Tuning phase transitions and magnetocaloric properties of novel materials for magnetic refrigeration

Precious Shamba
University of Wollongong

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Tuning Phase Transitions and Magnetocaloric Properties of Novel Materials for Magnetic Refrigeration

By

Precious Shamba, BSc (Hons), MSc

This thesis is presented as part of the requirements for the Award of the Degree of Doctor of Philosophy of the University of Wollongong

December 2012
DECLARATION

I, Precious Shamba, declare that this thesis, submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials (ISEM), Faculty of Engineering, University of Wollongong, Australia, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for a qualification at any other academic institution.

Precious Shamba

December, 2012
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Abstract

In this thesis, the magnetocaloric materials namely, the $\beta$-Co(OH)$_2$ nanosheets, La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds, La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds and the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy have been systematically investigated with their structural, magnetic and magnetocaloric properties being studied in detail.

We report the synthesis of $\beta$-Co(OH)$_2$ nanosheets using microwave assisted hydrothermal and conventional chemical reaction methods. A magnetic transition at an onset temperature, $T_1 = 96$ K, and a sign of antiferromagnetic state transition at the Néel temperature, $T_N = 9 \sim 10$ K, can be determined from M-T curves and M-H curves magnetic properties investigation. It is found that a sign of field-induced first order transition below 9 K, acts the role of reversing the magnetocaloric effect from negative to positive value. The large reversible magnetic-entropy change $\Delta S_M$ of 17 J/kg K around 11 K for a field change of 5 T indicates that this material is useful for refrigeration applications at low temperatures.

The effects of boron doping on the itinerant-electron metamagnetic (IEM) transition and the magnetocaloric effects (MCEs) in the cubic NaZn$_{13}$-type La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ compound have been investigated. The Curie temperature, $T_C$, of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds with $x = 0, 0.03, 0.06, 0.2$ and 0.3 was found to increase from 200 K to 222 K with increase in boron doping, $x$. The maximum values of the isothermal magnetic entropy change, $\Delta S_M$, (derived using the Maxwell relation for a field change $\Delta B = 0 \sim 5$ T) in La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ with $x = 0, 0.03, 0.06, 0.2$ and 0.3 are 14.8, 16, 15, 7.5 and 6.6 J kg$^{-1}$ K$^{-1}$ respectively, with corresponding values of the refrigerant capacity, $RCP$ of 285, 361, 346, 222 and 245 J kg$^{-1}$. 1
The large $\Delta S_M$ value observed for the low level B doped $\text{La}_{0.8}\text{Gd}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_{0.03}$ and $\text{La}_{0.8}\text{Gd}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_{0.06}$ compounds is attributed to the first order nature of the IEM transition while the decrease of $\Delta S_M$ at $x = 0.2$ and 0.3 is due to a change to a second order phase transition with increase in B doping. The nature of the magnetic phase transitions is also reflected by the magnetic hysteresis of $\sim 3.7, 9, 5.7, 0.4$ and 0.3 J kg$^{-1}$ for $x = 0.0, x = 0.03, 0.06, 0.2$ and 0.3 respectively.

In an effort to improve the magnetocaloric effects (MCEs) of the $\text{NaZn}_{13}$-type $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}$ compound, the effect of boron doping on the magnetic properties and magnetocaloric properties has been investigated. The magnetic entropy change ($\Delta S_M$) for the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}$ compound, obtained for a field change of $0 - 5$ T using the Maxwell relation exhibits a spike and appears to be overestimated and is thus corrected by using the Clausius-Clapeyron equation (CC). The $\Delta S_M$ determined from the CC equation is estimated to be $19.6$ J kg$^{-1}$K$^{-1}$. However, large hysteretic losses which are detrimental to the magnetic refrigeration efficiency, occur in the same temperature range. In this work, we report a significant reduction in hysteretic losses by doping the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}$ compound with a small amount of boron to get $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ compounds. The hysteresis loss decreases from 131.5 to 8.1 J kg$^{-1}$ when $x$ increases from 0 to 0.3, while $\Delta S_M$, obtained for a field change of $0 - 5$ T, varies from 19.6 to 15.9 J kg$^{-1}$K$^{-1}$. This also simultaneously shifts the $T_C$ from 174 K to 184 K and significantly improves the effective refrigerant capacity ($R_C_{eff}$) of the material from 164 to 305 J kg$^{-1}$. 


Structural, magnetic and magnetocaloric properties of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy have been investigated using x-ray diffraction, DC magnetization and neutron diffraction measurements. Two phase transitions have been detected at $T_{\text{str}} = 235$ K and $T_C = 270$ K, respectively. A giant magnetocaloric effect has been obtained around $T_{\text{str}}$ associated with a structural phase transition from the low temperature orthorhombic TiNiSi-type structure to the high temperature hexagonal Ni$_2$In-type structure, which is confirmed by neutron study. In the vicinity of the structural transition, $T_{\text{str}}$, the magnetic entropy change, $-\Delta S_M$ reached a maximum value of 14.8 Jkg$^{-1}$K$^{-1}$ under a magnetic field of 5T which is much higher than that previously reported on the parent compound MnCoGe. To investigate the nature of the magnetic phase transition around $T_C = 270$ K from ferromagnetic to paramagnetic state, we performed a detailed critical exponent study. The critical components, $\gamma$, $\beta$ and $\delta$ determined using the Kouvel-Fisher method, the modified Arrott plot as well as the critical isotherm analysis agree well and are close to the theoretical prediction of the mean-field model.

Structural and magnetic properties of Mn$_{0.94}$Ti$_{0.06}$CoGe have been studied by a combination of bulk magnetisation and neutron diffraction measurements over the temperature range 5 K - 350 K. The crystal structural transition occurs at $T_{\text{str}}$ (~ 235 K) with a change in symmetry from the low temperature orthorhombic TiNiSi-type structure (space group Pnma) to the high temperature hexagonal Ni$_2$In-type structure (space group P63/mmc) and the magnetic phase transition takes place around $T_C = 270$ K. It is found that the structural transition around $T_{\text{str}}$ is incomplete and there is a co-existence of the orthorhombic and hexagonal structures between $T_{\text{str}}$ and $T_C$ (~ 270 K).

High pressure x-ray diffraction studies up to 10.4 GPa were performed on the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy using synchrotron radiation and a diamond anvil cell. No structural
phase transitions occurred in the entire range of our measurements. Unit cell parameters were determined up to 10.4 GPa and the calculated unit cell volumes were found to be well represented by a third order Birch-Murnaghan equation of state. The bulk modulus determined from the pressure – volume data was found to be, $B_0 = 231.72 \pm 7.79$ GPa. This study, employing high resolution synchrotron x-rays has helped clarify the behaviour of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy under high pressure.
Chapter 1

INTRODUCTION

1.1 Overview and Motivation

Conventional gas compression refrigerators currently in use today, either use ozone depleting or global warming volatile refrigerants. The use of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) as working fluids in conventional refrigeration technology has raised serious environmental concerns. Currently, some measures, such as the Montreal and Kyoto protocols, have been put in place to protect the environment [1, 2]. The Montreal Protocol is an international treaty governing the protection of stratospheric ozone, originally signed in 1987 and substantially amended in 1990 and 1992 [1]. This protocol requires that countries phase out the production of numerous ozone-depleting substances (ODS) (such as CFCs and halons). The Montreal Protocol has been a success, specifically in stabilizing or decreasing levels of ozone depleting substances in the atmosphere. According to the World Meteorological Organization (WMO), amounts of the total amount of human produced ODS’s in the atmosphere had decreased by approximately 8 - 9 % from the peak observed from 1992 to 1994 [3]. The Kyoto Protocol, on the other hand is an international agreement on the reduction of greenhouse gas emissions and on mechanisms aimed at cutting the costs of reducing emissions, in order to address possible changes in the climate [2]. This protocol requires the world's developed countries to cut greenhouse gas emissions by 5 % from 1990 levels by 2008 - 2010. The Kyoto Protocol signatories succeeded in cutting emissions, however, worldwide atmospheric CO₂ levels continue to soar, now up 35 % since 1997, with most of that increase coming from the countries that were not included in the
protocol. Since approximately 15% of the total energy consumption worldwide is used for refrigeration purposes, even marginal efforts in reducing power consumption in household and industrial refrigeration will have a significantly large economic and ecological impact due to the size of this area [4]. The fact that conventional gas compression refrigeration has reached such a state of maturity that any improvements in this technology will only be incremental, coupled with a serious concern for the environment reiterates the need to shift our attention to alternative technologies such as magnetic refrigeration (MR). Scientists have expended a lot of research effort in this new cooling technology recently because it has several advantages over gas compression refrigeration. Magnetic refrigeration is a relatively novel technique that employs magnetically ordered materials and is based on the magnetocaloric effect (MCE) which results from the coupling of a system of magnetic moments with an external magnetic field resulting in the cooling or heating of a system. This magnetocaloric phenomenon was discovered in pure iron in 1881 by Emil Warburg [5]. Research in this field is therefore focused on the development of new materials with properties appropriate for practical magnetic cooling applications. Numerous efforts in the past years have been directed towards understanding the nature of the intrinsic relationships between the composition, structure, and magneto-thermal properties in improving MCE effects [6 - 13].

A notable achievement in magnetic refrigeration was made in 1976 by Brown who proved magnetic refrigeration could work at ambient temperatures by generating a temperature difference of 47 K with a ferromagnetic refrigerant [14, 15]. In 1997, there was a major breakthrough at Ames laboratory/Astronautics Corporation of America with Profs. Karl A. Gschneider, Jr and V.K. Percharsky unveiling a proof of concept magnetic refrigerator showing that magnetic refrigeration was competitive with conventional gas compression
cooling [16, 17]. Astronautics Corporation made a breakthrough in 2001 with the realisation of the world’s first successful room temperature magnetic refrigerator, in which permanent magnets were used to generate the field [16]. To date about twenty (20) magnetic refrigerators have been built and tested all over the world, a strong indication of the potential of this technology [18]. These notable achievements continue to move the magnetic refrigerator a step closer to commercial applications.

The cooling efficiency of the best proof-of-principle magnetic refrigerator reaches 60% of the Carnot efficiency, which is the maximum theoretical limit, whereas the most efficient conventional gas compression refrigerator operates well below the Carnot efficiency at around 40%, making MR a cost effective technology [18]. The use of MR eliminates the use of ozone depleting chemicals as well as consumption of fossil fuels, thereby reducing CO₂ emissions. Low cost, non-toxicity, compact size as well as lack of noise pollution count as some of the considerable advantages of the MR technology.

The essential part of any magnetic refrigeration device is the magnetocaloric material that undergoes a temperature change when subjected to a magnetic field and the characteristics of a magnetic refrigerator are determined to a large extent by the magnetic working material, which is figuratively speaking, the “heart” of the device. However, most magnetocaloric materials that are promising for intermediate to room temperature applications require magnetic fields as high as 5-10 T for efficient operation. Thus, the main aim of this work is to seek new materials that are cost-effective and exhibit large magnetic entropy change induced by a moderate magnetic field that can be supplied using permanent magnets. Such materials will be vital for creating highly efficient magnetic refrigerators with commercialization potential. This thesis will therefore focus on fundamental studies related to the critical issues facing the application of MR.
1.2 Objectives of research

Generally, the objective of the present thesis is to explore novel magnetic materials with considerable MCE for use in magnetic refrigerators. It is the aim of this work to contribute towards a better understanding of the fundamental material characteristics, with an emphasis on understanding the relationship between a defined structure, the crystallographic phase and magnetic phase structure, and alteration in the magneto-thermal properties.

The specific objectives are:

1. Study the effect of stoichiometric modifications or atomic substitutions to tune transition temperature, $T_C$, for phase transitions to occur at higher temperatures to enable materials to be used in room temperature devices.

2. Explore effects of the variation in composition and fabrication conditions on the types of magnetic phase transitions and the related magneto-structural coupling.

3. Study magnetocaloric properties of these systems, by quantifying the MCE using magnetic measurements to determine the magnetic entropy change ($\Delta S_M$) and magnetic thermal measurements to determine the adiabatic temperature change ($\Delta T_{ad}$).

4. Ultimate aim of the study is to synthesize high quality magnetocaloric materials suitable for use in magnetic refrigeration. Thus, the characterization of these magnetocaloric materials forms a critical part of the study.
1.3 Organization of Thesis

The present thesis aims to provide a comprehensive guidance on the optimization of the MCE in novel magnetic materials for use in magnetic refrigeration. This thesis is organised as follows:

The overview and motivation of the PhD research work as well as the specific objectives of the work are outlined in Chapter 1. For a better understanding of the variation of the magnetocaloric effect in different material systems, a thorough literature review with the emphasis on the MCE of materials with phase transitions occurring in the room temperature range is presented in Chapter 2.

The synthesis procedures of the various material systems investigated in this study and the main characterization techniques used are outlined in Chapter 3. Chapter 4 details the magnetic and magnetocaloric properties of β–Co(OH)$_2$ 2D nanostructures which, according to the best of our knowledge, has not been reported before.

Chapter 5 details the results of the first study on the effect of boron doping on the magnetocaloric properties of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$. This study brings new light on the role of boron (B) in tuning the magnetocaloric properties of the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ compound. A significant enhancement of the Curie temperature, $T_C$, and the refrigerant capacity was achieved in La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ due to boron doping. This study demonstrated how boron doping at high levels tunes the magnetic transition from 1$^{st}$ to 2$^{nd}$ order.

In Chapter 6, the experimental results of a study on the magnetic and magnetocaloric properties of boron doped La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ with the main aim of investigating the effect of boron doping on the hysteresis and consequently, the refrigerant capacity of this material
system are presented. Neutron measurement results of the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ material system are also presented in this chapter.

In Chapter 7, results on the magnetic properties and critical behaviour analysis of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy are presented. Results of a temperature dependent neutron diffraction study of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy are also presented in this chapter so as to elucidate the existence of a coupling of the magneto-structural transition.

In Chapter 8, results on the high pressure x-ray diffraction studies up to 10.4 GPa performed on the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy using synchrotron radiation are presented. The final chapter, Chapter 9, describes the conclusions drawn from this study as well as recommendations regarding future work.
References:


CHAPTER 2

LITERATURE REVIEW

2.1 Historical Background of Magnetic Refrigeration

Magnetic refrigeration is a relatively novel technique which employs magnetically ordered materials and is based on the magnetocaloric effect (MCE). The magnetocaloric phenomenon was discovered in pure iron in 1881 by Emil Warburg [1]. He discovered that when iron was placed in a magnetic field it was immediately warmed, and on removal of the magnetic field the iron sample cooled down, with the cooling effect varying between 0.5 to 2 K / T. Langevin, in 1905, demonstrated that the changing of a paramagnet magnetization causes a reversible temperature change [2].

