text{kg}^{-1}$ under an applied magnetic field of 5 T, large working temperature span (δT) of ~ 200 K, resulting in large RCP of $\sim 435 \text{ J kg}^{-1}$. The T_C can be easily tuned from 200 to 350 K by varying the boron content. The RCP of FeCrMoCuGaPCB alloys is more than those of other bulk amorphous alloys with similar T_C .⁵⁵

The temperature and field dependence of the MCE in a bulk amorphous $\text{Pd}_{40}\text{Ni}_{22.5}\text{Fe}_{17.5}\text{P}_{20}$ alloy exhibits a minimum value at the superparamagnetic-to-ferromagnetic transition and a maximum at the ferromagnetic-to-spin-glass transition.⁵⁶ At 80 K, and for $H = 5$ T, the ΔS_M is -0.029 k_B per Fe atom in the alloy. The MCE of melt-spun $\text{Fe}_{64}\text{Mn}_{15-x}\text{Co}_x\text{Si}_{10}\text{B}_{11}$ ($x = 0, 0.2, 0.5, 0.7$, and 1.0) amorphous alloys has been evaluated close to room temperature.⁵⁷ The maximum ΔS_M for $\text{Fe}_{64}\text{Mn}_{15}\text{Si}_{10}\text{B}_{11}$ at 309 K at $H = 1.5$ T was limited to $0.82 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$. The maximum ΔS_M for amorphous $\text{Fe}_{91-x}\text{Y}_x\text{Zr}_9$ alloys was found to be 1.22, 0.89 and $1.12 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for $x = 0, 5$ and 10, respectively, corresponding T_C was 223, 284 and 470 K, respectively.⁵⁸

Boutahar et al. studied the effect of vanadium on magnetocaloric properties of morphous $\text{Fe}_{80-x}\text{V}_x\text{B}_{12}\text{Si}_8$ ribbons fabricated by melt spinning technique. The addition of V to the $\text{Fe}_{80}\text{B}_{12}\text{Si}_8$ alloy results in a decrease of the T_C from 473.5 K to 335 K. With an increasing of V content, the maximum value of ΔS_M decrease. $\text{Fe}_{66.3}\text{V}_{13.7}\text{B}_{12}\text{Si}_8$ alloy exhibits the maximum RCP of $93.7 \text{ J}\cdot\text{kg}^{-1}$ and moderate ΔS_M of $1.034 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for $\Delta H = 2 \text{ T}$.⁵⁹

Figure 2.5 shows comparison of RCP at an applied magnetic field of 1.5 T and T_C for iron based MCM.

Fig. 2.5. Relative cooling power (below red line) with applied magnetic field of 1.5 T and Curie temperature (upper blue line) for iron based magnetocaloric materials^{27,29,30,36,40,42,45,48,55,60,61}

For some materials, RCP was estimated from the figure in the references and for others using the power law $RCP \propto H^N$ where $N = 1.15$ for transition metal based alloys^{30,40}

2.4.4 Manganites

Perovskite manganites also exhibit MCE for near room temperature applications. One can express them by the general formula $R_{1-x}M_xMnO_3$ with $R = La, Pr$ or Nd and $M = Ca, Ba$ or Sr . Manganites are SOMT materials and therefore exhibit lower MCE than those of FOMT materials. They are interesting because

their T_C can be tuned over a range of temperature by changing the value of x in $R_{1-x}M_x\text{MnO}_3$. Among these manganites, $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ compounds have been studied extensively⁶². The host compound, LaMnO_3 , where Mn ions with +3 valence, is an antiferromagnetic insulator, characterized by super exchange coupling between Mn^{3+} sites⁶³. The introduction of a divalent or monovalent ion instead of La into perovskite results in mixed valence states of Mn^{3+} and Mn^{4+} . The mixed valence state exhibits a major role in the double exchange mechanism, which is responsible for the metallic character and ferromagnetic (FM) properties in these oxides⁶⁴.

The T_C of the manganites $\text{La}_{0.67}\text{Ca}_{0.33-x}\text{Sr}_x\text{MnO}$ can be tuned from 267 to 369 K by changing the x value from 0 to 0.33⁶⁵. The ΔS_M values for this compound also depend on x and decreases from $5.9 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ ($x = 0$, $T_C = 267 \text{ K}$) to $2.8 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ ($x = 0.055$, $T_C = 285$). Cetin et al. studied the MCE of $(\text{La}_{1-x}\text{Sm}_x)_{0.67}\text{Pb}_{0.33}\text{MnO}_3$ polycrystalline materials with $x = 0, 0.1, 0.2, 0.3$.⁶³ T_C decreases with increasing Sm-content from 358 K for $x = 0$ to 286 K for $x = 0.3$, which is useful for room temperature magnetic cooling. The ΔS_M values were determined as 3.32, 3.33, 3.29 and $2.60 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for $x = 0, 0.1, 0.2$ and 0.3 , respectively, for applied magnetic field change ΔH of 2 T. Thanh et al. reported MCE of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Ba}_x\text{MnO}_3$ nanoparticles for $x = 0.025$ and 0.05 , synthesized by solid-state reaction and mechanical ball milling methods⁶⁶. The T_C values were about the same (256 K for $x = 0.025$ and 258 K for $x = 0.05$) for both the samples. From critical analysis they found that these samples exhibit second-order magnetic phase transition. The maximum ΔS_M value was $\sim 4.4 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ corresponding to RCP value $\sim 140 \text{ J}\cdot\text{kg}^{-1}$, under a magnetic field of 3 T.

Bettaibi et al. studied the effect of Cr concentration on the MCE of praseodymium-calcium manganite. The Cr substitution defeats the charge ordering state and the ferromagnetic coupling is weakened, and therefore the magnitude of the maximum ΔS_M reduced in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ series⁶⁷. Recently, a series of manganites with non-stoichiometric composition of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1+\delta}\text{O}_3$ ($\delta=0, \pm 0.05$ and ± 0.1) has been reported⁶⁸. The $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1+\delta}\text{O}_3$ with $\delta=-0.05, 0, 0.05$ and 0.1 undergo T_C at 220, 240, 248 and 222 K, respectively. The magnetization measurement at lower temperature indicates that the saturation magnetization is

lowered in the non-stoichiometric manganites. The maximum values of ΔS_M were found to be 2.10, 2.94 and 2.90 J·kg⁻¹·K⁻¹ for $\delta = -0.05$, 0 and 0.05, respectively, for $\Delta H = 5$ T.

2.4.5 Other recent work on MCE

In this section, we have reviewed very recent work in which peoples have used different concepts to improve the MCE. The multiferroic hexagonal single crystal DyMnO₃ exhibits a giant anisotropic and reversible MCE at T_C of 8 K. The RCP of the hexagonal DyMnO₃ was comparable with other promising magnetocaloric materials with similar T_C . The value of the volumetric ΔS_M of composite La(Fe,Mn,Si)₁₃H_x (~ 63 mJ cm⁻³ K⁻¹) was found to be comparable with bulk La(Fe,Co,Si)₁₃ (~ 70 mJ cm⁻³ K⁻¹) and larger than that of Gd (~ 40 mJ cm⁻³ K⁻¹)⁶⁹. The thermal conductivity of the polymer-bonded La(Fe,Mn,Si)₁₃H_x was about 5 W K⁻¹ m⁻¹, less than those of bulk La(Fe,Co,Si)₁₃ and Gd metal⁶⁹. The effect of the short milling times on MCE of R₅(Si,Ge)₄ (with R = Gd, Tb) was investigated⁷⁰. With short milling times (< 2.5 h), a reduction of the particle size of Gd₅Si_{1.3}Ge_{2.7} and Tb₅Si₂Ge₂ was achieved ~ 3.5 μ m. In the Gd₅Si_{1.3}Ge_{2.7} case, a decrease in the MCE of 35% after 150 min of milling was obtained. On the other hand, an opposite effect was observed in Tb₅Si₂Ge₂ where a 23% increase of the MCE was achieved. This finding may be related to the enhancement of the coupling between magnetic and structural transitions arising from internal strain in the milling process⁷⁰. The Ni₄₃Mn₄₆Sn₈In₃ alloy exhibits structural and magnetic phase transitions at T_C of the martensitic phase ($T_C^M = 166$ K), at the martensitic to austenitic transformation ($T_{M-A} = 260$ K) and at T_C of the austenitic phase ($T_C^A = 296$ K)⁷¹. The good value of RCP around T_{M-A} and T_C^A were found to be $RC_{M-A} = 172.6$ and $RC_A = 155.9$ J kg⁻¹, respectively, under magnetic field of 3 T.

The MCE in double perovskite Gd₂NiMnO₆ and Gd₂CoMnO₆ samples has been observed by magnetic and heat capacity measurements⁷². The T_C was at ~ 130 K and ~ 112 K in Gd₂NiMnO₆ and Gd₂CoMnO₆, respectively, while the Gd exchange interactions lead for $T < 20$ K. A maximum ΔS_M was found to be ~ 35.5 J Kg⁻¹ K⁻¹

and $\sim 24 \text{ J Kg}^{-1} \text{ K}^{-1}$ in $\text{Gd}_2\text{NiMnO}_6$ and $\text{Gd}_2\text{CoMnO}_6$, respectively, for a field change of 7 T. CsCl-type HoZn exhibits two magnetic transitions; (a) paramagnetic to ferromagnetic at $T_C \sim 72 \text{ K}$ and (b) a spin reorientation at $T_{SR} \sim 26 \text{ K}$ ⁷³. Two sequential magnetic transitions in HoZn induce one broad obvious peak together with a shoulder in the T vs $-\Delta S_M$ curves, yielding in a large RCP value of 1124 J-kg^{-1} for $\Delta H = 7 \text{ T}$. Dudek et al. proposed a mechanically driven MCE in magneto-auxetic systems near to room temperature⁷⁴. These systems represent a novel class of metamaterials having magnetic insertions embedded within a non-magnetic matrix. The auxetic behaviour of the non-magnetic matrix may be helpful to enhance the magnetic ordering or it may result in a transition to the disordered phase. They have shown the possibility to improve the MCE by changing the geometry of current MCE materials in such way that they exhibit auxetic behaviour.

A lot of research has been done and still continuing on MCE of manganites, which was systematically reviewed by Phan et al⁶². These materials are potential candidates for near room temperature magnetic cooling applications. The RCP or working temperature span of a magnetic cooling system can be increased by a suitable combination of R and M in $\text{R}_{1-x}\text{M}_x\text{MnO}_3$.

As discussed above many MCM have been developed by expecting that the higher density of magnetocaloric materials will result a compact design of cooling devices. However, the slow heat transfer in the bulk is a constraining factor in a magnetic cooling devices. Therefore, a suspension of magnetic particles in suitable fluid for magnetic cooling has been proposed in several studies as an alternative of bulk MCM^{75,76}. Nanoparticles with increased surface area suspended in a suitable fluid has better heat transfer compared to bulk devices. Therefore, most of the work done in this thesis is focused on nanoparticles, which would assist their suspension in a carrier fluid. The magnetic behaviour of any material varies with particle size, morphology, crystal structure and the interaction of the particle with adjacent particles. Nanostructures can have higher MCE over a broad temperature distribution, exhibiting more cooling efficiency compared to bulk materials. The magnitude of entropy change varies for different materials based on the number of particles per unit volume, magnetic moment of the particles, and the order

parameter. The MCE peak can be shifted to other temperatures or broadened by changing the particle size. The main limitation of ferrofluid cooling technology is the dispersion of magnetic nanoparticles in the fluid and their stability under magnetic field for long time⁷⁷. This problem can be resolved by suitable surface chemistry on the nanoparticles, which can result in helpful for long term dispersion even under magnetic field.

2.5 Critical Exponent Analysis

Besides the urgent need for low cost MCE materials, analysis of the critical behavior of such materials is of high interest, since it is directly related to the MCE.⁷⁸ The critical exponents α , β , γ and δ correspond to specific heat, spontaneous magnetization, magnetic susceptibility and critical isotherm, respectively. These exponents are directly related to the MCE of the materials. For example, with the help of the Arrott-Noakes equation of state, the magnetic entropy change at $T = T_C$ can be expressed by the following relations⁷⁹

$$\Delta S_M = \frac{-a\beta\gamma}{b^{\frac{\beta+\gamma}{\beta+\gamma}} (2\beta+\gamma-1)} H^{\frac{\beta-1}{\beta+\gamma}+1} = AH^n \quad (2.14)$$

where $n = 1 + [(\beta-1)/(\beta+\gamma)]$, a and b are constants and A is a function of the critical exponents. The field dependence of RCP can be expressed as a power law of $RCP \propto H^N$, where $N = 1 + 1/\delta$. Hence the determination of critical exponents (α , β , γ and δ) is useful to evaluate the MCE performance of materials even at high field, which may not be available in many laboratories as well as to compare MCE results obtained by various investigators using different maximum fields. In addition, the critical behavior study is a powerful approach to understand the mechanism of the magnetic phase transition and the nature of ordering around T_C . In the critical region, a simple equation of state $(M)^{1/\beta} = A(T - T_C)/T_C + B(H/M)^{1/\gamma}$ has been proposed by Arrott and Noakes, where A and B are constants. Arrott and Noakes determined the critical exponents of pure Ni as $1/\gamma = 0.75$ and $1/\beta = 2.5$ from the magnetization curves at fields up to 18 kOe near T_C . $(H/M)^{0.75}$ vs $M^{2.5}$ plots for fixed temperature

lie on straight lines which are parallel to each other¹¹⁰. These plots are referred to as the Arrott-Noakes plots. This fact suggests that this material is magnetically homogeneous, i.e., the spin correlation length is large enough in comparison of structural inhomogeneity.

According to Banerjee's criterion, the order of the magnetic phase transition can be determined from the slope of the magnetic isotherms. A negative (positive) slope of the Arrott plot M^2 versus H/M , suggests that the magnetic phase transition is first (second) order⁸⁰. Theoretical models; 3D-Heisenberg ($\beta = 0.365$, $\gamma = 1.336$ and $\delta = 4.66$), 3D-Ising ($\beta = 0.325$, $\gamma = 1.24$ and $\delta = 4.81$) and tricritical model ($\beta = 0.25$, $\gamma = 1.0$ and $\delta = 5.0$) are useful to explain the magnetic behaviour at ordering temperature. The scaling hypothesis is used to calculate the critical exponents β , γ and δ near T_C . The critical exponents (β , γ) and T_C can be accurately determined from the Kouvel-Fisher (KF) method⁸¹, equations (2.15) and (2.16).

$$\frac{Ms(T)}{dMs(T)/dT} = \frac{T - T_C}{\beta} \quad (2.15)$$

$$\frac{\chi_0^{-1}(T)}{d\chi_0^{-1}(T)/dT} = \frac{T - T_C}{\gamma} \quad (2.16)$$

According to this method $M_s (dM_s/dT)^{-1}$ versus T and $\chi_0^{-1} (d\chi_0^{-1}/dT)^{-1}$ versus T should show straight lines with slope $1/\beta$ and $1/\gamma$, respectively. The value of T_C can be determined by extrapolation of these straight lines to the ordinate equal to zero on the T axis. Widom's scaling relation⁸² $\delta = 1 + (\gamma/\beta)$ is useful to determine the third exponent δ . The critical behavior near T_C can also be verified by the universal scaling hypothesis. In the critical region, the magnetic equation of state⁸³ can be written as

$$m = f_{\pm}(h) \quad (2.17)$$

where m is the scaled magnetization, $m = |\varepsilon|^{-\beta} M(H, \varepsilon)$, h is the scaled field $h = |\varepsilon|^{-\beta\delta} H$ and ε is the reduced temperature $(T - T_C)/T_C$. The m as a function of

h yields two universal curves: $f_+(h)$ for $T > T_C$ and $f_-(h)$ for $T < T_C$. We have summarized the critical exponents for relevant materials in the table 2.1.

Table 2.1 Critical exponents of relevant materials

Material/Model (Method)	α	B	γ	δ	Ref.
3D-Heisenberg	0.115	0.365	1.336	4.8	83
Mean-field theory	0.0	0.5	1.0	3.0	83
3D-Ising	0.11	0.325	1.241	4.82	83
Tricritical mean field	0.5	0.25	1	5	84
Fe ₉₀ Zr ₁₀ (KF)	-	0.368	1.612	5.32	85
Fe ₈₅ Ni ₅ Zr ₁₀ (KF)	-	0.425	1.323	4.11	85
Fe ₇₇ Co _{5.5} Ni _{5.5} Zr ₇ B ₄ Cu (KF)	-	0.53	1.34	3.5	78
Fe _{89.5} Zr _{10.5} (KF)	0.93	0.47	2.0	5.31	86
Fe ₉₁ Zr ₇ B ₂	-	0.325	1.38	-	87
Fe ₈₈ Zr ₈ B ₄		0.39	1.38		87
Fe ₈₇ Zr ₆ B ₆ Cu		0.40	1.38		87
Fe ₈₆ Mn ₄ Zr ₁₀		0.369	1.368		88
Fe ₈₄ Mn ₆ Zr ₁₀		0.341	1.358		88
Fe ₈₂ Mn ₈ Zr ₁₀		0.365	1.387		88
Fe ₈₀ Mn ₁₀ Zr ₁₀		0.368	1.384		88
Fe ₇₈ Mn ₁₂ Zr ₁₀		0.359	1.378		88
Fe ₈₀ P ₁₃ C ₁₀		0.38±0.02	1.30±0.05	4.47±0.05	89
Fe _{75.5} Cr ₄ B ₁₃ Si _{7.5}		0.366	1.286		90
Fe ₂₀ Ni ₆₀ P ₁₄ B ₆		0.39	1.33	4.45	91
Fe ₄₀ Ni ₄₀ P ₁₄ B ₆		0.38	1.31	4.46	92
Fe ₈₈ Zr ₈ B ₄ (MAP)	-	0.39	1.38	-	87
Er ₂ Fe ₁₇ (MAP)	0.59	0.42	1.74	5.1	22
Fe	0.11	0.389	1.333	4.35	83
Ni	-0.10	0.378	1.34	4.58	93
Co	-0.095	0.435	1.225	3.35	83
Gd	0.04	0.381	1.196	3.615	83
Pr _{0.75} Ca _{0.25} MnO ₃ (MAP)	-	0.351±003	1.372±.002	4.9±.002	94
Pr _{0.71} Ca _{0.29} MnO ₃ (MAP)	-	0.521±002	0.912±005	2.71±002	94
Gd ₆₀ Co ₁₅ Al ₂₅ (MAP)	-	0.432	1.244	3.51	95
AMn _{0.825} Ga _{0.175} O ₃ (KF)		0.365	1.218	4.22	96
Co ₅₀ Cr ₂₅ Al ₂₅ (KF)		0.482	1.148	3.382	97

*A = La_{0.75}Ca_{0.08}Sr_{0.17}

2.6 Magnetothermal fluid

Resler and Rosenweig were the pioneers of magnetothermal energy conversion using magnetic fluids⁹⁸. In 1985, Rosenweig wrote a book on Ferrohydrodynamics in which he described magnetothermal energy conversion using magnetic fluids⁷⁶. Only a couple of studies can be found in the literature from 1990 to 2005, however, later, number of publications have been published on magnetothermal fluid⁹⁹⁻¹⁰⁴. So far, these magnetothermal fluids have not been used commercially for magnetic cooling or heat pumping. Therefore, magnetothermal fluid is a promising field of research, which can be applicable in many applications. The use of magnetothermal fluid can be based on self-pumping.

2.6.1 Magnetothermal fluid self-pumping

Rosenweig described the principle of self-pumping using ferrohydrodynamic equations⁷⁶. Fig 2.6 shows the schematic diagram of magnetothermal self-pumping, having a tube filled by ferrofluid, constant magnetic field and 4 regions represented by 1, 2, 3 and 4. The Bernoulli equation for fluid flow inside the magnetic field is:

$$\frac{dp}{ds} + \rho v \frac{dv}{ds} + \rho g \frac{dh}{ds} - \mu_0 M \frac{dH}{ds} = 0 \quad (2.18)$$

Where v is the fluid velocity along distance s and h is the height with a reference to ground level. The variable p refers to pressure. The integration of Eq. 2.18 from section denoted by 1 to a section denoted by 2 can be represented by

$$\int_1^2 \frac{dp}{\rho} + \frac{v_2^2 - v_1^2}{2} + g(h_2 - h_1) - \mu_0 \int_1^2 \frac{M}{\rho} dH = 0 \quad (2.19)$$

Let us consider that the ferrofluid is an incompressible fluid with a constant density. The Eq 2.19 can be written as¹⁰⁵:

$$p_1 + \rho \frac{v_1^2}{2} + \rho g h_1 - \mu_0 \int_0^{H_2} M dH = p_2 + \rho \frac{v_2^2}{2} + \rho g h_2 - \mu_0 \int_0^{H_2} M dH \quad (2.20)$$

Fig 2.6 Schematic diagram of magnetothermal self-pumping

In fig. 2.6, a tube filled with ferrofluid has two sections represented by cold and hot regions. A constant magnetic field was applied in the middle of the tube. The magnetization of ferrofluid is higher in the cold region, the ferrofluid will be attracted by the magnetic field. When the ferrofluid reached to the hot region, it gets hot and loses its magnetization. If we apply the Bernoulli equation, (Eq.2.20), neglecting gravitational potential energy and letting kinetic energy be constant, the following expressions for region 1 and 2 can be obtained ^{76,105}:

$$p_1 = p_2 - \mu_0(\bar{M}H)_2 \quad (2.21)$$

where

$$\bar{M} = \frac{1}{H} \int_0^H M dH \quad (2.21)$$

Similarly, application of the ferrohydrodynamic Bernoulli equation between regions 3 and 4, i.e., the pressure difference between region 3 and 4 yields

$$p_4 = p_3 - \mu_0(\bar{M}H)_3 \quad (2.22)$$

The ferrohydrodynamic Bernoulli equation is not applicable to the part of the tube where magnetic field is applied, since the assumption of an isothermal flow field is not satisfied. By neglecting acceleration, gravity and friction, Rosenweig showed the following governing equation holds inside the magnetic field⁷⁶.

$$0 = -\nabla p^* + \mu_0 \nabla H \quad (2.23)$$

where p^* is the composite pressure. The change in the pressure between region 4 and 1 can now be defined as:

$$\Delta p = p_4 - p_1 = \mu_0 H [\bar{M}(T_1) - \bar{M}(T_1)] = \mu_0 H \Delta \bar{M} \quad (2.24)$$

Actually, this pressure difference (Δp) can be considered as the basis for the self-pumping of magnetocaloric fluid. Self-pumping of magnetothermal fluid may be used for thermal management of electronic systems and in heat driving pumps.

Love et al. suggested a magnetocaloric pumping by having only thermal and magnetic fields using the principle proposed by Rosenweig^{99,106}. A uniform magnetic field with a temperature gradient yields a force on the magnetic fluid. They provided a long description of the process and its limitations, and developed a finite-element model and conducted a series of experiments.

Ganguly et al. simulated thermomagnetic convection and explained the origin of this kind of convection¹⁰⁷. A parametric study was showed to relate heat transfer, temperature difference, cavity dimension, magnetic field strength and fluid viscosity. Thermomagnetic convection is the result of both magnetic field and temperature gradients; warmer fluid moves away from the field while colder fluid moves toward the magnetic field.

In 2005, Mukhopadhyay et al. used scaling analysis to characterize thermomagnetic heat transfer in a two-dimensional enclosure filled with a ferrofluid¹⁰⁸. Their results matched excellently with numerical simulation.

In 2008, Li et al. established a miniature automatic cooling device without any moving mechanical part. It was demonstrated that no additional energy required to run the device.

In 2009, Lian et al. developed an automatic energy transport device using a temperature sensitive magnetocaloric ferrofluid as a coolant^{102,103}. The magnetic field gradient and fluid temperature variation results in fluid motion in a loop. They stated that the changing magnetic field and temperature variation of the magnetic fluid can control energy transport in such devices.

In 2011, Xuan and Lian presents a practical design of thermomagnetic convection in electronic cooling¹⁰⁴. A permanent magnet and the waste heat generated from a hot source (e.g. a chip) were used to maintain the flow of a

ferrofluid. This cooling device do not use any additional energy as the waste heat is used to drive the ferrofluid, it is a completely self-powered device. As the heat load increases (i.e. initial temperature of chip increased), higher heat dissipation rate can be achieved due to more thermomagnetic convection. Therefore, devices based on thermomagnetic convection can be treated as self-regulating devices. For actual electronic cooling applications, magnetic shielding with extremely small magnetic field leakage is required.

In 2011, Pal et al. invented a thermomagnetic pump without any external pressure gradient¹⁰⁹. The increased temperature of the ferrofluid from the heat load and magnetic field gradients results in driving forces to move the ferrofluid. Such kind of self-pumping can have many applications in cooling, especially microelectronic devices. The performance of the thermomagnetic pump was also experimentally studied to characterize pump pressure head and discharge under different working conditions.

In 2015, Rahman and Suslov explained the linear stability of magneto-convection of a ferrofluid contained between two heated plates under uniform applied magnetic field¹¹⁰. They also explained that the thermomagnetic convection arises due to the variation in magnetisation with temperature.

Based on the literature, the advantages of thermomagnetic convection include (a) no moving mechanical part (b) no external energy required to run the devices (c) there is no need for dynamic seals (d) the service temperature can be tuned by choosing ferrofluid having suitable T_C (e) potential applications can be range from cooling of small electronic devices to cooling of large space crafts.

References

- ¹ J. Y. Law, Thesis, Nanyang Technological University Singapore, 2012.
- ² A. M. Tishin, Spichkin, Y. I. , *The Magnetocaloric Effect and its Applications* (Bristol: Institute of Physics Publishing, 2003).
- ³ R. A. Swalin, *Thermodynamics of Solids* (New York: Wiley, 1962).

- ⁴ R. K. Pathria, B. D. Beale, *Statistical Mechanics* (Butterworth Heinemann publications, 2011).
- ⁵ B. F. Yu, Q. Gao, B. Zhang, X. Z. Meng, and Z. Chen, *International Journal of Refrigeration* **26**, 622 (2003).
- ⁶ M. H. Phan, H.-X. Peng, S.-C. Yu, N. Duc Tho, and N. Chau, *Journal of Magnetism and Magnetic Materials* **285**, 199 (2005).
- ⁷ B. Ekkes, *Journal of Physics D: Applied Physics* **38**, R381 (2005).
- ⁸ M. Halder, S. M. Yusuf, M. D. Mukadam, and K. Shashikala, *Physical Review B* **81**, 174402 (2010).
- ⁹ K. A. Gschneidner Jr, V. K. Pecharsky, and A. O. Tsokol, *Reports on Progress in Physics* **68**, 1479 (2005).
- ¹⁰ A. M. Tishin, K. A. Gschneidner, and V. K. Pecharsky, *Physical Review B* **59**, 503 (1999).
- ¹¹ V. Chaudhary, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, *IEEE Magnetics Letters* **5**, 6800104 (2014).
- ¹² V. Chaudhary, X. Chen, D. V. M. Repaka, A. Chaturvedi, Z. Wang, and R. V. Ramanujan, 6th IIF-IIR International Conference on Magnetic Refrigeration THERMAG VI, Victoria, BC, 7-10 Sept 2014 (2014).
- ¹³ V. Chaudhary, D. V. Maheswar Repaka, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, *Journal of Applied Physics* **116**, 163918 (2014).
- ¹⁴ V. Chaudhary and R. V. Ramanujan, *MRS Online Proceedings Library* **1708**, vv10 (2014).
- ¹⁵ V. Chaudhary and R. V. Ramanujan, *Journal of Physics D: Applied Physics* **48**, 305003 (2015).
- ¹⁶ V. Chaudhary and R. V. Ramanujan, *Magnetics Letters, IEEE* **6**, 6700104(4) (2015).
- ¹⁷ V. Franco, J. S. Blázquez, B. Ingale, and A. Conde, *Annual Review of Materials Research* **42**, 305 (2012).
- ¹⁸ P. Durga, V. K. Pecharsky, and J. K. A. Gschneidner, *Journal of Physics: Condensed Matter* **20**, 235235 (2008).