In the late 1920’s cooling via adiabatic demagnetization was independently proposed by two scientists: Debye [3] and Giauque [4]. This cooling technology was first demonstrated experimentally by William F. Giauque and Dr. D.P. MacDougall in 1933 for cryogenic purposes when they attained a temperature of 0.25 K from an initial temperature of 1.5 K with a magnetic field change of 8 kOe using gadolinium sulfate Gd$_2$(SO$_4$)$_2$ ∙8H$_2$O [5]. The cooling process was performed in two stages namely, isothermal magnetization and adiabatic demagnetization.

In 1933 de Haas et al. achieved 0.08 K starting from a temperature of 1.35 K with a magnetic field change of 27.6 kOe using cerium ethylsulfate Ce(C$_2$H$_5$SO$_4$)$_3$ ∙9H$_2$O [6]. In the 1950’s
several magnetic refrigerators operating at temperatures between 1 and 30 K were made. However, these could only run for a couple of days and thus were too inefficient to be used commercially. The interest in the investigation of MCE has steadily increased over the years with research focusing on the use of the MCE process to perform refrigeration near room temperature.

A notable achievement was made in 1976 by Zimm and later in 1978 by Brown who proved magnetic refrigeration could work at ambient temperatures by generating a temperature difference of 47 K with a ferromagnetic refrigerant [7 - 8]. In 1997, Prof. Karl A. Gschneider, Jr at Ames laboratory/Astronautics Corporation of America unveiled a proof of concept magnetic refrigerator showing that magnetic refrigeration was competitive with conventional gas compression cooling [9]. Astronautics Corporation made a breakthrough in 2001, with the realisation of the world’s first successful room temperature magnetic refrigerator, in which permanent magnets were used to generate the field [10]. This achievement moved the magnetic refrigerator a step closer to commercial applications.

2.2 Basic Theory of the Magnetocaloric Effect

MCE is the response of a magnetic solid to a changing magnetic field which is manifests itself as a change in its temperature [11]. The essential part of any magnetic refrigeration device is the magnetocaloric material that undergoes a temperature change when subjected to a magnetic field. It is worth noting that all magnetic materials exhibit the magnetocaloric effect. This effect indicates that paramagnetic or soft ferromagnetic materials absorbs heat and their magnetic entropy decreases when the magnetic field is applied isothermally or otherwise expel heat and their magnetic entropy increases when the magnetic field is reduced.
isothenrally. In order to understand the physics behind the magnetocaloric effect, it is important to gain an insight into the behaviour of magnetic materials under the influence of a magnetic field.

Magnetic materials can order their magnetic moments in a variety of ways as shown in Figure 2.1, with the simplest being the so-called ferromagnetic order, in which the interactions between the moments act to align them [12]. These interactions have a much larger effect on the alignment than the magnetic fields we apply. When a magnetic field is applied to a magnetic material, the unpaired spins partially comprising the material’s magnetic moment are aligned parallel to the magnetic field as shown in Figure 2.2. This spin ordering lowers the entropy of the system since disorder has decreased. To compensate for the aligned spins, the atoms of the material begin to vibrate in attempt to randomize the spins and lower the entropy of the system again. In doing so, the temperature of the material increases. An opposite effect occurs on removal of the applied magnetic field. At very low temperatures

![Figure 2.1 Examples of magnetic order. Arrows represent the magnetic moments of atoms in a cubic lattice. (a) ferromagnetic order where all the spins align in the same direction. (b) antiferromagnetic order where the spins align opposite each other [12].](image-url)
or very high fields all the moments may be aligned and an increase in field will not yield a further increase in the magnetization. The magnetization is a measurement of how much the magnetic moments are aligned. All magnetic materials have a phase transition temperature below which its moments are ordered and above which the moments are disordered. In the disordered state the magnetic materials are said to be paramagnetic. Near the transition temperature the magnetization \( M \), changes rapidly, whereas the changes at other temperatures are small.

The MCE is quantified through a definition of the entropy at constant pressure in a system as a function of temperature and magnetic field, \( S(T, H) \). The entropy of a magnetic material consists of the magnetic entropy \( S_M \), the lattice entropy \( S_L \) and the electronic entropy \( S_E \) as show below:

\[
S(T, H) = S_M(T, H) + S_L(L) + S_E(T)
\]  

(2.1)

where \( S_M \) is a function of both \( H \) and \( T \), whereas \( S_L \) and \( S_E \) are both functions of \( T \) only. Thus, only the magnetic entropy \( S_M \) can be controlled by changing the strength of the magnetic field. Figure 2.3 is an S-T diagram for a ferromagnetic solid, showing the total

---

**Figure 2.2** Illustration of the effect of applying an external magnetic field, \( H \) to a ferromagnetic material [12].
entropy in magnetic field $H_0$ and $H_1$ ($H_1 > H_0$). The diagram also illustrates the MCE which is represented by $\Delta T_{ad}$ or $\Delta S_M$ in the vicinity of the magnetic ordering temperature (Curie temperature, $T_C$). The vertical arrow shows the isothermal magnetic entropy change, $\Delta S_M$ whilst the horizontal arrow shows the adiabatic temperature change, $\Delta T_{ad}$ [13]. These arrows represent two different transformations, described in the preceding paragraph, elucidating further the thermodynamics of the magnetocaloric effect [13].

**Figure 2.3** S - T diagram demonstrating the magnetocaloric effect [13].

In order to explain the thermodynamics of the magnetocaloric effect, two different transformations, mentioned in the previous paragraph, are explained below:
i. The variation of the applied external magnetic field under isothermal conditions:

When the magnetic field is changed from $H_0$ to $H_1$ at a constant temperature $T$, the magnetocaloric effect is then described as:

$$\Delta S_M(T)_{T,\Delta H, p} = [S_M(T)_{H1} - S_M(T)_{H0}]_{T, p} = [S(T)_{H1} - S(T)_{H0}]_{T, p}$$  \hspace{2cm} (2.2)

The relationships between $S(T)_{H0}$ and $S(T)_{H1}$ at constant pressure determines the magnitude, sign and behaviour of $\Delta S_M$.

ii. The variation of the applied external magnetic field under adiabatic conditions:

When the magnetic field is changed from $H_0$ to $H_1$ under adiabatic conditions, the magnetic entropy changes, but the total entropy remains constant i.e.: $\Delta S = \Delta S_E + \Delta S_L + \Delta S_M = 0$.

Since the magnetic entropy changes, the combined lattice and electronic entropy must change by $\Delta(S_L + S_E) = -\Delta S_M$. Thus the lattice and electronic entropy vary resulting in a measurable adiabatic temperature change $\Delta T_{ad}$. This isentropic difference between the corresponding $S(T)_{H}$ curves known as the adiabatic temperature change can be used as a measurement of the magnetocaloric effect of the material. The $\Delta T_{ad}(T)_{\Delta H}$ is a function of temperature and for a fixed $\Delta H$ and an arbitrary $T$ it is defined as:

$$\Delta T_{ad}(T)_{T,\Delta H, p} = [T(S)_{H1} - T(S)_{H0}]_{T, p}$$  \hspace{2cm} (2.3)

According to equation (2.2) and (2.3) when the behaviour of the total entropy of a magnetic material is known as a function of both temperature and magnetic field, the magnetocaloric effect can thus be fully characterized.
2.2.1 Basic Thermodynamics of the magnetocaloric effect

The MCE is essentially the application of the first and second law of thermodynamics to a magnetic system. A description of the MCE in a magnetic system involves the use of thermodynamic functions such as:

i. The internal energy $U$

ii. The free energy $F$ and

iii. The Gibbs free energy $G$

The internal energy $U$, is a function of the total entropy $S$, the volume $V$ and the magnetization $M$ as shown below

$$U = U(S, V, M)$$ \hspace{1cm} (2.4)

The free energy of Helmholtz is used for systems with constant volume and is a function of $V$, $H$ and absolute temperature $T$. It can be written as:

$$F = F(T, V, H)$$ \hspace{1cm} (2.5)

It can also be expressed as:

$$F = U - TS$$ \hspace{1cm} (2.6)

The Gibbs free energy is a function of $T, H$ and $p$ and it is used for systems with constant pressure. It can be expressed as:

$$G = U - TS + PV - \mu_0MH$$ \hspace{1cm} (2.7)
Figure 2.4 Illustration of the first order phase transition with the corresponding equations describing the transition\(^1\).

Equation (2.7) is a very important expression as it is possible to define the first order and second order transitions on the basis of this equation. A phase transition is defined to be first order if the first derivative of the Gibbs free energy is discontinuous at the phase transition. Generally in a first order transition the volume, magnetization and entropy of the magnetic material might be discontinuous as shown in Figure 2.4.

Figure 2.5 Illustration of the second order phase transition\(^1\).

\(^{1}\text{Adapted from http://www.helsinki.fi/~serimaa/soft-luenso/soft-2-phase.html}\)
For a second order phase transition, the first derivative of the Gibbs free energy as well as the entropy is continuous at the phase transition as shown in Figure 2.5.

The differentials of $U, S$ and $G$ are given below as:

$$dU = TdS - pdV - \mu_0 HdM$$  \hspace{1cm} (2.8)

$$dF = -SdT - pdV - \mu_0 HdM$$  \hspace{1cm} (2.9)

$$dG = Vdp - SdT - \mu_0 MdH$$  \hspace{1cm} (2.10)

Considering the free energy $F$, the following equations determine the internal parameters $S, p$ and $H$.

$$S(T,H,V) = -\left( \frac{\partial F}{\partial T} \right)_{H,V}$$  \hspace{1cm} (2.11)

$$H(T,M,V) = -\left( \frac{\partial F}{\partial M} \right)_{V,T}$$  \hspace{1cm} (2.12)

$$p(T,H,V) = -\left( \frac{\partial F}{\partial V} \right)_{H,T}$$  \hspace{1cm} (2.13)

Considering the Gibbs free energy, the following equations determine, the internal parameters $S,M,V$:

$$S(T,H,p) = -\left( \frac{\partial G}{\partial T} \right)_{H,p}$$  \hspace{1cm} (2.14)

$$M(T,H,p) = -\left( \frac{\partial G}{\partial H} \right)_{T,p}$$  \hspace{1cm} (2.15)
\[ V(T, H, p) = \left( \frac{\partial G}{\partial p} \right)_{T, p} \]  
\hspace{1cm} (2.16)

Replacing the magnetic field \( H \) with the magnetic moment \( M \) as the external variable we get:

\[ H = \left( \frac{\partial G}{\partial M} \right)_{T, p} \]  
\hspace{1cm} (2.17)

Deriving the Maxwell equations using equations (2.14) and (2.15), (2.14) and (2.16) and (2.14) and (2.17) we get:

\[ \left( \frac{\partial S}{\partial H} \right)_{T, p} = \left( \frac{\partial M}{\partial T} \right)_{H, p} \]  
\hspace{1cm} (2.18)

\[ \left( \frac{\partial S}{\partial p} \right)_{T, H} = \left( \frac{\partial V}{\partial T} \right)_{H, p} \]  
\hspace{1cm} (2.19)

\[ \left( \frac{\partial S}{\partial M} \right)_{T, p} = -\left( \frac{\partial H}{\partial T} \right)_{M, p} \]  
\hspace{1cm} (2.20)

From the second law of thermodynamics, the enthalpy variation of a reversible process can be expressed as

\[ \partial S = \left( \frac{\partial Q}{\partial T} \right) \]  
\hspace{1cm} (2.21)

Accordingly, the heat capacity \( C_x \) of a system at constant parameters \( x \) is defined by:

\[ C_x = \left( \frac{\partial Q}{\partial T} \right)_x \]  
\hspace{1cm} (2.22)
Where \( \partial Q \) is the amount of heat exchanged by the solid at temperature \( T \) giving rise to a temperature change \( \partial T \). Since \( \partial Q = T \partial S \), the heat capacity of the system can be expressed as:

\[
C_s = T \left( \frac{\partial S}{\partial T} \right)_s
\]  
(2.23)

From equation (2.25), the total entropy can be expressed as:

\[
dS(T)_s = \frac{C(T)}{T} dT
\]  
(2.24)

The total differential of the total entropy of a magnetic system as a function of \( T, p \) and \( H \) can be written as:

\[
dS = \left( \frac{\partial S}{\partial T} \right)_{H,p} dT + \left( \frac{\partial S}{\partial H} \right)_{T,p} dH + \left( \frac{\partial S}{\partial p} \right)_{T,H} dp
\]  
(2.25)

Considering an adiabatic \((dS = 0)\) and isobaric \((dp = 0)\) process and using the Maxwell relations (2.18) and (2.23), the temperature change due to a change in the magnetic field is expressed as:

\[
dT = -\frac{T}{C_{H,p}} \left( \frac{\partial M}{\partial T} \right)_{H,p} dH
\]  
(2.26)

Using equations (2.20) and (2.24) the temperature change caused by an adiabatic and isobaric change of magnetization is given by:

\[
\partial T = -\frac{T}{C_{M,p}} \left( \frac{\partial H}{\partial T} \right)_{M,p} dM
\]  
(2.27)

\( C_{H,p} \) and \( C_{M,p} \) are the heat capacity of the material at constant pressure and constant field or magnetization respectively.
If the total entropy of the system is expressed a function of $T$, $p$ and $M$ respectively, its total differential can be written as:

$$dS = \left( \frac{\partial S}{\partial T} \right)_{M,p} \, dT + \left( \frac{\partial S}{\partial M} \right)_{T,p} \, dM + \left( \frac{\partial S}{\partial p} \right)_{T,M} \, dp$$

(2.28)

To obtain the finite temperature change $\Delta T_{ad}$ for an adiabatic magnetization, equations (2.26) and (2.27) are integrated as shown below:

$$\Delta T_{ad}(T, \Delta H) = - \int_{H_1}^{H_f} \left( \frac{H}{C(T,H)} \right)_H \left( \frac{\partial M(T,H)}{\partial T} \right)_H \, dH$$

(2.29)

$$\Delta T_{ad}(T, \Delta M) = - \int_{M_i}^{M_f} \left( \frac{H}{C(T,M)} \right)_M \left( \frac{\partial H(T,M)}{\partial T} \right)_M \, dM$$

(2.30)

The integration of the Maxwell relation, equation (2.18) to give the finite entropy change under isothermal and isobaric conditions is expressed below:

$$\Delta S_M(T, \Delta H) = \int_{H_1}^{H_f} \left( \frac{\partial M(T,H)}{\partial T} \right)_H \, dH$$

(2.31)

From these equations it follows that the MCE (absolute values of $\Delta S_M(T)_{\Delta H}$ or $\Delta T_{ad}(T)_{\Delta H}$) is large when $\left| \frac{\partial M}{\partial T} \right|$ which is sometimes written as $\left| \frac{\partial \sigma}{\partial T} \right|$ is large, that is the magnetization changes rapidly with temperature.
2.3 Research Progress of magnetic materials for room temperature magnetic refrigeration

Recently, several materials with a so called giant MCE have been discovered. This includes amongst others, Gd$_5$Si$_2$Ge$_2$, MnAs$_{1-x}$Sb$_x$, (Mn,Fe)$_2$(P,As) and La(Fe,Si)$_{13}$ [14 - 72]. These materials are the main contenders for near-room temperature magnetic refrigeration based on the MCE which is set to replace the conventional gas-compression/expansion technique. Conventional refrigeration technologies based on the gas-compression/expansion cooling mechanisms may gradually be replaced by the environmentally friendly and more efficient magnetic refrigeration in the nearly future [73 – 77]. The magnetic refrigeration is based on the magnetocaloric effect (MCE) which results from the coupling of a system of magnetic moments with an external magnetic field resulting in the cooling or heating of a system. An ideal material for magnetic refrigeration should be composed of relatively inexpensive raw materials, have a high MCE demonstrated by a high change in magnetic entropy ($\Delta S_M$) and a high adiabatic temperature change ($\Delta T_{ad}$) and have little or no thermal or magnetic hysteresis [78]. First order transitions possess the above mentioned characteristics and have been shown to have a consistently higher MCE than second-order transitions.