- ¹⁹ K. A. Gschneidner and V. K. Pecharsky, *Annual Review of Materials Science* **30**, 387 (2000).
- ²⁰ V. K. Pecharsky and J. K. A. Gschneidner, *Physical Review Letters* **78**, 4494 (1997).
- ²¹ G. Pedro, L. S. L. José, Á. Pablo, P. María José, M. Jorge Sánchez, and A. B. Jesús, *Journal of Physics D: Applied Physics* **41**, 192003 (2008).
- ²² Á. Pablo, G. Pedro, F. Victorino, M. J. Sánchez, J. P. María, L. S. L. José, O. I. Puente, and A. B. Jesús, *Journal of Physics: Condensed Matter* **22**, 216005 (2010).
- ²³ P. Alvarez-Alonso, J. L. S. Llamazares, C. F. Sánchez-Valdés, G. J. Cuello, V. Franco, P. Gorria, and J. A. Blanco, *Journal of Applied Physics* **115**, 17A929 (2014).
- ²⁴ P. Alonso, P. Gorria, J. A. Blanco, J. S. Marcos, G. J. Cuello, I. P. Orench, J. A. R. Velamazán, G. Garbarino, I. Pedro, J. R. Fernández, and J. L. S. Llamazares, *Physical Review B* **86**, 184411 (2012).
- ²⁵ Á. A. Pablo, G. Pedro, M. J. Sánchez, L. S. L. José, and A. B. Jesús, *Journal of Physics: Condensed Matter* **25**, 496010 (2013).
- ²⁶ C. F. S. Valdés, P. J. I. Gaytán, J. L. S. Llamazares, M. Á. Borja, P. Á. Alonso, P. Gorria, and J. A. Blanco, *Applied Physics Letters* **104**, 212401 (2014).
- ²⁷ J. Y. Law, V. Franco, and R. V. Ramanujan, *Applied Physics Letters* **98**, 192503 (2011).
- ²⁸ J. Y. Law, V. Franco, and R. V. Ramanujan, *Journal of Applied Physics* **111**, 3919 (2012).
- ²⁹ J. Y. Law, V. Franco, and R. V. Ramanujan, *Journal of Applied Physics* **110**, 023907 (2011).
- ³⁰ J. Y. Law, R. V. Ramanujan, and V. Franco, *Journal of Alloys and Compounds* **508**, 14 (2010).
- ³¹ J. W. Lai, Z. G. Zheng, X. C. Zhong, V. Franco, R. Montemayor, Z. W. Liu, and D. C. Zeng, *Journal of Magnetism and Magnetic Materials* **390**, 87 (2015).
- ³² H. C. Tian, X. C. Zhong, Z. W. Liu, Z. G. Zheng, and J. X. Min, *Materials Letters* **138**, 64 (2015).

- ³³ F. Johnson and R. D. Shull, *Journal of Applied Physics* **99**, 08K909 (2006).
- ³⁴ Y. K. Fang, C. C. Yeh, C. C. Hsieh, C. W. Chang, H. W. Chang, W. C. Chang, X. M. Li, and W. Li., *Journal of Applied Physics* **105**, 07A910 (2009).
- ³⁵ X. Li and Y. Pan, *Journal of Applied Physics* **116**, 093910 (2014).
- ³⁶ V. Franco, J. S. Blázquez, and A. Conde, *Journal of Applied Physics* **100**, 064307 (2006).
- ³⁷ K. E. Knipling, M. Daniil, and M. A. Willard, *Journal of Applied Physics* **117**, 172611 (2015).
- ³⁸ H. Ucar, M. Craven, D. E. Laughlin, and M. E. McHenry, *Journal of Electronic Materials* **43**, 137 (2014).
- ³⁹ S. Mandal, J. Panda, and T. K. Nath, *Journal of Alloys and Compounds* **653**, 453 (2015).
- ⁴⁰ R. C. Flores, V. Franco, A. Conde, K. E. Knipling, and M. A. Willard, *Applied Physics Letters* **96**, 182506 (2010).
- ⁴¹ D. Mishra, M. Gurram, A. Reddy, A. Perumal, P. Saravanan, and A. Srinivasan, *Materials Science and Engineering: B* **175**, 253 (2010).
- ⁴² V. Franco, A. Conde, and L. F. Kiss, *Journal of Applied Physics* **104**, 033903 (2008).
- ⁴³ D. Wang, K. Peng, B. Gu, Z. Han, S. Tang, W. Qin, and Y. Du, *Journal of Alloys and Compounds* **358**, 312 (2003).
- ⁴⁴ Y. Wang and X. Bi, *Applied Physics Letters* **95**, 262501 (2009).
- ⁴⁵ V. Franco, C. F. Conde, J. S. Blázquez, A. Conde, P. Švec, D. Janičkovič, and L. F. Kiss, *Journal of Applied Physics* **101**, 093903 (2007).
- ⁴⁶ I. Škorvánek, J. Kováč, J. Marcin, P. Švec, and D. Janičkovič, *Materials Science and Engineering: A* **449–451**, 460 (2007).
- ⁴⁷ I. Škorvánek and J. Kováč, *Czechoslovak Journal of Physics* **54**, 189 (2004).
- ⁴⁸ R. Caballero-Flores, V. Franco, A. Conde, and L. F. Kiss, *Journal of Applied Physics* **108**, 073921 (2010).
- ⁴⁹ J. T. Serra, P. Bruna, S. Roth, J. Rodriguez-Viejo, and M. T. Clavaguera-Mora, *Journal of Physics D: Applied Physics* **42**, 095010 (2009).
- ⁵⁰ Y. Wang and X. Bi, *Applied Physics Letters* **97**, 022503 (2010).

- ⁵¹ S. G. Min, K. S. Kim, S. C. Yu, H. S. Suh, and S. W. Lee, *Journal of Applied Physics* **97**, 10M310 (2005).
- ⁵² S. G. Min, K. S. Kim, S. C. Yu, Y. C. Kim, K. Y. Kim, K. W. Lee, J. R. Rhee, S. Y. Cha, and Y. S. Kim, *Journal of Magnetism and Magnetic Materials* **310**, 2820 (2007).
- ⁵³ H. Zhang, R. Li, T. Xu, F. Liu, and T. Zhang, *Journal of Magnetism and Magnetic Materials* **347**, 131 (2013).
- ⁵⁴ P. Álvarez, P. Gorria, J. S. Marcos, L. F. Barquín, and J. A. Blanco, *Intermetallics* **18**, 2464 (2010).
- ⁵⁵ V. Franco, J. M. Borrego, C. F. Conde, A. Conde, M. Stoica, and S. Roth, *Journal of Applied Physics* **100**, 083903 (2006).
- ⁵⁶ T. D. Shen, R. B. Schwarz, J. Y. Coulter, and J. D. Thompson, *Journal of Applied Physics* **91**, 5240 (2002).
- ⁵⁷ J. H. Lee, S. J. Lee, W. B. Han, H. H. An, and C. S. Yoon, *Journal of Alloys and Compounds* **509**, 7764 (2011).
- ⁵⁸ K. S. Kim, S. G. Min, S. C. Yu, S. K. Oh, Y. C. Kim, and K. Y. Kim, *Journal of Magnetism and Magnetic Materials* **304**, 642 (2006).
- ⁵⁹ A. Boutahar, A. Ettayfi, G. Alouhmy, H. Lassri, E. K. Hlil, and D. Fruchart, *Journal of Superconductivity and Novel Magnetism* **27**, 2401 (2014).
- ⁶⁰ V. Franco, J. M. Borrego, A. Conde, and S. Roth, *Applied Physics Letters* **88**, 132509 (2006).
- ⁶¹ V. Franco, C. Conde, A. Conde, and L. Kiss, *Applied physics letters* **90**, 052509 (2007).
- ⁶² M.H. Phan and S.-C. Yu, *Journal of Magnetism and Magnetic Materials* **308**, 325 (2007).
- ⁶³ S. K. Çetin, M. Acet, M. Güneş, A. Ekicibil, and M. Farle, *Journal of Alloys and Compounds*.
- ⁶⁴ C. Zener, *Physical Review* **82**, 403 (1951).
- ⁶⁵ A. R. Dinesen, S. Linderöth, and S. Mørup, *Journal of Physics: Condensed Matter* **17**, 6257 (2005).

- ⁶⁶ T. D. Thanh, D. C. Linh, N. T. Uyen Tuyen, T.-L. Phan, and S.-C. Yu, *Journal of Alloys and Compounds* **649**, 981 (2015).
- ⁶⁷ A. Bettaibi, R. M'Nassri, A. Selmi, H. Rahmouni, N. Chniba-Boudjada, A. Cheikhrouhou, and K. Khirouni, *Journal of Alloys and Compounds* **650**, 268 (2015).
- ⁶⁸ G. F. Wang, Z. R. Zhao, L. R. Li, and X. F. Zhang, *Journal of Magnetism and Magnetic Materials* **397**, 198 (2016).
- ⁶⁹ I. A. Radulov, K. P. Skokov, D. Y. Karpenkov, T. Gottschall, and O. Gutfleisch, *Journal of Magnetism and Magnetic Materials* **396**, 228 (2015).
- ⁷⁰ A. L. Pires, J. H. Belo, J. Turcaud, G. N. P. Oliveira, J. P. Araújo, A. Berenov, L. F. Cohen, A. M. L. Lopes, and A. M. Pereira, *Materials & Design* **85**, 32 (2015).
- ⁷¹ T. D. Thanh, W. Z. Nan, G. Nam, H. T. Van, T. S. You, T. L. Phan, and S. C. Yu, *Current Applied Physics* **15**, 1200 (2015).
- ⁷² J. K. Murthy, K. D. Chandrasekhar, M. Sudipta, D. Topwal, and A. Venimadhav, *Journal of Physics D: Applied Physics* **48**, 355001 (2015).
- ⁷³ L. Li, Y. Yuan, Y. Zhang, R. Pöttgen, and S. Zhou, *Journal of Alloys and Compounds* **643**, 147 (2015).
- ⁷⁴ M. R. Dudek, K. W. Wojciechowski, J. N. Grima, R. Caruana-Gauci, and K. K. Dudek, *Smart Materials and Structures* **24**, 085027 (2015).
- ⁷⁵ J. A. Barclay, *Journal of Applied Physics* **53**, 2887 (1982).
- ⁷⁶ R. E. Rosenweig, *Ferrohydrodynamics* (Cambridge University Press, 1985).
- ⁷⁷ J. Romero Gómez, R. Ferreira Garcia, A. De Miguel Catoira, and M. Romero Gómez, *Renewable and Sustainable Energy Reviews* **17**, 74 (2013).
- ⁷⁸ V. Franco, R. Caballero-Flores, A. Conde, K. E. Knipling, and M. A. Willard, *Journal of Applied Physics* **109**, 07A905 (2011).
- ⁷⁹ V. Franco, J. S. Blazquez, and A. Conde, *Applied Physics Letters* **89**, 2512 (2006).
- ⁸⁰ B. K. Banerjee, *Physics Letters* **12**, 16 (1964).
- ⁸¹ J. S. Kouvel and M. E. Fisher, *Physical Review* **136**, A1626 (1964).
- ⁸² L. P. Kadanoff, *Physics* **2**, 263 (1966).

- ⁸³ S. N. Kaul, *Journal of Magnetism and Magnetic Materials* **53**, 5 (1985).
- ⁸⁴ K. Huang, (Wiley, New York, , 1987).
- ⁸⁵ T. D. Thanh, N. Huy Dan, T.-L. Phan, H. Kumarakuru, E. J. Olivier, J. H. Neethling, and S.-C. Yu, *Journal of Applied Physics* **115**, 023903 (2014).
- ⁸⁶ K. Winschuh and M. Rosenberg, *Journal of Applied Physics* **61**, 4401 (1987).
- ⁸⁷ P. Álvarez, J. S. Marcos, P. Gorria, L. F. Barquín, and J. A. Blanco, *Journal of Alloys and Compounds* **504**, S150 (2010).
- ⁸⁸ A. Perumal, V. Srinivas, K. S. Kim, S. C. Yu, V. V. Rao, and R. A. Dunlap, *Physical Review B* **65**, 064428 (2002).
- ⁸⁹ K. Yamada, Y. Ishikawa, Y. Endoh, and T. Masumoto, *Solid State Communications* **16**, 1335 (1975).
- ⁹⁰ I. M. Kyprianidis, C. A. Achilleos, I. A. Tsoukalas, H. Bremers, and J. Hesse, *Journal of Magnetism and Magnetic Materials* **161**, 203 (1996).
- ⁹¹ S. N. Kaul, *Physical Review B* **23**, 1205 (1981).
- ⁹² S. N. Kaul, *Physical Review B* **24**, 6550 (1981).
- ⁹³ G. Böhnke, S. N. Kaul, W. Kettler, and M. Rosenberg, *Solid State Communications* **48**, 743 (1983).
- ⁹⁴ T. A. Ho, T. D. Thanh, Y. Yu, D. M. Tartakovsky, T. O. Ho, P. D. Thang, A. T. Le, T. L. Phan, and S. C. Yu, *Journal of Applied Physics* **117**, 17D122 (2015).
- ⁹⁵ D. Xing, H. Shen, S. Jiang, J. Liu, M. H. Phan, H. Wang, F. Qin, D. Chen, Y. Liu, and J. Sun, *physica status solidi (a)* **212**, 1905 (2015).
- ⁹⁶ A. Omri, E. Dhahri, and E. K. Hlil, *Phase Transitions* **88**, 1098 (2015).
- ⁹⁷ J. Panda, S. N. Saha, and T. K. Nath, *Journal of Alloys and Compounds* **644**, 930 (2015).
- ⁹⁸ E. L. Resler and R. E. Rosensweig, *AIAA Journal* **2**, 1418 (1964).
- ⁹⁹ L. J. Love, J. F. Jansen, T. E. McKnight, Y. Roh, and T. J. Phelps, *NanoBioscience, IEEE Transactions on* **3**, 101 (2004).
- ¹⁰⁰ Y. Z. Shao, J. K. L. Lai, and C. H. Shek, *Journal of Magnetism and Magnetic Materials* **163**, 103 (1996).

- ¹⁰¹ Q. Li, W. Lian, H. Sun, and Y. Xuan, International Journal of Heat and Mass Transfer **51**, 5033 (2008).
- ¹⁰² W. Lian, Y. Xuan, and Q. Li, International Journal of Heat and Mass Transfer **52**, 5451 (2009).
- ¹⁰³ W. Lian, Y. Xuan, and Q. Li, Energy Conversion and Management **50**, 35 (2009).
- ¹⁰⁴ Y. Xuan and W. Lian, Applied Thermal Engineering **31**, 1487 (2011).
- ¹⁰⁵ U. T. J. Tušek, A. Kitanovski, U. Plaznik, M. Ožbolt and A. Poredoš, *Magnetocaloric Energy Conversion* (Springer International Publishing Switzerland, 2015).
- ¹⁰⁶ L. Love, J. Jansen, and T. McKnight, (Google Patents, 2006).
- ¹⁰⁷ R. Ganguly, S. Sen, and I. K. Puri, Physics of Fluids **16**, 2228 (2004).
- ¹⁰⁸ A. Mukhopadhyay, R. Ganguly, S. Sen, and I. K. Puri, International Journal of Heat and Mass Transfer **48**, 3485 (2005).
- ¹⁰⁹ S. Pal, A. Datta, S. Sen, A. Mukhopdhyay, K. Bandopadhyay, and R. Ganguly, Journal of Magnetism and Magnetic Materials **323**, 2701 (2011).
- ¹¹⁰ H. Rahman and S. A. Suslov, Journal of Fluid Mechanics **764**, 316 (2015).
- ¹¹⁰ H. Hiroyoshi, A. Hoshi and Y. Nakagawa, J. Appl. Phys. **53**, 2453 (1982)

Chapter 3

Experimental procedures

In this chapter, the experimental methods and characterization techniques employed in the thesis are discussed. Nanoparticles were synthesized by high speed ball milling while arc melting was used for bulk samples. X-ray diffractometer (XRD), Transmission electron microscope (TEM), Energy dispersive spectroscopy (EDS), Electron probe micro analyser (EMPA) and Physical property measurement system (PPMS) were used to characterize the samples. Therefore, the working principle of these techniques and used parameter during characterization are described.

3.1. Rationale for selection of methods

High energy ball milling is a suitable technique for production of micro- and nanoparticles for several applications. In addition, ball milling is straight forward process to alloy materials in compared to chemical synthesis. Chemical synthesis can produce high purity samples but for ternary alloys this can be difficult because the precursor reduces at different temperatures. Ball milling also has some limitations, e.g., it cannot be used if the elements are immiscible or volatile, e.g., Fe-Ag and W-Cu cannot made by this technique. The advantage of this technique are (a) to enlarge the solid-solubility limit (b) grain size in nanometer range can be obtained (c) to produce crystalline, quasi-crystalline and amorphous phases (d) alloying of elements which are difficult by conventional techniques.

In addition of nanoparticles produced by ball milling, we have synthesized bulk samples by arc melting. In arc melting technique, an electrical arc generated by a large voltage between two electrodes is used to melt the alloy in the desired stoichiometry. For bulk sample arc melting is considered as one of the best techniques. This can be used for alloying of several elements. However, during arc melting oxidation is possible; to control it, titanium, zirconium or tantalum foil, which work as an oxygen getter can be placed inside the arc melter chamber.

3.1.1. Nanoparticles preparation - ball milling

Mechanical alloying is actually consistent process of flattening, welding, fracturing and rewelding of grinding powder. Fig 3.1 shows a schematic of high energy ball milling of Fe-Ni-B/Mn/Cr alloy particles. The milling balls and a mixture of starting elements is filled in a rotating reaction chamber (vial) (Fig 3.1). After an optimized time at a definite speed (revolution per min (rpm)) alloying is obtained by repeated fracturing and welding.

Fig 3.1 Schematic of high energy ball milling synthesis mechanism for Fe-Ni-B/Mn/Cr alloy nanoparticles (a) Rotating reaction chamber (vial) with milling balls and a mixture of starting elements (b) Repeated welding fracture provides the final alloyed powder

Mechanical alloying is a complex process for which optimization of many variables, e.g., (a) type of mill and milling container, (b) milling speed and time, (c) ball to powder ratio, (d) atmosphere and temperature of milling, are essential to obtain the desired product. These variables are interlinked e.g., optimum milling time depends on size of the grinding medium, type of mill, ball to powder ratio, etc. First, we will give a brief introduction to each variable and then the experimental procedure will be discussed.

3.1.2. Type of mill and milling container

Many types of mills are available for alloying and/or synthesis of powder samples. These differ in their capacity, temperature of the medium, ability to control contamination from etc. Based on the final requirements, a suitable mill should be selected. Our main concern is to obtain alloy particles in the nano size range, therefore high energy ball mill has been used. High energy ball mills can produce up to ~ 60 gm of powders in one run.

Choice of the appropriate grinding vial (vessel) is also needed. If vial and grinding powder are made of the same material, the chemistry/composition of final product can be changed. On the other hand, if the vial material is different than from of the grinding powder, final product can get contaminated. There are many grinding media such as hardened steel, stainless steel, sintered corundum, tungsten carbide, zirconium oxide etc. Here, zirconium oxide vial and balls have been used.

3.1.3. Milling speed and time

Every mill has a maximum milling speed. In general, the faster the speed, the higher the energy transformed to the powder, however, this is not always true. There is a critical speed above which the balls get pinned on the wall and do not fall down, therefore the collisions with the powder decrease¹. In addition, high speed increases the chance of contamination in the powder.

The time of milling is also important. For a particular mill, the times required depends on milling speed, ball-sample ratio, milling temperature. An optimum value of milling time has to be fixed to obtain the desired phase because if excess time can result in contamination and/or undesired phases. In this study we have chosen different milling speed and found that 10 h milling time is enough to get the desired phase.

3.1.4. Ball to powder ratio

Ball to powder ratio sometimes called charge ratio is another key variable which is directly related to milling time, temperature inside the mill and alloy formation. High ball to powder ratio results in high temperatures and high collision frequency during milling, therefore energy transferred to the powders will increase, which can decrease the time for alloying. By changing milling time and ball to powder ratio, one can change the particle size of the final product.

3.1.5. Atmosphere and temperature inside the mill

Milling atmosphere can lead to oxidation and/or composition change during the milling. Inert gases are found to be the best to minimize the oxidation of grinding powder. Therefore, milling vials were first evacuated and filled with Ar gas to reduce contamination and oxidation.

The temperature inside the vials depends on many factors such as (a) friction between balls and vials, (b) kinetic energy transformed from balls to particles, (c) exothermic reaction during grinding and (d) electric motor.

Regarding MCE results, ball milling technique has been used widely to study for both rare earth and transition metal based materials. For example, $\text{Gd}_5\text{Si}_2\text{Ge}_2$,^{2,3} $\text{La}(\text{FeSi})_{13}$,^{4,5} $\text{RE}_2\text{Fe}_{17}$,⁶⁻⁸ MnAs ,^{9,10} $\gamma\text{-FeNi}$,^{1,11-14} Heusler alloys,^{15,16} and amorphous alloys^{17,18} have been synthesized by ball milling. Generally, ball milled samples exhibit smaller ΔS_M than those of bulk materials while greater working temperature span leads to enhancement of relative cooling power.^{6-8,19}

The balls rotate with high energy inside a vial and hit the solid mixture. A high energy collision of balls and mixture of powder results in powder in nano form as well as alloying. The total sum of impact energy of collision events n can be defined as $E_i = \sum_{j=1}^n \frac{1}{4M} m v^2$, where M , m and u are mass of vial, mass of ball and velocity of grinding ball, respectively²⁷. Because of higher speed of our ball miller than conventional, the produce impact energy is high. Therefore, this process called as high energy ball milling.

Other milling media (tungsten carbide or stainless steel) can also be used, however these media may increase the hardness (coercivity) of the samples which is not good for magnetocaloric applications. ZrO_2 milling media was used because it is relatively less hard than tungsten carbide and stainless steel.

3.2. Bulk sample preparations – arc melting

A pellet of stoichiometric amount of starting elements with purity greater than 99.9% was prepared using hydraulic pressure of 10 N. This pellet was then melted

in an arc furnace. The furnace contains a copper hearth which is cooled by chilled water and a tungsten electrode. The furnace was flushed 5 times with Ar gas to minimize oxygen in the chamber, preventing oxidation of the sample. By turning a millimetric screw, the cathode was moved toward the pellet which is placed on a copper crucible. When the cathode is close enough, an arc that melts the elements is discharged by ionizing the gas. After some seconds of melting, all the elements are mixed. Melting, turning and remelting were repeated at least 5 times to ensure sample homogeneity.

The γ -phase stabilization is very important for this study. The materials was sealed in quartz ampoules with a high pressure of 10^{-5} torr. The ampoules were placed in a box furnace at 700 °C for 2 h. 700 °C is the temperature for γ – phase formation. Then, the samples were quenched in water at a rate of ~ 100 °C/S.

3.3. Ferrofluid preparation

$\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles were synthesized via the hydrothermal method²⁰. Manganese (II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 99%), zinc chloride, anhydrous (ZnCl_2 , 98%), Iron (III) chloride hexahydrate, ACS ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), were used as starting precursors. Sodium hydroxide (NaOH) was used to adjust the pH value. Each precursor was dissolved separately in appropriate molar quantities of purified water. 5M-NaOH was added to the iron chloride solution until the pH value reached 8. The precipitate was centrifuged and washed four times with DI water. The salt solutions were then added together and vigorously stirred while adding sodium hydroxide drop wise until pH reached 11. The resulting slurry was decanted in a pressure vessel and placed in an oven at 190°C for 4 h. The resulting nanoparticles were washed several times with DI water followed by overnight vacuum drying. These particles were functionalized by oleic acid and ammonium hydroxide and then dispersed into water to make a water based ferrofluid.

3.4. Materials characterizations

3.4.1. X-ray diffraction

Wilhelm Conrad Rontgen, a German physicist demonstrated X-rays in 1895 and got the Nobel Prize for physics in 1901. Max von Laue was honored by the Nobel Prize for diffraction of X-rays by crystals in 1914. The next year in 1915, Bragg and his father, Sir William Henry Bragg got Nobel Prize for their analysis of crystal structure by means of X-rays^{21,22}.

X-ray diffraction provides structural information of materials and is therefore a powerful tool for phase identification. A X-ray diffractometer made up of three main components (a) x ray tube, (b) sample holder and (c) x-ray detector (fig. 3.2). When X-rays are generated by the cathode tube, they bombard the inner shell electrons of the target material which generate X-rays characteristic of the material.

Fig 3.2 Schematic of X-ray diffractometer

Target materials may be Cu, Mo, Fe or Cr which produce monochromatic wavelengths. When the diffracted X-ray beams satisfy Bragg's equation, $2d \sin \theta = n\lambda$, the result in constructive interference. All the samples were studied by x-ray diffraction (XRD) using a Bruker D8 ADVANCE Diffractometer with Cu $K\alpha$ radiation, $\lambda=0.154$ nm. The measurements were performed at a scan speed of 0.02

%step. Some samples were investigated by in-situ high temperature X-ray diffraction (XRD) using a SIEMENS diffractometer (D5005), Cu K α radiation, $\lambda=0.154$ nm, equipped with a high temperature chamber, in the scan range (2θ) from 20° to 80° and step size of 0.05° . To prevent oxidation, XRD measurements were performed under a vacuum of 10^{-3} torr.

XRD diffraction patterns were used for lattice parameter, phase(s) and particle size analysis. The calculation of lattice parameters, determination of crystal structure, indexing of the peaks and structure refinement were carried out by TOPAS software (Bruker AXE, 2005). The CIF files were collected with the help of FINDIT.

The average crystallite size (d) of phase(s) has been deduced from the Scherrer formula, $d = 0.89 \lambda / B_s \cos \theta$, where λ is the X-ray wavelength, θ is the Bragg angle and B_s is the corrected full width at half maximum of peak, taking silicon as standard. The peak broadening may be because of instrumentation effects, lattice strain and small particle size, although, the Scherrer equation only considers broadening because of crystallite size.

3.4.2. Transmission electron microscopy

For transmission electron microscopy, the samples were dispersed in hexane and ultra-sonicate for 2h. These suspended particles were dropped on a holey carbon coated copper grid followed by vacuum drying for couple of hours. Images were collected using a JEOL 2010 transmission electron microscopy (TEM) at operating voltage and current of 200kV and 106 mA, respectively. The JEOL-2010 is a microscopy with a field emission electron gun that produces high brightness, essential for high resolution and analysis.

3.4.3. Energy dispersive X-ray spectroscopy

In a scanning electron microscope (SEM), the interaction between a focused beam of electrons and the specimen generates a signal, yields the information about

morphology and composition of the sample. The composition was analysed by energy dispersive X-ray spectroscopy using a JEOL JSM-7600F scanning electron microscope. For this, the powder product was dispersed over a copper stub and coated with gold to avoid charging and improve secondary electron (SE) signal.

3.4.4. Electron probe micro analyser (EPMA)

Electron probe micro analyser (EPMA) (JEOL JXA-8530F) can measure the composition of the materials qualitatively and quantitatively. An EPMA is a micro-beam instrument used primarily for *in situ* non-destructive chemical analysis of tiny solid samples. It works on the same principle as SEM with the added capability of chemical analysis. The EPMA has the ability to get exact quantitative analyses at very small spot sizes (1-2 μm) by wavelength-dispersive spectroscopy. In addition to elemental analysis, it has the ability to create detailed images of the sample. An EPMA works on the principle that when a solid material is bombarded by an accelerated electron beam, the electron beam has enough energy to release both energy and electron from the target. The interactions between electron and target release heat, electrons and x-rays. The secondary and back-scattered electrons are useful for compositional analysis of the material. EPMA is a non-destructive technique because x-rays generated by electron interactions do not result any loss in the volume of the sample, so that the same material can reuse for analysis.

3.4.5. Physical properties measurement system

The magnetic properties were measured using a physical property measuring system (PPMS) (EverCool-II, Quantum Design), equipped with a vibrating sample magnetometer (VSM) probe. The VSM equipped with PPMS is a very sensitive (can measure the moment up to 10^{-6} emu) and fully automatic DC magnetometer. The VSM detection coil was inserted into the PPMS sample chamber. The operating temperature range of standard PPMS is from 1.9 K to 400 K. The range of applied magnetic field in our PPMS is ± 9 T. However, for high Curie temperature

materials to calculate the T_C and RCP, high temperature measurements are required. Therefore, for high temperature magnetic measurements, an oven (model P527) was installed with a VSM head. High temperature measurements were performed under a vacuum of 10^{-5} torr. To drive the linear motor transport system and detect the response from the pickup coil, MultiVu software was used.

Fig. 3.3 shows the operating principle for the VSM option in the PPMS. VSM motor module is used to control the precise position and amplitude of oscillation. The voltage induced in the pickup coil is amplified and detected in the VSM detection module.

Fig. 3.3 Working principle for VSM²³

The principle of a VSM is that a changing magnetic field induces a voltage in a pickup coil. This coil voltage can be defined as

$$V_{Coil} = \frac{d\phi}{dt} = \left(\frac{d\phi}{dz}\right) \left(\frac{dz}{dt}\right) \quad (3.1)$$

where Φ is the magnetic flux, t is the time and Z is the vertical position of the sample with respect to the coil. For oscillating sample position

$$V_{Coil} = 2\pi f C m A \sin(2\pi f t) \quad (3.2)$$

where f is the frequency of the oscillation, A is the amplitude, m is the DC magnetic moment, and C is the coupling constant.

The magnetic measurements involve measuring the coefficient of the sinusoidal voltage response from the coil.

3.5. Property evaluation of the magnetocaloric effect

In the design of magnetic cooling device, MCMs as the refrigerant are the most important element. We have evaluated the following properties:

3.5.1. Curie temperature

Curie temperature is the temperature at which the ferromagnetic phase changes to the paramagnetic phase. For the application of MCM, the first condition is to know about the T_C of that material. It should be noted that MCE of any material is maximum at its T_C and relatively small or almost zero (depending on the T_C distribution and the order of the phase transition) at temperatures beyond T_C .

There are many techniques in the literature to determine the T_C (a) The point where the specific heat is maximum in the heat capacity measurement with and without magnetic field, (b) The maximum change in magnetization with respect to temperature i.e. the minimum of dM/dT , (c) the point where initial susceptibility becomes zero, (d) the extremum of the temperature coefficient of the electrical resistance. The temperature dependence of magnetization $M(T)$ of the studies samples under a field of 0.1T was used in this thesis to estimate the T_C . The minimum of the plot of dM/dT versus T was used as the T_C .

Fig. 3.4 illustrates the FeNi phase diagram for a range of temperatures from 200 °C to 1600 °C, and T_C for the γ -phase and the α -phase²⁴. In the iron rich side of the FeNi phase diagram, especially in the γ -phase region, the T_C is not well

characterized. Miller et al. reported that the γ -phase of $(\text{Fe}_{73}\text{Ni}_{27})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ can be stabilized by annealing at 700 °C for 2 h, followed by water quenching. The experimental T_C value for $(\text{Fe}_{73}\text{Ni}_{27})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ powder was 120 °C which matched well with the T_C calculated by extrapolation of the γ -phase to metastable phase in the phase diagram. However, a small deviation in the stoichiometry of a few weight/atomic percent is sufficient to result in a large change in T_C in the Fe rich FeNi alloys, as extrapolated curve is very steep. For this research, we have fixed the Fe-Ni composition in a 70:30 ratio, and the γ -phase was stabilized by water quenching in the γ -phase region (700 °C). The reason why we fixed this composition is that in the Fe rich side, the γ -phase phase could not be stabilized and in the nickel rich side the T_C was very high.

Fig. 3.4 Fe–Ni phase diagram. Dashed red line is extrapolation in the γ -phase region, showing T_C for corresponding composition in the iron rich region²⁴.

$\text{Fe}_{70}\text{Ni}_{30}$ alloy nanoparticles were synthesized by high energy ball milling (the detailed synthesis is same as FeNiB, described in chapter 4). Fig. 3.5 shows the temperature dependence of magnetization, $M(T)$ (left) and dM/dT (right) for γ - $(\text{Fe}_{70}\text{Ni}_{30})$ nanoparticles, measured from 400 K to 600 K under a field of 0.1 T in the VSM equipped with PPMS.

Fig 3.5. Left axis shows the temperature dependence of magnetization $M(T)$ for the γ - $\text{Fe}_{70}\text{Ni}_{30}$ nanoparticles while the right axis shows corresponding derivative with respect to temperature (dM/dT).

The T_C of γ -($\text{Fe}_{70}\text{Ni}_{30}$) nanoparticles was found to be 438 K, determined from the minima of the plot of dM/dT versus T . The T_C for γ -($\text{Fe}_{70}\text{Ni}_{30}$), measured from an extrapolation to metastable phase in the phase diagram was found to be 443 K. Therefore, the γ - $\text{Fe}_{70}\text{Ni}_{30}$ nanoparticles can be produced by high energy ball milling, followed by an annealing treatment in the γ -phase region and water quenching. As mentioned in chapter 1 and 2, we are interested in tuning T_C near room temperature. Hence, a suitable third element has been added, as explained in later chapters.

3.5.2. Magnetic entropy change (ΔS_M)

Magnetization isotherms $M(H)$ obtained in a range of temperatures in the particular temperature range for decreasing and increasing magnetic field up to 5 T, were used to determine ΔS_M using the Maxwell relation $\Delta S_M = \int_0^H (\partial M / \partial T)_H dH$, where the partial derivative $(\partial M / \partial T)_H$ was evaluated using finite difference and the integration was done numerically.

If shape factor is included, then above Maxwell equation must be recalculated using the internal field ($H = H_{ap} - NM$, where N is the demagnetization factor; $N =$

1/3 for spherical particles), instead of the applied field. However, this correction does not significantly affect ΔS_M (~5 % reduction in magnitude)²⁵.

3.5.3. Magnetic and thermal Hysteresis

In simple words, if positive and negative magnetic field sweep follow the different magnetization paths, the resultant difference is called magnetic hysteresis. Thermal sweep (cooling and heating) is associated with thermal hysteresis. FOMT materials, in general, exhibit large magnetic and thermal hysteresis due to structural change during magnetic and thermal sweep. SOMT materials, generally, do not exhibit hysteresis. The hysteresis represents a loss in energy, hysteresis can significantly diminish MCE during thermodynamic cycles and therefore reduce the performance of magnetic cooling system. For better performance of a magnetocaloric material in magnetic cooling, magnetic and thermal hysteresis should be as small as possible. Thus, SOMT materials are more preferable for magnetic cooling, one of the best examples is gadolinium.

3.5.4. Relative cooling power

High ΔS_M only at T_C and zero at other temperatures is not suitable for magnetic cooling devices. MCM should have a large MCE over a wide temperature range. The relative cooling power (RCP) is a measure that includes both ΔS_M and working temperature span. As described in chapter 2, there are several methods to calculate the relative cooling power (RCP). We will calculate RCP as the product of maximum ΔS_M and full temperature width at half maximum of peak entropy change, i.e. $RCP(S) = \Delta S_M \times \delta T_{FWHM}$.

3.6. Self-pumping magnetic cooling prototype

A prototype has been built for automatic magnetic cooling system using a 5.2 mm inner diameter, 60 cm circumference polymer tube. A heat load (electric heater made by kanthal wire) and a heat sink (ice bath) were placed opposite each other. A permanent

magnet which can provide a maximum field of 0.3 T, was placed close to the heat load. A temperature data logger with SD card was used to record changes in temperature in time. The power of the heat load (and therefore the initial temperature) was fixed by tuning the current and voltage in a Keithley power supply (Model: 2231 A-30-3). To avoid the buoyance effect, a spirit level was used to fix the prototype horizontally. Fig 3.6 shows the picture of our magnetic cooling prototype.

Fig 3.6 Magnetic cooling prototype

3.7. Simulation

For modelling, COMSOL Multiphysics simulation software version 4.4 was used with finite element method and normal mesh. To describe the magnetic field, the following equations can be used²⁶

$$\Delta \cdot \mathbf{B} = 0 \quad (3.3)$$

$$\mathbf{B} = \mu_o(\mathbf{H} + \mathbf{M}) = \mu_o(1 + \chi)\mathbf{H} = \mu_r \mathbf{H} \quad (3.4)$$

where, χ is the local susceptibility of the ferrofluid diluted by the carrier fluid. The vector $\mathbf{B}$, $\mathbf{M}$, $\mathbf{H}$, μ_o and μ_r represent the magnetic flux density, magnetization, vacuum permeability and relative permeability, respectively.

The volume force term F_f (N/m³) in the Navier-Stokes equation is the sum of the magnetic force vector $\mathbf{F}_m$ and the gravitational force vector $\mathbf{F}_g$

$$\mathbf{F}_f = \mathbf{F}_m + \mathbf{F}_g \quad (3.5)$$

We assume that there is no effect of gravitational force vector as our experimental setup was horizontally fixed, therefore

$$\mathbf{F}_f = \mathbf{F}_m = \frac{\chi}{\mu_o} (\mathbf{B} \cdot \nabla \mathbf{B}) \quad (3.6)$$

In the model, it also assumed that the temperature sensitive ferrofluid is an electrically nonconductive, single phase and incompressible Newtonian fluid.

Reference

- ¹ H. Ucar, Ph.D. Thesis, Carnegie Mellon University, 2013.
- ² T. B. Zhang, V. Provenzano, Y. G. Chen, and R. D. Shull, Solid State Communications **147**, 107 (2008).
- ³ D. M. Rajkumar, M. Manivel Raja, R. Gopalan, and V. Chandrasekaran, Journal of Magnetism and Magnetic Materials **320**, 1479 (2008).
- ⁴ K. Mandal, D. Pal, O. Gutfleisch, P. Kersch, and K.-H. Müller, Journal of Applied Physics **102**, 053906 (2007).
- ⁵ M. Phejar, V. P. Boncour, and L. Bessais, Intermetallics **18**, 2301 (2010).
- ⁶ P. A. Alonso, J. L. Sánchez Llamazares, C. F. Sánchez-Valdés, G. J. Cuello, V. Franco, P. Gorria, and J. A. Blanco, Journal of Applied Physics **115**, 17A929 (2014).
- ⁷ Á. Pablo, G. Pedro, F. Victorino, M. J. Sánchez, J. P. María, L. S. L. José, O. Inés Puente, and A. B. Jesús, Journal of Physics: Condensed Matter **22**, 216005 (2010).
- ⁸ G. Pedro, L. S. L. José, Á. Pablo, P. María José, M. Jorge Sánchez, and A. B. Jesús, Journal of Physics D: Applied Physics **41**, 192003 (2008).
- ⁹ W. B. Cui, W. Liu, X. H. Liu, S. Guo, Z. Han, X. G. Zhao, and Z. D. Zhang, Materials Letters **63**, 595 (2009).
- ¹⁰ N. K. Sun, S. N. Xu, Y. B. Gao, T. B. Ji, and Y. B. Li, Physica B: Condensed Matter **406**, 2731 (2011).

- ¹¹ J. J. Ipus, H. Ucar, and M. E. McHenry, IEEE Transactions on Magnetics **47**, 2494 (2011).
- ¹² H. Ucar, J. J. Ipus, D. E. Laughlin, and M. E. McHenry, Journal of Applied Physics **113**, 17A918 (2013).
- ¹³ H. Ucar, J. J. Ipus, M. E. McHenry, and D. E. Laughlin, Journal of Metals **64**, 782 (2012).
- ¹⁴ H. Ucar, M. Craven, D. E. Laughlin, and M. E. McHenry, Journal of Electronic Materials **43**, 137 (2014).
- ¹⁵ L. Zhang, E. Brück, O. Tegus, K. H. J. Buschow, and F. R. de Boer, Physica B: Condensed Matter **328**, 295 (2003).
- ¹⁶ A. G. Varzaneh, P. Kameli, F. Karimzadeh, B. Aslibeiki, G. Varvaro, and H. Salamati, Journal of Alloys and Compounds **598**, 6 (2014).
- ¹⁷ J. J. Ipus, J. S. Blázquez, V. Franco, and A. Conde, Journal of Alloys and Compounds **496**, 7 (2010).
- ¹⁸ J. S. Blázquez, V. Franco, and A. Conde, Intermetallics **26**, 52 (2012).
- ¹⁹ J. S. Blázquez, J. J. Ipus, L. M. M. Ramírez, J. M. Borrego, S. L. Pérez, V. Franco, C. F. Conde, and A. Conde, Metallurgical and Materials Transactions E **2**, 131 (2015).
- ²⁰ V. Chaudhary and R. V. Ramanujan, MRS Online Proceedings Library **1708**, vv10 (2014).
- ²¹ G. Hildebrandt, Crystal Research and Technology **28**, 747 (1993).
- ²² M. Eckert, Annalen der Physik **524**, A83 (2012).
- ²³ Q. Design. <http://www.qdusa.com/>
- ²⁴ K. J. Miller, M. Sofman, K. McNerny, and M. E. McHenry, Journal of Applied Physics **107**, 09A305 (2010).
- ²⁵ L.M. Moreno-Ramírez, J.J. Ipus, V. Franco, J.S. Blázquez, A. Conde Journal of Alloys and Compounds 622 606–609 (2015)
- ²⁶ Zhaomeng Wang, V. B. Varma, Huan Ming Xia, Z. P. Wang, and R. V. Ramanujan, Phys. Fluids **27**, 052004 (2015)
- ²⁷ C. F. Burmeister and A. Kwade, Chem. Soc. Rev., 42, 7660 (2013)

Chapter 4*

Magnetocaloric effect and critical behaviour of FeNiB nanoparticles

Low cost magnetocaloric nanomaterials have attracted considerable attention for energy efficient applications. We found very high relative cooling power (RCP) in a study of the magnetocaloric effect (MCE) in FeNiB nanoparticles. RCP increases from 89.8 to 640 J·kg⁻¹ for a field change of 1 and 5 T, respectively, these values are the largest for rare earth free iron based magnetocaloric nanomaterials. To investigate the MCE around the Curie temperature (T_C), the critical behavior of quenched nanoparticles was studied. Detailed analysis of the magnetic phase transition using the modified Arrott plot, Kouvel-Fisher method and critical isotherm plots yields critical exponents of $\beta = 0.364$, $\gamma = 1.319$, $\delta = 4.623$ and $\alpha = -0.055$, which are close to the theoretical exponents obtained from the 3D-Heisenberg model. Our results indicate that these FeNiB nanoparticles are potential candidates for magnetocaloric fluid based heat pumps and low grade waste heat recovery.

*This section published substantially as reference: V. Chaudhary, D. V. Maheswar Repaka, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, Journal of Applied Physics **116**, 163918 (2014).

4.1 Introduction

Environmental degradation and energy efficiency are of high interest due to global warming and finite energy resources¹. Low grade waste heat recovery and heat pumps are of special interest because of their tremendous potential to improve energy efficiency^{2,3}. Low grade waste heat is expelled to the atmosphere during production and consumption of energy, this waste heat can be recycled using the magnetocaloric effect (MCE). A heat pump is a device which can transfer heat from a cool region to a hot region⁴. MCE based heat pumps are more cost effective and energy efficient than conventional heat pumps⁵. The MCE is the change in temperature, corresponding to the magnetic entropy change (ΔS_M), of a material due to the adiabatic application (or removal) of an external magnetic field⁶⁻⁹. Generally, MCE is large close to the Curie temperature (T_C), where the magnetic spins undergo an order $\leftrightarrow$ disorder phase transition^{7,10}. The relative cooling power (RCP) is another important performance metric to rank magnetocaloric materials, it quantifies the magnitude of heat extracted in a thermodynamic cycle¹¹. High RCP, reasonable ΔS_M , as well as low thermal and magnetic hysteresis are required for MCE based heat pumps.

Gd based materials exhibit very high ΔS_M ,^{12,13} however, materials containing rare earths such as Gd are very expensive, of limited availability, involve radioactive mining etc., which precludes large scale commercialization. On the other hand, transition metal (TM) based alloys are low cost, readily available, earth abundant and environmentally friendly¹⁴. Hence, there is considerable interest in developing rare earth free magnetocaloric materials. Magnetic nanoparticles (MNPs) can exhibit superior magnetocaloric properties compared to the bulk but there are very few reports of the MCE of nanoparticles^{15,16}. The RCP of nanoparticles can be increased through a broad magnetic phase transition, which will be useful for low grade waste heat recovery and heat pumps¹⁷. Ucar *et al.*, reviewed the RCP (in Joule/\$) of various magnetocaloric materials and found that FeNi based materials are very useful for such applications¹⁶. For self-pumping cooling systems, MNPs are suitable if the T_C lies between room temperature and the device operating temperature¹⁸.

Besides the urgent need for low cost MCE materials, analysis of the critical behavior of such materials is of high interest since it is directly related to the MCE¹⁹. The critical exponents α , β , γ and δ correspond to specific heat, spontaneous magnetization, magnetic susceptibility and critical isotherm, respectively. These exponents are directly related to the MCE of the materials. For example, with the help of the Arrott-Noakes equation of state, the magnetic entropy change at $T = T_C$ can be expressed by the relation:²⁰ $\Delta S_M = AH^n$, where $n = 1 + [(\beta-1)/(\beta+\gamma)]$, a and b are constants and A is a function of the critical exponents. The field dependence of RCP can be expressed as power law of $RCP \propto H^N$, where $N = 1 + 1/\delta$. The determination of critical exponents (α , β , γ and δ) is useful to evaluate MCE performance of the materials even at high field, which may not be available in many laboratories, as well as to compare the MCE results obtained by various investigators using different maximum fields. In addition, the critical behavior study is a powerful approach to get the mechanism of the magnetic phase transition and the nature of ordering around T_C .

We report the synthesis and structure of Fe–Ni–B nanoparticles possessing a metastable face centered cubic (fcc) crystalline structure. Boron was added to reduce the T_C to ~ 100 °C, suitable for low grade waste heat recovery. Previous work on $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Zr}_7\text{B}_4$ nanoparticles showed attractive magnetocaloric properties²¹. However, zirconium is not preferred for waste heat recovery applications due to their pyrophoric nature. These particles have to be suspended such as water and pyrophoric materials will not be useful. Here, Zr was replaced by B and the composition of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ was selected, which was found in this work to yield superior MCE ($\Delta S_M = -2.1 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, $RCP = 640 \text{ J}\cdot\text{kg}^{-1}$ at $\Delta H = 5 \text{ T}$) properties compared to $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Zr}_7\text{B}_4$. The MCE is much more dramatic near T_C . Hence, the critical exponents of the magnetic phase transition near T_C were obtained using Landau's mean field model, 3D-Ising, 3D-Heisenberg and tricritical mean field models²². The obtained critical exponents ($\beta = 0.364$, $\gamma = 1.319$, $\delta = 4.623$ and $\alpha = -0.055$) were very close to the 3D-Heisenberg model and used to determine the field dependence of MCE.

4.2 Experimental details

(Fe₇₀Ni₃₀)₈₉B₁₁ alloy nanoparticles were prepared by planetary ball milling (FRITSCH) at 600 rpm under Ar atmosphere from elemental Fe (99.99%, Sigma Aldrich), Ni (99.998%, Fisher ChemAlert Guide) and B (97%, Sigma Aldrich) powders. To prevent cold welding, a small quantity of ethanol was also added in the material mixture. The ball to powder ratio was 10:1. The vials and balls were made of zirconium oxide, and the volume of the vial was 125 ml, which contains 15 balls (10 mm in diameter). To prevent oxidation during heat treatment, the magnetic nanoparticles were sealed under high vacuum (10⁻⁵ torr) in a quartz tube. The sealed tube was heated at 700 °C (γ - phase region)²³ for 2h and quenched in water. The structure and phase were determined by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer (CuK α radiation). The composition was confirmed by energy dispersive X-ray spectroscopy using a JEOL JSM-7600F scanning electron microscope. To determine the particle size and morphology, transmission electron microscopy (TEM) was carried out on a JEOL 2010 TEM with an operating voltage of 200 kV. Samples were prepared by ultrasonically dispersing a small quantity of powder in hexane followed by placing a drop of the suspension on a holey carbon-coated copper grid, the sample is then dried in air. The magnetic properties were measured using a physical property measuring system (PPMS) (EverCool-II, Quantum Design), equipped with a vibrating sample magnetometer probe and an oven (model P527).

4.3 Results and discussion

4.3.1 Phase analysis

Fig.4.1 (a) shows the XRD patterns of (Fe₇₀Ni₃₀)₈₉B₁₁ nanoparticles after 4, 5, 7, 8 and 10 h milling times. Rietveld refinement showed that the product after 4h milling is a mixture of both body centered cubic (bcc) and fcc FeNiB phases. As milling time increased to 5h, the intensity of the diffraction peaks increased slightly and shifted to higher “2 θ ” values (fig.4.1 (b)), indicating greater crystallinity and

lower cell volume. The mass fraction of the bcc phase reduced with milling time and only the γ -FeNi was observed after 10 h milling time (fig.4.1 (b)). The γ - phase has lattice parameters $a = 3.59893(6) \text{ \AA}$, $V = 46.61465 \text{ \AA}^3$, $Z = 2$ and space group Fm-3m. In mechanical alloying, the composition ranges of the bcc and fcc phase regions were extended compared to their equilibrium range. The average crystalline size, calculated by the Scherrer's formula, was $\sim 18 \text{ nm}$ and $\sim 10 \text{ nm}$ for bcc (4 h milling) and fcc (10 h milling) phases, respectively²⁴. Fig.4.2 shows the bright field transmission electron micrograph for $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ after 10 h milling time. The particle size is in the range of 6 to 17 nm with an average size of 12 nm, close to the value obtained from the XRD data.

Fig.4.1 (a) XRD patterns of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles after milling times 4, 5, 7, 8 and 10 h under Ar atmosphere. (b) Higher magnification of 110(bcc) and 111(fcc) diffraction peaks.

Fig 4.2 Bright field TEM of γ -(Fe₇₀Ni₃₀)₈₉B₁₁ nanoparticles with magnified inset showing lattice spacing corresponding to 111 planes.

The lattice fringe of 2.5 Å, corresponding to the 111 planes of the fcc phase is shown in the magnified portion of fig.4.1. The XRD and TEM results demonstrate that high speed ball milling has produced a nanocrystalline structure. Small particles are easy to suspend in fluids, even at high fields, thus providing versatile applications for heat pumps and waste heat recovery²⁵.

4.3.2 Magnetocaloric effect

Fig. 4.3 (a) shows the temperature dependence of magnetization $M(T)$ of (Fe₇₀Ni₃₀)₈₉B₁₁ nanoparticles with and without water quenching, under a field of 0.1T. T_C of the as milled sample was above 400 K, whereas the quenched sample shows $T_C = 381$ K, as determined from the minima of the plot of dM/dT versus T (inset of fig. 4.3 (a)). Our T_C value for quenched nanoparticles is lower than that reported in the Fe-Ni phase diagram²⁶. We attribute this change to atomic rearrangements (short-range ordering or clustering by addition of boron) and quenching.

Fig.4.3 (a) $M(T)$ versus T of as milled and water quenched $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles for $\mu_0 H = 0.1$ T, the inset of (a) shows dM/dT versus T plot for the quenched sample. (b) M versus H at 10 K for the quenched sample.

Recently, Moreno *et al.* also reported a large reduction in T_C of $\text{Co}_{62}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ alloys by quenching.²⁷ Fig.4.3 (b) shows the magnetic field dependence of magnetization $M(H)$ at $T = 10$ K. The sample exhibits ferromagnetic behavior with coercivity ~ 30 Oe. The absence of significant field hysteresis in $M(H)$ is a great advantage for efficient magnetic cooling, since it permits high cycle operating frequency²⁸.

For further tune the T_C , more boron was added i.e., $(\text{Fe}_{70}\text{Ni}_{30})_{1-x}\text{B}_x$, $x = 0.15$, 0.18 were prepared and water quenched in the γ -phase region. The temperature dependence of magnetization for water quenched samples in the temperature range of 10 to 400 K for an external magnetic field of 0.1 T is shown in fig.4.4. As the boron content is raised to 15% and 18%, the magnetization values decreased, and there is little change in their values with temperature, which indicates that these

samples have their FM-PM phase transition above 400K. The magnetization and Curie temperature (T_C) of FeB and CoB alloys with respect to boron concentration was measured previously²⁹⁻³¹. They found that T_C increases with B in FeB while it decreases in the case of the CoB alloy. The magnetization value was also obtained to decrease with boron content in both cases similar to the present findings. Hasegawa *et al.* reported that rapidly quenched $\text{Fe}_{100-x}\text{B}_x$ with $x = 12 - 28$ shows an increment in Curie temperature and reduction in saturation magnetization similar to our results³¹. This change in T_C is related to atomic rearrangements, such as short-range ordering or clustering during heating and quenching³².

Fig. 4.4 The temperature dependence of magnetizations for water quenched $(\text{Fe}_{70}\text{Ni}_{30})_1\text{B}_{1-x}$ ($x=0, 0.11, 0.15, 0.18$) at applied magnetic field 0.1 T.

Fig.4.5 shows the full cycle $M(H)$ isotherms on both side of T_C , from 100 to 600 K, which will be used to determine ΔS_M using the Maxwell relation

$$\Delta S_M = \int_0^H (\partial M / \partial T)_H dH .$$

Fig.4.6 (a) shows the $-\Delta S_M$ versus T plots for field changes (ΔH) of 1, 2, 3, 4, and 5 T. At T_C equal to 381K, $-\Delta S_M^{\text{peak}}$ increased from 0.51 to 2.1 J $\cdot\text{kg}^{-1}\text{K}^{-1}$ for field changes $\Delta H = 1$ T and $\Delta H = 5$ T, respectively.

Fig. 4.5 Magnetization isotherms obtained from temperature 100 to 600 K for a maximum applied magnetic field of 5 T. The temperature difference between two isotherms from 100 K to 300 K and from 500 K to 600 K was 10 K, while from 300 K to 500 K it was 5 K.

These curves show a symmetric peak at T_C , indicating that the paramagnetic (PM) to ferromagnetic (FM) phase transition is second-order. RCP is calculated as the product of maximum entropy change and temperature at full width of half maximum, *i.e.*, $RCP(S) = \Delta S_M \times \delta T_{FWHM}$. Because of the large δT_{FWHM} in our nanoparticles, the RCP increases from 89.8 to 640 J·kg⁻¹ for a field change ΔH equal to 1 T to 5 T, respectively. Fig.4.6 (b) shows the ' $-\Delta S_M^{peak}$ ' (left) and RCP (right) as a function of ΔH . Recently, Ucar *et al.* reported $-\Delta S_M$ and RCP values of 0.5 J·kg⁻¹ K⁻¹ and 84 J·kg⁻¹ for a γ -Fe₇₂Ni₂₈ alloy for a field change ΔH of 1.5 T²³. The $-\Delta S_M$ and RCP values of our (Fe₇₀Ni₃₀)₈₉B₁₁ nanoparticles for the same field change are 48 and 86% higher than Fe₇₂Ni₂₈. For $\Delta H = 5$ T, our RCP = 640 J·kg⁻¹ value is 36% higher than that of Fe₇₀Ni₃₀ and even larger than the benchmark magnetocaloric material, Gd₅Ge_{1.9}Si₂Fe_{0.1} (630 J·kg⁻¹)²⁸.

Fig.4.6 (a) $-\Delta S_M$ versus T for quenched $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles for ΔH ranging from 1 T to 5 T. (b) $-\Delta S_M^{\text{peak}}$ (left scale) and RCP (right scale) as a function of ΔH .

Another benchmark material, Gd, with 12 nm particle size, has a RCP of 400 $\text{J}\cdot\text{kg}^{-1}$, which is $\sim 46\%$ less than our nanoparticles with the same average size¹⁵. In addition, we have made a comparison of the magnetocaloric properties of our nanoparticles with Gd, $\text{Pr}_2\text{Fe}_{17}$, $\text{Nd}_2\text{Fe}_{17}$, $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Zr}_7\text{B}_4$ nanoparticles in table 4.1.