Due to rising concerns about global warming, there has been renewed interest in the magnetic refrigeration cooling technology. Figure 2.6, shows that the number of published papers per annum on the magnetocaloric effect has grown at an exponential rate in the past years. Scientists are expending a lot of research effort in this field mainly because of the issue of global warming. Global warming is exacerbated by the fact that the world’s energy demands keep on increasing, meaning that it will become even worse in future.
Figure 2.6 Rate of increase of published research papers per annum on the magnetocaloric effect. The triangle represents the number of papers abstracted during the first three-fourths of the year 2007 [9].

2.3.1 La(Fe,Si)$_{13}$ based compounds

La(Fe$_{13-x}$M$_x$) compounds have been studied since the late 1960s [79 - 80]. The magnetic properties of these compounds were initially measured in the mid 1980’s by Palstra et al. [81 - 82]. Compounds with cubic NaZn$_{13}$ - type structure have attracted a lot of attention in recent years because of their interesting magnetocaloric properties and low cost. Below their Curie temperature, these compounds are ferromagnetic with high saturation magnetization due to the high concentration of 3d metal and cubic symmetry structure. LaFe$_{13-x}$Si$_x$
compounds in the ground state are ferromagnetic and have high magnetization. With increasing Si content, the moments of Fe atoms decrease and the Curie temperature increases, which is usually found in Invar-type alloys [81]. These compounds are enjoying renewed interest in the magnetic materials community due to the observation of a large MCE, which shows a large magnetic entropy change, $\Delta S_M = 19.4$ Jkg$^{-1}$ at $T_C = 208$ K [83].

In the La(Fe$_{1-x}$Si$_x$)$_{13}$ system, at lower Si concentration or under higher annealing temperature, the cubic NaZn$_{13}$ - type structure occurs [84]. Preparation of homogeneous La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds is difficult and requires a lengthy homogenization heat treatment because of the formation of a large amount of primary Fe-Si phase dendrite crystals in the cast alloys. A simple consideration of the diffusion law suggests that refinement of the cast structure by means of rapid solidification should significantly contribute to reducing the time required for homogenization [83]. Bodak and Gladyshevskij investigated the phase equilibrium relations of the La-Fe-Si ternary system, and found that the NaZn$_{13}$ - derived structure within the homogeneous composition range of LaFe$_{11.3} - 9.8$Si$_{1.7} - 3.2$ but they did not present more detailed structural information [85]. Phase equilibria in the Fe-La-Si system are not well known. The Fe-La and Fe-Si phase diagrams have been studied and reviewed [86,87]. However, the La-Si phase diagram is not known but six La-Si intermediate phases are known in literature. According to the La-Fe quasi binary diagram, the temperature point of the peritectic reaction in LaFe$_{13-x}$Si$_x$ compounds is around 1673 K [88].

Wen et al. prepared LaFe$_{13-x}$Si$_x$ compounds with $x = 2.4$, 2.6 and 2.8 by arc melting and subsequently carried out magnetization measurements on these samples [89]. XRD patterns of these samples confirmed that they crystallized in a single NaZn$_{13}$ type phase. The Curie
temperature decreases nearly 50 K with \( x \) increasing from 2.4 to 2.8. The samples exhibit a
typical second order phase transition. The maximum values of the magnetic entropy change
of \( \text{LaFe}_{13-x}\text{Si}_x \) samples are found to be 5.85, 5.9 and 3.7 J/kg K for \( x = 2.4, 2.6 \) and 2.8 under
a field change of 0 - 5 T.

Ilyn \textit{et al.} investigated the MCE in the itinerant electron metamagnetic (IEM) compounds
\( \text{LaFe}_{11.7}\text{Si}_{1.3} \) and \( \text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1} \) by measuring directly or calculating from magnetization
data using Maxwell relation [90]. The largest values of the MCE were observed at 188 K for
\( \text{LaFe}_{11.7}\text{Si}_{1.3} \) and at 274 K for \( \text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1} \). The isothermal magnetic entropy change
\((-\Delta S_M)\) reached in \( \text{LaFe}_{11.7}\text{Si}_{1.3} \) and \( \text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1} \) is 29 J/kg K and 20.3 J/kg K
respectively, at a magnetic field change of 5 T. The adiabatic temperature was measured
directly and the maximum values of \( \Delta T \) for \( \text{LaFe}_{11.7}\text{Si}_{1.3} \) and \( \text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1} \) were 4 and
2.4 K respectively. The normalized adiabatic temperature changes of 2.9 and 2.2 K/T are
comparable with that of 2.85 K/T in Gd.

Nane \textit{et al.} investigated the low field magnetic and magnetocaloric properties of \( \text{LaMn}_{1.9}\text{Fe}_{0.1}\text{Si}_2 \) [91]. The magnetic entropy change \( \Delta S_M \) as a function of temperature and magnetic
field was derived from the Maxwell relation using M-H data measured at various
temperatures. The peak values of \( \Delta S_M \) for the fields of 0.2 and 0.9 T are about 0.2 J/kgK and
0.53 J/kgK respectively. The small values in this material system is probably due to the small
value of saturation magnetization and the nature of the phase transition which is found to be
second order. The results also show that \( \text{LaMn}_{1.9}\text{Fe}_{0.1}\text{Si}_2 \) is ferromagnetically ordered around
285 K.
Liu et al. investigated the effect of annealing on the arc-melted LaFe$_{11.6}$Si$_{1.4}$ compound. This compound was annealed at high temperatures of 1423 K, 1473 K and 1573 K for an hour, respectively [92]. Metallographic microscopy and powder X-ray diffraction analyses show that the as-cast LaFe$_{11.6}$Si$_{1.4}$ compound mainly consists of $\alpha$-Fe and LaFeSi phases. However, after annealing, the main phase of the annealed LaFe$_{11.6}$Si$_{1.4}$ compound becomes the cubic NaZn$_{13}$-type phase, which increases with an increase in annealing temperature. The maximal magnetic entropy change the sample annealed at 1573 K is 17.56 J/kg K at a magnetic field change of 0 - 5 T.

Tsuji et al. investigated the phase formation of La(Fe,Si)$_{13}$ compounds with NaZn$_{13}$ – type structure using an electron probe micro analyser (EPMA) and x-ray diffraction [93]. Synthesis of the La(Fe,Si)$_{13}$ compounds was via a solid-state reaction of fine elemental powders using a spark plasma sintering (SPS) technique. This technique consists of only one process which does not require melting, annealing, grinding or molding. The structure of these samples were then compared to those synthesized by conventional methods including a melt and solidification process. The conventional methods, namely, arc-melting and melt spinning, easily caused segregation of the Fe-rich phase. However, the remarkable NaZn$_{13}$ – type structure was observed in the SPS sample. Conclusions from these experiments include the fact that homogeneous distribution of the elements and short-range atomic diffusion are important for forming NaZn$_{13}$ - type structure efficiently.

So many studies have been devoted to the increase of the Curie temperature by substituting Fe and La by other transition metals and rare-earths respectively or by introducing interstitial atoms such as C, N, B or H materials [94]. This process of introducing small atoms into the
structure, usually from the gas phase at elevated temperatures and pressures, can lead to very
dramatic changes in the magnetic properties of these interstitially modified materials. In
particular, hydriding and nitriding lead to an expanded crystal lattice and a modified
electronic structure, commonly in the form of an increase in the density of states at the Fermi
level. Such a situation results in an elevated Curie temperature and a dramatically enhanced
MCE.

The most remarkable feature of LaFe$_{13-x}$Si$_x$ besides the significant MCE is the strong
dependence of its Curie temperature ($T_C$) on element doping or external perturbations such as
magnetic field and pressure. It has been confirmed that the $T_C$ of LaFe$_{13-x}$Si$_x$ can be increased
by introducing N, H, C or B atoms. The intrusion of the interstitial N, H, C or B atoms into
the lattice leads to lattice expansion, which makes the Fe 3d band narrow and bring about the
increase in $T_C$ by reducing the Fe 3d overlap wave functions [95]. Small atoms like N change
the electronic structure of the compounds, which can influence the intrinsic magnetic
properties of Fe-based compounds, improving the Curie temperature due to the fact that N
weakens the negative Fe-Fe exchange by increasing the Fe-Fe distance [96]. Carbon is
usually chosen as the interstitial atom because its content can be easily controlled by direct
arc melting using Fe-C alloy compared with that for H and N by gas-solid reaction.
However, hydrides are usually chemically unstable above 150 °C, which is an underlying
problem for practical applications [97]. It has also been noted that the N or C addition in
LaFe$_{13-x}$Si$_x$ compounds as interstitial atoms has a negative impact on the MCE due to the
reduced magnetic moments and loss of the first order nature of the structural/magnetic
transition of the compound [98].
Xie et al. studied the influence of boron addition on the phase formation, Curie Temperature and magnetic entropy change of NaZn$_{13}$ – type La(Fe$_{0.9}$Si$_{0.1}$)$_{13}$B$_x$ compounds with $x = 0, 0.03, 0.06, 0.1, 0.2, 0.3, 0.5$ and $0.6$ [99]. Results show that a small amount of B addition in La(Fe$_{0.9}$Si$_{0.1}$)$_{13}$ forms the solid solution NaZn$_{13}$ – type structure phase by substituting B for Si or doping B into interstitial position of the lattice, preserves its giant magnetocaloric effects due to their first order structural/magnetic transition, as well as increasing its Curie temperature slightly. In $\Delta S_M$ the magnetic field change of $0 – 1.6$ T are around $29$ Jkg$^{-1}$K$^{-1}$ for samples with $B < 0.3$, whilst improving the $T_C$ by $2$ K.

Fujita et al. revealed that the insertion of hydrogen into the LaFe$_{13-x}$Si$_x$ lattice considerably increases $T_C$ towards room temperature without significantly affecting the MCE [100]. Chen et al. also noted the same behaviour [101]. Balli et al. studied the effect of nitrogen insertion on the crystal structure, magnetic and magnetocaloric properties of LaFe$_{11.7}$Si$_{1.3}$ [94]. The Curie temperature increased with an increase in nitrogen concentration on account of volume expansion. Compared to hydrides the entropy change of LaFe$_{11.7}$Si$_{1.3}$ decreased drastically after nitrogenation. The relative cooling power of the nitride, however, remained comparable to that of reference materials. Nitrogenation had a strong effect on the cubic phase, including a large lattice expansion (6.2 to 10.8 %) and an increase of Curie temperature (52 K to 80 K) and spontaneous magnetization (approximately 10 %).

Lyubina et al. investigated the structure and magnetic properties of LaFe$_{13-x}$Si$_x$ and Co-substituted LaFe$_{11.8-x}$Co$_x$Si$_{1.2}$ alloys prepared by melt spinning as well as LaFe$_{11.5}$Si$_{1.43}$H$_x$ hydrides prepared by reactive milling it was noted that the hysteresis in the temperature and
field induced phase transitions is significantly reduced as compared with conventional bulk alloys [102].

Fujieda et al. investigated the partial substitution of Ce for La in LaFe$_{13-x}$Si$_x$ compounds. They noted that this partial substitution enhanced the MCE ($-\Delta S_M$) but decreases the Curie temperature $T_C$ [103]. Due to the weak ferromagnetic band character of iron, the LaFe$_{13-x}$Si$_x$ compounds exhibit rather low Curie temperatures because of the short Fe-Fe distances existing in LaFe$_{13-x}$Si$_x$. The same also applies for many Fe-rich R-Fe series (R-rare-earth). Applying an external pressure, however, causes a lattice contraction. It has been reported that a pressure of 1GPa reduces $T_C$ by approximately 100 K, whereas a magnetic field of 5T lifts $T_C$ by approximately 25 KpA [95].

Fujita et al. demonstrated that LaFe$_{13-x}$Si$_x$ compounds exhibit a first order magnetic phase transition at the Curie temperature, $T_C$, as well as an IEM transition above $T_C$. The magnetic moment induced by the IEM transition exceeds 1 $\mu_B$ just above $T_C$, accompanied by a large volume change [104, 105]. Fujita et al. investigated the magnetovolume effect due to the IEM transition in La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ by x-ray diffraction measurements in high magnetic fields [106]. After the IEM transition no crystal structure change was observed. A significant increase in the lattice constant of about 0.4 % is caused by the IEM transition. The magnetic field dependence of the relative change in the lattice constant measured perpendicular to the magnetic field direction is similar to that of the longitudinal linear magnetorestriction. Thus, it is concluded that the volume change due to the IEM transition is isotropic in the studied La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound.
Sun et al. studied the effect of pressure on the magnetocaloric effect in a polycrystalline in LaFe$_{11.6}$Si$_{1.4}$ sample [107]. At ambient pressure the Curie temperature, $T_C$, of the sample was measured to be 191 K, however, after the application of 8.3 kbar pressure, the Curie temperature rapidly decreased to 80 K. At temperatures above $T_C$, the metamagnetic transition induced by the field becomes extremely sharp under high pressure and the critical field $H_C$ of the transition increases fast with increasing temperature. Under 8.3 k bar pressure, the maximum value of entropy change is 60 J/kgK for a 5T field variation. For a field variation of 1 T, however, the maximum value of the entropy change is 34 J/kgK thus confirming that the MCE in LaFe$_{11.6}$Si$_{1.4}$ is greatly enhanced by pressure, especially at low fields. It has been proposed that the enhancement of MCE by pressure is due to the contribution from the lattice entropy where there is a strong magnetostructural coupling associated with the first order magnetic phase transition. It has since been proven that there exists a strong magnetovolume effect which accompanies the first order metamagnetic transition in LaFe$_{13-x}$Si$_{x}$ thus the above mentioned proposal seems also true for LaFe$_{11.6}$Si$_{1.4}$.