Table 4.1 Curie temperature (T_C), grain size, change in entropy (ΔS_M) and relative cooling power (RCP) for selected magnetocaloric nanomaterials

Nominal composition	T_C (K)	grain size (nm)	$\mu_0 H$	$ \Delta S_M \text{ J kg}^{-1} \text{ K}^{-1}$	RCP ($\text{J}\cdot\text{kg}^{-1}$)	Ref.
Gd	295	12	2	3.5	~ 180	¹⁵
Gd	295	12	5	7.2	~ 400	¹⁵
$\text{Pr}_2\text{Fe}_{17}$	290	11	1.5	~ 0.6	60	³³
$\text{Pr}_2\text{Fe}_{17}$	~ 292	20	5	4.5	573	³⁴
$\text{Nd}_2\text{Fe}_{17}$	340	11	1.5	~ 1	118	³⁵
$\text{Nd}_2\text{Fe}_{17}$	340	14	1.5	1.6	87	³⁵
$(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Zr}_7\text{B}_4$	353	20	1.5	0.7	-	²¹
$(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Zr}_7\text{B}_4$	353	20	5	~ 2.8	~ 330	²¹
$(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$	381	12	1	0.51	89.8	This work
$(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$	381	12	1.5	0.73	155	This work
$(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$	381	12	5	2.1	640	This work

It can be concluded from table 4.1 that the RCP values for FeNiB nanoparticles are higher than those of rare earth and FeNi based nanoparticles, with Curie temperature suitable for low grade waste heat recovery.

The enhanced spin disorder at the surface is common in magnetic nanoparticles when particle size decreases to the same size range as the magnetic domain size. On the other hand, surface atoms experience large anisotropy due to the broken symmetry of their surroundings, called Neel surface anisotropy. The broadening in the ΔS_M versus T curve and therefore high RCP arises from the asymmetric nature of the exchange parameter and fluctuations in the interatomic spacing due to increased spin disorder at the surface of the nanoparticles^{36,37}. For small particle size, the total magnetization $M(H) = M_{core} + M_{surface}$ suggests that $\Delta S_M = \Delta S_{core} + \Delta S_{surface}$. Xi *et al.*, Garnin *et al.* and Biasi *et al.* described in detail how surface and core contributions are different in magnetic nanoparticles³⁸⁻⁴⁰. The ΔS_M of our nanoparticles (~ 12 nm size), which can be considered as a single domain, is the sum of the change in entropy of the core (ΔS_{core}) and the change in entropy of the disordered surface ($\Delta S_{surface}$). As the particle size decreases, the surface to volume ratio of the atoms increases. In nanoparticles, M_{core} decreases while $M_{surface}$ is less dependent on T (less $\partial M_{surface} / \partial T$), resulting in moderate ΔS_M and broad δT_{FWHM} . Mathew *et al.* also found an increment in broadening (δT_{FWHM}) in the ΔS_M versus T using nanostructuring of Gd and suggested that average nanocrystallite size can be used to tune the full width and half maximum of ΔS_M ¹⁵.

Although second order transition materials (SOTM) generally exhibit lower ΔS_M^{peak} compared to first order transition materials (FOTM), their high RCP and absence of field hysteresis can make them better candidates for magnetic cooling.^{41,42} The RCP is 4/3 times the cooling capacity $q = -\int_{T_1}^{T_2} \Delta S_M(T)_{\Delta H} dT$ of the material⁴³. Cooling capacity is the heat transferred from cold end (T_1) to the hot end (T_2) in one ideal thermodynamic cycle. The Cooling power (CP), an important parameter for device applications, is directly proportional to heat absorbed per cycle (q) and operating frequency. Engelbrecht *et al.* used different model materials in a device simulation and reported that a material with a broad peak in entropy change (large δT_{FWHM}) provides significantly better cooling power than a material

with a sharp peak⁴⁴. Cooling power for material with low ΔS_M and high δT_{FWHM} is about 50% more than that of material with high ΔS_M and low δT_{FWHM} , for the same normalized fluid flow rate. Thus, for a single regenerator, our material with broad temperature distribution of MCE is more attractive than with sharp ΔS_M peaks (low δT_{FWHM}). Franco *et al.* has reviewed the RCP and ΔS_M^{peak} for first and second order transition materials, our nanoparticles exhibit ΔS_M^{peak} comparable with most rare earth free SOTM and also exhibit higher RCP.⁷ This implies that these nanoparticles could be potential candidates for low grade waste heat recovery.

4.3.3 Critical behavior of (Fe₇₀Ni₃₀)₈₉B₁₁ nanoparticles

4.3.3.1 Arrott plots

To understand the MCE, the nature of the magnetic phase transition responsible for the MCE needs to be determined. $M(H)$ isotherms for quenched nanoparticles were measured around T_C at each 2 K interval from 364 to 400 K (fig.4.7 (a)). According to the Banerjee criteria, the order of the magnetic phase transition can be determined from the slope of the Arrott plot, M^2 versus H/M . A negative (positive) slope of the Arrott plot suggests that the magnetic phase transition is first (second) order⁴⁵. Fig.4.7 (b) shows M^2 versus H/M curves for (Fe₇₀Ni₃₀)₈₉B₁₁ nanoparticles. The nanoparticles exhibit a positive slope, indicating that the PM-FM phase transition is second order. However, all curves of the Arrott plots exhibit non parallel behavior, even at high magnetic fields.

This indicates that the Arrott-Noakes equation⁴⁶ of state, i.e., $(H/M)^{1/\gamma} = (T - T_C)/T_C + (M/M_I)^\beta$, where M_I is a materials constant, is not satisfied with critical exponents $\gamma = 1$ and $\beta = 0.5$. Generally, second order magnetic phase transition materials show straight parallel curves in the Arrott plot when spontaneous magnetization occurs due to long range ordering. In our case, however, the nonparallel nature of Arrott plots results the existence of inhomogeneous magnetic phases and short range order near T_C .

Fig.4.7 (a) $M(H)$ isotherms around T_C (b) Arrott plot (Mean-field model) (c) 3D-Ising model (d) 3D-Heisenberg model (e) Triclinic mean field model and (f) Relative slope (RS) as a function of temperature.

The critical behavior and nature of transition for our materials could be explained by the modified Arrott plot, as proposed by Noakes. In the high magnetic field region, the effect of charge, lattice, and orbital degrees of freedom are suppressed in a ferromagnet and the order parameter can be identified with macroscopic magnetization⁴⁷. Three models, i.e., 3D-Heisenberg model ($\beta = 0.365$, $\gamma = 1.336$), 3D Ising model ($\beta = 0.325$, $\gamma = 1.24$) and the tricritical mean field model ($\beta = 0.25$, $\gamma = 1.00$) were used to obtain experimental β and γ values (fig. 4.7 (c, d and e)). To find the best model, the relative slopes (RS) of the straight lines, $RS = S(T)/S(T_C)$ were calculated. Fig.4.7 (f) shows the RS versus T plots for all three models. The value of RS for the tricritical and 3D-Ising models deviate from 1, while for the 3D-Heisenberg model it is much closer to 1. Therefore, the critical

properties (β , and γ) and T_C of the $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles were calculated on the basis of the 3D-Heisenberg model.

4.3.3.2 Determination of critical exponents β , γ , δ and α

Linear extrapolation from high fields to the intercept with the axis $(H/M)^{1/\gamma}$, for $T > T_C$ and $M^{1/\beta}$ for $T < T_C$, yields the spontaneous magnetization ($M_s(T, 0)$) and the inverse magnetic susceptibility ($\chi^{-1}(T, 0)$). The critical exponents and T_C can be accurately determined from the Kouvel-Fisher (KF) method⁴⁸ equations given in chapter 3. According to this method $M_s(dM_s/dT)^{-1}$ versus T and $\chi_0^{-1}(d\chi^{-1}/dT)^{-1}$ versus T should show straight lines with slope $1/\beta$ and $1/\gamma$, respectively. The value of T_C can be determined by extrapolation of these straight lines to the ordinate equal to zero on the T axis. Experimental data were fit with the Kouvel-Fisher method, yielding exponents $\beta = 0.364$ with $T_C = 380.96\text{K}$ and $\gamma = 1.319$ with $T_C = 381.32\text{K}$ (fig.4.8 (a)). These values of critical exponents are in good agreement with the 3D-Heisenberg model.

The third critical exponent δ can be experimentally determined from the $M(H)$ at T_C (fig.4.8 (b)). The slope ($1/\delta$) of $\ln(M)$ versus $\ln(H)$ plot (the inset of fig.4.8 (b)) yields $\delta = 4.60$. This exponent δ can also be determined by Widom's scaling relation⁴⁹ $\delta = 1 + (\gamma/\beta)$, which results in a δ value of 4.623. This value is close to our experiment value, implying that the critical exponents β and γ values are reliable. The critical behavior near T_C was also verified by the universal scaling hypothesis. In the critical region, the magnetic equation of state⁵⁰ can be written as $m = f_{\pm}(h)$, where m is the scaled magnetization, $m = |\varepsilon|^{-\beta} M(H, \varepsilon)$, h is the scaled field $h = |\varepsilon|^{-\beta\delta} H$ and ε is the reduced temperature $(T - T_C)/T_C$. Eq.(4) implies that m as a function of h yields two universal curves: $f_+(h)$ for $T > T_C$ and $f_-(h)$ for $T < T_C$. The isothermal magnetization around T_C is plotted (fig.4.8 (c)) as a prediction of the scaling theory. The experimental data fall on two curves, below and above T_C . The inset of fig.4.8 (c) plotted on the log-log scale shows that all the points

collapse into two universal curves. This indicates that our critical exponents and T_C are reliable and best match the 3D-Heisenberg model.

Fig.4.8 (a) Kouvel-Fisher (KF) plot for M_s , $(dM_s/dT)^{-1}$ (left) and χ_0^{-1} , $(d\chi_0^{-1}/dT)^{-1}$ (right) versus T . (b) $M(H)$ at $T_c = 381$ K, inset shows $\ln M$ versus $\ln H$. (c) Scaling plots of $M(H)$ isotherms above and below T_c , using β and γ from the KF equations. Inset of (c) shows the same plot in log-log scale.

A fourth critical exponent (α), which is correlated to specific heat (C_H) and MCE (change in adiabatic temperature $\Delta T \propto 1/C_H$) can be defined by the homogeneous function approach: $\alpha = 2 - 2\beta - \gamma$, which yields $\alpha = -0.055$. For a

negative value of α and a second order phase transition, short range disorder should not affect the sharpness of the transition while long range disorder will smear the transition. The experimental critical parameters for some materials and for theoretical models are listed in Table 2. Most of the alloys reveal short range ferromagnetic disordered interactions with critical exponents near the 3D-Heisenberg model (table 4.2).

Table 4.2 Experimental values of the critical exponents of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$, results from theoretical models as well as critical exponents of other related ferromagnets.

Material/Model (Method)	α	β	γ	δ	Ref.
$(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ (KF)	-0.055	0.364	1.319	4.623	This work
3D-Heisenberg	-0.115	0.365	1.336	4.8	50
Mean-field theory	0.0	0.5	1.0	3.0	50
3D-Ising	0.11	0.325	1.241	4.82	50
Tricritical mean field	0.5	0.25	1	5	22
$\text{Fe}_{90}\text{Zr}_{10}$ (KF)	-	0.368	1.612	5.32	51
$\text{Fe}_{85}\text{Ni}_5\text{Zr}_{10}$ (KF)	-	0.425	1.323	4.11	51
$\text{Fe}_{77}\text{Co}_{5.5}\text{Ni}_{5.5}\text{Zr}_7\text{B}_4\text{Cu}$ (KF)	-	0.53	1.34	3.5	19
$\text{Fe}_{89.5}\text{Zr}_{10.5}$ (KF)	-0.93	0.47	2.0	5.31	52
$\text{Fe}_{88}\text{Zr}_8\text{B}_4$ (MAP)	-	0.39	1.38	-	53
$\text{Er}_2\text{Fe}_{17}$ (MAP)	-0.59	0.42	1.74	5.1	35
Fe	-0.11	0.389	1.333	4.35	50
Ni	-0.10	0.378	1.34	4.58	54
Co	-0.095	0.435	1.225	3.35	50
Gd	0.04	0.381	1.196	3.615	50

* KF : Kouvel-Fisher method, MAP : Modified Arrott plots.

Nevertheless, some alloys such as $\text{Fe}_{77}\text{Co}_{5.5}\text{Ni}_{5.5}\text{Zr}_7\text{B}_4\text{Cu}$, $\text{Fe}_{85}\text{Ni}_5\text{Zr}_{10}$ and $\text{Fe}_{89.5}\text{Zr}_{10.5}$ exhibit coexistence of short and long range interactions as the β value deviated from both of 3D-Heisenberg and mean field model^{19,51,52}.

4.3.3.3 Field dependence of $\Delta S_M(n)$ and RCP (N)

The mean field approach on the field dependence of the magnetic entropy change at T_C yields a prediction of $n = 2/3$. In the case of our material, which does not follow the mean field model, the field dependence of ΔS_M and RCP has been

obtained from the Arrott Noakes equation of state. Moreover, insight into the magnetocaloric properties with applied magnetic field can be obtained from finding out which of the theoretical models matches the experimental observations. The mean field model, 3D-Heisenberg model, 3D-Ising model and tricritical mean field model yield n equal to 0.66, 0.68, 0.57 and 0.4, respectively. Fig. 4.9 shows the field dependence of the ΔS_M and RCP, which is measured by a linear fit of the values of ΔS_M and RCP for different fields on the ln-ln scale. The field dependence of RCP ($RCP \propto H^N$) i.e., the value of $N=1.215$ calculated from the linear fit of experimental data agrees very well with the value obtained from the critical exponents using the 3D-Heisenberg model ($N=1.216$).

Fig.4.9 Field dependence of change in entropy ΔS_M^{peak} (left scale) and relative cooling power RCP (right scale) in ln-ln scale

However, the value of n obtained from the slope of ΔS_M versus ΔH is 0.875, which is somewhat higher than that obtained from the critical exponents (0.62) and does not match any of the models. $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Cr}_{0.1}\text{O}_3$ and $\text{La}_{0.6}\text{Nd}_{0.4}(\text{CaSr})_{0.3}\text{Mn}_{0.9}\text{V}_{0.1}\text{O}_3$ also exhibit higher values of n from the slope of

ΔS_M versus ΔH than those obtained from the modified Arrott plot^{55,56}. The values of ΔS_M and RCP depend not only on n and N but also on the proportionality factor (Eq.13). Large value of N (*i.e.*, small δ) favors large RCP, but in our material it is expected that proportionality factor between RCP, and H , which depends on the other critical exponents, dominates. These critical exponents depend on the dimensionality of the material, the number of components, and the range of microscopic interactions⁵⁷

4.4 Conclusions

The magnetocaloric properties and critical behavior of FeNiB nanoparticles, with a Curie temperature suitable for low grade waste heat recovery was investigated. $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles possessing a fcc crystal structure and an average particle size of 12 nm were synthesized *via* ball milling. We find very high relative cooling power (RCP) of $640 \text{ J}\cdot\text{kg}^{-1}$ for $\Delta H = 5 \text{ T}$ in $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles. These values of RCP are larger than those of giant magnetocaloric materials. Absence of field hysteresis and broad $-\Delta S_M$ versus T behavior are added advantages of this material. We evaluated the critical exponents ($\alpha, \beta, \gamma, \delta$) through the modified Arrott plot and the Kouvel-Fisher plot. Our experimental results agreed well with the 3D-Heisenberg model. The field dependence of the RCP shows a $H^{1+1/\delta}$ dependence with the critical exponent δ value measured from 3D-Heisenberg model. Broad operating temperature range along with moderate change in entropy and very high RCP make these nanoparticles potential candidates for magnetic cooling applications. Moreover, these finding can be used as a point of reference for understanding the MCE and critical behavior of FeNiB nanoparticles.

References

- ¹ S. W. Lee, Y. Yang, H. W. Lee, H. Ghasemi, D. Kraemer, G. Chen, and Y. Cui, Nat Commun **5**, 3942 (2014).

- ² L. D. Zhao, S. H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, and M. G. Kanatzidis, *Nature* **508**, 373 (2014).
- ³ S. Chu and A. Majumdar, *Nature* **488**, 294 (2012).
- ⁴ X. Moya, S. Kar-Narayan, and N. D. Mathur, *Nat Mater* **13**, 439 (2014).
- ⁵ O. Gutfleisch, M. A. Willard, E. Brück, C. H. Chen, S. G. Sankar, and J. P. Liu, *Advanced Materials* **23**, 821 (2011).
- ⁶ V. Franco, J. S. Blázquez, B. Ingale, and A. Conde, *Annual Review of Materials Research* **42**, 305 (2012).
- ⁷ J. Y. Law, Thesis, Nanyang Technological University Singapore, 2012.
- ⁸ J. Y. Law, V. Franco, and R. V. Ramanujan, *Applied Physics Letters* **98**, 192503 (2011).
- ⁹ M. H. Phan and S.-C. Yu, *Journal of Magnetism and Magnetic Materials* **308**, 325 (2007).
- ¹⁰ J. Y. Law, V. Franco, and R. V. Ramanujan, *Journal of Applied Physics* **111**, 3919 (2012).
- ¹¹ V. K. Pecharsky and J. K. A. Gschneidner, *Physical Review Letters* **78**, 4494 (1997).
- ¹² Q. Zhang, B. Li, X. G. Zhao, and Z. D. Zhang, *Journal of Applied Physics* **105**, 053902 (2009).
- ¹³ L. H. Lewis, M. H. Yu, and R. J. Gambino, *Applied Physics Letters* **83**, 515 (2003).
- ¹⁴ R. C. Flores, V. Franco, A. Conde, K. E. Knipling, and M. A. Willard, *Applied Physics Letters* **98** (2011).
- ¹⁵ S. P. Mathew and S. N. Kaul, *Applied Physics Letters* **98**, 2505 (2011).
- ¹⁶ H. Ucar, J. J. Ipus, M. E. McHenry, and D. E. Laughlin, *Journal of Metals* **64**, 782 (2012).
- ¹⁷ R. E. Rosensweig, *International Journal of Refrigeration* **29**, 1250 (2006).
- ¹⁸ K. Raj and R. Moskowitz, (Google Patents, 1995).
- ¹⁹ V. Franco, R. Caballero-Flores, A. Conde, K. E. Knipling, and M. A. Willard, *Journal of Applied Physics* **109**, 07A905 (2011).

- ²⁰ V. Franco, J. S. Blazquez, and A. Conde, *Applied Physics Letters* **89**, 2512 (2006).
- ²¹ J. J. Ipus, H. Ucar, and M. E. McHenry, *IEEE Transactions on Magnetics* **47**, 2494 (2011).
- ²² K. Huang, (Wiley, New York, , 1987).
- ²³ H. Ucar, J. J. Ipus, D. E. Laughlin, and M. E. McHenry, *Journal of Applied Physics* **113**, 17A918 (2013).
- ²⁴ P. Dutta, A. Manivannan, M. S. Seehra, N. Shah, and G. P. Huffman, *Physical Review B* **70**, 174428 (2004).
- ²⁵ R. E. Rosenweing, *Ferrohydrodynamics* (Cambridge University Press, 1985).
- ²⁶ L. J. Swartzendruber, V. P. Itkin, and C. B. Alcock, *Journal of Phase Equilibria* **12**, 288 (1991).
- ²⁷ L. M. Moreno, J. S. Blázquez, J. J. Ipus, J. M. Borrego, V. Franco, and A. Conde, *Journal of Applied Physics* **115**, 17A302 (2014).
- ²⁸ V. Provenzano, A. J. Shapiro, R. D. Shull, *Nature* **429**, 853 (2004)
- ²⁹ V. Dolocan and E. Dolocan, *J. Phys. III France* **2**, 915 (1992).
- ³⁰ N. S. Kazama, T. Masumoto, and M. Mitera, *Journal of Magnetism and Magnetic Materials* **15–18, Part 3**, 1331 (1980).
- ³¹ R. Hasegawa and R. Ray, *Journal of Applied Physics* **49**, 4174 (1978).
- ³² M. R. Gallas and J. A. H. d. Jornada, *Journal of Physics: Condensed Matter* **3**, 155 (1991).
- ³³ C. F. S. Valdés, P. J. I. Gaytán, J. L. S. Llamazares, M. Á. Borja, P. Á. Alonso, P. Gorria, and J. A. Blanco, *Applied Physics Letters* **104**, 212401 (2014).
- ³⁴ G. Pedro, L. S. L. José, Á. Pablo, P. M. José, M. J. Sánchez, and A. B. Jesús, *Journal of Physics D: Applied Physics* **41**, 192003 (2008).
- ³⁵ Á. Pablo, G. Pedro, F. Victorino, M. J. Sánchez, J. P. María, L. S. L. José, O. Inés Puente, and A. B. Jesús, *Journal of Physics: Condensed Matter* **22**, 216005 (2010).
- ³⁶ N. J. Jones, H. Ucar, J. J. Ipus, M. E. McHenry, and D. E. Laughlin, *Journal of Applied Physics* **111**, 07A334 (2012).

- ³⁷ V. Chaudhary and R. V. Ramanujan, MRS Online Proceedings Library **1708**, vv10 (2014).
- ³⁸ S. B. Xi, W. J. Lu, H. Y. Wu, P. Tong, and Y. P. Sun, Journal of Applied Physics **112**, 123903 (2012).
- ³⁹ D. A. Garanin and H. Kachkachi, Physical Review Letters **90**, 065504 (2003).
- ⁴⁰ E. De Biasi, C. A. Ramos, R. D. Zysler, and H. Romero, Physical Review B **65**, 144416 (2002).
- ⁴¹ C. M. Bonilla, J. H. Albillos, F. Bartolomé, L. M. García, M. P. Borderías, and V. Franco, Physical Review B **81**, 224424 (2010).
- ⁴² V. Pecharsky and K. Gschneidner Jr, Journal of Applied Physics **90**, 4614 (2001).
- ⁴³ A. M. Tishin, Spichkin, Y. I. , *The Magnetocaloric Effect and its Applications* (Bristol: Institute of Physics Publishing, 2003).
- ⁴⁴ K. Engelbrecht and C. R. H. Bahl, Journal of Applied Physics **108**, 123918 (2010).
- ⁴⁵ B. K. Banerjee, Physics Letters **12**, 16 (1964).
- ⁴⁶ A. Arrott and J. E. Noakes, Physical Review Letters **19**, 786 (1967).
- ⁴⁷ J. Fan, L. Ling, B. Hong, L. Zhang, L. Pi, and Y. Zhang, Physical Review B **81**, 144426 (2010).
- ⁴⁸ J. S. Kouvel and M. E. Fisher, Physical Review **136**, A1626 (1964).
- ⁴⁹ L. P. Kadanoff, Physics **2**, 263 (1966).
- ⁵⁰ S. N. Kaul, Journal of Magnetism and Magnetic Materials **53**, 5 (1985).
- ⁵¹ T. D. Thanh, N. Huy Dan, T. L. Phan, H. Kumarakuru, E. J. Olivier, J. H. Neethling, and S. C. Yu, Journal of Applied Physics **115**, 023903 (2014).
- ⁵² K. Witschuh and M. Rosenberg, Journal of Applied Physics **61**, 4401 (1987).
- ⁵³ P. Álvarez, J. S. Marcos, P. Gorria, L. F. Barquín, and J. A. Blanco, Journal of Alloys and Compounds **504**, S150 (2010).
- ⁵⁴ G. Böhnke, S. N. Kaul, W. Kettler, and M. Rosenberg, Solid State Communications **48**, 743 (1983).

- ⁵⁵ P. Nisha, S. S. Pillai, M. R. Varma, and K. G. Suresh, *Solid State Sciences* **14**, 40 (2012).
- ⁵⁶ A. Dhahri, F. I. H. Rhouma, S. Mnefui, J. Dhahri, and E. K. Hlil, *Ceramics International* **40**, 459 (2014).
- ⁵⁷ R. K. Pathria, B. D. Beale, *Statistical Mechanics* (Butterworth Heinemann publications, 2011).

Chapter 5*

Magnetocaloric Effect of FeNiMn Nanoparticles

In this chapter, we investigated the magnetocaloric properties of $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mn}_x$ with $x = 5, 8, 11$. The alloying of FeNi with Mn and fcc (γ) phase stabilization results in a shift of Curie temperature to near room temperature. $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ was chosen to examine the phase stability by in situ XRD. The MCE were measured before and after γ -phase stabilization. It was shown that quenching is required for γ -phase stabilization. Our results demonstrate the feasibility of developing high RCP, low cost, rare earth free Fe-Ni-Mn magnetocaloric nanoparticles for near room temperature applications.

*This section published substantially as references:

1. V. Chaudhary, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, IEEE Magnetics Letters **5**, 6800104 (2014).
2. V. Chaudhary and R. V. Ramanujan, Journal of Physics D: Applied Physics **48**, 305003 (2015).

5.1 Introduction

FeNi¹ and FeNi based alloys, such as Fe-Ni-Mo², Fe-Ni-Zr-B³, Fe-Ni-B,⁴ are affordable magnetocaloric materials. Stabilization of the fcc γ -FeNi phase at room temperature with reasonable magnetization values as well as tuning T_C to near room temperature are challenges.⁵ Alloying by Mn in Fe₇₀Ni₃₀ results in lowering the T_C to near room temperature and broadening of the magnetic entropy vs temperature curve, yielding high RCP. It was reported that superparamagnetic SOTM in nanoparticle form shows high RCP compared to bulk materials.⁶⁻⁸ Nanoparticles exhibit additional advantages, e.g., they can be dispersed in a suitable liquid and used as a ferrofluid. Ferrofluid based self-pumping has a wide range of applications, e.g., cooling of microelectronic and power electronics devices.⁹

The magnetocaloric effect is most pronounced in the vicinity of T_C . Hence, critical behavior studies were undertaken to understand the magnetic phase transition mechanism, magnetocaloric behavior and the nature of ordering in the vicinity of T_C . Previous critical behavior studies on Fe based materials suggest that magnetic order strongly depends on composition. For example, Fe₈₅Ni₅Zr₁₀¹⁰, Fe₇₇Co_{5.5}Ni_{5.5}Zr₇B₄Cu¹¹, and (Fe_{0.74}Cu_{0.26})₈₅Zr₁₅¹² alloys exhibit coexistence of short and long range order, while other alloys e.g., (Fe₇₀Ni₃₀)₈₉B₁₁⁴ and Fe₉₀Zr₁₀¹⁰ show only short range interactions near the transition temperature. The critical exponents depend on the dimensionality of the system, nature of nearest neighbor atoms, symmetry of the materials, number of components, and range of microscopic interactions.¹³ The critical exponents (β , γ and δ) are related to the MCE by power laws: $\Delta S_M \propto H^{1+[(\beta-1)/(\beta+\gamma)]}$ and $RCP \propto H^{(1+1/\delta)}$.¹⁴ Therefore, we studied the critical behavior of γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles around T_C using modified Arrott plots¹⁵ and Kouvel-Fisher methods.¹⁶

We report the synthesis, structural and magnetic phase transition, magnetocaloric properties and critical behavior of FeNiMn nanoparticles. Critical exponent analysis for γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles was performed; the field dependence of RCP was experimentally measured and also theoretically modeled. It was found that our nanoparticles are attractive candidates for near room

temperature magnetic cooling (T_C of the γ -phase ~ 317 K, 338 and 340) and low grade waste heat recovery applications (T_C of the α -phase ~ 380 K).

5.2 Experimental details

Alloys of $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mn}_x$ with $x = 5, 8, 11$ were produced by high speed ball milling (FRITSCH, Pulverisette 7, premium line). Elemental Fe (99.99%, Sigma Aldrich), Ni (99.998%, Fisher ChemAlert Guide) and Mn (99.95%, Alfa Aesar) powders were mixed and sealed in a vial under Ar gas atmosphere^{7,17}. To prevent cold welding, a small quantity of ethanol was also added in the material mixture. The ball to powder ratio was 10:1. The vials and balls were made of zirconium oxide, and the volume of the vial was 125 ml, which contains 15 balls (10 mm in diameter). The magnetic nanoparticles were sealed under high vacuum (10^{-5} torr) in a quartz tube. The sealed tube was heated at 700°C (fcc γ - phase region) for 2h and quenched in water. The structure and phase were determined by X-ray diffraction (XRD) using Bruker D8 Advance diffractometer ($\text{CuK}\alpha$ radiation). In addition, as milled $\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ sample was investigated by in-situ high temperature X-ray diffraction (XRD) using a SIEMENS diffractometer in the scan range (2θ) from 20° to 80° and step size of 0.05° . The composition was confirmed by energy dispersive X-ray spectroscopy using a JEOL JSM-7600F scanning electron microscope. To determine the particle size and morphology, transmission electron microscopy (TEM) was carried out on a JEOL 2010 TEM with an operating voltage of 200 kV. The magnetic properties were measured using the physical property measuring system (PPMS) (EverCool-II, Quantum Design).