Jia et al. experimentally studied a field induced magnetic entropy change under high pressure for the LaFe$_{1.5}$Si$_{1.5}$ compound [108]. The high pressure caused a linear decrease of the Curie temperature from 194 to 88 K, corresponding to a variation of pressure from ambient to 1 GPa. Appropriate pressures enhance the magnetic entropy change significantly whilst decreasing the Curie temperature.
2.3.2 MnCoGe based compounds

Materials which experience simultaneous crystallographic and magnetic phase transitions have garnered a lot of interest owing to their promising applications as multifunctional materials [109 – 111]. The intermetallic compounds MnCo$_{1-x}$Ge, with (0 ≤ $x$ ≤ 0.1) have an orthorhombic TiNiSi –type structure at room temperature whilst the compositions with $x > 0.1$ have a Ni$_2$In-type structure [112].

MnCoGe behaves like a typical ferromagnet with a second-order magnetic phase transition. It has previously been shown that, the magnetic saturation moment $M_S$ and the magnetic ordering temperature $T_C$ are different for these two phases. In the orthorhombic structure, the values of $M_S$ and $T_C$ are 4.13 $\mu_B$ and 345 K, respectively [113]. The hexagonal form, on the other hand exhibits a lower $M_S$ and also a lower $T_C$, namely 2.76 $\mu_B$ and 275 K, respectively [114]. It has been established that for the MnCoGe compound, the structural transition

![Figure 2.7 Volume and lattice parameters of the MnCoGe alloy as a function of temperature.](image)
temperature, \( T_{\text{str}} \), between the orthorhombic and hexagonal phase can be changed by either changing the composition \([115 – 117]\), or applying an external pressure \([118 – 122]\).

Kanomata et al. \([112]\) clearly point out that the structural transition in MnCoGe, as shown in Figure 2.7, is accompanied by strong thermal hysteresis \((\Delta T_{\text{hys}} \sim 40 \text{ K})\) and a large volume change \((\Delta V/V \sim 4\%)\). In order to modify the interatomic distances resulting in the tuning of the magnetostructural coupling in MnCoGe compound, several different ways such as substitutions, dopings and the application of physical pressure have been used \([123 – 125]\).

Compared to the La(Fe,Si)\(_{13}\) based group of compounds, the MnCoGe compounds have not been studied as much, however several research groups worldwide have reported on the MCE of MnCoGe and related alloys, some of these finding are discussed in detail below. Wang et al. reported on the \textit{ab initio} total energy calculations on the first-order structural transition of the ferromagnetic MnCo\(_{1-x}\)Ge intermetallic compound. They show that increasing Co vacancies induce a transition from an orthorhombic structure to a hexagonal structure they also observed that a concomitant high to low moment magnetic transition and a large magnetovolume effect occur due to the change of the symmetry and the resulting coupling distance between the magnetic atoms \([114]\).

Markin et al. studied the concentrical dependences of the lattice parameters, spontaneous magnetic moment, and magnetic ordering temperature of nonstoichiometric Mn\(_{1.9-x}\)Co\(_x\)Ge \((0.8 < x < 1.65)\) compounds with a hexagonal crystal structure \([126]\). On increasing the Co content, \( x \) from 1.1 to 1.2, the Curie temperature and magnetic moment were found to increase abruptly.
Lin et al. [113], reported on the iron doping where a structural transformation from the orthorhombic to the hexagonal phase was observed in the MnCo_{1-x}Fe_{x}Ge alloys. For undoped MnCoGe, the maximum magnetic entropy change is about -5.6 Jkg^{-1}K^{-1} for a magnetic field change ΔB = 0-5 T. Meanwhile, an enhanced ΔS_M value up to -9 Jkg^{-1}K^{-1} was reported for the x = 0.2 sample. For Sn and Ge doped MnCoGe compounds for low magnetic field change, moderate values of magnetic entropy change were obtained [127 – 128].

Trung et al. systematically studied the structural, magnetic and magnetocaloric properties of MnFe(P,Ge) and related compounds on both bulk samples and melt-spun ribbons. By changing either the compositions or the annealing conditions, the critical behavior of the phase transition can be controlled. Also, the thermal hysteresis is tunable to very small values while maintaining a large MCE in a large range of working temperatures [129].

Trung et al. studied the substitution of some Cr for Mn atoms in MnCoGe to control the magnetic and structural transitions in this alloy to coincide, leading to a single first-order magnetostructural transition from the ferromagnetic to the paramagnetic state with a giant magnetocaloric effect observed near room temperature. Further increase in the Cr content in the Mn_{1-x}Cr_{x}CoGe alloys induces another first-order magnetoelastic transition from the antiferromagnetic to the ferromagnetic state occurring at lower temperature [124].

Caron et al. investigated the effects of physical and chemical pressures in the Mn_{1-x}Cr_{x}CoGe series of compounds. Cr substitution and hydrostatic pressure play similar roles in displacing T_C to lower temperatures and coupling or decoupling magnetic and crystallographic transitions. In this work the similarities and differences between the effects of chemical and
physical pressures were explored, helping unveil the nature of the first-order phase transition presented by MnCoGe-based compounds [123].

2.3.3 Nanocomposite Systems

Nanomaterials are the latest class of materials to be characterized for the magnetocaloric effect. Nanoparticles which are magnetic and have a size below the size domain limit are known to exhibit superparamagnetism. Each nanoparticle by itself exhibits ferromagnetic behaviour with a large moment, but there is no long range correlation with other neighboring nanoparticles. So each nanoparticle behaves as a “superspin” with the whole system showing a paramagnetic response. This magnetic character is known as superparamagnetism. Superparamagnetic materials are synthesized by the rapid cooling of a corresponding melt. One of the earliest investigations of the MCE of nanocomposite materials was done by Shao et al., who prepared nanocomposite ribbons of Gd_{0.85}Tb_{0.15}, Gd_{0.85}Y_{0.15} and Gd_{0.75}Zr_{0.25} alloys by a copper-sheathed rolling technique, which briefly consists of the following steps [130 -131]. Heat capacity measurements made on the ribbons in the temperature range from 280 to 310K revealed its increase in all three samples with a maximum mean value of 57.9% for Gd_{0.85}Y_{0.15}. On the other hand, the Curie temperature in the ribbons was reduced. Shao et al. related these experimental results to the large amount of interface atoms arranged in disorder, which changed the interatomic distances and lowered the number of nearest neighbours [130]. Figure 2.8 shows temperature dependences of the magnetic entropy change of the nanopowder ribbon Gd_{0.85}Y_{0.15} sample and bulk alloy with the same composition. The ribbon was considered to be in a superparamagnetic state (T_C of the bulk alloy is 240 K). As one can see, ΔS_M in the ribbon is higher than in bulk material in the temperature interval under consideration, which is typical for superparamagnets. However, no enhancement in the
Figure 2.8 Temperature dependences of the magnetic entropy change induced by the application of a field on the Gd$_{0.85}$Y$_{0.15}$alloy in bulk and nanosized states [130].

MCE was observed in the investigated nanopowder Gd$_{0.85}$Tb$_{0.15}$ and Gd$_{0.75}$Zr$_{0.25}$ ribbons in comparison with the corresponding bulk materials.

Yamamoto et al. studied the influence of the magnetocaloric effect of superparamagnetic nanocomposites by evaluating their $\Delta S_M$ from magnetization data sets. They investigated the influence of distribution of the magnetic moment size on $\Delta S_M$. They concluded that a narrow size distribution was favourable for high performance of the MCE [132]. Kinoshita et al. investigated the MCE of the superparamagnetic nanocomposites composed of magnetic grains isolated by gold as a function of the size distribution width. The evaluated $\Delta S_M$ was found to increase with particle size. They concluded that a narrow size distribution would considerably enhance the MCE of the superparamagnetic nanocomposites [133].
Gorsse et al. investigated the magnetic behaviour, magnetocaloric effect and refrigeration capacity of the Gd$_{60}$Al$_{10}$Mn$_{30}$ metallic glass containing nanocrystallites of Gd. It was found that the temperature dependence of the magnetization exhibited multiple second-order magnetic transitions due to the composite effect. The resulting magnetic entropy change and adiabatic temperature change compared well with the MCE of known magnetic refrigerants. A high refrigeration capacity of 660 J kg$^{-1}$, a large operating temperature range around 150 K and a soft magnetic behavior make this nanocomposite an attractive candidate as magnetic refrigerants in a temperature range where pure Dy is the best material currently available [134].

Recently, Jones et al. investigated the temperature dependence of the magnetization of the (Fe$_{70}$Ni$_{30}$)$_{88}$Zr$_7$B$_4$Cu nanocomposite alloy and a good fit with a modified Handrich-Kobe equation with an asymmetric exchange fluctuation parameter combined with the Arrott-Noakes equation was obtained. They investigated the broadening of the second-order transition arising from asymmetric exchange parameters and resulting from the fluctuations of interatomic spacing found in an amorphous matrix and the asymmetric dependence of exchange energy on interatomic spacing. The obtained magnetic entropy curve revealed extra broadening with a refrigeration capacity (RC) value of 135 J/kg at 5 T. Broadening of the magnetic entropy can lead to larger RC values and a wider working temperature range, making nanocomposite alloys promising for magnetocaloric [135].
2.3.4 Comparisons of different materials and outlook

Figure 2.9 $\Delta S_M$ values of different materials measured at 2 T [98].

A plot of $\Delta S_M$ under a 2 T field for different materials is shown in Figure 2.9. This figure clearly shows that the transition metal based alloys exhibit the best MCE properties at room temperature. However, below room temperature several rare - earth compounds perform better and their cost versus performance analysis is shown in Table 2.1 below. With all different requirements for magnetic refrigerants taken into account, the ideal magnetocaloric material should be composed of at least 80 % transition metals with a large magnetic moment like Fe or Mn. The preparation route and time as well as material cost also play an important factor for the practical application which is not suitable for those materials.
Table 2.1 Advantages and disadvantages of various magnetic refrigerants [98].

<table>
<thead>
<tr>
<th>Factor</th>
<th>Gd</th>
<th>Gd₅T₄</th>
<th>RMnO₃</th>
<th>LaFeSi</th>
<th>MnAs</th>
<th>FeMnPAs</th>
<th>Ni₂MnGa</th>
</tr>
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<tr>
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<td>0</td>
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<td>++</td>
<td>++</td>
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<td>+</td>
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<tr>
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<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Fabrication (sheet)</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MCE, $\Delta S_M$</td>
<td>0</td>
<td>++</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>MCE, $\Delta T_{ad}$</td>
<td>0</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>?</td>
</tr>
<tr>
<td>Refrigeration Capacity</td>
<td>0</td>
<td>+</td>
<td>?</td>
<td>+</td>
<td>?</td>
<td>+</td>
<td>?</td>
</tr>
<tr>
<td>Hysteresis</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Time dependence of $\Delta T_{ad}$</td>
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<td>-</td>
<td>?</td>
<td>-</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Environmental concern</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Corrosion</td>
<td>0</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>-</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

0 neither advantageous nor disadvantageous
+ advantageous
++ more advantageous
- disadvantageous
-- more disadvantageous
--- most disadvantageous
? unknown
References:


CHAPTER 3

EXPERIMENTAL METHODS AND PROCEDURES

The basic principles of equipment used to synthesize and characterize the properties of the materials presented in this thesis are outlined in this chapter. Owing to the emphasis on establishing a correlation between the structure, magnetic properties and the MCE in the studied magnetic materials, the investigated samples were first characterized structurally and then magnetic and magnetocaloric measurements were performed.

3.1 Sample Preparation

3.1.1 Nano-sized sample Preparation – Microwave assisted hydrothermal process

Analytically pure reagents were dissolved in appropriate amounts of distilled water under stirring. Appropriate amounts of potassium hydroxide (KOH) was added to the solution until the required pH was attained. This solution was stirred for 30 minutes, after which it was transferred into a double-walled Teflon flask which consists of an inner liner and a cover made of Teflon PFA and an outer high strength sleeve. Microwave - assisted hydrothermal treatment was performed by placing the sealed Teflon flask in a Microwave Accelerated Reaction System (MARS-5, CEM Corporation, USA) at 140°C for 3 h. This system was operated at a frequency of 2.45 GHz with a maximum power of 1200 W and could be controlled by temperature (maximum, 300°C) and pressure (maximum, 1500 psi). On completion of the reaction, the resultant black precipitates were centrifuged, washed with distilled water and then ethanol to eliminate excess ions in the final product. Finally, the precipitate was dried.
3.1.2 Bulk sample Preparation – Arc melting

The arc melting furnace is divided into two main sections; the chamber and the electrical power supply. During the melting procedure, a non-consumable tungsten electrode is used on a water cooled copper hearth. For the melting process, the power supply a high current, low voltage power. The melting is done on a copper stage which is cooled by water supplied to the chamber. Before starting the melting process, the copper stage is disconnected from the chamber and is cleaned by sandblasting and is subsequently rinsed with alcohol. The copper stage is loaded with materials, usually consisting of small pieces or pellets to be melted and is reconnected to the chamber. The system is evacuated, filled with argon gas and the tungsten tip is lowered until it touches the material on the copper stage. During the melting, the tip is constantly moved uniformly over the whole area containing the material. Furthermore, the melted samples are turned over and remelted several times to achieve homogeneous melting. Finally, the ingot is wrapped in tantalum foil and annealed for the required time.

3.2 Structural and physical characterization of the samples

The determination of the structural properties as well as the quantification of the phases therein was carried out using x-ray diffraction (XRD), neutron diffraction and scanning electron microscopy (SEM). These techniques are elaborated below.

3.2.1 X-Ray Diffraction

The XRD technique is a simple non-destructive method for crystal structure analysis requiring no elaborate sample preparation with just a finely ground powder of the sample being used for the measurement. In the kinematical theory, as illustrated in Figure 3.1, a monochromatic x-ray beam incident upon a crystal with lattice planes separated by a distance $d$, is reflected by each plane. The path difference between two adjacent planes is $2d\sin\theta$. The
reflected radiation from adjacent planes will experience constructive interference when the Bragg condition is satisfied:

\[ n\lambda = 2d \sin \theta \]  

(3.1)

where \( n \) is an integer and \( \lambda \) is the wavelength of the incident x-ray beam. This Bragg reflection is only possible if \( \lambda \leq 2d \). CuK\( _\alpha \) radiation is used for this type of measurement since \( d \) is of the order angstrom. In this work, the x-ray diffraction patterns were collected in a Philips PW1730 diffractometer using monochromated Cu K\( _\alpha \) radiation of wavelength, \( \lambda = 1.5418 \text{Å} \) to analyze the crystalline nature of the magnetocaloric materials.