5.3 Results and discussion

5.3.1 In-situ XRD: $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ nanoparticles

Fig.5.1 shows the in-situ high temperature XRD patterns, during heating and cooling, of $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ at temperatures of 300 K (RT), 573 K, 773 K and 973 K. Rietveld refinement of these patterns showed that, at RT the sample consists the

body centered cubic (bcc) α -FeNiMn phase with lattice parameters (a) = 2.9302 Å, unit cell volume (v) = 25.1693 Å³ and space group Im-3m. As the temperature increased from room temperature to 573 K, the formation of the face centered cubic (fcc) γ -FeNiMn with space group Fm-3m was observed.

Fig.5.1 X-ray diffraction patterns of $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ recorded at temperatures between room temperature and 973K during heating ($\uparrow$) and cooling ($\downarrow$). The star (*) is showing an impurity of spinel phase. (b) Selected diffraction peaks (bcc, 110 and fcc, 111) in “ 2θ ” range 40 to 45° , inset shows the bright field transmission electron micrograph for as milled sample.

Selected diffraction peaks (bcc, 110 and fcc, 111) in the “2 θ ” range of 40 to 45° (fig.5.1 (b)) show the change from the bcc to the fcc crystal structure. The shift of the main diffraction peak of fcc phase (111) to lower “2 θ ” values indicates that the unit cell parameters (unit cell volume) increased from 3.7025 Å (50.7557 Å³) to 3.7140 Å (51.2302 Å³) when the temperature was raised from 573 K to 973 K.

During cooling, the diffraction peak shifted to higher “2 θ ” values, indicating that the unit cell parameters (unit cell volume) contracted from 3.7025 Å (50.7557 Å³) to 3.6822 Å (49.9255 Å³) when the temperature was reduced from 973 K to RT. The crystallite size of the α - and γ -FeNiMn phase, calculated by Scherrer’s equation, was ~13 nm and 25 nm, respectively. The inset of fig. 5.1 (b) shows the bright field transmission electron micrograph of as milled (Fe₇₀Ni₃₀)₉₂Mn₈ at RT (for α -FeNiMn). The particle size is in the range of 4 nm to 20 nm, with an average size of 12 nm, close to the value obtained from XRD data at room temperature. The maximum particle size d is less than $(6kT/\pi MH)^{1/3}$ (ratio of thermal and magnetic energy),⁹ implying that our average size is suitable for making ferrofluids for self-pumping applications.

5.3.2 XRD: (Fe₇₀Ni₃₀)₉₅Mn₅, (Fe₇₀Ni₃₀)₉₂Mn₈ and (Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles

Fig.5.2 (a) shows the room temperature XRD patterns of (Fe₇₀Ni₃₀)₉₅Mn₅, (Fe₇₀Ni₃₀)₉₂Mn₈ and (Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles after water quenching. All the samples exhibit pure γ -FeNiMn phase. The average crystalline size, calculated by the Scherrer’s formula, was ~14 nm, ~13 nm and 11 nm for (Fe₇₀Ni₃₀)₉₅Mn₅, (Fe₇₀Ni₃₀)₉₂Mn₈ and (Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles, respectively¹⁸.

Fig.5.2 XRD patterns of $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$, $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ and $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Mn}_{11}$ nanoparticles after annealing at 700 °C for 2 h and then quenching in water.

5.3.3 Curie temperature, change in entropy, relative cooling power: $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ Nanoparticles

Fig.5.3 (a) shows the temperature dependence from 10 K to 400 K of magnetization, $M(T)$ of $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ nanoparticles, with and without quenching, under a field of 0.1 T. The transition temperature of the as milled sample was above 400 K, whereas the quenched sample shows $T_C = 338$ K, as determined from the minima of the plot of dM/dT versus T (inset of fig.5.3 (a)). Our T_C value is lower than that obtained from the Fe-Ni phase diagram⁵. This change in T_C is due to the change in exchange energy interactions due to the addition of Mn and by quenching. Recently, Moreno *et. al.* also reported a large reduction in T_C of $\text{Co}_{62}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ by quenching¹⁹. Fig.5.3 (b) shows the field dependence of magnetization $M(H)$ for as milled and quenched $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ nanoparticles at room temperature ($T = 300$ K).

Fig. 5.3 (a) The temperature dependence of magnetization for as milled (black square) and after water quenching (red circle) of $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ nanoparticles at applied magnetic field 0.1 T. Inset a) shows dM/dT versus T plot for quenched sample, (b) Isothermal magnetization M at 300 K for as milled and quenched $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ nanoparticles. The inset of (b) is the zoom portion to show the hysteresis.

Both the samples exhibit ferromagnetic behavior with small hysteresis (coercivity < 100 Oe). The low field hysteresis in $M(H)$ is a great advantage for efficient magnetic cooling, since it permits high cycle frequency of operation^{20,21}.

Fig. 5.4 (a) shows the magnetic isothermal curves (M - H curves) which were used to determine the magnetic entropy change (ΔS_M) with the help of the Maxwell relation; $\Delta S_M = \int_0^H (\partial M / \partial T)_H dH$. The nature of magnetic transitions can be determined by the Banerjee criterion²², plotting H/M versus M^2 curves around T_C . The slope of the resulting curves indicates whether the transition is first order or second order. We found a positive slope of H/M versus M^2 curves, denoting second order behavior.

Fig. 5.4 (a) Magnetization isotherms for a maximum applied magnetic field 5 T, (b) Magnetic entropy changes for quenched $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ nanoparticles as a function of temperature for different field

Fig. 5.4 (b) shows the magnetic entropy change ($-\Delta S_M$) for the quenched samples as a function of temperature under different magnetic fields (0.5 T to 5 T). As expected, the magnitude of entropy change is larger around the ferromagnetic to paramagnetic (FM-PM) transition temperature. This is because of the continuous decrease in magnetization close to the FM-PM transition in second-order phase

transitions. The $-\Delta S_M$ versus T curves are approximately symmetric near T_C but the peak shape is diffuse. The maximum entropy change ($-\Delta S_M^{\max}$) increases from 0.20 J·kg⁻¹ K⁻¹ for a field of 0.5 T to 1.45 J·kg⁻¹ K⁻¹ for 5 T field near room temperature (338 K).

Giant magnetocaloric materials exhibit higher change in entropy near the PM-FM transition temperature. However, these materials only exhibit entropy change in a narrow temperature range. For practical magnetic cooling systems, both ΔS_M and the temperature range over which the system can operate are important. The RCP of (Fe₇₀Ni₃₀)₉₅Mn₅ nanoparticles increases from 26 to 470 J·kg⁻¹ for field change of $\Delta H = 0.5$ T and $\Delta H = 5$ T, respectively. Fig. 5.5 shows $\Delta S_M^{\max}$ (left) and RCP (right) as a function of applied magnetic field. The insets (a and b) of fig 5.5 show the field dependence of ΔS_M and RCP, measured by a linear fit of the values of ΔS_M and RCP for different fields. The field dependence of RCP ($RCP \propto H^N$) and change in entropy ($\Delta S_M \propto H^n$) show that the value of N and n are 1.245 and 0.861, respectively.

Fig. 5.5 Variation of $\Delta S_M^{\max}$ (left scale) and RCP (right scale) as a function of ΔH . Insets (a and b) depicts the same graphs in Log-Log scale, respectively.

For further information on the field dependence of RCP, the critical exponent δ was determined experimentally by fitting the isotherm $M(H)$ at T_C using the scaling relation $M = D H^{1/\delta}$, where D is the critical amplitude (fig.5.6). Linear fitting of $\ln(M)$ versus $\ln(H)$ plot (inset of fig.5.6) yields a straight line with a slope of $1/\delta$ when $\mu_0 H > 0.5$ T. The critical exponent δ was found to be 4.34.

Fig. 5.6 $M(H)$ magnetic isotherm at $T_C = 338$ K, inset shows $\ln(M)$ versus $\ln(H)$ with $H > 0.5$ T.

Both the N values, *i.e.*, those calculated from the Arrott-Noakes equation of state and from linear fitting of RCP versus ΔH are very close to each other, demonstrating that the N value is reliable. The high RCP, absence of field hysteresis and low cost make these materials attractive candidates for near room temperature magnetic cooling applications.

5.3.4 Curie temperature, change in entropy, relative cooling power: $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ Nanoparticles

Our *in-situ* XRD results were supported by the magnetization (M) versus temperature (T) results shown in fig 5.7. During heating, T_C of 380 K was observed, corresponding to the bcc α -($\text{Fe}_{70}\text{Ni}_{30}$) $_{92}\text{Mn}_8$ phase. T_C shifted to a lower temperature

of 340 K during cooling, corresponding to the T_C of the fcc γ -(Fe₇₀Ni₃₀)₉₂Mn₈ phase. Interestingly, if the measurement was repeated in heating mode, the M - T curve follows the same path as that of cooling, indicating stabilization of the fcc structure. However, this value of T_C of γ -(Fe₇₀Ni₃₀)₉₂Mn₈ (~340 K) is almost equal to the T_C of γ -(Fe₇₀Ni₃₀)₉₅Mn₅ (~338 K, measured in section 5.3.3) which was quenched in water. Why did alloying of Mn of 5% and 8% resulting in approximately the same T_C ? The γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles were just annealed unlike the water quenched of γ -(Fe₇₀Ni₃₀)₉₅Mn₅. To check this point, we sealed as milled (Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles in a quartz tube with high vacuum (10^{-5} torr) followed by annealing at 700 °C for 2h and quenching in water. The magnetometry measurement for water quenched (Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles, shown in fig 5.6 (b) results in T_C of 317 °C, close to room temperature.

Fig. 5.7 (a) Magnetization as a function of temperature for as milled sample at a magnetic field of 0.1 T in the temperature range from RT to 973 K in three modes; during heating (black circle), cooling (red square) and again heating (blue triangle). The inset of (a) is dM/dT versus T plot during heating and cooling. (b) Magnetization as a function of temperature for quenched sample at a magnetic field of 0.1 T in the temperature range from 10 K to 400 K. The inset of b is dM/dT versus T plot during heating and cooling.

Therefore, quenching is necessary for stabilization of the γ -phase. The coexistence of exchange interactions $J_{NiNi} > 0$, $J_{NiFe} > 0$, $J_{FeFe} < 0$, $J_{NiMn} > 0$, $J_{FeMn} < 0$, and $J_{MnMn} < 0$ in the γ -FeNiMn phase will result a lower Curie temperature

compared to the γ -FeNi phase.²³ This can be understood by the mean field model: $T_C = J(r)_{eff} Z_T S (S+1) / 3k_B$, where $J(r)_{eff}$ is the effective exchange interaction, Z_T is the coordination number, S is the atomic spin quantum number and k_B is Boltzmann's constant. When the magnitude of J_{MnMn} is larger than the values of J_{FeMn} and J_{NiMn} , the effective exchange interaction $J(r)_{eff}$ will decrease, leading to lower T_C .²⁴ Lara et al. calculated the exchange interaction parameters for $(Fe_{65}Ni_{35})_{1-x}Mn_x$ alloy using a random bond Blume-Caple model with the values $J_{NiNi} = 17.01$ meV, $J_{NiFe} = 5.92$ meV, $J_{FeFe} = -2.05$ meV, $J_{NiMn} = -4.32$ meV, $J_{FeMn} = -4.63$ meV, and $J_{MnMn} = -10.42$ meV.²⁵ The large antiferromagnetic character of the Fe-Fe bond in γ -phase results in lower saturation magnetization and Curie temperature than that of the α -phase.²⁶

Fig.5.8 (a) and (b) show the isothermal curves of the temperature dependence of magnetization $M(H, T)$ for α -(Fe₇₀Ni₃₀)₉₂Mn₈ and γ -(Fe₇₀Ni₃₀)₉₂Mn₈, respectively. The absence of magnetic hysteresis in the forward and backward field sweeps of the $M(H)$ isotherms is a great advantage for the efficient magnetic cooling system.²⁷ Fig.5.8 (c) and (d) show the “ $-\Delta S_m$ ” vs T plot for α -(Fe₇₀Ni₃₀)₉₂Mn₈ and γ -(Fe₇₀Ni₃₀)₉₂Mn₈, respectively, determined by the Maxwell relation for ΔH in the range of 1 to 5 T. In both cases, the symmetric nature and coincidence of peak temperatures for all fields suggest that ferromagnetic (FM) to paramagnetic (PM) phase transition is second order. The $-\Delta S_m$ for α -(Fe₇₀Ni₃₀)₉₂Mn₈ increases from 0.32 J·kg⁻¹ K⁻¹ (for a field of 1 T) to 1.57 J·K⁻¹ K⁻¹ (for 5 T) at 380 K. For γ -(Fe₇₀Ni₃₀)₉₂Mn₈, $-\Delta S_m$ increases from 0.41 J·kg⁻¹ K⁻¹ (for a field of 1 T) to 1.67 J·K⁻¹ K⁻¹ (for 5 T) at 340 K. The RCP is an important parameter which quantifies the magnitude of the heat extracted in a thermodynamic cycle.²⁸ The RCP for α -(Fe₇₀Ni₃₀)₉₂Mn₈ and γ -(Fe₇₀Ni₃₀)₉₂Mn₈ increased from 83 J·kg⁻¹ to 507 J·kg⁻¹ and from 78 J·kg⁻¹ to 466 J·kg⁻¹, respectively, as the field increases from $\Delta H = 1$ T to $\Delta H = 5$ T.

Fig.5.9 (a) and (b) show the isothermal curves of the temperature dependence of magnetization $M(H, T)$ and the “ $-\Delta S_m$ ” vs T plot for quenched γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles, respectively.

Fig. 5.8 Magnetization isotherms $M(H)$ obtained for a maximum applied magnetic field of 5 T (a) from 10 to 570 K for the α - phase, (b) from 10 to 500 K for the γ - phase. Magnetic entropy change as a function of temperature for a range of magnetic field from 1 T to 5 T (c) for γ -FeNiMn and (d) α -FeNiMn nanoparticles.

Fig. 5.9 (a) Magnetization isotherms $M(H)$ obtained for a maximum applied magnetic field of 5 T from 100 to 400 K for the quenched γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles (b) Magnetic entropy change as a function of temperature for a range of magnetic field from 1 T to 5 T for quenched γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles.

The $-\Delta S_m$ for quenched γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles increases from 0.37 J·kg⁻¹ K⁻¹ (for a field of 1 T) to 1.45 J·Kg⁻¹K⁻¹ (for 5 T) at 317 K. The RCP for quenched γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles increased from 66 J·kg⁻¹ to 415 J·kg⁻¹ as the field increases from $\Delta H = 1$ T to $\Delta H = 5$ T.

5.3.5 Curie temperature, change in entropy, relative cooling power: (Fe₇₀Ni₃₀)₈₉Mn₁₁ Nanoparticles

Fig. 5.10 (a) shows the $M(T)$ curve for (Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles from 10 K to 400 K at applied magnetic field of 0.1 T. It can be seen from the graph that at low temperature the sample exhibits antiferromagnetic behavior. The antiferromagnetic behavior can be seen more clearly in the dM/dT versus T graph (inset of fig 5.10 (a)). In this alloy, antiferromagnetic behavior at low temperatures may be associated with higher percentage of Mn, which has antiferromagnetic interactions. The T_c was found to be 220 K, as determined from the minima of the plot of dM/dT versus T (inset of fig.5.10 (a)). Fig.5.10 (b) shows the field dependence of magnetization at temperature of 300 K. This sample exhibit coercivity of ~300 Oe, higher than those of (Fe₇₀Ni₃₀)₉₅Mn₅ and (Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles. Higher percentage of Mn in (Fe₇₀Ni₃₀) results in antiferromagnetic interaction at low temperature. In addition, higher percentage of Mn in (Fe₇₀Ni₃₀) yields increased magnetic hysteresis which is not preferred for MCE applications.

Fig.5.11 (a) and (b) show the magnetic isotherm curves and the “ $-\Delta S_m$ ” versus T plot for fast quenched γ -(Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles, respectively. The $-\Delta S_m$ for fast quenched γ -(Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles increases from 0.26 J·kg⁻¹ K⁻¹ (for a field of 1 T) to 1.02 J·Kg⁻¹K⁻¹ (for 5 T) at 220 K. The RCP for fast quenched γ -(Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles increased from ~37.5 J·kg⁻¹ to 237.8 J·kg⁻¹ as the field increases from $\Delta H = 1$ T to $\Delta H = 5$ T. The ΔS_m and RCP values for γ -(Fe₇₀Ni₃₀)₈₉Mn₁₁ nanoparticles are less than those of γ -(Fe₇₀Ni₃₀)₉₂Mn₈ and γ -(Fe₇₀Ni₃₀)₉₅Mn₅ nanoparticles.

Fig. 5.10 (a) The temperature dependence of magnetization for quenching $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Mn}_{11}$ nanoparticles at applied magnetic field 0.1 T. Inset a) shows dM/dT versus T plot, the T_C for this sample is 220 K (b) Isothermal magnetization M at 10 K.

Fig. 5.11 (a) Magnetization isotherms $M(H)$ obtained for a maximum applied magnetic field of 5 T from 10 K to 400 K for the quenched $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Mn}_{11}$ nanoparticles (b) Magnetic entropy change as a function of temperature for a range of magnetic field from 1 T to 5 T for quenched $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Mn}_{11}$ nanoparticles.

For comparison, fig.5.12 shows the “ $-\Delta S_m$ ” versus T plot for $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ (quenched), $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ (as milled), $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ (vacuum annealed), $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ (quenched), $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Mn}_{11}$ (quenched) nanoparticles, at a magnetic field of 5 T.

Fig. 5.12 Magnetic entropy change as a function of temperature at applied magnetic field of 5 T for $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Mn}_5$ (quenched), $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ (as milled), $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ (vacuum annealing), $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ (quenched), $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{Mn}_{11}$ (quenched) nanoparticles.

Table 5.1 shows a comparison of the MCE of our nanoparticles with other promising nanoparticles including manganite nanoparticles. Manganites, e.g., $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO), $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) and $\text{La}_{1-x-y}\text{Ca}_x\text{Sr}_y\text{MnO}_3$ (LCSMO) are generally believed to exhibit good magnetocaloric properties.²⁹⁻³⁵ From table 1 it is clear that most of our nanoparticles have reasonable ΔS_m and high RCP, which may arise from the asymmetric nature of the exchange parameters due to increased spin disorder at the surface of the nanoparticles.^{8,20} For example, Alvarez-Alonso *et al.* studied the broadening of magnetic entropy change with temperature in $\text{Pr}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}$ alloys produced by high energy ball milling and found enhancement in the full width at half maximum with increasing milling time.³⁶

The RCP values for Fe-Ni-Mn nanoparticles are less than those of our previous studied γ -FeNiB, however Fe-Ni-Mn nanoparticles have lower T_C which makes these materials more promising for room temperature applications.⁴

Table 5.1 Curie temperature (T_C), particle size (d), the magnitude of change in magnetic entropy ($|\Delta S_m|$) and relative cooling power (RCP) for selected magnetocaloric nanoparticles

Nominal composition	T_C (K)	d (nm)	$ \Delta S_m $ J kg ⁻¹ K ⁻¹ ($\mu_0 H = 1.5$ T)	RCP (J·kg ⁻¹)	Ref.
γ -(Fe ₇₀ Ni ₃₀) ₉₅ Mn ₅ (quenched)	338		0.51	116	This work
α -(Fe ₇₀ Ni ₃₀) ₉₂ Mn ₈ (as milled)	380	12	0.5	139	This work
γ -(Fe ₇₀ Ni ₃₀) ₉₂ Mn ₈ (vacuum annealed)	340	25	0.6	125	This work
γ -(Fe ₇₀ Ni ₃₀) ₉₂ Mn ₈ (quenched)	317		0.52	107	This work
γ -(Fe ₇₀ Ni ₃₀) ₈₉ Mn ₁₁ (quenched)	220		0.37	61	This work
γ -(Fe ₇₀ Ni ₃₀) ₈₉ B ₁₁	381	12	0.74	164	⁴ (chapter 4)
γ -(Fe ₇₀ Ni ₃₀) ₈₉ Zr ₇ B ₄	353	20	0.7	~65	³
Gd	295	12	~2.7	~90	⁶
Pr ₂ Fe ₁₇	290	11	~0.6	60	³⁶
Nd ₂ Fe ₁₇	340	11	~1	118	³⁶
Nd ₂ Fe ₁₇	340	14	1.6	87	³⁷
La _{0.67} Sr _{0.33} MnO ₃	362	32	0.32	20.5	²⁹
La _{0.6} Sr _{0.4} MnO ₃	364	20	1	64	³⁰
La _{0.7} Ca _{0.11} Sr _{0.19} MnO ₃	295	30-40	~0.65	~60	³²
La _{0.7} Ca _{0.3} MnO ₃	267	44	1.2	65	³⁴
La _{0.7} Cr _{0.3} MnO ₃	260	30	1.01	64	³⁵

The thermal conductivity of the material also plays an important role in cooling applications. Transition metal alloys possess better thermal conductivity than those of oxides, therefore our nanoparticles would provide superior performance compared to manganites.

5.4 Critical behavior of γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles

The critical behavior of SOTM near T_C can be characterized by a set of critical exponents: β corresponding to the saturation magnetization M_S ; γ corresponding to the initial magnetic susceptibility χ_0 , and δ corresponding to the critical magnetization isotherm at T_C . Fig. 5.13 (a) shows the $M(H)$ isotherms of γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles from 320 K to 360 K, for magnetic fields ranging from 0 to 5 T. The magnetic phase transition can be determined by the Arrott -Noakes equation¹⁵ of state, i.e., $(H/M)^{1/\gamma} = (T - T_C)/T_C + (M/M_l)^\beta$, where M_l is a materials constant, and γ and β are critical exponents. Fig. 5.13 (b) shows that the Arrott plot M^2 v/s H/M exhibits a positive slope (for $\beta = 0.5$ and $\gamma = 1$), indicating that the PM-FM phase transition is second order. SOTM show straight parallel curves in the

Arrott plot when the spontaneous magnetization occurs at T_C . This is due to long range ordering, as suggested by mean field theory ($\beta = 0.5$ and $\gamma = 1$). In our case, inhomogeneous magnetic phases and short range order at T_C results in non-parallel lines in the Arrott plot, suggesting a change in the nature of the magnetic phase transition and the critical exponents.

Fig. 5.13 (a) $M(H)$ isotherm around T_C , (b) Arrott plot (mean field model), M^2 versus H/M and (c) 3D-Heisenberg model.

Three models, *i.e.*, 3D- Heisenberg model, 3D-Ising model and triclinic model were used to obtain the critical exponents β and γ . It was found that a modified Arrott plot using the 3D-Heisenberg model ($\beta = 0.365$, $\gamma = 1.336$) results in parallel

straight lines (Fig. 5.13 (c)). The other two models (not shown) did not yield parallel straight lines.

The spontaneous magnetization $M_s(T)$ and inverse initial susceptibility $\chi^{-1}(T)$ were calculated for each straight line by extrapolating the modified Arrott plots from the high field region to $(\mu_0 H/M)^{1/\gamma} = 0$ for $T < T_C$ and $(M)^{1/\beta} = 0$ for $T > T_C$. The critical exponents β and γ associated with M_s and χ^{-1} , respectively, as well as T_C were calculated by the Kouvel-Fisher (KF) method,^{4,16,38} The plots $M_s(T)(dM_s/dT)^{-1}$ vs T and $\chi_0^{-1}(T)(d\chi_0^{-1}/dT)^{-1}$ vs T should result in straight lines with slopes of $1/\beta$ and $1/\gamma$, respectively. Extrapolation of these lines to the ordinate equal to zero yields critical exponents $\beta = 0.319$ with $T_C = 339.73\text{K}$ and $\gamma = 1.195$ with $T_C = 340.15\text{ K}$ (fig.5.14 (a)). The third critical exponent δ was experimentally determined by fitting the isotherm $M(H)$ using the scaling relation³⁸⁻⁴⁰: $M = D H^{1/\delta}$ at $T = T_C$, where D is the critical amplitude. Linear fit of the $\ln(M)$ versus $\ln(H)$ plot (fig.5.14 (b)) yields a straight line with slope $1/\delta$ when $\mu_0 H > 0.3\text{T}$. The critical exponent δ was found to be 4.71. δ was also determined by Widom's scaling relation⁴¹ $\delta = 1 + (\gamma/\beta)$, which yields $\delta = 4.75$. This value is close to the value obtained from our experimental results.

Next, we studied the critical behavior of our sample by the universal scaling hypothesis. Near the FM-PM transition temperature, the magnetic equation of state⁴² can be written as $m = f_{\pm}(h)$, where m is the scaled magnetization, $m = |\varepsilon|^{-\beta} M(H, \varepsilon)$, h is the scaled field $h = |\varepsilon|^{-\beta\delta} H$, ε is the reduced temperature $(T - T_C)/T_C$, '+' and '-' signs denote temperatures above and below T_C . The plot of m as a function of h yields two universal curves; $f_+(h)$ for $T > T_C$ and $f_-(h)$ for $T < T_C$. Fig.5.13 (c) shows $M |\varepsilon|^{\beta}$ versus $H |\varepsilon|^{\beta\delta}$ around T_C , clearly displaying two different branches, corresponding to magnetization data for temperatures above T_C and temperatures below T_C . The inset of Fig. 5.14 (c) plotted on the log-log scale shows that all the points collapse into two universal curves, which confirms that our critical exponents and T_C are reliable.

Fig. 5.14 (a) Kouvel-Fisher (KF) plot for $M_s \cdot (dM_s/dT)^{-1}$ (left) and $\chi_0^{-1} \cdot (d\chi_0^{-1}/dT)^{-1}$ (right) v/s T . (b) $\ln(M)$ v/s $\ln(H)$ for $H > 3000$ Oe at $T_C = 340$ K. (c) Scaling plots of $M(H)$ isotherms above and below T_C using β and γ from the KF equations, inset shows the same plot in log-log scale.

The value of critical exponents ($\delta = 4.71$, $\beta = 0.319$, $\gamma = 1.195$) derived for the γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles are close to those of the 3D- Heisenberg model ($\delta = 4.66$, $\beta = 0.365$, $\gamma = 1.336$), indicating that short range interactions dominate critical behavior around T_C in these nanoparticles. The linear fitting of field dependence of RCP for γ - FeNiMn nanoparticles yields a straight line, with slope $N = 1.18 \pm 0.01$ (not shown). Using the values of critical exponents we have determined the field dependence of RCP, i.e., $RCP \propto H^{(1+1/\delta)}$; for our case $RCP \propto H^{1.21}$. This dependence of RCP, calculated from the critical exponents, is within 2.5% of the value calculated from the linear fit of RCP v/s $\mu_0 H$ plots.

5.5 Conclusions

The magnetocaloric properties and critical behavior of FeNiMn nanoparticles were investigated. The bcc α -(Fe₇₀Ni₃₀)₉₂Mn₈ and fcc γ -(Fe₇₀Ni₃₀)₉₂Mn₈ nanoparticles possess high relative cooling power (RCP), varying from 83 J·kg⁻¹ to 507 J·kg⁻¹ and from 78 J·kg⁻¹ to 466 J·kg⁻¹, respectively, for a field change from $\Delta H=1$ to 5 T. water quenching of these nanoparticles results further shifting of T_C very near to room temperature (317 K) Good agreement was found between the critical exponents of the γ -(Fe₇₀Ni₃₀)₉₂Mn₈ alloy nanoparticles determined by the modified Arrott plot and those obtained from the Kouvel-Fisher method. The Widom's scaling relation showed good agreement with the critical exponents $\beta = 0.319$, $\gamma = 1.195$ and $\delta = 4.71$. High relative cooling power, minimal magnetic and thermal hysteresis, low cost and high corrosion resistance make these nanoparticles suitable for low grade waste heat recovery and near room temperature thermal management application.

References

- ¹ H. Ucar, J. J. Ipus, D. E. Laughlin, and M. E. McHenry, Journal of Applied Physics **113**, 17A918 (2013).
- ² H. Ucar, M. Craven, D. E. Laughlin, and M. E. McHenry, Journal of Electronic Materials **43**, 137 (2014).
- ³ J. J. Ipus, H. Ucar, and M. E. McHenry, IEEE Transactions on Magnetism **47**, 2494 (2011).
- ⁴ V. Chaudhary, D. V. Maheswar Repaka, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, Journal of Applied Physics **116**, 163918 (2014).
- ⁵ L. J. Swartzendruber, V. P. Itkin, and C. B. Alcock, Journal of Phase Equilibria **12**, 288 (1991).
- ⁶ S. P. Mathew and S. N. Kaul, Applied Physics Letters **98**, 2505 (2011).

- ⁷ V. Chaudhary, X. Chen, D. V. M. Repaka, A. Chaturvedi, Z. Wang, and R. V. Ramanujan, 6th IIF-IIR International Conference on Magnetic Refrigeration THERMAG VI, Victoria, BC, 7-10 Sept 2014 (2014).
- ⁸ V. Chaudhary and R. V. Ramanujan, MRS Online Proceedings Library **1708**, vv10 (2014).
- ⁹ R. E. Rosenweig, *Ferrohydrodynamics* (Cambridge University Press, 1985).
- ¹⁰ T. D. Thanh, N. Huy Dan, T. L. Phan, H. Kumarakuru, E. J. Olivier, J. H. Neethling, and S.-C. Yu, Journal of Applied Physics **115**, 023903 (2014).
- ¹¹ V. Franco, R. C. Flores, A. Conde, K. E. Knipling, and M. A. Willard, Journal of Applied Physics **109**, 07A905 (2011).
- ¹² F. J. Castaño, J. M. G. Beneytez, P. Crespo, M. Multigner, M. Vazquez, and A. Hernando, Journal of Physics: Condensed Matter **11**, 5671 (1999).
- ¹³ J. Rogel-Salazar, Contemporary Physics **52**, 619 (2011).
- ¹⁴ H. Oesterreicher and F. T. Parker, Journal of Applied Physics **55**, 4334 (1984).
- ¹⁵ A. Arrott and J. E. Noakes, Physical Review Letters **19**, 786 (1967).
- ¹⁶ J. S. Kouvel and M. E. Fisher, Physical Review **136**, A1626 (1964).
- ¹⁷ V. Chaudhary, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, IEEE Magnetics Letters **5**, 6800104 (2014).
- ¹⁸ P. Dutta, A. Manivannan, M. S. Seehra, N. Shah, and G. P. Huffman, Physical Review B **70**, 174428 (2004).
- ¹⁹ L. M. Moreno, J. S. Blázquez, J. J. Ipus, J. M. Borrego, V. Franco, and A. Conde, Journal of Applied Physics **115**, 17A302 (2014).
- ²⁰ N. J. Jones, H. Ucar, J. J. Ipus, M. E. McHenry, and D. E. Laughlin, Journal of Applied Physics **111**, 07A334 (2012).
- ²¹ Provenzano, V, A. J. Shapiro, Shull, and D. Robert; *Vol. 429* (Nature Publishing Group, London, ROYAUME-UNI, 2004), p. 5.
- ²² B. K. Banerjee, Physics Letters **12**, 16 (1964).
- ²³ A. Z. Menshikov, P. Burlet, A. Chamberod, and J. L. Tholence, Solid State Communications **39**, 1093 (1981).

- ²⁴ A. Z. Menshikov, V. A. Kazantsev, N. N. Kuzmin, and S. K. Sidorov, *Journal of Magnetism and Magnetic Materials* **1**, 91 (1975).
- ²⁵ D. Peña Lara, G. A. Pérez Alcázar, L. E. Zamora, and J. A. Plascak, *Physical Review B* **80**, 014427 (2009).
- ²⁶ A. Bohórquez, L. E. Zamora, and G. A. Pérez Alcázar, *Physical Review B* **49**, 16035 (1994).
- ²⁷ V. Provenzano, A. J. Shapiro, and R. D. Shull, *Nature* **429**, 853 (2004).
- ²⁸ M. E. Wood and W. H. Potter, *Cryogenics* **25**, 667 (1985).
- ²⁹ W. J. Lu, X. Luo, C. Y. Hao, W. H. Song, and Y. P. Sun, *Journal of Applied Physics* **104**, 113908 (2008).
- ³⁰ M. H. Ehsani, P. Kameli, M. E. Ghazi, F. S. Razavi, and M. Taheri, *Journal of Applied Physics* **114**, 223907 (2013).
- ³¹ S. B. Xi, W. J. Lu, H. Y. Wu, P. Tong, and Y. P. Sun, *Journal of Applied Physics* **112**, 123903 (2012).
- ³² E. Ohayona and A. Gedanken, *Journal of Magnetism and Magnetic Materials* **331**, 45 (2013).
- ³³ L. Paula, P. Archana, P. Manh-Huong, and S. Hariharan, *Journal of alloys and compounds* **512**, 6 (2012).
- ³⁴ H. Yang, Y. H. Zhu, T. Xian, and J. L. Jiang, *Journal of Alloys and Compounds* **555**, 150 (2013).
- ³⁵ J. H. Xu, W. Y. Yang, Q. H. Du, Y. H. Xia, H. L. Du, J. B. Yang, C. S. Wang, J. Z. Han, S. Q. Liu, Y. Zhang, and Y. C. Yang, *Journal of Physics D: Applied Physics* **47**, 065003 (2014).
- ³⁶ P. A. Alonso, J. L. S. Llamazares, C. F. S. Valdés, G. J. Cuello, V. Franco, P. Gorria, and J. A. Blanco, *Journal of Applied Physics* **115**, 17A929 (2014).
- ³⁷ Á. Pablo, G. Pedro, F. Victorino, M. J. Sánchez, J. P. María, L. S. L. José, O. Inés Puente, and A. B. Jesús, *Journal of Physics: Condensed Matter* **22**, 216005 (2010).
- ³⁸ P. Lampen, M. H. Phan, H. Srikanth, K. Kovnir, P. Chai, and M. Shatruk, *Physical Review B* **90**, 174404 (2014).

- ³⁹ M. Seeger and H. Kronmüller, Journal of Magnetism and Magnetic Materials **78**, 393 (1989).
- ⁴⁰ J. Fan, L. Ling, B. Hong, L. Zhang, L. Pi, and Y. Zhang, Physical Review B **81**, 144426 (2010).
- ⁴¹ L. P. Kadanoff, Physics **2**, 263 (1966).
- ⁴² S. N. Kaul, Journal of Magnetism and Magnetic Materials **53**, 5 (1985).

Chapter 6

Magnetocaloric Effect of FeNiCr Nanoparticles

Low cost, earth abundant and rare earth free magnetocaloric materials have attracted enormous amount of attention for green and energy efficient applications. Hence, we have investigated the magnetic and magnetocaloric properties of transition metal based $(\text{Fe}_{70}\text{Ni}_{30})_{1-x}\text{Cr}_x$ ($x= 1, 3, 5, 6$, and 7) nanoparticles. 5 % of Cr alloying with $\text{Fe}_{70}\text{Ni}_{30}$ is able to decrease the T_C from ~ 438 K to 258 K. All the samples exhibit broadening in the entropy curve and therefore high working temperature span, which is useful to enhance an important figure of merit, relative cooling power.

6.1 Introduction

Energy efficient magnetocaloric materials for magnetic cooling have attracted intense research interest due to unsustainable energy consumption and limitations of current cooling technology. Magnetic cooling is a low noise and low vibration technique which does not use ozone layer depleting hydrofluorocarbons and is therefore environmentally friendly. $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ and other R_5T_4 materials exhibit promising magnetocaloric performance and are therefore known as “Giant magnetocaloric materials”. However, the issues around rare-earths are very complex due to international politics and economics. China is the main supplier of rare earths since several decades, accounting for ~97% and ~90 % of world production in 2009 and 2013, respectively¹. The control of rare earths by one country can results in supply instabilities. In addition, these materials are corrosion prone and not earth abundant. The combination of these undesirable factors motivates us to develop non rare earth based magnetocaloric materials.

First order transition materials (FOTM), which exhibit simultaneous paramagnetic to ferromagnetic transformation and structural transition, results in enhanced total isothermal entropy change by the application of magnetic field. The narrow working temperature span and large magnetic and thermal hysteresis in FOTM limit real-world applications²⁻⁵. This magneto-structural transition is often connected with field and temperature hysteresis which reduces the system efficiency. In addition, repeated structural transition in FOTM promotes mechanical instability, which can causes failure of the system⁶⁻⁸. On the other hand, second order materials (SOTM) do not exhibit structural transition with magnetic transition. These materials in general have lesser isothermal entropy change than those of FOTM. However, SOTM are good in terms of negligible magnetic and temperature hysteresis and can exhibit large working temperature span and therefore high relative cooling power^{3-5,9,10}. Hence, there is a considerable interest in rare earth free, cost effective and easily available Fe based materials.

The $\gamma\text{-Fe}_{80-x}\text{Ni}_x\text{Cr}_{20}$ ($14 \leq x \leq 30$) alloys have competing exchange interactions and hence the local spin orientation depends on its environment¹¹. The effective exchange interaction can be positive, negative, or nearly zero. From the Heisenberg

principle, the effective interaction can be governed by the concentration, distribution, and strength of the six different possible exchange interactions J_{ij} between different magnetic atoms. By using neutron scattering technique, Men'shikov et al¹² has reported the exchange integrals J_{ij} (Ni–Ni) = 52 meV, J_{ij} (Fe–Ni) = 36 meV, J_{ij} (Ni–Cr) = 122 meV, J_{ij} (Fe–Cr) = 39 meV, J_{ij} (Fe–Fe) = –7 meV, J_{ij} (Cr–Cr) = –227 meV.

Chapter 4 and chapter 5 shows that the γ -(Fe₇₀Ni₃₀)₈₉B₁₁ nanoparticles are potential candidates for low grade waste heat recovery while γ -(Fe₇₀Ni₃₀)₉₂Mn₈ can be used for slightly above room temperature applications^{3,5}. Ucar et al,¹³ reported tuning of T_C at room temperature by alloying of Mo in Fe₇₀Ni₃₀. In this chapter, Cr alloyed FeNi was selected to tune T_C for below room temperature applications. The alloying of Cr with iron based material is also good to improve corrosion resistance¹⁴. Increasing Cr content in Fe_{73.5-x}Si_{13.5}B₉Nb₃Cu₁Cr_x alloys results in improved corrosion resistance in marine or SiO₂ contaminated environments.^{15,16}

We report the effect on the magnetic phase transition temperature and magnetocaloric properties of alloying of Cr in Fe₇₀Ni₃₀. Five samples (Fe₇₀Ni₃₀)₉₉Cr₁, (Fe₇₀Ni₃₀)₉₇Cr₃, (Fe₇₀Ni₃₀)₉₅Cr₅, (Fe₇₀Ni₃₀)₉₄Cr₆, and (Fe₇₀Ni₃₀)₉₃Cr₇ were synthesized and denoted as Cr1, CCr3, Cr5, Cr6 and Cr7, respectively. The theoretical values of T_C were compared with experimental results.

6.2 Experimental details

Nanoparticles of (Fe₇₀Ni₃₀)_{100-x}Cr_x alloy were prepared by planetary ball milling (FRITSCH) at 600 rpm under Ar atmosphere from elemental Fe (99.99%, Sigma Aldrich), Ni (99.998%, Fisher ChemAlert Guide) and Cr (> 99%, Sigma Aldrich) powders. The ball to powder ratio was 10:1. The vials and balls were made of zirconium oxide, and the volume of the vial was 125 ml, which contains 15 balls (10 mm in diameter). To prevent oxidation during heat treatment, the magnetic nanoparticles were sealed under high vacuum (10⁻⁵ torr) in a quartz tube. The sealed tube was heated at 700 °C (γ - phase region) for 2h and quenched in water⁵. The rate of quenching was ~ 125 °C/ sec. The structure and phase were determined by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer (CuK α radiation).

The composition was confirmed by energy dispersive X-ray spectroscopy using a JEOL JSM-7600F scanning electron microscope. The magnetic properties were measured using a physical property measuring system (PPMS) (EverCool-II, Quantum Design), equipped with a vibrating sample magnetometer probe and an oven (model P527).

6.3 Results and discussion

Fig. 6.1 shows the bright field transmission electron micrograph of Cr3 and Cr5 nanoparticles. The particle size for Cr3 is in the range of 3 nm to 21 nm, with an average size of 9 nm, while the particle size for Cr5 is in the range of 4 nm to 25 nm range, with an average size of 12 nm. These values are close to the value obtained from XRD data. The lattice fringe of $2.1\text{\AA}$ and $2.11\text{\AA}$ for Cr3 and Cr5, respectively, corresponding to the 111 planes of the fcc phase, are shown in the magnified portions of fig 6.1.

Fig. 6.1 Bright field TEM of (a) Cr3 and (b) Cr5 nanoparticles with magnified insets showing lattice spacing corresponding to 111 planes.

Fig.6.2 shows the temperature dependence of magnetization, $M(T)$ (left) and dM/dT (right) for $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$ ($x = 0, 1, 3, 5, 6$ and 7) nanoparticles, measured upon cooling under a field of 0.1 T. The Curie temperature of Cr0, Cr1, Cr3, Cr5, Cr6 and Cr7 were found to be 438 K, 398 K, 323 K, 258 K, 245 K and 215 K, respectively, determined from the minima of the plot of dM/dT versus T .

Fig. 6.2 Left axis show the temperature dependence of magnetization $M(T)$ for (a) Cr0, (b) Cr1, (c) Cr3, Cr5, Cr6 and Cr7 while the right axis show corresponding derivative with respect to temperature (dM/dT). The Curie temperature for Cr0, Cr1, Cr3, Cr5, Cr6 and Cr7 is 438 K, 398K, 323K, 258K, 245K and 215K, respectively.

The reduction of T_C below room temperature is consistent with the mean field model $T_C = J(r)_{eff} Z_T S(S+1)/3k_B$, where $J(r)_{eff}$ is the effective exchange interaction, Z_T is coordination number, S is the atomic spin quantum number and k_B is the Boltzmann constant. For the same value of x , the T_C for $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$ is smaller than the T_C of $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mn}_x$ alloys^{3,9}(chapter 5). This is because the value of J_{CrCr} is more negative than that of J_{MnMn} . Hence, the effective exchange interaction ($J(r)_{eff}$) is less in the case of $(\text{Fe}_{70}\text{Ni}_{30})_{1-x}\text{Cr}_x$ and the coordination number (Z_T) is

the same in both cases (due to the same crystal structure), which results in a reduction in T_C .

The experimental values of T_C were compared with the theoretical values calculated from the expression $T_C = T_{C1} + (dT_C/dc) c$. T_{C1} is the Curie temperature for the parent alloy $\text{Fe}_{70}\text{Ni}_{30}$ and dT_C/dc is the rate of change of Curie temperature with concentration c . The dT_C/dc value for Cr is $-3.2 \times 10^3 \text{ K/at } \%$.¹⁷ To plot this expression, T_{C1} (443 K) was obtained by extrapolation to the metastable region of the Fe-Ni phase diagram which was reasonably close to experimental T_C (438 K).

Fig 6.3 shows the change in Curie temperature with Cr content in ternary system $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$. The dashed blue line and black square dot represent the theoretical expression $T_C = T_{C1} + (dT_C/dc) c$ and experimental data, respectively.

Fig. 6.3 Phase diagram for ternary system $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$ with $x = 0$ to 8. Solid line represents the theoretical values predicted from FeNi phase diagram and empirical equation $T_C = T_{C1} + (dT_C/dc) c$, while points (black square) are experimental results.

We found that the experimental T_C values for Cr0, Cr1, Cr3, Cr6 and Cr7 are reasonable close to those of calculated from the empirical formula $T_C = T_{C1} + (dT_C/dc)c$. Small amount of contamination and/or oxidation in the sample can influence T_C . The compositional tuning of T_C with minimal change in magnetization makes these alloys important for near room temperature cooling applications

We have also fitted the experimental Curie temperature for $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mn}_x$ nanoparticles, synthesized in chapter 5. Fig 6.4 shows the change in Curie

temperature with Mn content in ternary system $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mn}_x$. The dashed blue line and black square dot represent the theoretical expression $T_C = T_{C1} + (dT_C/dc) c$ and experimental data, respectively. The dT_C/dc value for Mn is found to be $-1.9 \times 10^3 \text{ K/wt } \%$.

Fig. 6.4 Phase diagram for ternary system $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mn}_x$ with $x = 0$ to 11. Solid line represents the theoretical values predicted from FeNi phase diagram and empirical equation $T_C = T'_C + (dT_C/dc) c$, while points (black square) are experimental results.

The $M(H)$ isotherms for all the samples were recorded for hysteresis and ΔS_M measurements. Negligible hysteresis in all the samples make them useful for magnetocaloric devices operating at high operational frequency. The isothermal magnetic entropy change due to the applied magnetic field has been calculated using the Maxwell equation $\Delta S_m = \int_0^H (\partial M / \partial T)_H dH$, where ΔS_M is the magnetic entropy change, T is the temperature, M is the magnetization. Figs. 6.5 (a), (b), (c), (d) and (e) show temperature dependence of the magnetic entropy change ($-\Delta S_M$) under magnetic field ranging from 0.5 T to 5 T for Cr1, Cr3, Cr5, Cr6 and Cr7 alloy, respectively. In all the cases, the $-\Delta S_M$ versus T curves are very broad and the exact peak entropy cannot be defined. It has been suggested that such “table like” plots of the magnetic entropy v/s temperature are useful for device applications^{18,19}. For comparison of our data with the literature, the $-\Delta S_M$ and RCP values were calculated at the Curie temperature. For 1 T applied magnetic field, the ΔS_M for Cr1, Cr3, Cr5,

Cr6 and Cr7 at their T_C was found to be $0.38 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, $0.27 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, $0.37 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, $0.29 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ and $0.28 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, respectively. When the field was increased to 5 T, the ΔS_M for Cr1, Cr3, Cr5, Cr6 and Cr7 was found to be $1.58 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, $1.49 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, $1.45 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, $1.22 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ and $1.11 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, respectively.

Fig. 6.5 Temperature dependence of the magnetic entropy change ($-\Delta S_M$) under magnetic field ranging from 0.5 T to 5 T for (a) Cr1, (b) Cr3, (c) Cr5, (d) Cr6 and (e) Cr7 alloy. (f) Dependence of $-\Delta S_M$ (left axis, black square) and RCP (right axis, blue circle) on Chromium percentage in $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$ nanoparticles at applied magnetic field 5 T.

Fig. 6.5 (f) show magnetic entropy change (left axis) and RCP (right axis) v/s Cr content in $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$ alloy nanoparticles at applied field of 5 T. It is obvious from the fig 6.4 (f) that both ΔS_M and RCP decrease with increasing the Cr content in $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$ which can be attribute from the antiferromagnetic interaction in Cr atoms.

Fig. 6.6 (a) shows the variation of full width at half maximum of the entropy v/s temperature curves which is also known as working temperature span. The δT_{FWHM} for Cr1, Cr3, Cr5, Cr6 and Cr7 was found to be 216 K (347 K), 220 K (293

K), 209 K (280 K), 213 K (300 K) and 166 K (306 K) at magnetic field 1 T (5 T), respectively. Our δT_{FWHM} values are higher than those of Gd (~ 35 K)²⁰, Pr₂Fe₁₇ (~ 78 K)²¹, Nd₂Fe₁₇ (~ 95 K)²¹, (Fe₇₀Ni₃₀)₈₉Zr₇B₄ (133 K)²² at applied magnetic field 1 T. However, single and multiphase alloys of (Fe₇₀Ni₃₀)₈₉B₁₁ have δT_{FWHM} value of 174 K and 322 K, at 1 T magnetic field, respectively^{5,23}. The high working temperature span produces high RCP, which quantifies the magnitude of the heat extracted in a thermodynamic cycle.

Fig. 6.6 (b) and (c) show the field dependence of ΔS_M and RCP, on the log-log scale and the corresponding linear fit. The RCP for Cr1, Cr3, Cr5, Cr6 and Cr7 increased from 82 J·kg⁻¹, 59 J·kg⁻¹, 77 J·kg⁻¹, 62 J·kg⁻¹ and 47 J·kg⁻¹ to 548 J·kg⁻¹, 436 J·kg⁻¹, 406 J·kg⁻¹, 366 J·kg⁻¹ and 306 J·kg⁻¹ as the field increases from $\Delta H=1$ T to $\Delta H=5$ T, respectively.

Fig. 6.6 (a) Field dependence of working temperature span (δT_{FWHM}) for Cr1, Cr3, Cr5, Cr6 and Cr7 alloys. (b) Maximum change in entropy ($-\Delta S_M^{\max}$) as a function of applied field and (c) Variation in relative cooling power (RCP). The plots (b) and (c) are in log-scale.

For comparison with other magnetocaloric materials, table 6.1 shows the values of ΔS_M , RCP and δT_{FWHM} for our materials, and selected relevant materials. The RCP values for our alloy nanoparticles are close to those of other key magnetocaloric materials. In addition, these alloys are affordable and are easily available.

Table 6.1 Curie temperature (T_C), change in magnetic entropy (ΔS_M) and relative cooling power (RCP) for selected magnetocaloric materials.

Nominal Composition	T_C (K)	ΔS_M (J·kg ⁻¹ ·K ⁻¹) ($\mu_0 H = 5T$)	RCP (J·kg ⁻¹) ($\mu_0 H = 5T$)	Ref.
(Fe ₇₀ Ni ₃₀) ₉₉ Cr ₁	398	1.58	548	This work
(Fe ₇₀ Ni ₃₀) ₉₇ Cr ₃	323	1.49	436	This work
(Fe ₇₀ Ni ₃₀) ₉₅ Cr ₅	258	1.45	406	This work
(Fe ₇₀ Ni ₃₀) ₉₄ Cr ₆	245	1.22	366	This work
(Fe ₇₀ Ni ₃₀) ₉₃ Cr ₇	215	1.11	306	This work
(Fe ₇₀ Ni ₃₀) ₉₅ Mn ₅	338	1.45	470	⁹
(Fe ₇₀ Ni ₃₀) ₉₂ Mn ₈	340	1.67	466	³
(Fe ₇₀ Ni ₃₀) ₈₉ Zr ₇ B ₄	353	2.8	330	²²
(Fe ₇₀ Ni ₃₀) ₈₉ B ₁₁	381	2.1	640	⁵
(Fe ₇₀ Ni ₃₀) ₉₆ Mo ₄	300	1.67	432	¹³
Gd ₅ Ge _{1.9} Si ₂ Fe _{0.1}	300	7.1	630	²⁴

From the Arrott-Noakes equation of state, the magnetic entropy change at T_C can be expressed by the relation $\Delta S_M \propto H^n$, the field dependence of RCP can be expressed by power law $RCP \propto H^N$, where $n = 1 + [(\beta - 1)/(\beta + \gamma)]$ and $N = 1 + 1/\delta$. β , γ and δ are the critical exponents²⁵. The linear fit of field dependence of ΔS_M (Fig 6.6 (b)) and RCP (Fig 6.6 (c)) at T_C results in the values of local exponents “n” and “N”, respectively. The values of local exponent “n” at T_C for Cr1, Cr3, Cr5, Cr6 and Cr7 were 0.92, 1.08, 0.84, 0.90 and 0.84 respectively, and, the values of local exponent “N” at T_C for Cr1, Cr3, Cr5, Cr6 and Cr7 were 1.24, 1.25, 1.05, 1.14 and 1.25, respectively. The variation in local exponent can be attributed to changes in microscopic interactions due to differences in Cr content.

6.4 Conclusions

Cr was used to tune the Curie temperature of Fe-Ni alloy from more than 400 K to below room temperature. Mean field theory and Bethe Slater curve were used to explain the reduction of T_C and therefore experimental results were compared with calculated values from the theory. These findings can be used as a point of reference to calculate T_C for other compositions. The ΔS_M for Cr1, Cr3, Cr5, Cr6 and Cr7 was found to be $1.58 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, $1.49 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, $1.45 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, $1.22 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ and $1.11 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, respectively. The RCP for Cr1, Cr3, Cr5, Cr6 and Cr7 increased from $82 \text{ J}\cdot\text{kg}^{-1}$, $59 \text{ J}\cdot\text{kg}^{-1}$, $77 \text{ J}\cdot\text{kg}^{-1}$, $62 \text{ J}\cdot\text{kg}^{-1}$ and $47 \text{ J}\cdot\text{kg}^{-1}$ to $548 \text{ J}\cdot\text{kg}^{-1}$, $436 \text{ J}\cdot\text{kg}^{-1}$, $406 \text{ J}\cdot\text{kg}^{-1}$, $366 \text{ J}\cdot\text{kg}^{-1}$ and $306 \text{ J}\cdot\text{kg}^{-1}$ as the field increases from $\Delta H = 1 \text{ T}$ to $\Delta H = 5 \text{ T}$, respectively. The mean field theory and Bethe Slater curve were used to explain the reduction of T_C .

References

- ¹ J. A. Nekuda Malik, MRS Bulletin **40**, 206 (2015).
- ² K. A. Gschneidner Jr, Y. Mudryk, and V. K. Pecharsky, Scripta Materialia **67**, 572 (2012).
- ³ V. Chaudhary and R. V. Ramanujan, Journal of Physics D: Applied Physics **48**, 305003 (2015).
- ⁴ V. Chaudhary and R. V. Ramanujan, MRS Online Proceedings Library **1708**, vv10 (2014).
- ⁵ V. Chaudhary, D. V. Maheswar Repaka, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, Journal of Applied Physics **116**, 163918 (2014).
- ⁶ V. Franco, J. S. Blázquez, B. Ingale, and A. Conde, Annual Review of Materials Research **42**, 305 (2012).
- ⁷ K. A. Gschneidner Jr, V. K. Pecharsky, and A. O. Tsokol, Reports on Progress in Physics **68**, 1479 (2005).
- ⁸ J. R. Gómez, R. F. Garcia, A. D. M. Catoira, and M. R. Gómez, Renewable and Sustainable Energy Reviews **17**, 74 (2013).

- ⁹ V. Chaudhary, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, *IEEE Magnetics Letters* **5**, 6800104 (2014).
- ¹⁰ V. Chaudhary, X. Chen, D. V. M. Repaka, A. Chaturvedi, Z. Wang, and R. V. Ramanujan, 6th IIF-IIR International Conference on Magnetic Refrigeration THERMAG VI, Victoria, BC, 7-10 Sept 2014 (2014).
- ¹¹ S. Mandal, J. Panda, and T. K. Nath, *Journal of Alloys and Compounds* **653**, 453 (2015).
- ¹² A. Z. Men'shikov, N. N. Kuz'min, V. A. Kazantsev, S. K. Sidorov, and V. N. Kalinin, *Physics of Metals and Metallography* **40**, 174 (1975).
- ¹³ H. Ucar, M. Craven, D. E. Laughlin, and M. E. McHenry, *Journal of Electronic Materials* **43**, 137 (2014).
- ¹⁴ K. Fukamichi, K. Shirakawa, T. Kaneko, and T. Masumoto, *Journal of Applied Physics* **53**, 2246 (1982).
- ¹⁵ A. Pardo, E. Otero, M. C. Merino, M. D. López, M. Vázquez, and P. Agudo, *Corrosion Science* **44**, 1193 (2002).
- ¹⁶ A. Pardo, E. Otero, M. C. Merino, M. D. López, M. Vázquez, and P. Agudo, *Corrosion Science* **43**, 689 (2001).
- ¹⁷ C. W. Chen, *Magnetism and Metallurgy of Soft Magnetic materials* (North Holland Publishing Company, 1977).
- ¹⁸ H. Fu, Z. Ma, X. J. Zhang, D. H. Wang, B. H. Teng, and E. Agurto Balfour, *Applied Physics Letters* **104**, 072401 (2014).
- ¹⁹ A. Chaturvedi, S. Stefanoski, M.-H. Phan, G. S. Nolas, and H. Srikanth, *Applied Physics Letters* **99**, 162513 (2011).
- ²⁰ S. P. Mathew and S. N. Kaul, *Applied Physics Letters* **98**, 2505 (2011).
- ²¹ P. A. Alonso, J. L. S. Llamazares, C. F. S. Valdés, G. J. Cuello, V. Franco, P. Gorria, and J. A. Blanco, *Journal of Applied Physics* **115**, 17A929 (2014).
- ²² J. J. Ipus, H. Ucar, and M. E. McHenry, *IEEE Transactions on Magnetics* **47**, 2494 (2011).
- ²³ V. Chaudhary and R. V. Ramanujan, *Magnetics Letters, IEEE* **6**, 6700104(4) (2015).
- ²⁴ V. Provenzano, A. J. Shapiro, R. D. Shull, *Nature* **429**, 853 (2004)

- ²⁵ V. Franco, J. S. Blazquez, and A. Conde, Applied Physics Letters **89**, 2512 (2006).