![Figure 3.1 Kinematical interpretation of Bragg diffraction by adjacent crystal planes.](image)

3.2.2 Scanning Electron Microscopy

The SEM generates a variety of signals at the surface of solid specimens by using a focused beam of high energy electrons. Electron – sample interactions generate a signal which reveals information about the sample such as the morphology, chemical composition and crystalline structure. Precise measurements of very small features of the sample down to the nanometer (nm) size is possible using SEM. The SEM is also capable of quantitatively determining the
chemical composition using energy dispersive x-ray spectroscopy (EDS). In this technique, only solid samples can be analysed. For electrically insulating samples, the low vacuum mode is used or an electrically conductive coating is applied to the sample.

**3.2.3 Neutron Measurements**

The neutron diffraction technique is used for the determination of the atomic and/or magnetic structure of a material. We performed our neutron experiments at The Australian Nuclear Science and Technology Organisation (ANSTO), which houses the Open Pool Australian Lightwater (OPAL) reactor, which is a state of the art 20 Megawatt reactor that uses low enriched uranium fuel. A high continuous flux of neutrons is produced in the core of this fission reactor. These neutrons are moderated to thermal velocities close to the source and then transported to the neutron scattering instruments in neutron guide systems to targets in a series of instruments.

For this study, Echidna and Wombat neutron beam instruments were used for the determination of the atomic and magnetic structure of a few selected magnetocaloric materials. A schematic diagram of the Echidna neutron diffractometer is shown in Figure 3.2. As mentioned previously, an intense beam of neutrons is produced at the nuclear reactor and this neutron beam is channelled through a collimator which narrows the beam such that only neutrons travelling normal to the reactor surface are used. The neutron beam is then targeted on a monochromators (usually graphite), which will reflect neutrons with a wavelength close to a value determined by the angular setting of the graphite monochromator. The monochromatic beam is then directed to the sample under investigation. When these neutrons
strike the target material, they scatter, producing distinctive patterns that deliver information to researchers.

3.2.4 Synchrotron Measurements

![Schematic diagram of the Australian Synchrotron](image)

**Figure 3.3** Schematic diagram of the Australian Synchrotron.

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Figure 3.3 is a schematic of the synchrotron which functions as described below:

1. Electrons are produced at the electron gun by thermionic emission from a heated tungsten cathode. After that, the emitted electrons are then accelerated to energy of 90 keV by a 90 kV potential difference applied across the gun, and move into the linear accelerator.

2. The linear accelerator (linac) accelerates the electron beam to energy of 100 MeV over a distance of about 10 metres.

3. The booster is an electron synchrotron 130 metres in circumference that takes the 100 MeV beam from the linac and increases its energy to 3 GeV. The beam is then accelerated by a simultaneous ramping of magnet strength and cavity fields.

4. The storage ring, which can hold 200 mA of stored current with a beam lifetime of over 20 hours is the final destination for the accelerated electrons.

5. Individual beamlines are positioned to capture the synchrotron light given off by the storage ring. The photon delivery system (also called the ‘beamline optics’) which incorporates filters, monochromators, mirrors, attenuators and other devices is used to focus and select appropriate wavelengths for particular research techniques.

6. Experiments employing synchrotron light are conducted in customised facilities called end-stations which are housed inside radiation shielding enclosures called ‘hutches’ to protect personnel from potentially harmful x-rays. Each beamline utilises the synchrotron light to gather data in the form of images, chemical spectra, and/or scattered light. In our work we used the powder diffraction beamline which has been designed to operate over the energy range 5-30 keV.

---

3.3 Physical Property Measurement System (PPMS)

The Quantum Design PPMS is a variable temperature – field system, designed to perform a range of automated measurements. Samples can be measured in magnetic fields up to 14 T in a temperature range of 1.9 – 400 K. The PPMS has the following different options:

- DC and AC magnetometry
- Heat capacity
- Electro – transport
- Thermal transport

In this work, only the DC magnetometry was used and it is described briefly below.

3.3.1 Vibrating Sample Magnetometer (VSM)

The VSM is composed of a linear motor for vibrating the sample, a coil-set puck for detections, electronics for controlling the linear motor transport and software for automatic control. The sample is magnetized by a constant magnetic field and the magnetic moment of the sample is measured, producing a DC magnetization curve which can be a function of field or temperature.
A SIGN OF FIELD-INDUCED FIRST ORDER MAGNETIC STATE TRANSITION AND GIANT REVERSIBLE MAGNETOCALORIC EFFECT IN COBALT HYDROXIDE NANOSHEETS

4.1 Introduction

An ideal material for magnetic refrigeration should be composed of relatively inexpensive raw materials, have a high MCE demonstrated by a high change in magnetic entropy ($\Delta S_M$) and a high adiabatic temperature change ($\Delta T_{ad}$) and have little or no thermal/magnetic hysteresis [1 – 6]. First order transitions possess the above mentioned characteristics and have been shown to have a consistently higher MCE than second-order transitions. Recently, there has been an interest in the investigation of magnetic and MCE properties in various nanoparticle systems [7 – 10]. Magnetic nanoparticles exhibit a higher refrigerant capacity as compared to their bulk counterparts, owing to their reasonably large MCE over a wide temperature range [11]. It has now been established that the shapes of nanostructured materials have a considerable influence on their physical properties [12]. In the past decade, one-dimensional nanostructures such as wires, rods and tubes were the main focus of intense research, owing to their novel properties and potential applications in the fabrication of nanostructure devices. In recent years, however, there has been a growing interest in the investigation of two – dimensional (2D) nanosheets due to the interesting properties they possess, owing to their high anisotropy and thinness [13]. Enhanced magnetic properties are also expected in 2D nanostructures. For $\beta$-Co(OH)$_2$, this area is poorly explored, and to date,
only a few reports on the preparation of 2D \( \beta \)-Co(OH)\(_2\) nanostructures have appeared in print [12, 14]. Liang \textit{et al.} and Liu \textit{et al.} both synthesized single crystalline \( \beta \)-Co(OH)\(_2\) nanosheets. However, these studies have not investigated the magnetic properties of the 2D \( \beta \)-Co(OH)\(_2\) to investigate whether the expected enhanced magnetic properties would be observed. To the best of our knowledge, this is the first report on the magnetic and magnetocaloric properties of 2D \( \beta \)-Co(OH)\(_2\) nanostructures. Herein, we report a novel process of synthesizing \( \beta \)-Co(OH)\(_2\) nanosheets through a microwave assisted hydrothermal process. It is the aim of this work to investigate the magnetic and magnetocaloric properties of 2D \( \beta \)-Co(OH)\(_2\) nanosheets and compare with those of \( \beta \)-Co(OH)\(_2\) nanoparticles reported in literature.

### 4.2 Experimental Procedures

Analytically pure reagents were used in this experiment. A precipitation and microwave hydrothermal process was used for the synthesis of cobalt hydroxide nanoplatelets. 10 mmol Co(NO\(_3\))\(_2\).6H\(_2\)O was dissolved in 50 ml distilled water under stirring, then 2 M KOH solution was added into the solution at a rate of 2 mL.min\(^{-1}\), until the pH value of the solution reached 11. This solution was stirred for 30 minutes, after which it was transferred into a double-walled vessel which consists of an inner liner and a cover made of Teflon PFA and an outer high strength sleeve. The vessel was sealed and maintained in a Microwave Accelerated Reaction System (MARS-5, CEM Corporation, USA) at 140°C for 3 h. This system was operated at a frequency of 2.45 GHz with a maximum power of 1200 W and could be controlled by temperature (maximum, 300°C) and pressure (maximum, 1500 psi). On completion of the reaction, the resultant black precipitates were centrifuged, washed with distilled water and then ethanol in an attempt to minimize the extra ions in the final product. Finally, the black precipitates were dried at 80°C in air.
The as-prepared sample was characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The magnetization measurements for the sample was carried out using the vibration sample magnetometer (VSM) option of a quantum design 14 T Physical Property Measurement System (PPMS) in the temperature range of 3 – 22 K at applied fields up to 5T. The MCE was evaluated from the calculated isothermal magnetic entropy change $\Delta S_M(T, H)$ in the vicinity of the magnetic phase transition temperature according to equation (4.1) below.

$$\Delta S_M(T, \Delta H) = \int_{H_1}^{H_2} \left( \frac{\partial M(T, H)}{\partial T} \right) dH$$

### 4.3 Results and Discussion

![Image](image.png)

**Figure 4.1** The x-ray diffraction pattern of $\beta$-Co(OH)$_2$ nanosheets.
The XRD pattern and index of the cobalt hydroxide sample is shown in Figure 4.1, most of the β-Co(OH)$_2$ phase (~ 95%) and small amount of secondary phase (~ 5% Co$_3$O$_4$) was determined through XRD Rietveld refinement.

The morphology of the β-Co(OH)$_2$ nanoparticles was investigated by SEM, as shown in Figure 4.2 The β-Co(OH)$_2$ is shown to have a platelet morphology with the diameter distribution range being 1 - 2 µm. The platelet particle is consisted of agglomerated nanosheets with thickness of 20 to 80 nm. However, the average thickness of a single β-Co(OH)$_2$ nanosheet was about 10 nm, estimated from the isolated nanosheets.

Figure 4.2 The SEM image of β-Co(OH)$_2$ nanosheets.
The temperature dependence of the inverse magnetic susceptibility in a magnetic field of 100 Oe under field cooling (FC) and zero FC (ZFC), which contains $1/\chi - T$ curves ($1/\chi_{FC} - T$ curve and $1/\chi_{ZFC} - T$ curve). A sign of antiferromagnetism (AFM) transition at temperature $T_N = 9 \sim 10$ K can be found from these $1/\chi - T$ curves. The $T_N$ value for $\beta$-Co(OH)$_2$ nanoparticles in the present work is lower than the previously reported values of 11 and 12.3 K reported in Refs. 15 and 16, respectively. A decrease in $T_N$ was observed in many nanosized AFM systems as the grain size decreased [17 – 19]. We have established from the SEM images that the $\beta$-Co(OH)$_2$ nanoparticles investigated in this work had a considerably smaller grain size, compared to those described in Refs. 15 and 16; hence the lower value of $T_N$ in the present work could be ascribed to nanosize effects. The $1/\chi - T$ curves also indicate that paramagnetic to spin glass (SG) - like (we suspect it is the surface spin present SG - like...
behaviour) transition seems to start at onset temperature defined as $T_1 \sim 96$ K since the slope of the curve start changing from the constant straight line (PM state) to lower value (SG – like state) at that temperature (96 K), then the value of the slope increases (AFM state) at temperature of $9 \sim 10$ K. The SG - like behaviour of the surface spins is clearly seen as an open hysteresis loop, as shown in Figure 4.4. This indicates that it has a loss of magnetization during one hysteresis [20 – 21].

Figure 4.4 shows the selected isothermal M - H loops of the $\beta$-Co(OH)$_2$ nanosheets, which are plotted as a function of the applied magnetic field (ranging from $\mu_0H = -5$ T to 5 T) at the temperatures of 3, 10, 20, and 100K. This figure depicts the hysteresis loop of the $\beta$-Co(OH)$_2$ nanosheets at temperature 3K, 10K, 20K, 100K.

![Figure 4.4 Selected M - H loops of $\beta$-Co(OH)$_2$ nanosheets at temperature 3K, 10K, 20K, 100K.](image)
nanosheets obtained at different temperatures in the presence of a magnetic field which was scanned in the interval ± 5T. We found a magnetic hysteresis of approximately 20 Oe which is very low. It should be noted that the M – H loops show straight-type line (PM behaviour) at temperatures higher than 100 K, show bent-type line (SG-like behaviour of the surface spin) at temperatures lower than 100 K, and show step-type line (field-induced AFM to FM behaviour) at temperatures lower than 9 K.

Figure 4.5 shows the isothermal magnetization curves of the β-Co(OH)₂ nanosheets, which are plotted as a function of the applied magnetic field (ranging from $\mu_0H = 0$ to 5 T) in the temperature range between 3 and 22 K. It should be noted that at temperatures below 9 K,
and under a low field, the variation of the isotherm magnetizations with temperature are rather dramatic as compared to the isotherm magnetizations at temperatures above 9 K. However, under high magnetic field values, the variation of the isotherm magnetizations (in the whole temperature range) becomes gradual with no saturation being observed. This non-saturation of the magnetization confirms the presence of a large anisotropy in the $\beta$-Co(OH)$_2$ nanosheets. Also, the fact that the M – H curves are non-saturating with gradual curvature indicates superparamagnetic behaviour.

The Arrott plots $M^2$ versus H/M at selected temperatures in the range 3 – 22K are shown in Figure 4.6. Below the temperature of 9 K, Fig 4.6 shows S-shaped Arrott plots which demonstrate that the transition temperature is around 9 K, and the field induced transition from the AFM to FM state is first order in nature.

![Arrott plot curves of $\beta$ - Co(OH)$_2$ nanosheets.](image)
The isothermal magnetization data was analyzed using the well-known Maxwell relation shown in Eq. (4.1). The magnetic entropy changes (ΔS_M) versus temperature under different fields are shown in Figure 4.7; ΔS_M was calculated from the isothermal curves according to Eq. (4.1) of the Maxwell relation, which is discussed in detail in Refs. 22 - 24. It is apparent that, the peak of ΔS_M at T_c = 11 K for the different magnetic field changes, corresponds to second order PM to FM - like phase transition, the ΔS_M value exhibits a positive value below 9 K and under low field range, but it changes to a negative value under high field range.

Figure 4.8 shows the magnetic entropy change, ΔS_M, as a function of applied field at different temperatures. This positive ΔS_M indicates inverse MCE, which has also been previously observed in β-Co(OH)_2 nanoparticles [15]. The peak value of ΔS_M is 17 J/kg K at 11 K for a

![Graph](image)

**Figure 4.7** Magnetic-entropy changes versus temperature curves of β-Co(OH)_2 nanosheets.
Figure 4.8 Magnetic-entropy changes versus applied field of $\beta$-Co(OH)$_2$ nanosheets.

field change of 5 T. This is slightly higher than the previously reported value of $\Delta S_M = 15$ J / kg K at 5 T for $\beta$-Co(OH)$_2$ nanoparticles [15]. It is also worth noting that the XRD analysis of our sample shows a small amount of a secondary phase (~ 5% Co$_3$O$_4$), which obviously has a detrimental effect on the determined value of $\Delta S_M$. This therefore means that we expect our samples to exhibit an even higher value of $\Delta S_M$ once their purity has improved.

Following the above results and discussions, we find that: (i) the SG-like surface spin may have a significant effect on the MCE (Ref. 11) and (ii) similar to what was observed by Zhong et al. [25] the surface bond contraction effect on the magnetic performance of the $\beta$-Co(OH)$_2$ nanoparticles will also have a significant effect on the MCE and (iii) the sign of field-induced first order magnetic phase transition is possibly due to the result of the
competition or interaction coupling of the surface spin, impure phase [Co$_3$O$_4$ shown in Figure 4.1], and for β-Co(OH)$_2$ bulk magnetic behaviour. Thus more work (outlined in Chapter 9) needs to be done to understand the nanomagnetism of this material. The β-Co(OH)$_2$ nanosheets, however, show a very high magnetic moment, the $M_S \sim 110 \text{ emu/g at } 3 \text{ K}$, as shown in Figure 4.4, which causes a highly reversible giant MCE effect even with second transition at a temperature above $11 \text{ K}$, is a sign of field-induced first order transition from the AFM to the FM below $9 \text{ K}$, and acts as a role of reversing the MCE value from negative to positive value in the low field range.