Chapter 7*

Magnetocaloric properties of bulk Fe-Ni-B alloy

Low cost magnetic cooling, based on the magnetocaloric effect is an energy efficient, environmentally friendly, thermal management technology. However, inadequate temperature span is often a challenge in developing magnetic cooling system. In this chapter, we report the novel use of multiphase materials to enhance the working temperature span (δT_{FWHM}) of the magnetic entropy change and the relative cooling power of a Fe-Ni-B bulk alloy. The coexistence of bcc, fcc and spinel phases results in large working temperature spans of 322.3 K and 439.0 K for magnetic field change of 1 T and 5 T, respectively. δT_{FWHM} for this multiphase $(Fe_{70}Ni_{30})_{89}B_{11}$ alloy is about 86 % higher than the corresponding value for single phase γ - $(Fe_{70}Ni_{30})_{89}B_{11}$ alloy for $\Delta H = 1$ T. These values are the largest for any bulk magnetocaloric material and even higher than most magnetocaloric nanoparticles.

*This section published substantially as reference: V. Chaudhary and R. V. Ramanujan, Magnetism Letters, IEEE **6**, 6700104(4) (2015)

7.1 Introduction

Magnetic cooling, based on the magnetocaloric effect (MCE) is of high interest due to its technological significance for energy efficient thermal management.¹⁻³ Moreover, magnetic cooling does not use ozone layer depleting gases and global warming substances and is therefore green and environmentally friendly.^{2,4-8} MCE is a magneto-thermodynamic phenomenon in which a magnetic material exhibits a change in temperature by the application or removal of magnetic field.

To achieve high relative cooling power, a cooling system needs high working temperature span. However, conventional magnetocaloric materials (e.g., Gd_2CoGa_3 , Dy_2CoGa_3 , Ho_2CoGa_3 , GdCoAl) exhibit low working temperature span, ranging from 10 to 50 K, with applied magnetic field up to 5 T.⁹⁻¹¹ To achieve larger working temperature span, layering of materials with a range of Curie temperature has been used in magnetic cooling systems.¹²⁻¹⁵ In addition, there is extensive efforts towards increasing working temperature span through processing, including mechanical alloying, amorphization, annealing and nanocrystallization.^{10,16-19} For example, nanocrystallization of Fe-Ni-B, Pr-Fe and Nd-Fe by ball milling results in large working temperature span.^{10,19} Ucar et al. suggested that the magnetocaloric properties of the fcc phase of FeNi can be controlled by the oxidation kinetics.²⁰ Caballero-Flores et al. reported an enhancement in RCP of 37% in a two phase $\text{Fe}_{88-2x}\text{Co}_x\text{Ni}_x\text{Zr}_7\text{B}_4\text{Cu}_1$ alloy ($x=0$ to 1).¹⁸

We report for the first time high working temperature span (δT_{FWHM}) in multiphase bulk alloy, their high working temperature span is due to the coexistence of the fcc, bcc and spinel phases. The coexistence of these phases results in large working temperature spans of 322.3 K and 439.0 K for magnetic field change of 1 T and 5 T, respectively. These δT_{FWHM} values are larger than that of many other magnetocaloric bulk alloys and even higher than nanocrystalline Fe-Ni-B, Fe-Ni-Zr-B, Pr-Fe and Nd-Fe alloys.

7.2 Experimental details

A multiphase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy was prepared by arc melting under argon atmosphere from elemental Fe (99.99%, Sigma Aldrich), Ni (99.998%, Fisher ChemAlert Guide) and B (97%, Sigma Aldrich) powders. The ingot was annealed at 700° C for 2h under argon gas atmosphere and cooled at a rate of $\sim 8^\circ \text{C/min}$. Structural characterization was performed by X-ray diffractometry (XRD) using a Bruker D8 Advance diffractometer in the scan range (2θ) from 30 to 90° and step size of 0.02°. The instrument was operated at 35kV and 25 mA with Cu-K α radiation ($\lambda=0.154 \text{ nm}$). The composition and microstructure were determined by Energy dispersive X-ray spectroscopy (JEOL JSM-7600F scanning electron microscopy) and an Electron probe micro analyzer (EPMA) (JXA-8560F). Magnetic measurements were carried out in the temperature range from 300 K to 973 K, with magnetic fields up to 5 T, using a Physical Property Measurement System (PPMS) (EverCool-II, Quantum Design) equipped with a vibrating sample magnetometer (VSM) probe and an oven (Model P527).

7.3 Results and discussions

7.3.1 Phase analysis

Room temperature X-ray diffraction was used to determine the crystal structure and unit cell parameters of the phases present in our bulk $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy. The X-ray diffraction pattern of the arc melted $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy, along with its Rietveld refinement is shown in Fig 7.1. The Rietveld refinement of the diffraction pattern shows that the sample exhibits a mixture of a face centered cubic ($Fm-3m$) phase, a body centered cubic ($Im-3m$) phase and a spinel ($Fd-3ms$) phase. The mass fractions of fcc, bcc and spinel phases were 71.75%, 20.95% and 7.30%, respectively. A possible oxidation reaction can be $\text{Fe}_{70-3x}\text{Ni}_{30-3x} + 2x\text{O}_2 \rightarrow x(\text{Fe,Ni})_3\text{O}_4$. The majority fcc phase is maximum since the annealing was conducting in the γ -phase region (700 °C). The bcc and spinel phases form during slow cooling from the γ -phase region to room temperature and oxidation in the arc

melter and furnace, respectively. A small mass fraction of an unidentified phase, shown by star (*) in the XRD pattern, was also present. Table 7.1 shows the structural data obtained from the X-ray diffraction pattern.

Fig. 7.1 Room temperature X-ray diffraction pattern of arc melted FeNiB. Blue line, red line and bottom black line are observed, calculated and differences, respectively. The Rietveld refinement of the diffraction pattern shows that the sample exhibits a mixture of a face centered cubic (*Fm-3m*, 71.75 %) phase, a body centered cubic (*Im-3m*, 20.95 %) phase and a spinel (*Fd-3ms*, 7.30 %) phase.

Table 7.1 Crystal structure, Space groups, weight fractions, unit cell parameters and Bragg R factor obtained from Rietveld refinement of X-ray diffraction patterns.

Crystal structure	fcc	bcc	spinal
Space group	Fm-3m	Im-3m	Fd-3m
Weight fraction (%)	71.75	20.95	7.30
Lattice parameters (Å)	3.600(2)	2.854(4)	8.521(1)
Cell Volume (Å ³)	46.689(3)	23.270(2)	618.719(2)
Bragg R factor	1.698	0.465	1.623

Fig. 7.2(a) shows the temperature dependence of magnetization $M(T)$ of the quenched $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy under magnetic fields of 0.05 T, 0.1 T, 0.5 T and 1 T in the temperature range from 300 K to 973 K. The overlap of temperature sweep curves in cooling and heating modes shows that there is no temperature hysteresis in our sample. All the curves have similar shape and exhibit two transitions. To determine the phase transition temperature between the paramagnetic (PM) and ferromagnetic (FM) states, dM/dT versus T plots for all the fields were constructed (Fig. 7.2(b)).

Fig. 7.2 (a) Temperature dependence of magnetization in cooling (filled symbols) and heating (open symbols) mode for $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy at applied magnetic fields of 0.05 T, 0.1 T, 0.5 T and 1 T, the hysteresis is negligible. (b) The corresponding dM/dT versus T curves, showing the Curie temperature for the γ - and α - phase. Inset of (b) shows changes in transition temperature (T_C^γ and T_C^α) with applied magnetic fields.

Two minima (T_C^γ and T_C^α) in the plots of dM/dT versus T and a kink (at ~ 770 K) suggest that the sample contains more than one phase. The transition temperatures (T_C^γ and T_C^α) shift to higher temperatures as the field increases because more thermal energy is required to randomize the magnetic spin at high magnetic fields. The dependence of T_C^γ and T_C^α with applied magnetic field is shown in the inset of fig 7.2 (b). T_C^γ increased from 381 K to 400 K while T_C^α increased from 891 K to 898 K for magnetic fields of 0.05 T and 1 T, respectively. In our previous study¹⁹, it was shown that the γ phase of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy nanoparticles shows a FM $\rightarrow$ PM transition temperature of 381 K which is exactly equal to the T_C^γ for the bulk $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy at applied magnetic field of 0.1 T. This suggests that T_C^γ is associated with γ phase of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy. From the phase diagram of Fe-Ni, T_C^α for our ternary $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy (891 K) is bit higher than that of the FM $\rightarrow$ PM transition temperature for the binary α -Fe $_{70}\text{Ni}_{30}$ (~ 773 K). The kink at ~ 770 K in fig. 7.2 (b) is probably due to magnetic ordering of the spinel phase.

7.3.2 Magnetocaloric studies

Fig. 7.3 (a) shows the magnetization isotherms $M(H)$ obtained in the temperature range of 10 K to 950 K for decreasing and increasing magnetic fields up to 5 T. The overlap of forward and backward field sweeps of the $M(H)$ isotherms is due to the absence of magnetic hysteresis which permits high operating frequency and is therefore a great advantage for an efficient magnetic cooling system. These $M(H)$ isotherms were used to determine the change in entropy using the Maxwell relation $\Delta S_M = \int_0^H (\partial M / \partial T)_H dH$. Fig. 7.3(b) shows the “ $-\Delta S_m$ ” vs T plots for $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy, for ΔH values in the range of 1 to 5 T. The magnitude of the ΔS_m is larger around T_C^γ and T_C^α and a shift of ΔS_m^{peak} was observed with increasing magnetic field. The $-\Delta S_m^{peak}$ for $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy increases from 0.31 J $\cdot\text{kg}^{-1}\text{K}^{-1}$ for a field of 1 T to 1.46 J $\cdot\text{kg}^{-1}\text{K}^{-1}$ for 5 T at T_C^γ .

The working temperature span, calculated from the full width at half maximum of the “ $-\Delta S_m$ ” vs T plots, was 322.3 K and 439.0 K, for magnetic field change of 1 T and 5 T, respectively. We have studied in previous work, the MCE

of the single γ -phase of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy nanoparticles synthesized by high speed ball milling.¹⁹

Fig. 7.3 (a) Magnetization isotherms obtained from temperature 10 K to 950 K for a maximum applied magnetic field 5 T, showing almost zero magnetic hysteresis in magnetic field sweep cycles. (b) Magnetic entropy changes for $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy as a function of temperature for ΔH ranging from 1 T to 5 T, resulting two peak values at transition temperature of γ - and α - phase.

The working temperature span for multiphase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy was compared with the single γ -phase of $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy (Fig. 7.4(a)). Interestingly, δT_{FWHM} (322.3 K) for the multiphase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy at $\Delta H=1$ T is much higher

than δT_{FWHM} for pure γ - $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy (307.5 K) with five times applied magnetic field ($\Delta H=5\text{T}$).

Fig. 7.4 (a) Field dependence of working temperature span (δT_{FWHM}) for multiphase bulk alloy $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ and γ - $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles (b) RCP as a function of change in applied magnetic field.

The reasons for high δT_{FWHM} are the difference in Curie temperature of the three phases in $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ and non zero magnetization in over a broad temperature range of M versus T curves. For the same applied magnetic field of 1 T, δT_{FWHM} for multiphase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy is about 86 % higher than that of δT_{FWHM} of the single phase γ - $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ particles. The high working

temperature span results in high relative cooling power (RCP), which quantifies the magnitude of the heat extracted in a thermodynamic cycle. The RCP increased from 100 J·kg⁻¹ to 641 J·kg⁻¹ respectively, as the field increases from $\Delta H = 1$ T to $\Delta H = 5$ T. Fig. 7.4 (b) shows the field dependence of RCP for both the samples on the ln-ln scale and the corresponding linear fit. RCP for multiphase (Fe₇₀Ni₃₀)₈₉B₁₁ alloy (100 J·kg⁻¹) at $\Delta H = 1$ T is higher than that of RCP for the single phase γ -(Fe₇₀Ni₃₀)₈₉B₁₁ alloy (89.8 J·kg⁻¹) while at $\Delta H = 5$ T, they are almost equal (Table 2). A comparison with other recently reported MCE materials has been made in Table 7.2.

Table 7.2 working temperature span (δT_{FWHM}), Relative cooling power (RCP), change in entropy ($-\Delta S_m$), transition temperature (T_C) and exponent (n) for different magnetocaloric materials including Multi-phase (Fe₇₀Ni₃₀)₈₉B₁₁

Sample	T_C (K)	$-\Delta S_m$ (J kg ⁻¹ K ⁻¹) ($\mu_0 H = 1$ T)	δT_{FWHM} (K) ($\mu_0 H = 1$ T)	RCP(J·kg ⁻¹) ($\mu_0 H = 1$ T)	n at T_C
Multi-phase(Fe ₇₀ Ni ₃₀) ₈₉ B ₁₁ *	381 (T_C^γ)	0.31	322.3	100	0.925
γ -(Fe ₇₀ Ni ₃₀) ₈₉ B ₁₁ # (Ref. ¹⁹)	381	0.51	173.8	89.8	0.875
Gd # (Ref. ²¹)	295	~2	~35	~70	0.67
(Fe ₇₀ Ni ₃₀) ₈₉ Zr ₇ B ₄ # (Ref. ²²)	353	~0.3	~133	~40	-
Pr ₂ Fe ₁₇ # (Ref. ¹⁰)	290	~0.45	~78	~35	-
Nd ₂ Fe ₁₇ # (Ref. ¹⁰)	340	~0.63	~95	~60	-

*bulk, # nanoparticles

It can be concluded from Table 7.2 that the multiphase (Fe₇₀Ni₃₀)₈₉B₁₁ alloy have broad working temperature span and higher RCP than other materials. Engelbrecht *et al.* reported that a material with a wide peak in isothermal entropy change (large temperature span, δT_{FWHM}) provides significantly larger cooling power than a material with a sharp peak in a practical active magnetic regenerator system. Thus, for a single magnetic regenerator, our multiphase material with wide temperature distribution of MCE is more attractive than with sharp ΔS_m peaks. By controlling the synthesis parameters such as annealing temperature/time and

cooling rate, the mass fraction of the phases can be tuned, which would control the change in entropy, working temperature span and RCP.

Fig 7.5 shows the temperature dependence of exponent n , described by $\Delta S_M = a H^n$, where a is a proportionality constant, for single (data were collected using the temperature versus entropy curve of our previous study)¹⁹ and multiphase Fe-Ni-B. For single phase γ -Fe-Ni-B, the $n(T)$ exhibits three regimes ($T < T_C$, $T = T_C$ and $T > T_C$) which is similar to other second order phase transition materials.

Fig. 7.5 Temperature dependence of the exponent “ n ” for single and multiphase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloys calculated by linear fitting of change in entropy versus applied magnetic field for $\Delta H = 5$ T. The exponent “ n ” for multiphase is higher than that of single phase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$.

However, the $n(T)$ for multiphase Fe-Ni-B exhibits five regimes ($T < T_C^\gamma$, $T = T_C^\gamma$, $T_C^\alpha > T > T_C^\gamma$, $T = T_C^\alpha$ and $T > T_C^\alpha$). Both samples exhibit the minimum values of $n(T)$ at the Curie temperature of their phase/s. Multiphase system $\text{Nd}_{1.25}\text{Fe}_{11}\text{Ti}$ ($\text{Fe}_{17}\text{Nd}_2$, Fe_7Nd and $\text{Fe}_{11}\text{TiNd}$) also exhibits similar behavior for the exponent $n(T)$ ²³. At FM-PM transition, the exponent n of multiphase Fe-Ni-B (~ 0.925) is

higher than that of single phase Fe-Ni-B (~0.875). We expected that high value of exponent n for multiphase γ -Fe-Ni-B at transition temperature (T_C) is because of partial contribution of ferromagnetic interactions of the α -Fe-Ni-B phase

7.4 Conclusions

It has been shown that enhancement in working temperature span and therefore relative cooling power can be attained by having multiple different phases in a composite. The presence of three phases in arc melted Fe-Ni-B alloy was confirmed by Rietveld refinement of X-ray diffraction patterns. Magnetometry reveals that a very large working temperature span of 322.3 K was obtained by the application of small magnetic field 1T. These results can be extended to other materials to increase in the working temperature span.

References

- ¹ A. Tishin, M., *Magnetocaloric effect : Current situation and future trends* (Elsevier, Amsterdam, PAYS-BAS, 2007).
- ² V. Franco, J. S. Blázquez, B. Ingale, and A. Conde, *Annual Review of Materials Research* **42**, 305 (2012).
- ³ H. Ucar, J. J. Ipus, M. E. McHenry, and D. E. Laughlin, *Journal of Metals* **64**, 782 (2012).
- ⁴ V. Chaudhary, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, *IEEE Magnetism Letters* **5**, 6800104 (2014).
- ⁵ X. Chen, V. B. Naik, R. Mahendiran, and R. V. Ramanujan, *Journal of Alloys and Compounds* **618**, 187 (2015).
- ⁶ A. Biswas, S. Chandra, S. Stefanoski, J. S. Blázquez, J. J. Ipus, A. Conde, M. H. Phan, V. Franco, G. S. Nolas, and H. Srikanth, *Journal of Applied Physics* **117**, 033903 (2015).
- ⁷ J. S. Blázquez, J. J. Ipus, L. M. Moreno-Ramírez, J. M. Borrego, S. Lozano-Pérez, V. Franco, C. F. Conde, and A. Conde, *Metallurgical and Materials Transactions E* **2**, 131 (2015).

- ⁸ A. Boutahar, A. Ettayfi, G. Alouhmy, H. Lassri, E. K. Hlil, and D. Fruchart, *Journal of Superconductivity and Novel Magnetism* **27**, 2401 (2014).
- ⁹ L. C. Wang, L. Cui, Q. Y. Dong, Z. J. Mo, Z. Y. Xu, F. X. Hu, J. R. Sun, and B. G. Shen, *Journal of Applied Physics* **115**, 233913 (2014).
- ¹⁰ P. A. Alonso, J. L. S. Llamazares, C. F. S. Valdés, G. J. Cuello, V. Franco, P. Gorria, and J. A. Blanco, *Journal of Applied Physics* **115**, 17A929 (2014).
- ¹¹ K. A. Gschneidner Jr, Y. Mudryk, and V. K. Pecharsky, *Scripta Materialia* **67**, 572 (2012).
- ¹² A. Rowe and A. Tura, *International Journal of Refrigeration* **29**, 1286 (2006).
- ¹³ K. L. Engelbrecht, G. F. Nellis, and S. A. Klein, in *Cryocoolers 13*, edited by R. Ross, Jr. (Springer US, 2005), p. 471.
- ¹⁴ M. A. Richard, A. M. Rowe, and R. Chahine, *Journal of Applied Physics* **95**, 2146 (2004).
- ¹⁵ T. Mukherjee, S. Sahoo, R. Skomski, D. J. Sellmyer, and C. Binek, *Physical Review B* **79**, 144406 (2009).
- ¹⁶ V. Chaudhary and R. V. Ramanujan, *MRS Online Proceedings Library* **1708**, vv10 (2014).
- ¹⁷ G. Pedro, L. S. L. José, Á. Pablo, P. María José, M. Jorge Sánchez, and A. B. Jesús, *Journal of Physics D: Applied Physics* **41**, 192003 (2008).
- ¹⁸ R. C. Flores, V. Franco, A. Conde, K. E. Knipling, and M. A. Willard, *Applied Physics Letters* **98** (2011).
- ¹⁹ V. Chaudhary, D. V. Maheswar Repaka, A. Chaturvedi, I. Sridhar, and R. V. Ramanujan, *Journal of Applied Physics* **116**, 163918 (2014).
- ²⁰ H. Ucar, J. J. Ipus, D. E. Laughlin, and M. E. McHenry, *Journal of Applied Physics* **113**, 17A918 (2013).
- ²¹ S. P. Mathew and S. N. Kaul, *Applied Physics Letters* **98**, 2505 (2011).
- ²² J. J. Ipus, H. Ucar, and M. E. McHenry, *IEEE Transactions on Magnetics* **47**, 2494 (2011).
- ²³ R. C. Flores, V. Franco, A. Conde, Q. Y. Dong, and H. W. Zhang, *Journal of Magnetism and Magnetic Materials* **322**, 804 (2010).

Chapter 8

Self-pumping Magnetic Cooling

A series of experiments were conducted to determine the effect of heat load, magnetic particle content and magnetic field on self-pumping magnetic cooling. It was found that the performance of the cooling device strongly depends on these factors. Cooling by $\sim 16^\circ\text{C}$ and $\sim 27^\circ\text{C}$ was achieved by the application of 0.3 T magnetic field when fluid density was 5 % and 10 %, respectively. These results were compared to simulations performed with COMSOL Multiphysics. Our system is a self-regulating device since, as the heat load increases, magnetization of the ferrofluid decreases, the driving force for fluid motion increases with faster heat transfer from the heat source to the heat sink.

8.1 Introduction

Many thermal management solutions have been suggested for cooling. Current cooling approaches for thermal management like micro jet cooling and spray cooling have been widely used in electronic devices¹⁻⁶. However, these techniques have some drawbacks, e.g., vibration, noise, leakage, high maintenance and power consumption due to mechanical pumps and other moving parts. To overcome these drawbacks, researchers are avoiding mechanical pumps and have proposed membrane based actuators, e.g., magnetic, piezoelectric, thermopneumatic and shape memory alloy actuators⁷⁻⁹. However, these techniques generally provide pulsatile flow rate, resulting in temperature fluctuations which creates instabilities.

Cooling devices based on field induced flow are very attractive for thermal management in electronic devices. The interaction between a magnetic field and a ferrofluid results in pumping force. These interactions can be divided into three classes: (i) Electrohydrodynamics (EHD), corresponding to electric force effect i.e., the Coulomb force on a low electrical conductor fluid, (ii) Magnetohydrodynamics (MHD), corresponding to Lorentz force i.e., the force between magnetic field and fluid conductors of electricity and (iii) Ferrohydrodynamics (FHD), corresponding to forces of magnetic polarization¹⁰. Systems based on EHD and MHD have no moving parts and therefore a simple structure, but to find a working fluid with suitable electrical conductivity is still a challenge. In addition, MHD systems require high magnetic force to generate significant flow because of high viscous fluid. Therefore, EHD and MHD are usually unsuitable for practical applications.

The body force in FHD is the result of change in the magnetization of materials with temperature in the presence of an applied magnetic field. The mechanics of the FHD depends on the properties of a colloidal suspension of ferri- or ferromagnetic nanoparticles in a suitable liquid carrier, called ferrofluid. A ferrofluid experiences a change in magnetization when the fluid temperature changes. Magnetization is higher in the low temperature region compared to the high temperature region. With constant applied magnetic field, a driving force is

produced for fluid flow. This ferrofluid can therefore be used as a heat transfer medium.

Previous studies in which ferrofluids were used to cool electronic devices, have been called thermomagnetic convection¹¹⁻¹³. These self-cooling devices have several applications, especially where maintenance is difficult, such as space craft, because there is no moving mechanical part. Zhou et al. proposed an engine in which performance can be controlled by external magnetic field or temperature of the ferrofluid¹⁴. The application of this technique can be enlarged to overcome recent problems in heating of solar panels. By controlling temperature rise, we can enhance efficiency of solar panels. Several experimental and theoretical investigations has been carried out for thermomagnetic convection of magnetic fluids and for energy transport devices^{11,15-25}. Lian et al. established a mathematical model to predict flow and heat transport features of the ferrofluid and to design an energy transport device based on the thermomagnetic effect¹¹. Xuan et al. designed a cooling device based on the thermomagnetic effect, in which waste heat from electronic device was used as the driving force for fluid flow.

There is still considerable scope for improvement of these devices. Hence, a proof of concept device was constructed. Modeling was also performed. In this chapter, we have characterized thermomagnetic convection for different temperatures and external magnetic fields.

8.2 Experimental details

Mn_{0.4}Zn_{0.6}Fe₂O₄ nanoparticles, synthesized by the hydrothermal method, were used to make the ferrofluid. The detailed synthesis of nanoparticles can be found in our previous work²⁶. The magnetic properties of the nanoparticles were measured using a physical property measurement system (PPMS, EverCool-II Quantum Design). The Curie temperature (T_C) and saturation magnetization at room temperature were found to be 80°C and 100 emu/g, respectively. These particles were first functionalized by oleic acid and ammonium hydroxide, and then

dispersed into water to make the ferrofluid. The average diameter of the suspended nanoparticles was ~ 11 nm, which was confirmed from TEM micrographs (Fig. 8.1)

Figure 8.1 Bright field TEM of MnZn Ferrite nanoparticles with the histogram of particle size distributions

We have attempted to use Fe-Ni based nanoparticles developed in the previous chapters to prepare ferrofluids. $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ and $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Cr}_5$ nanoparticles were used for preparing the ferrofluid. These particles were added with oleic acid and ammonium hydroxide into the vial and milled for 10h. Further, these coated nanoparticles were dispersed in the silicone oil, oleyl-amine, octadecane. However, due to the high density of these nanoparticles, the particles settled to the bottom of the tube too quickly to conduct the experiments. Stabilization of the particles using oleic acid did not increase the time for settling sufficiently for us to conduct the experiment. $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Cr}_5$ nanoparticles in oleic acid were more dispersed than those of $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ nanoparticles. Therefore, some experiments were performed based on ferrofluid of $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Cr}_5$ nanoparticles and oleic acid.

Fig. 8.2 shows a schematic of the magnetic cooling system. A 5.2 mm inner diameter, 60 cm circumference, polymer tube was used for circular flow. A heat

load (electric heater made by Kanthal wires) and a heat sink (ice bath) were placed opposite each other.

Fig. 8.2 Schematic layout of automatic magnetic cooling system

A permanent magnet, which can provide a maximum field of 0.3 T, was placed close to the heat load. A temperature data logger with SD card was used to record temperature v/s time. The power of the heat load, and therefore initial temperature was tuned by changing the current through the Kanthal wire and voltage using a Keithley power supply (Model: 2231 A-30-3). To avoid buoyancy, a spirit level was used to fix prototype horizontally.

The experiments were carried out for heat power source of 3.25 W, 4.4 W and 5.75 W corresponding to the temperature of 64 °C, 74 °C and 87 °C, respectively. For modelling, COMSOL Multiphysics simulation software version 4.4 was used with finite element method and normal mesh.

8.3 Governing equations

The value of magnetic susceptibility in the model was calculated from the magnetic susceptibility of the magnetic particles and its volume concentration in the fluid. Water is a diamagnetic material and the typical value of volume magnetic

susceptibility is $\sim -9.0 \times 10^{-6}$. The Navier-Stokes equation describes the behavior of the incompressible and viscous laminar flow inside the tube:

$$\frac{\partial}{\partial t}(\rho \mathbf{u}) + \mathbf{u} \cdot \nabla(\rho \mathbf{u}) = -\nabla p + [\eta(\nabla \mathbf{u} + \nabla \mathbf{u}^T)] + F_f \quad (8.1)$$

where ρ , $\mathbf{u}$, p , η and F_f represent the local density of the flow, flow velocity, pressure, fluid viscosity and external volume force vector within each mesh cell, respectively.

8.4 Magnetic field equation

To describe the magnetic field the following equations were used:

$$\Delta \cdot \mathbf{B} = 0 \quad (8.2)$$

$$\mathbf{B} = \mu_o(\mathbf{H} + \mathbf{M}) = \mu_o(1 + \chi)\mathbf{H} = \mu_r \mathbf{H} \quad (8.3)$$

where, χ is the local susceptibility of the ferrofluid diluted by the carrier fluid. The vector $\mathbf{B}$, $\mathbf{M}$, $\mathbf{H}$, μ_o and μ_r represent the magnetic flux density, magnetic field strength, magnetization, vacuum permeability and relative permeability, respectively.

The volume force term F_f (N/m^3) in the Navier-Stokes equation is the sum of the magnetic force vector $\mathbf{F}_m$ and gravitational force vector $\mathbf{F}_g$

$$\mathbf{F}_f = \mathbf{F}_m + \mathbf{F}_g \quad (8.4)$$

The direction of gravity is perpendicular to the flow plane in our experimental, therefore, the effect of gravitational force vector has been neglected

$$\mathbf{F}_f = \mathbf{F}_m = \frac{\chi}{\mu_o}(\mathbf{B} \cdot \nabla \mathbf{B}) \quad (8.5)$$

In the model, the magnetic fluid is assumed to be a single phase, incompressible, and Newtonian fluid. No slip boundary condition was applied to the channel walls.