4.4 Conclusions

In conclusion, β-Co(OH)$_2$ nanosheets have been successfully prepared by a microwave assisted hydrothermal and conventional chemical reaction method. This material displays a high magnetic moment and a large reversible magnetic entropy change of $17 \text{ J/kg K at } 11 \text{ K}$ in a magnetic field change of $5 \text{ T}$ thereby indicating the suitability of this material for use in magnetic refrigeration.
References:


CHAPTER 5

ENHANCEMENT OF THE REFRIGERANT CAPACITY IN
LOW LEVEL BORON DOPED La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$

5.1 Introduction

Magnetic refrigeration is regarded as a promising, more efficient, and environmentally friendly alternative to gas-compression-based refrigeration due to its potential applications in a wide range of temperatures [1 - 5]. Materials exhibiting first-order magnetic phase transitions are of special interest since they intrinsically present a high MCE originating from the discontinuous character of the transition [6 - 7]. The LaFe$_{11.4}$Si$_{1.6}$ alloy exhibits a first-order magnetic transition and also belongs to the so-called giant magnetocaloric effect (GMCE) group of materials which undergo a phase transition from one form of magnetic order to another with an associated "giant" change of entropy. With the potential for high temperature operation in mind, a drawback of this system is the relatively low ordering temperature of $T_C \sim 195$ K [8] although $T_C$ can be tuned by introducing small atoms like B, N or C [9 – 11]. Introduction of the interstitial N, H, C or B atoms leads to expansion of the lattice which makes the Fe 3d band narrow and brings about the increase in $T_C$ by reducing the Fe 3d overlap wave functions [10]. Such small atoms change the electronic structure of the compounds, which can influence the intrinsic magnetic properties of Fe-based compounds [12].
The refrigerant capacity \( (RCP) \) is a measure of the heat that can be transferred between the cold and hot reservoirs and, together with \( \Delta S_M \), is a key parameter for characterising the performance of magnetocaloric materials. We have therefore carried out a systematic study of the influence of boron doping on the \( \Delta S_M \) and \( RCP \) of La\(_{0.8}\)Gd\(_{0.2}\)Fe\(_{11.4}\)Si\(_{1.6}\)B\(_x\) compounds (with boron doping level, \( x = 0, 0.03, 0.06, 0.2 \) and 0.3). It has been previously shown that the partial substitution of La with Gd enhances the LaFe\(_{11.4}\)Si\(_{1.6}\) magnetocaloric properties, hence for this purpose for all our samples we substituted 20 at. % La with Gd [13]. Our results reveal that, for low boron doping levels, the magnetic field induced phase transition remains first order and causes a significant enhancement of \( RCP \). However, high boron doping levels change the phase transition from first order to second order and accordingly decreases both \( \Delta S_M \) and \( RCP \) compared to undoped La\(_{0.8}\)Gd\(_{0.2}\)Fe\(_{11.4}\)Si\(_{1.6}\). We also show that for La\(_{0.8}\)Gd\(_{0.2}\)Fe\(_{11.4}\)Si\(_{1.6}\)B\(_x\) compounds (with boron doping level, \( x = 0, 0.03, 0.06, 0.2 \) and 0.3), an increase in boron doping shifts \( T_C \) towards room temperature.

### 5.2 Experimental Procedures

Ingots of polycrystalline alloys with nominal compositions La\(_{0.8}\)Gd\(_{0.2}\)Fe\(_{11.4}\)Si\(_{1.6}\)B\(_x\) (\( x = 0, 0.03, 0.06, 0.2 \) and 0.3), where \( x \) is the boron doping level, were prepared by arc-melting appropriate amounts of the high purity constituent elements under a high purity argon atmosphere in a water cooled copper crucible. The purities of the starting materials were 99.9% for La, Si and Fe, 99.99% for Gd and 99.999% for B. During the arc melting process, each ingot was turned over and remelted several times to ensure its homogeneity. The total weight loss after the arc-melting procedure was less than 1 wt %, corresponding to La and Gd evaporation during the fusion, which was compensated with an La and Gd mass excess (10 at. %) to ensure the compound stoichiometry. The resulting ingots were wrapped in tantalum foil, annealed at 1323 K for 14 days in an evacuated quartz tube to improve the crystallization
of the samples and then quenched in water. X-ray diffraction (XRD) measurements on powder samples were performed using Cu Kα radiation to identify the crystal structure and the crystal lattice parameter. The magnetization was measured as a function of temperature and magnetic field for the samples and was carried out using the vibration sample magnetometer (VSM) option of a quantum design 14 T Physical Property Measurement System (PPMS) in the temperature range of 150 – 300 K under applied magnetic field values up to 5 T.

5.3 Results & Discussion

A Rietveld plot of XRD data profile refinement with the program FULLPROF for a selected sample La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.06} is shown in Figure 5.1. The XRD indicates that the alloys crystallize well in the NaZn_{13}-type cubic structure with a small amount of α-Fe and LaFeSi existing as minor phases. It is imperative to note that the majority of published data on LaFe_{13-x}Si_{x} alloys, no single-phase LaFe_{13-x}Si_{x} alloys could be obtained [14 – 17]. Table 5.1 shows the lattice parameter, \(a\), determined by using the Rietveld refinement as a function of the \(B\) concentration. It is clear from Table 5.1 that the addition of boron in La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{x} results in a linear increase of the lattice constant from 11.464 to 11.473 for \(x = 0\) to \(x = 0.3\) The lattice parameters of the NaZn_{13}-type structure phase for the alloys increase on the addition of boron, suggesting that the boron atoms occupy interstitial sites resulting in the expansion of the lattice. The lattice expansion caused by the addition of \(B\) is shown in Table 5.1 and was calculated to be \(~8\%\) for La_{0.8}Gd_{0.2}Fe_{11.4}Si_{1.6}B_{0.3} compared to the undoped sample.
Figure 5.1 Rietveld plot of X-ray diffraction data for a selected sample, $x = 0.06$ at 300 K.

Table 5.1 Magnetic hysteresis loss, lattice parameter, $RC_{\text{eff}}$ and bond angles of La$_{1-x}$Gd$_x$Fe$_{11.4}$Si$_{1.6}$ compounds, measured at 5 T.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Loss (J/kg)</th>
<th>$RC_{\text{eff}}$ (J/kg)</th>
<th>$a$ (Å)</th>
<th>$La(8a)$-$Fe(96i)$ (Å)</th>
<th>$Fe(8b)$-$Fe(96i)$ (Å)</th>
<th>$Fe(96i)$-$Fe(96i)$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$</td>
<td>3.7</td>
<td>281</td>
<td>11.4637(4)</td>
<td>3.3468(7)</td>
<td>2.4519(2)</td>
<td>2.8292(8)</td>
</tr>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$B$_{0.03}$</td>
<td>9.1</td>
<td>352</td>
<td>11.4641(8)</td>
<td>3.3470(2)</td>
<td>2.4520(3)</td>
<td>2.8294(1)</td>
</tr>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$B$_{0.06}$</td>
<td>5.7</td>
<td>341</td>
<td>11.4646(2)</td>
<td>3.3471(4)</td>
<td>2.4521(1)</td>
<td>2.8295(1)</td>
</tr>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$B$_{0.2}$</td>
<td>0.4</td>
<td>226</td>
<td>11.4649(9)</td>
<td>3.3472(5)</td>
<td>2.4522</td>
<td>2.8296(1)</td>
</tr>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$B$_{0.3}$</td>
<td>0.3</td>
<td>249</td>
<td>11.4728(6)</td>
<td>3.3495(6)</td>
<td>2.4538(9)</td>
<td>2.8315(5)</td>
</tr>
</tbody>
</table>
The temperature-dependent magnetization was been measured in the zero-field-cooled (ZFC) and field-cooled (FC) process for all samples in order to determine the transition temperature and the nature of the transition. The sample was first cooled in zero-field to 5 K, then a small field of 200 Oe was applied to the sample and after that the magnetization was measured in the heating process up to 300 K, thus obtaining the ZFC magnetization curve (which is not shown to enhance clarity). The FC magnetization was measured in the process of cooling sample to 5 K with the same field. Figure 5.2 shows the FC magnetization obtained under a magnetic field of 0.02 T for the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples with boron doping level, $x = 0, 0.03, 0.06, 0.2$ and $0.3$. The ferromagnetic ordering $T_C$ of the samples is defined as the temperature at which the $dM/dT$ of the warming $M$ - $T$ curves is a minimum. The $T_C$ values for the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples with $x = 0$ to 0.3 are found to increase linearly with

![Diagram](image)

**Figure 5.2** Thermomagnetization curves of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds (with boron doping level, $x = 0, 0.03, 0.06, 0.2, 0.3$).
The samples were measured on warming in a magnetic field of $B = 0.02$ T after first cooling to 100 K in zero field. The increase in $T_C$ for La(Fe,Si)$_{13}$ compounds with increasing $B$ concentration to $T_C = 200, 204, 205, 215$ and 222 K respectively is consistent with results reported in literature by Xie et al. [10]. Normally, the $T_C$ increases as the lattice expands, or equivalently as the $Fe - Fe$ distances increase. However, for $Fe$ - rich rare - earth (RE) compounds, $T_C$ depends mainly on the $Fe - Fe$ and $Fe - RE$ direct exchange interactions which the $Fe - Fe$ distance strongly influences [18]. In this work the BLOKJE program was used to compute the La(8$a$) - Fe(96$i$), Fe(8$b$) - Fe(96$i$) and Fe(96$i$)-Fe(96$i$) bond lengths to help explain the increase in $T_C$. As expected, Table 5.1 shows the increase in bond length in all the above mentioned bonds with an increase in boron doping, $x$. Thus, the observed enhancement of $T_C$ in La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds with an increase of boron doping, $x$, can be attributed to an increase in the $Fe - Fe$ exchange interactions caused by the increasing $Fe - Fe$ distances.

Figure 5.3 shows the isothermal magnetization curves of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ (with boron doping level, $x = 0, 0.03, 0.06, 0.2$ and 0.3) over the temperature range 180 – 250 K which span the paramagnetic to ferromagnetic transition regions. The magnetization isotherms were measured for increasing and decreasing magnetic fields in the range $\Delta B = 0 - 5$ T with the PM - FM transitions evident in the behaviour of all five samples. The change in the saturation magnetization is probably related to the presence of different amounts of the $\alpha$-Fe in the compounds. Figure 5.3 also demonstrates hysteresis for the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$, La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.03}$ and La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.06}$ samples compared with the insignificant hysteresis in the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.2}$ and La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.3}$ samples. These hysteretic effects confirm the first-order nature of the magnetic transitions for the $x = 0.0, 0.03$ and 0.06
Figure 5.3 Magnetization isotherms of $\text{La}_{0.8}\text{Gd}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}B_x$ compounds with boron doping level, $x = 0$ and 0.03 measured in the field ascending and the field descending processes in a range of temperatures around $T_C$. 
Figure 5.3 Magnetization isotherms of $\text{La}_{0.8}\text{Gd}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ compounds with boron doping level, $x = 0.06$ and 0.2 measured in the field ascending and the field descending processes in a range of temperatures around $T_C$. 
Figure 5.3 Magnetization isotherms of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds with boron doping level, $x = 0.3$ measured in the field ascending and the field descending processes in a range of temperatures around $T_C$.

samples while the behaviour of the $x = 0.2$ and 0.3 samples is typical of a second order magnetic transition. The isothermal magnetisation curves exhibit typical ferromagnetic behaviour for all samples below their respective magnetic ordering temperatures. The La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples with boron doping level, $x = 0$, 0.03 and 0.06 show $S$-shaped magnetization curves typical for the itinerant electro-metamagnetism [12] while the magnetization curves for La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.3}$ are characteristic of a second order transition. These results are confirmed by the Arrott plots in Figure 5.4. The Arrott plots were used to determine the type of phase transition of the sample near $T_C$ according to the Inoue-
Shimizu model\textsuperscript{19}. In this model, the free energy \( F \) of a magnetic system is expressed by the Landau expansion in powers of magnetization, \( M \) shown in Equation (5.1) below:

\[
F(M, T) = \frac{1}{2} c_1(T)M^2 + \frac{1}{4} c_3(T)M^4 + \frac{1}{6} c_5(T)M^6 - MH
\]  

(5.1)

The type of transition is related to the sign of the Landau coefficient \( c_3(T) \) at the Curie temperature \( (c_3(T_C)) \). If \( c_3(T_C) \) is negative, the transition is first order, otherwise the transition will be second order. The sign of \( c_3(T_C) \) can be obtained from the Arrott plots. If there are \( S \)-shaped curves near \( T_C \) in the Arrott plots, \( c_3(T_C) \) is negative, otherwise, it is positive. As seen in Figure 5.4, the La\textsubscript{0.8}Gd\textsubscript{0.2}Fe\textsubscript{11.4}Si\textsubscript{11.6}B\textsubscript{x} samples (with boron doping level, \( x = 0, 0.03, 0.06, 0.2 \) and 0.3) near their respective \( T_C \) exhibit \( S \)-shaped curves with negative slopes. The negative slopes and inflection points in these three samples confirms the occurrence of metamagnetic transitions from \( FM \) to \( PM \) state above \( T_C \), indicating that both compounds undergo a first-order transition. This therefore means that for the low level boron doping, the \( B \) atoms do not significantly influence the shape of the density of states around the Fermi level and a strong IEM behaviour is still retained. However, the absence of \( S \)-
Figure 5.4 Arrott plots of isotherms in the vicinity of $T_C$ of $\text{La}_{0.8}\text{Gd}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}B_x$ compounds with boron doping level, $x = 0$ and 0.03.
Figure 5.4 Arrott plots of isotherms in the vicinity of $T_C$ of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds with boron doping level, $x = 0.06$ and 0.2.
Figure 5.4 Arrott plots of isotherms in the vicinity of $T_C$ of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds with boron doping level, $x = 0.3$.

shaped curves with negative slope or an inflection point in the Arrott plot for La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.2}$ and La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.3}$ (but rather an almost linear behaviour of the Arrott plot), confirms the occurrence of a second-order transition in these samples.