The properties of water and ferrite based ferrofluid in the models are: density $\rho = 1044 \text{ kg-m}^3$, specific heat $C_P = 1616 \text{ J-kg}^{-1}\text{K}^{-1}$, thermal conductivity $k = 0.16 \text{ W-m}^{-1}\text{K}^{-1}$. For thermal boundary condition, a constant surface temperature is applied to the heat sink section (273.15 K) and to the tube wall in the section where the heat load was placed. The properties of the oleic acid and $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Cr}_5$ base

ferrofluid in the model are; density $\rho = 895 \text{ kg}\cdot\text{m}^{-3}$, specific heat $C_P = 2800 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, thermal conductivity $k = 0.16 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$.

The driving force is actually the result of magnetic and thermal gradients; the temperature distribution of the fluid can be controlled by changing the applied magnetic field. The effect of magnetic field and load temperature on cooling has been studied.

8.5 Experiments with $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles based ferrofluid

8.5.1 Effect of magnetic field

A series of experiments has been carried out to determine the effect of magnetic field on cooling. Fig 8.3 shows the temperature distribution of the fluid in the circular loop with and without magnetic field. From the temperature distribution, it can be concluded that the fluid starts to flow only when field is applied i.e., the driving force is the result of both magnetic and thermal field.

Fig. 8.3. Schematic of 2D model showing the temperature distribution (a) without magnetic field (b) with magnetic field.

Fig 8.4 shows the heating coil temperature under a 4.4 W heat load i.e., initial temperature of heating coil without magnetic field was fixed at 74 °C, with magnetic field of 0 T, 0.2 T, 0.25 T and 0.3 T for both the experimental and simulation results. The magnetic field was fixed by changing the distance of permanent magnet from the tube. It is evident that the temperature of the heating

coil drops with increasing magnetic field, which indicates that thermomagnetic convection, induced by magnetic field, increases with increasing magnetic field.

The combination of temperature gradient and applied magnetic field results in thermomagnetic convection. The magnetization of the magnetic fluid decreases with increasing temperature, the magnetic fluid in the load section possesses less magnetization than other sections. It has been reported in our previous work that the magnetization of MnZn ferrite nanoparticles increases with increasing magnetic field²⁶. The volume force (F_M) depends directly on the applied magnetic field, therefore higher field results in larger cooling. In both experiments and simulations, with non-zero magnetic field, the temperature profiles exhibit a transient behavior (marked by an ellipse in fig 8.4). This behavior can be understood by the fact that the cold magnetic fluid from the heat sink did not reach the hot section by that time. Once the magnetic fluid from the cold section reaches the magnet (and therefore near the heat load), the temperature gradient increases, which results in greater thermomagnetic convection. Xuan et al., also reported that the surface temperature of the chip shows a peak before steady state¹². Jin et al. reported an enhancement in heat transfer with increasing applied magnetic field²⁷. The temperature differences after 25 min, for both experimental and simulation, are plotted in fig 8.5.

Fig.8.4 Effect of magnetic field in the cooling of heat load.

Fig 8.5. Temperature difference of the heat load with and without magnetic field for both experiment (black square) and simulated data (red circle)

8.5.2 Effect of load temperature

To determine the effect initial temperature of heat load on cooling, the initial temperatures of 64 °C, 74 °C and 87 °C were used. A magnetic field of 0.3 T was applied near to the heat load. Fig 8.6 shows the temperature profiles for heating coil with magnetic field of 0.3 T and without magnetic field. An obvious reduction in temperature can be seen in all the cases. Our experimental results were in good agreement with the simulations for the same magnetic field, other parameters are the same as those used in the experiments.

Fig 8.6 Temperature v/s time for initial temperature of heat load of (a) 64°C , (b) 74°C and (c) 87°C , respectively, without and with magnetic field of 0.3 T.

Fig 8.7 shows the temperature difference of the heat load with and without magnetic field for different initial temperatures. The experimental and simulated data were shown by symbol of black square and red circle, respectively. These experimental and simulated results indicate greater cooling with higher initial temperature, therefore such kind of devices have an attractive self-pumping regulating feature. However, the temperature limit of such devices is limited to the boiling temperature of the magnetic fluid²⁸.

Fig 8.7 Temperature difference of the heat load with and without magnetic field for different initial temperatures. The experimental and simulated data are shown by symbol of black square and red circle, respectively

8.5.3 Effect of fluid concentration

To examine the effect of volume fraction of the magnetic nanoparticles, we prepared magnetic fluids with 3%, 5%, 7% and 10% of magnetic nanoparticles in water. The initial temperature of the heat load was 74 °C. Fig 8.8 shows the effect of particle content on the cooling of the heat load with time. As particle content increases, the assumption that the particles do not aggregate is less valid, weakening the agreement between experiment and simulation. After certain time, at high field, particles start to settle in the magnetic field direction, which can reduce the velocity of the fluid and therefore less cooling. Fig 8.9 shows the temperature difference of

the heat load with different volume fraction of magnetic nanoparticles for experiments (black square) and simulated (red circle) results.

Fig.8.8 Effect of volume fraction of magnetic nanoparticles on the cooling of heat load.

Fig.8.9 Temperature difference of the heat load with different volume fraction of magnetic nanoparticles

8.5.4 Switching ('0' and '1') of magnetic field

Fig 8.10 shows the temperature profiles of heat load when magnetic field was applied and removal in between the measurements. The initial temperature without magnetic field was fixed at 87° C, 74° C and 64° C, and after having a study state, a magnetic field of 0.3 T was applied. After applying the magnetic field, a quick drop in temperature is obvious in all the cases.

Fig 8.10 The effect of application and removal of magnetic field of 0.3 T on the temperature profile for initial temperature of heat load of (a) 87° C, (b) 74° C and (c) 64° C, respectively. The temperature drop (cooling) in (a), (b) and (c) was ~ 20 ° C, ~ 24 ° C and ~ 28 ° C, respectively.

Interestingly, the temperature drop in every cycle is almost constant for fixed initial temperature. When field was removed, temperature of heat load again increases up to the initial temperature and steady state was obtained. The cooling (ΔT) increases from $\sim 20^\circ\text{C}$ to $\sim 29^\circ\text{C}$, when initial temperature of heat load was changed from 64°C to 87°C . Importantly, this change in temperature achieved in less than 3 min.

8.6 Experiments with $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Cr}_5$ nanoparticles based ferrofluid

As mentioned earlier, we prepared ferrofluid based on our nanoparticles synthesized in chapter 6. $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Cr}_5$ nanoparticles were coated with a mixture of oleic acid and ammonium hydroxide and then dispersed into the oleic acid. Fig 8.11 shows the temperature profiles for heat load with magnetic field (0.25 T) and without magnetic field, while using $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Cr}_5$ and oleic acid based ferrofluid.

Fig 8.11 Temperature v/s time for initial temperature of heat load of (a) 64.4°C , (b) 53.4°C and (c) 47.4°C , respectively, without and with magnetic field of 0.25 T.

A reduction in temperature can be seen in all cases. In case of oleic acid based ferrofluid, ice bath cannot be used as the heat sink, due to the freezing of oleic acid at $\sim 10^\circ\text{C}$.

The cooling for $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Cr}_5$ and oleic acid based ferrofluid is less than that of MnZn ferrite and water based ferrofluid. This low cooling may be because of the high viscosity of oleic acid. Suslov et al. reported that two mechanisms, i.e., magnetic and thermo-gravitational effects are responsible for instabilities in this kind of ferrofluid¹⁵. The simulated temperature profiles for initial temperature of 64.4°C , 53.4°C and 47.4°C are shown in fig 8.12.

Fig 8.12 Simulated temperature profiles for initial temperature of heat load of (a) 64.4°C , (b) 53.4°C and (c) 47.4°C , respectively, without and with magnetic field of 0.25 T.

We have also compared experimental and simulated results in fig 8.13. The small deviation between experimental and simulated results may be because of the assumption of incompressible flow of ferrofluid in the simulation.

Fig 8.13 Temperature difference of the heat load with and without magnetic field for different initial temperatures. The experiment and simulated data were shown by symbol of black square and red circle, respectively.

8.7 Conclusions

$\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles, synthesized by hydrothermal method were coated by oleic acid and these particles were dispersed into the water to make water based ferrofluid. The ferrofluid was used in a home-built prototype to examine the cooling of heat load. The prototype consists of magnet, heat load, heat sink, polymer tube, connectors and ferrofluid. It was found that the performance of the cooling device depends strongly on the heat load, magnetic particle content and magnetic field. Cooling of $\sim 16^\circ\text{C}$ and $\sim 27^\circ\text{C}$ was achieved by the application of 0.3 T magnetic field when fluid density was 5 % and 10 %, respectively. The *in-situ* application and removal of magnetic field of 0.3 T results the cooling of $\sim 20^\circ\text{C}$, $\sim 24^\circ\text{C}$ and 28°C , when initial temperature was of $\sim 87^\circ\text{C}$, $\sim 74^\circ\text{C}$ and $\sim 64^\circ\text{C}$.

C, respectively. Due to the high density of $(\text{Fe}_{70}\text{Ni}_{30})_{95}\text{Cr}_5$ nanoparticles and the high viscosity of oleic acid, the performance of this ferrofluid was not good as $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ containing water based ferrofluid, and $\sim 3^\circ\text{C}$ cooling of heat load was achieved. The experimental results were compared to simulation performed with COMSOL Multiphysics. These cooling systems do not need a pump and therefore these can consider more mechanically stable. Importantly, these magnetic cooling devices are self-regulating, i.e., the higher the heat load, the greater the driving force for ferrofluid motion.

Reference

- ¹ H. Yong, L. Boon Long, and Z. Xiaowu, *Electron Device Letters*, IEEE **36**, 502 (2015).
- ² M. Fabbri, S. Jiang, and V. K. Dhir, *Journal of Heat Transfer* **127**, 38 (2005).
- ³ B. W. Webb, and C. F., Ma, *Adv. Heat Transfer* **26**, 105 (1995).
- ⁴ D. Lytle and B. W. Webb, *International Journal of Heat and Mass Transfer* **37**, 1687 (1994).
- ⁵ J. Stevens and B. W. Webb, *Journal of Heat Transfer* **113**, 71 (1991).
- ⁶ Y. Zhang, L. P. Pang, Y. Q. Xie, S. C. Jin, M. Liu, and Y. B. Ji, *Experimental Heat Transfer* **28**, 564 (2015).
- ⁷ B. Wang, X. Chu, E. Li, and L. Li, *Ultrasonics* **44**, Supplement, e643 (2006).
- ⁸ E. Stemme and G. Stemme, *Sensors and Actuators A: Physical* **39**, 159 (1993).
- ⁹ Y. Shinozawa, T. Abe, and T. Kondo, in *A proportional microvalve using a bi-stable magnetic actuator*, 1997, p. 233.
- ¹⁰ R. E. Rosenweig, *Ferrohydrodynamics* (Cambridge University Press, 1985).
- ¹¹ W. Lian, Y. Xuan, and Q. Li, *International Journal of Heat and Mass Transfer* **52**, 5451 (2009).
- ¹² Y. Xuan and W. Lian, *Applied Thermal Engineering* **31**, 1487 (2011).
- ¹³ H. Yamaguchi, I. Kobori, and N. Kobayashi, *Journal of Magnetism and Magnetic Materials* **201**, 260 (1999).

- ¹⁴ L. Zhou, Y. Xuan, Q. Li, and W. Lian, *Frontiers of Energy and Power Engineering in China* **3**, 160 (2009).
- ¹⁵ S. A. Suslov, *Physics of Fluids* **20**, 084101 (2008).
- ¹⁶ X.-D. Niu, H. Yamaguchi, and K. Yoshikawa, *Physical Review E* **79**, 046713 (2009).
- ¹⁷ Q. Li, W. Lian, H. Sun, and Y. Xuan, *International Journal of Heat and Mass Transfer* **51**, 5033 (2008).
- ¹⁸ A. Mukhopadhyay, R. Ganguly, S. Sen, and I. K. Puri, *International Journal of Heat and Mass Transfer* **48**, 3485 (2005).
- ¹⁹ S. Banerjee, A. Mukhopadhyay, S. Sen, and R. Ganguly, *Numerical Heat Transfer, Part A: Applications* **55**, 931 (2009).
- ²⁰ R. Ganguly, S. Sen, and I. K. Puri, *Physics of Fluids* **16**, 2228 (2004).
- ²¹ M. Petit, Y. Avenas, A. Kedous-Lebouc, W. Cherief, and E. Rullière, *International Journal of Refrigeration* **37**, 201 (2014).
- ²² M. Bahiraei and M. Hangi, *Journal of Magnetism and Magnetic Materials* **374**, 125 (2015).
- ²³ M. Kaneda, H. Kano, and K. Suga, *Heat and Mass Transfer* **51**, 1263 (2015).
- ²⁴ A. Ghofrani, M. H. Dibaei, A. Hakim Sima, and M. B. Shafii, *Experimental Thermal and Fluid Science* **49**, 193 (2013).
- ²⁵ K. Jahani, M. Mohammadi, M. B. Shafii, and Z. Shiee, *Journal of Electronic Packaging* **135**, 021005 (2013).
- ²⁶ V. Chaudhary and R. V. Ramanujan, *MRS Online Proceedings Library* **1708**, vv10 (2014).
- ²⁷ L. Jin, X. Zhang, and X. Niu, *Journal of Magnetism and Magnetic Materials* **324**, 44 (2012).
- ²⁸ W. Lian, Y. Xuan, and Q. Li, *Energy Conversion and Management* **50**, 35 (2009).

Chapter 9

Summary and future work

Globally, a high percentage of energy utilization in residential and commercial sectors is used for thermal management devices e.g., air conditioners, refrigerators. Therefore, improvement in cooling technology can save billions dollars. Magnetic cooling using MCE has high potential in addressing world-wide demands for environmentally friendly, green and energy efficient thermal management. Rare earth based materials possess good MCE but have low potential for commercialization due to their limited availability, high cost and poor corrosion resistance. The increasing energy demand and limited availability of rare earth materials provides significant motivation to develop rare-earth free magnetocaloric materials which can meet the needs of magnetic cooling applications. Cost effective and low magnetic and thermal hysteresis of Fe-Ni magnetic materials make them attractive for magnetic cooling. In addition, these FeNi based materials exhibit tunable T_C , relevant to commercialization for near room temperature applications.

9.1 Summary

In this work, the effect of B, Mn and Cr alloying on the MCE of Fe-Ni nanoparticle were studied. The importance of γ - phase stabilization on the MCE of Fe-Ni-X (X = B, Mn and Cr) nanoparticles was also investigated. A prototype of ferrofluid based magnetocaloric self-pump was constructed and a series of measurements were performed. These experimental finding were compared with the simulation results.

High energy ball milling, a suitable technique for large scale nanoparticles production was utilized for synthesizing Fe-Ni-X nanoparticles. In this technique, the milling balls and a mixture of starting elements in the desired composition ratio are filled in a rotating chamber along with hard balls. We have optimized the speed and time of the high energy ball milling to obtain the desired structure.

Our major findings are summarized below

1. The synthesis and structure of Fe-Ni-B nanoparticles possessing a metastable face centered cubic structure has been studied. Boron was added to reduce the T_C to $\sim 100^\circ\text{C}$, suitable for low grade waste heat recovery. We found a very high relative cooling power (RCP) in a study of the magnetocaloric effect (MCE) in quenched $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ nanoparticles. RCP increases from 89.8 to 640 $\text{J}\cdot\text{kg}^{-1}$ for a field change of 1 and 5 T, respectively, these values are the largest for rare earth free iron based magnetocaloric nanomaterials. Our T_C value for quenched nanoparticles is lower than that reported in the Fe-Ni phase diagram. We attribute this change to short-range ordering or clustering by addition of boron and quenching. To investigate the magnetocaloric behavior around the Curie temperature (T_C), the critical behavior of these quenched nanoparticles was studied. Detailed analysis of the magnetic phase transition using the modified Arrott plot, Kouvel-Fisher method and critical isotherm plots yields critical exponents of $\beta = 0.364$, $\gamma = 1.319$, $\delta = 4.623$ and $\alpha = -0.055$, which are close to the theoretical exponents obtained from the 3D-Heisenberg model. These particles exhibit broad operating temperature range along with moderate change in entropy and high RCP.

2. The magnetocaloric properties of $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Mn}_x$ with $x = 5, 8, 11$ has been studied. The alloying Fe-Ni with Mn and fcc (γ) phase stabilization results in high relative cooling power (RCP). Quenching is required for γ -phase stabilization. It was found that these nanoparticles are attractive candidates for near room temperature magnetic cooling ($T_C \sim 317$ K and 340 K) and low grade waste heat recovery applications ($T_C \sim 380$ K). The bcc α - $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ and fcc γ - $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ nanoparticles possess high relative cooling power (RCP), varying from $83 \text{ J}\cdot\text{kg}^{-1}$ to $507 \text{ J}\cdot\text{kg}^{-1}$ and from $78 \text{ J}\cdot\text{kg}^{-1}$ to $466 \text{ J}\cdot\text{kg}^{-1}$, respectively, for a field change from $\Delta H=1$ to 5 T. Quenching of these nanoparticles results in T_C shifting close to room temperature (317 K). Good agreement was found between the critical exponents of the γ - $(\text{Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ alloy nanoparticles determined by the modified Arrott plot and those obtained from the Kouvel-Fisher method. The Widom's scaling relation showed good agreement with the critical exponents $\beta = 0.319$, $\gamma = 1.195$ and $\delta = 4.71$. The RCP follows the power law $RCP \propto H^{1.21}$. These nanoparticles can be suitable for low grade waste heat recovery and near room temperature thermal management.
3. The magnetic and magnetocaloric properties of transition metal based $(\text{Fe}_{70}\text{Ni}_{30})_{100-x}\text{Cr}_x$ ($x = 1, 3, 5, 6$, and 7) nanoparticles were studied. 7 % of Cr alloying with $\text{Fe}_{70}\text{Ni}_{30}$ could reduce the T_C from ~ 338 K to 215 K. A Phase diagram for ternary system $(\text{Fe}_{70}\text{Ni}_{30})_{1-x}\text{Cr}_x$ with $x=0$ to 8 was plotted. All the samples exhibit broad entropy curve and therefore high working temperature span, which are useful to enhance an important figure of merit, relative cooling power.
4. It was shown that enhancement in working temperature span and therefore relative cooling power can be attained by having multiple different phases in a composite. We report the novel use of multiphase materials to enhance the working temperature span (δT_{FWHM}) of the magnetic entropy change and the relative cooling power of a Fe-Ni-B bulk alloy. The coexistence of bcc, fcc and spinel phases results in large working temperature spans of 322.3 K and 439.0 K for magnetic field change of 1 T and 5 T, respectively. δT_{FWHM} for this

multiphase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy is about 86 % higher than the corresponding value for single phase γ - $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy for $\Delta H = 1$ T.

The relative cooling power of our transition metal based alloy nanoparticles and gadolinium nanoparticles are shown in the following fig. 9.1

Fig 9.1 The relative cooling power of our iron based nanoparticles and gadolinium nanoparticles.

5. We report the novel use of multiphase materials to enhance the working temperature span (δT_{FWHM}) of the magnetic entropy change and the relative cooling power of a Fe-Ni-B bulk alloy. The coexistence of bcc, fcc and spinel phases results in large working temperature spans of 322.3 K and 439.0 K for magnetic field change of 1 T and 5 T, respectively. δT_{FWHM} for this multiphase $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy is about 86 % higher than the corresponding value for single phase γ - $(\text{Fe}_{70}\text{Ni}_{30})_{89}\text{B}_{11}$ alloy for $\Delta H = 1$ T.
6. We have constructed a self-pumping magnetic cooling prototype based on the thermomagnetic effect, which can be used to cool electronic devices. No energy input is required to operate this device. A series of experiments have been conducted to examine the effect of initial temperature, tube diameter, magnetic

particle content and magnetic field on cooling. The performance of cooling device strongly depends on heat load, magnetic field and volume of ferrofluid. Magnetic field of 0.3 T results in a cooling of $\sim 27^\circ\text{C}$. Experimental results compare well with simulation data. This technique has great potential since there is no moving mechanical part and therefore no maintenance. Our system is treated as a self-regulating device since, as heat load increases, fluid circulates with a higher velocity and transfer heat from the heat load to the heat sink more quickly. We have also used Fe-Ni based nanoparticles to prepare ferrofluids. These particles were added with oleic acid and ammonium hydroxide into the vial and milled for 10h. Further, these coated nanoparticles were tried to disperse in the silicon oil, oleyl-amine, octadecane. However, due to the high density of these nanoparticles, the particles settled to the bottom of the tube too quickly for us to conduct the experiments. Stabilization of the particles using oleic acid did not increase the time for settling sufficiently for us to conduct the experiments, and therefore only $\sim 3.8^\circ\text{C}$ cooling was achieved.

9.2 Proposed future research

The main focus of the thesis was to study Fe-Ni alloy nanoparticles for near room temperature magnetic cooling applications. However, these nanoparticles can also be studied for other applications such as cancer therapies and RF heating experiments. Magnetic nanoparticles are receiving increasing consideration for their promising biomedical and engineering applications. Raising the temperature typically in the range of $42\text{--}46^\circ\text{C}$ is useful to destroy malignant cells. The basic idea to use magnetic nanoparticles for this application is that magnetic nanoparticles can be heated up by the application of a.c magnetic field. Hyperthermia has been recognized as a suitable therapy in cancer treatments. Some of our nanoparticles, for example quenched $\gamma\text{-(Fe}_{70}\text{Ni}_{30})_{92}\text{Mn}_8$ nanoparticles which have T_C of about 44°C may be an ideal candidate for hyperthermia treatment. However, for biomedical applications of magnetic nanoparticles, tests for biocompatibility and toxicity are essential. It is confirmed by TEM and XRD

analysis that the average particle size of our nanoparticles is in the range of 11 to 25 nm. However, for hyperthermia application, particle size distribution is also very important as the local temperature depends on the particle size.

A thin oxide layer on the surface of the particles may be useful as a surfactant coating, a stable ferrofluid can be developed. The efficiency of self-pumping magnetic cooling can further increase as Fe-Ni based nanoparticles have more magnetization than ferrite nanoparticles.

In this thesis, the trend of decreasing T_C , while simultaneously obtaining high MCE has been studied experimentally and by modeling. First principle calculations may be helpful to understand the mechanism of local magnetic moments. The first principle calculations will also be helpful to understand quantitative values of T_C and therefore RCP.

It is clear that the γ -phase is very important for near room temperature magnetic cooling applications. Therefore, we have used *in-situ* XRD to understand phase stabilization. We found that there is negligible change in XRD patterns for annealed and quenched samples but they have different T_C . *In-situ* neutron diffraction may be useful to understand γ -phase stabilization and quenching. In addition, *in-situ* neutron diffraction may also be helpful to understand magnetic interactions between atoms/ions in the unit cell.

Publications

1. **V. Chaudhary**, I Sridhar and R. V. Ramanujan, Self-pumping magnetic cooling, submitted for patent.
2. **V. Chaudhary** and R. V. Ramanujan, Magnetocaloric properties of Fe-Ni-Cr nanoparticles, communicated with Scientific Report
3. **V. Chaudhary** and R. V. Ramanujan, Magnetic and structural properties of high relative cooling power (Fe₇₀Ni₃₀)₉₂Mn₈ magnetocaloric nanoparticles, **J. Phys D: Appl. Phys.** 48 305003 (7pp) (2015)
4. **V. Chaudhary** and R. V. Ramanujan, High relative cooling power in a multiphase magnetocaloric Fe-Ni-B alloy, **IEEE Magnetics Letters**, 6, 6700104(4pp) (2015)
5. **V. Chaudhary**, D. V. Maheswar Repaka, A. Chaturvedi, I. Sridhar and R. V. Ramanujan, Magnetocaloric properties and critical behavior of high relative cooling power FeNiB nanoparticles, **J. Appl. Phys.** 116 (16), 163918-163926 (2014)
6. **V. Chaudhary**, A. Chaturvedi, I. Sridhar and R. V. Ramanujan, Fe-Ni-Mn nanoparticles for magnetic cooling near room temperature, **IEEE Magnetics Letters**, 5, 6800114-6800118 (2014)
7. **V. Chaudhary**, X. Chen, D. V. M. Repaka, A. Chaturvedi, Z. Wang and R. V. Ramanujan, High relative cooling power iron based nanoparticles, **IIR-THERMAG VI Proc**, (2014)
8. **V. Chaudhary** and R. V. Ramanujan, Iron oxide based magnetic nanoparticles for high temperature span magnetocaloric applications, **Mater. Res. Soc. Pros.** 1708, 10-08 (2014).

Conference Presentations

1. **V. Chaudhary** and R. V. Ramanujan, "Iron based magnetocaloric nanomaterials" IEEE Magnetic symposium (2015) –**Singapore**, 01/10/2015-02/10/2015 (**Talk**)
2. **V. Chaudhary** and R. V. Ramanujan, "Magnetocaloric fluids" International conference on materials and advanced techniques (ICMAT-2015), Materials research society Singapore (MRS-S)-**Singapore**, 28/6/20- 03/07/2015 (**Poster**)
3. **V. Chaudhary**, and R. V. Ramanujan, "Low cost magnetocaloric nanoparticles for green, energy efficient thermal management" IEEE Magnetic Society Summer School (2015) University of Minnesota, **Minneapolis, USA**, 14/06/2015-19/06/2015 (**Poster**)

4. **V. Chaudhary**, I Sridhar, R. V. Ramanujan, “MagCool: Magnetic fluid based refrigeration” Joint Conference Between Shizouka University, Japan – Nanyang Technological University, **Singapore**, (2015), Singapore 04/03/2015-06/03/2015 (Talk)
5. **V. Chaudhary**, I. Sridhar and R. V. Ramanujan, “Magnetocaloric nanoparticles for energy efficient applications”, IEEE Magnetic symposium (2014) –**Singapore**, 22/09/2014-23/09/2014 (Talk)
6. **V. Chaudhary**, X. Chen, D. V. M. Repaka, A. Chaturvedi, Z. Wang and R. V. Ramanujan, “High relative cooling power iron based nanoparticles”, 6th IIR/IIF International Conference on Magnetic Refrigeration THERMAG VI (2014) - **Victoria, BC, Canada**, 7/9/2014-10/9/2014 (Talk)
7. **V. Chaudhary**, D. V. Maheswar Repaka, A. Chaturvedi, I. Sridhar and R. V. Ramanujan, “High performance, low cost magnetocaloric nanomaterials for energy efficient applications”, **6th MRS-S** conference on Advanced materials (2014) – **Singapore**, 22/07/2014-24/07/2014 (Poster)
8. **V. Chaudhary**, A. Chaturvedi, and R. V. Ramanujan, “Iron based magnetic nanoparticles for near room temperature magnetocaloric applications”, Materials research society (**MRS**) Spring Meeting (2014) - San Francisco, **California, USA** 21/4/2014-25/4/2014 (Talk)
9. **V. Chaudhary** and R. V. Ramanujan, Fe-Ni/Co based Magnetic Nanomaterials for Magnetocaloric Applications” International conference on materials and advanced techniques (ICMAT-2013), Materials research society Singapore (MRS-S)-**Singapore**, 30/6/2013- 05/07/2013 (Talk)
10. R. V. Ramanujan, X. Chen and **V. Chaudhary**, “Magnetic nanomaterials” IEEE Magnetic symposium (2014) –Singapore, 22/09/2014-23/09/2014 (Talk)
11. R. V. Ramanujan, X. Chen and **V. Chaudhary**, “Affordable High Performance Magnetocaloric Fluids, TMS (2014) 143rd Annual Meeting & Exhibition, San Diego, **California, USA**, 16/2/2014-20/2/2014 (Talk)
12. R. V. Ramanujan, X. Chen, **V. Chaudhary** and D. V. M. Repaka, “Low cost high performance magnetocaloric nanomaterials” TMS (2015) 144th Annual Meeting & Exhibition, **Orlando, Florida USA**, 15/03/2015-19/03/2015 (Talk)