It has been shown recently that the magnetic entropy change ($\Delta S_M$) of materials with hysteretic first order transitions should be calculated carefully using the Maxwell relation as the value of $\Delta S_M$ calculated from the increasing field differs from that calculated using the
decreasing field [20]. The $\Delta S_M$ calculated using the increasing field has been shown to exhibit an erroneous spike, whilst the $\Delta S_M$ calculated using the decreasing field consists of a much reduced spike with a plateau [20]. Hence, for this reason, in this work we calculated $\Delta S_M$ using the decreasing field. Thus, the magnetic entropy change ($\Delta S_M$) was calculated from the isothermal magnetization curves close to $T_C$ using the Maxwell relation shown in Equation (5.2) below:

$$-\Delta S_M = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH.$$  \hspace{1cm} (5.2)

Figure 5.5 shows the 3D plots of magnetic entropy change as a function of temperature and magnetic field, $H$ for La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds with boron doping level, $x = 0$, 0.03, 0.06, 0.2 and 0.3. Similar to what Demuner et al. observed, the $\Delta S_M$ curves for the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds with $x = 0$ and 0.03 have asymmetric peaks near $T_C$ which is attributed to the field induced metamagnetic transition above $T_C$ with the maximum magnetic entropy changes being 14.8 and 16 J kg$^{-1}$K$^{-1}$ respectively [13]. However, a further increase in the boron doping ($x = 0.03$, 0.06, 0.2 and 0.3) significantly broadens the $\Delta S_M$ versus $T$ curve and in the case for the samples with $x = 0.2$ and 0.3, reducing the maximum magnetic entropy change to 7.5 and 6.6 J kg$^{-1}$K$^{-1}$ respectively. This reduction in the magnetocaloric properties is explained by the fact that the increase of B content in La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ drives the FM – PM transition towards second order and eliminates the meta-magnetic transition. Also, the introduction of boron atoms leads to an increase of $T_C$, which results in the shift of $\Delta S_M$ peaks towards higher temperatures. Thus for the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds, optimum boron doping occurs at low levels since the lowly boron doped sample ($x = 0.03$) exhibits the highest magnetic entropy change.
Figure 5.5 Temperature and magnetic field dependence of the isothermal magnetic entropy change of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds with boron doping level, $x = 0, 0.03, 0.06, 0.2, 0.3$ measured at 5 T calculated from the Maxwell relation.
In order to assess the usefulness of the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ alloys as magnetic refrigerant materials, the $RCP$ is calculated according to equation (5.3) below:

$$RCP = -\Delta S_M \times \partial T_{FWHM}$$ \hspace{1cm} (5.3)

where $\partial T_{FWHM}$ is the width at half maximum obtained from the temperatures at half the maximum peak value of the $\Delta S_M$ versus $T$ curve. The calculated results of $RCP$ for La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples with boron level, $x = 0, 0.03, 0.06, 0.2$ and $0.3$ plotted as a function of the magnetic field are shown in Figure 5.6. For all the samples, the maximum values of $RCP$ are found to increase with an increase in the applied magnetic field and reach the values of 285, 361, 346, 222 and 245 J kg$^{-1}$ for the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples with boron level, $x = 0, 0.03, 0.06, 0.2$ and $0.3$ respectively under a field change of $0 - 5$ T. This figure, clearly illustrates the fact that the lowly doped sample ($x = 0.03$ and $0.06$) exhibit significantly higher $RCP$ compared to the undoped sample, whilst the highly doped samples ($x = 0.2$ and $0.3$) exhibit significantly lower $RCP$ values as compared to the undoped sample.

Table 5.1 shows the hysteresis loss, defined as the area enclosed by the ascending and descending branches of the magnetization curve. The maximal hysteresis losses around $T_C$ for La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples with boron level, $x = 0, 0.03, 0.06, 0.2$ and $0.3$ are $3.7, 9.1, 5.7, 0.4$ and $0.3$ J kg$^{-1}$ measured under a $5$ T field respectively. This reduction in hysteresis losses at high boron doping levels (i.e., $x = 0.2$ and $0.3$) is attributed to the weakening of the field induced first order magnetic transition (FOMT) from the paramagnetic to the ferromagnetic state due to the addition of boron. By subtracting the hysteresis loss from the calculated RCP, we obtained the effective refrigerant capacity, $RC_{eff}$ which is also shown in Table 5.1, calculated for magnetic field values of $5$ T. As boron
Figure 5.6 Field dependences of the refrigerant capacity for La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds with boron doping level, $x = 0, 0.03, 0.06, 0.2$ and $0.3$ measured at $5$ T.

Doping, $x$ varies from 0 to 0.3, the RC$_{eff}$ shows a similar trend to that observed in the RCP. These results indicate that the introduction of interstitial boron atoms significantly improves the cooling capacity of the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ material system at all values of the applied magnetic field, $H$

Clearly of the five samples investigated, La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.03}$ is the preferred magnetic refrigerant material as it would support the transport of the greatest amount of heat in a practical refrigerator. Therefore, low level boron doping enhances the $MCE$ in the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ material system.
Table 5.2 shows a summary of the present results, as well as the MCE properties of La$_{1-x}$Gd$_x$Fe$_{11.4}$Si$_{1.6}$ compounds with Gd and LaFe$_{11.4}$Si$_{1.6}$ included for comparison. The inconsistency of the reported MCE properties is apparent even for compounds with the same composition and is discussed in detail below. Investigation of La substitution by the rare-earth element Gd was first reported in 2007 by Passamani et al. They found that for 5 at. % La substituted by Gd, the first order transition is destroyed leading to a drastic reduction of its maximum magnetic entropy change [8]. This seems to be in disagreement with the work of Demunier et al. (2009) which shows that for 5 at. % La substituted by Gd, the magnetic transition remains first order and the maximum magnetic entropy change remains relatively

<table>
<thead>
<tr>
<th>Sample</th>
<th>Order of transition</th>
<th>$T_C$ (K)</th>
<th>$\Delta S_M$ (J kg$^{-1}$K$^{-1}$)</th>
<th>RCP (J kg$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>2$^{nd}$</td>
<td>294</td>
<td>10.2</td>
<td>410</td>
<td>22</td>
</tr>
<tr>
<td>*LaFe$<em>{11.4}$Si$</em>{1.6}$</td>
<td>1$^{st}$</td>
<td>195</td>
<td>18</td>
<td>324</td>
<td>8</td>
</tr>
<tr>
<td>La$<em>{0.95}$Gd$</em>{0.05}$Fe$<em>{11.4}$Si$</em>{1.6}$</td>
<td>2$^{nd}$</td>
<td>215</td>
<td>7</td>
<td>210</td>
<td>8</td>
</tr>
<tr>
<td>La$<em>{0.95}$Gd$</em>{0.05}$Fe$<em>{11.4}$Si$</em>{1.6}$</td>
<td>1$^{st}$</td>
<td>~210</td>
<td>~15</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$</td>
<td>2$^{nd}$</td>
<td>215</td>
<td>7.9</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$</td>
<td>1$^{st}$</td>
<td>200</td>
<td>14.8</td>
<td>285</td>
<td>This work</td>
</tr>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$B$_{0.03}$</td>
<td>1$^{st}$</td>
<td>204</td>
<td>16</td>
<td>361</td>
<td>This work</td>
</tr>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$B$_{0.06}$</td>
<td>1$^{st}$</td>
<td>205</td>
<td>15</td>
<td>346</td>
<td>This work</td>
</tr>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$B$_{0.2}$</td>
<td>2$^{nd}$</td>
<td>215</td>
<td>7.5</td>
<td>222</td>
<td>This work</td>
</tr>
<tr>
<td>La$<em>{0.8}$Gd$</em>{0.2}$Fe$<em>{11.4}$Si$</em>{1.6}$B$_{0.3}$</td>
<td>2$^{nd}$</td>
<td>222</td>
<td>6.6</td>
<td>245</td>
<td>This work</td>
</tr>
</tbody>
</table>

*These samples are shown for the purposes of comparison.
high [13]. In 2008, Kumar et al. investigated the MCE properties of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$. This group observed a drastic reduction in the maximum magnetic entropy change of the above mentioned compound with the first order transition being destroyed [21]. Thus, the discrepancies in the MCE properties of La$_{1-x}$Gd$_x$Fe$_{11.4}$Si$_{1.6}$ compounds studied by the several groups mentioned above can be attributed to the presence of different impurities in samples with the same composition thereby influencing the MCE properties. Also, it has been previously established that the $T_C$ of Si based compounds is strongly dependent on the Si content in the NaZn$_{13}$-type structure, hence the discrepancy in the $T_C$ of the La$_{1-x}$Gd$_x$Fe$_{11.4}$Si$_{1.6}$ compounds in Table 2 can be attributed to the different Si content in the actual compositions of the compounds even though they may have the same Si content in the nominal compositions [22 – 23].

Our investigation reveals that for 20 at. % La substituted by Gd, the maximum magnetic entropy change remains relatively high (compared to LaFe$_{11.4}$Si$_{1.6}$) whilst the magnetic transition remains first order, which is in contrast to Kumar et al. [15] We then studied the influence of boron doping on La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ and our results show that at low boron doping levels ($x = 0.03$ and $0.06$), the $T_C$, $\Delta S_M$ and $RCP$ are all significantly enhanced, whilst the magnetic transition remains first order. However, at high boron doping levels ($x = 0.2$ and $0.3$), $T_C$ increases whilst both $\Delta S_M$ and $RCP$ are significantly reduced with the first transition order being destroyed. MCE changes due to interstitial or substitutional modifications are common in La(Fe,Si)$_{13}$-based compounds due to the fact that the magnetic properties of these compounds are dominated by the characteristics of the Fe 3d electron band structures. Therefore, the variation of $T_C$ in these compounds is mainly associated with the lattice constant in keeping the characteristic band structure. As reported in the Ref 24, the hydrogen
atoms in the interstitial positions expand the lattice parameter and in so doing, changes the magnetic properties. So the interstitial atoms play two roles on modifying the magnetic properties: (1) expanding the lattice parameter and (2) varying the chemical environments. However, in the present case, unless we perform the external pressure experiment, it is difficult to separate these roles.

5.4 Conclusions

We have investigated the effect of boron doping on the magnetic and magnetocaloric properties of $\text{La}_{0.8}\text{Gd}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}B_x$ compounds (with boron doping level, $x = 0$, 0.03, 0.06, 0.2 and 0.3). We have shown that the paramagnetic to ferromagnetic transition in $\text{La}_{0.8}\text{Gd}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}B_x$ compounds, which is first-order for $x = 0$, 0.03 and 0.06 can be tuned to second-order at high boron doping levels ($x = 0.2$ and 0.3). A considerable enhancement of $T_C$, $\Delta S_M$ and $RCP$ was observed at low boron doping levels ($x = 0.03$ and 0.06). Thus, at low boron doping levels, the enhancement of MCE in $\text{La}_{0.8}\text{Gd}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}B_x$ alloys makes this material system a promising candidate for magnetic refrigeration near room temperature.
References:


CHAPTER 6

EFFECT OF BORON DOPING ON THE MAGNETOCALORIC AND STRUCTURAL PROPERTIES OF THE La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ REFRIGERANT

6.1. Introduction

Amid growing concerns regarding global warming and the ever-increasing energy consumption which is being worsened by the current use of conventional vapour-compression refrigeration technologies, scientists have expended a lot of research effort to find magnetic materials with a large ambient magnetic entropy change which can be used in magnetic refrigeration (MR) as an alternative cooling technology [1 - 5]. Magnetic materials having a first order transition exhibit large MCEs and are thus suitable candidates for magnetic refrigerants [6 - 8]. Of the several compounds discovered exhibiting large MCEs with first order magnetic phase transition (FOMT), the LaFe$_{13-x}$Si$_x$ compounds with cubic NaZn$_{13}$-type structure are one of the most attractive because of their considerably large MCEs and low cost. These large MCEs in LaFe$_{13-x}$Si$_x$ result from the itinerant-electron metamagnetic (IEM) transition in the vicinity of the first-order phase transition temperature [9 - 11]. However, the first order transition is usually accompanied by a considerable level of thermal and magnetic hysteresis, bringing about hysteresis loss which is detrimental to the refrigerant capacity. Under field or temperature cycling, this irreversibility appears as an undesirable heating of the magnetocaloric material. To date, several studies have been done to reduce or eliminate hysteresis in LaFe$_{13-x}$Si$_x$ based alloys [12 - 19]. These include a study by Lyubina et al. in 2008 where melt spinning was shown to significantly reduce hysteresis in
LaFe$_{13-x}$Si$_x$ based alloys compared to the bulk material [20]. However, the most common method of reducing the hysteretic losses in LaFe$_{13-x}$Si$_x$ based compounds is by the addition of substitutional or interstitial atoms [12 - 19, 21 - 24]. It has been shown that partially replacing La with Pr, Nd and Ce in LaFe$_{13-x}$Si$_x$ not only increases the MCE but leads also to a significant increase in hysteresis loss in the IEM transition process [21 - 24].

As such, the control of hysteresis due to the first order transition is imperative for the improvement in performance of magnetic refrigerants. In view of this, we have studied the magnetic and magnetocaloric properties of boron doped La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ with the main aim of investigating the effect of boron doping on the hysteresis and consequently, the refrigerant capacity of this material system. Since hysteretic losses add to the cost in energy and must be considered when calculating the usefulness of a magnetic refrigerant material when subjected to a cycling field, such a study is of paramount importance in determining the suitability of using this material system for practical applications in room temperature magnetic refrigerators.

6.2 Experimental details

Ingots of polycrystalline alloys with nominal compositions La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ ($x = 0, 0.03, 0.1, 0.3$ and $1$) were prepared by arc-melting appropriate amounts of the high purity constituent elements under a high purity argon atmosphere in a water cooled copper crucible. The purities of the starting materials were 99.9% for La, Si and Fe, 99.99% for Ce and 99.999% for B. 10 at. % excess La and Ce were used to compensate for the weight loss during the arc melting. During the arc melting process, each ingot was turned over and remelted several times to ensure its homogeneity. The resulting ingots were wrapped in tantalum foil, annealed at 1323 K for 14 days in an evacuated quartz tube to improve the
crystallization of the samples and then quenched in water. The crystal structure of the samples was determined by room temperature powder x-ray diffraction (XRD) with Cu K$_\alpha$ radiation. The magnetization was measured as a function of temperature and magnetic field for the samples and was carried out using the vibration sample magnetometer (VSM) option of a quantum design 14 T Physical Property Measurement System (PPMS) in the temperature range of 140 – 240 K at applied fields of up to 5T.

For the neutron diffraction experiment, the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}$, $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_{0.03}$ and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_{1}$ alloys were synthesized as described above, using a different arc melting system. The neutron data was collected in the temperature range 10 - 350 K and in the magnetic field range of 0 – 6 T at the high resolution powder diffractometer, $\textit{Echidna}$ at OPAL research reactor at the Australian Nuclear Science and Technology Organization (ANSTO) with an incident neutron wavelength of $\lambda = 2.4177 \, \text{Å}$. 
6.3 Results and Discussion

6.3.1 Reduction of hysteresis losses in the magnetic refrigerant La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ by the addition of boron

The x-ray diffraction (XRD) results, shown in Figure 6.1 indicate that all the alloys crystallized in a single phase with the NaZn$_{13}$-type cubic structure except for the presence of a few percent of α-Fe. Subsequent magnetic measurements were performed on the three samples namely, La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$, La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.1}$ and La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.3}$. Fig. 6.2
Figure 6.2 Magnetization as a function of temperature in the ZFC and FC process for the \( \text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x \) samples with \( x = 0, 0.1 \) and 0.3.

shows the temperature dependencies of the magnetization measured in the heating and cooling processes under a low magnetic field of 0.02T and temperature range from 140 K to 220 K of \( \text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x \) samples with \( x = 0, 0.1 \) and 0.3. The Curie temperature, \( T_C \), which is defined as the temperature at which the \( dM / dT \) of the heating M-T curves is a minimum is found to increase with an increase in boron content from 174 K, 182 K and finally to 184 K for \( x = 0, 0.1 \) and 0.3 respectively. This increase in \( T_C \) with increasing boron doping, \( x \), can be attributed to the lattice expansion caused by the introduction of interstitial boron atoms since previous investigations on the relation between unit cell volume and \( T_C \) for \( \text{LaFe}_{13-x}\text{Si}_x \) based compounds have verified that the introduction of interstitial boron can
cause $T_C$ to increase through expanding the lattice of the compounds [13]. In our study, the M-T curve for the undoped sample shows a considerable thermal hysteresis (17.4 K) which indicates the first-order nature of this transition. However, on increasing the boron doping, $x$, it is evident from Figure 6.2 that the thermal hysteresis is reduced to 12.7 K and 11.7 K for $x = 0.1$ and 0.3 respectively. This implies that the boron doping in the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}$ material system can decrease the thermal-induced first order magnetic transition at $T_C$.

Figure 6.3 displays the magnetization curves for the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ ($x = 0, 0.1$ and 0.3) alloys. The sweep rate of the field is slow enough to ensure that the M-H curves are recorded in an isothermal process. The M-H curves show a field induced metamagnetic transition. A stepwise magnetic behaviour is observed in the vicinity of $T_C$, signifying the coexistence of ferromagnetic and paramagnetic phases. The first abrupt increase of magnetization marks the contribution of the FM phase, while the subsequent step-like variation signifies the field-induced metamagnetic transition of the PM phase to the FM phase with the inflexion point of this step-like transitional region being the critical field value, $H_C$. For the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ samples with $x = 0, 0.1$ and 0.3, $H_C$ linearly depends on temperature with a rate of 0.21, 0.20 and 0.17 T / K respectively. A similar trend was observed in $\text{Mn}_{0.99}\text{Fe}_{0.01}\text{As}$ [25]. Furthermore, the M-H curves measured under increasing and decreasing fields exhibit significant magnetic hysteresis loops for $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ with $x = 0, 0.1$ and 0.3. For each sample, the magnetization curves above $T_C$, ($= 174$ K for $x = 0$, 181 K for $x = 0.1$ and 184 K for $x = 0.3$) exhibit a discontinuous magnetization change with hysteresis. It can be clearly seen that the hysteresis becomes smaller with an increase in boron doping, $x$. 
Figure 6.3 The magnetization curves measured in the increasing and decreasing field for the 
$La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ ($x = 0, 0.1$ and $0.3$).
Figure 6.3 shows the temperature dependence of the hysteresis loss, defined as the area enclosed by the ascending and descending branches of the magnetization curve. It can be seen that the hysteretic losses are negligible below $T_C$ and grow rapidly to reach a maximum around $T_C$ and then decrease with a further increase in temperature above $T_C$. The maximal hysteresis losses around $T_C$ are 131.5, 30.4 and 8.1 J kg$^{-1}$ measured under a 5T field for $x = 0$, 0.1 and 0.3 respectively and are shown in Figure 6.4. The insert shows the maximum hysteresis loss measured under a 2 T field, which is also found to decrease with an increase in $x$. This result indicates the effectiveness of the interstitial boron atoms introduced into the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ material system in depressing the hysteresis loss. This reduction in hysteresis losses is attributed to the weakening of the field induced FOMT from the paramagnetic to ferromagnetic state due to the addition of boron.

Figure 6.4 The temperature dependence of the hysteresis loss of La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ for values of $x$ of 0, 0.1 and 0.3 measured at 2 and 5 T.
Figure 6.5 Arrott plots of La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ for values of $x$ of 0, 0.1 and 0.3.
Figure 6.5 shows Arrott plots of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ for values of $x$ of 0, 0.1 and 0.3. It is clear enough to see that the experimental points near $T_\text{C}$ show $S$–shaped curves. Such $S$–shaped curves suggest the phase transitions of all three samples are first order.

The magnetic entropy changes reach maximum near their $T_\text{C}$. In an isothermal process, the magnetic entropy change of the materials can be derived from the Maxwell relation which is shown below.

$$\Delta S_M(T, p, \Delta H)_{\Delta H, p} = \int_{H_1}^{H_2} \left[ \frac{\partial M(T, p, H)}{\partial T} \right]_{H, p} dH$$ \hspace{1cm} (6.1)

The maximum $\Delta S_M$ for $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ samples with $x = 0, 0.1$ and 0.3 range from 72.2 J kg$^{-1}$K$^{-1}$ to 16.4 J kg$^{-1}$K$^{-1}$ measured under a field of 5T and are shown in Figure 6.6. The $\Delta S_M$ for the pure $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}$ compound derived from the Maxwell relation is in good agreement with Ref 24. However, the presence of the $\Delta S_M$ spikes shown in Figure 6.6 are a reason for concern as their presence implies that the $\Delta S_M$ predicted by the Maxwell relation could be erroneous. Previously, Pecharsky et al., [26] showed that no $\Delta S$ spikes are expected for a normal first order transition. Thus $\Delta S_M$ is recalculated using the CC equation which is shown below.

$$\Delta S_M = -\Delta M \frac{dH_C}{dT}$$ \hspace{1cm} (6.2)

Where $\Delta M$ is the difference of magnetization between the low and high field parts in the M-H curves shown in Figure 6.3.
Figure 6.6 $\Delta S_m$ vs $T$ plots of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ for values of $x$ of 0, 0.1 and 0.3.
Thus, Figure 6.7 shows a comparison of the $\Delta S_M$ calculated using the CC equation and the $\Delta S_M$ predicted by the Maxwell relation. The maximum $\Delta S_M$ calculated using the CC equation for the $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with $x = 0, 0.1$ and $0.3$ are $20.8, 12.4$ and $8.9$ J kg$^{-1}$K$^{-1}$ respectively and similar to what Balli et al. [25] observed in $Mn_{0.99}Fe_{0.01}As$, the $\Delta S_M$ peaks for these samples derived from the CC equation are centred at slightly higher temperatures than the MCE peaks derived from the Maxwell relation.

The efficiency or the performance of a solid-state cooling device is determined by the magnitude of the figure-of-merit, the refrigerant capacity, $RC$ (i.e. the heat that can be transferred between the cold and hot reservoirs), which is calculated by numerically

![Figure 6.7 Comparison of the $\Delta S_M$ calculated using the Clausius-Clapeyron equation and the $\Delta S_M$ predicted by the Maxwell relation.](image-url)
integrating the area under the $\Delta S_M - T$ curve, with the integration limits being the temperatures at half maximum of the peak. To enhance the performance of the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}$ material system, we carried out a boron doping study to optimize the RC. Tabulated values of the RC as a function of B field at 5 T calculated using $\Delta S_M$ obtained using the Maxwell relation and the Clausius-Clapeyron equation, RC (MR) and RC (CC) respectively are shown in Table 6.1. For the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ alloys with $x = 0$ to 0.3, both the RC (MR) and RC (CC) increase with an increase in magnetic field up to 5T. Also, there is an increase in both the RC (MR) and RC (CC) with an increase in boron doping, $x$. However, it is imperative to note that for most of the samples, the calculated RC (MR) is significantly higher than the RC (CC). This is due to the fact that in calculating RC (MR), an overestimated value of $\Delta S_M$, obtained from the Maxwell relation is used, thus leading to an overestimation of RC (MR). Hence for the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ material system, RC (CC) gives a reasonable estimate of the refrigerant capacity. Although $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ compounds exhibit high RC values, they also have a large hysteresis loss, demonstrated in Figure 6.3, which reduces the MCE of the material.

By subtracting the hysteresis loss from the calculated RC (MR) and RC (CC), we obtained the effective refrigerant capacities $\text{RC}_{\text{eff}}$ (MR) and $\text{RC}_{\text{eff}}$ (CC) which are shown in Table 6.1, calculated for magnetic field values of 5 T. For the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ alloys as $x$ varies from 0 to 0.3, both the $\text{RC}_{\text{eff}}$ (MR) and $\text{RC}_{\text{eff}}$ (CC) show a similar trend to that observed in the RC (MR) and RC (CC), with $\text{RC}_{\text{eff}}$ (CC) being a reasonable estimate of the effective refrigerant capacity. These results indicate that the introduction of interstitial boron atoms significantly improves the cooling capacity of the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}$ material system. Thus,
Table 6.1 Tabulated values of the refrigerant capacity RC (MR), RC (CC), and the effective refrigerant capacity $R_{C_{\text{eff}}}$ (MR) and $R_{C_{\text{eff}}}$ (CC), at 5T for $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ for $x$ values of 0, 0.1, and 0.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H</th>
<th>RC (MR)</th>
<th>RC (CC)</th>
<th>$R_{C_{\text{eff}}}$ (MR)</th>
<th>$R_{C_{\text{eff}}}$ (CC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$</td>
<td>5</td>
<td>176.6</td>
<td>295.5</td>
<td>45.1</td>
<td>164</td>
</tr>
<tr>
<td>$La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_{0.1}$</td>
<td>5</td>
<td>437.2</td>
<td>335.4</td>
<td>406.8</td>
<td>305</td>
</tr>
<tr>
<td>$La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_{0.3}$</td>
<td>5</td>
<td>461.8</td>
<td>306.1</td>
<td>453.7</td>
<td>298</td>
</tr>
</tbody>
</table>

A proper comparison between magnetocaloric materials can be made with the use of $R_{C_{\text{eff}}}$ as opposed to simply comparing the $\Delta S_M$.

6.3.2. Neutron powder diffraction studies on $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ alloys

![Figure 6.8](image)

Figure 6.8 Magnetization as a function of temperature in the ZFC and FC process for the $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with $x = 0$ and 0.03.
Figure 6.8 shows the FC and ZFC magnetization obtained under a magnetic field of 0.02 T for the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples with boron doping level, $x = 0$ and 0.03. The M-T curves of both samples confirm the presence of a large amount of the $\alpha$-Fe phase. Due to this reason, it was impossible to study the effect of boron doping on the magnetic structure of the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples. Figure 6.9 shows a Rietveld plot of the measured and calculated neutron diffraction patterns for the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ and La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.03}$ samples. The red points are the experimental data, while the solid black lines are the calculated results. The green vertical bars indicate the peak positions that are calculated by the refinement. The bottom blue line indicates the difference between the experimental and

![Rietveld plots](image)

**Figure 6.9** Neutron powder diffraction data collected from the *Echidna* diffractometer refined to the NaZn$_{13}$ structure for La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples with $x = 0$ and 0.03 at room temperature.
Figure 6.10 Neutron diffraction patterns measured at 0 T, for La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ samples with $x = 0$ and 0.03, showing negative thermal expansion.

calculated results. These neutron diffraction patterns confirm that both samples crystallize in the NaZn$_{13}$ structure with a significant amount of the alpha Fe phase. The Rietveld refinement was used to calculate the lattice parameters of the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ and La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.03}$ samples measured at different temperatures and fields, which will be discussed in detail in the ensuing paragraphs.

Figure 6.10 shows the neutron diffraction patterns of the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ and La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.03}$ samples measured at room temperature and at zero field. For both
Figure 6.11 Neutron diffraction patterns measured at 200 K, for La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples with $x = 0$ and 0.03, showing negative magneto-elastic expansion.

For both samples, an increase in temperature causes the peaks in Figure 6.10 to shift to the right, which is an indication of contraction of the unit cell. Therefore, for both samples an increase in temperature causes a negative thermal expansion.

Figure 6.11 shows the neutron diffraction patterns of the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ and La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.03}$ samples measured at 200 K and at 0, 1 and 6 T. For both samples, the application of a field causes the peaks in Figure 6.11 to shift to the right, which is an
Figure 6.12 Dependence of the lattice parameters extracted from Rietveld refinements on the temperature measured at different magnetic fields for La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ samples with $x = 0$ and 0.03.
indication of contraction of the unit cell. In this case, for both samples, an application of a magnetic field gives rise to a negative-magneto-elastic expansion.

Figure 6.12 shows a dependence of the lattice parameters to the temperature for the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ and La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.03}$ samples. At 0 T, a decrease in temperature from 300 to 200 K causes both compounds to undergo a normal thermal contraction. However, on decreasing the temperature further from 200 K, a large volume change occurs in the vicinity of the ferromagnetic to paramagnetic transition. In this region, a decrease in temperature results in an expansion of the lattice parameter. Wang et al. attributed this expansion to the spontaneous magnetostriction cancelling the normal contraction with a decrease in temperature [25]. Therefore, in this region, the co-existence of a large volume change as well as a spontaneous magnetostriction jump gives rise to a first order magnetic transition. The dependence of the lattice parameters on the temperature for the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ and La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{0.03}$ samples at 1 and 6 T follow a similar trend to the trend measured at 0 T described above.

6.4 CONCLUSIONS

In conclusion, we have found that large $\Delta S_M$ and RC values and a small hysteresis loss can be simultaneously achieved in the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds. Results obtained from this study show that the introduction of interstitial boron atoms into the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ material system could be a promising method of depressing the hysteresis loss whilst maintaining the large MCE, since the boron containing alloys are much improved magnetic refrigerants for near-room-temperature applications. The determination of $\Delta S_M$ for La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds using the Clausius-Clapeyron equation yields reasonable estimates of the MCE in these compounds. Our results demonstrate that the hysteresis
behaviour of a material is critical in evaluating its potential as a functional magnetic refrigerant. Also, high resolution neutron diffraction was employed to investigate the crystal structure of the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}\text{B}_x$ compounds. We found that, in the vicinity of the FM – PM transition there is co-existence of a large volume change as well as a spontaneous magnetostriction jump, which gives rise to a first order magnetic transition.
References

CHAPTER 7

MAGNETOCALORIC EFFECT, CRYSTAL STRUCTURE
AND CRITICAL BEHAVIOUR OF THE Mn$_{0.94}$Ti$_{0.06}$CoGe ALLOY

7.1 Introduction

Materials which experience simultaneous crystallographic and magnetic phase transitions have garnered a lot of interest owing to their promising applications as multifunctional materials [1 – 3]. Recently, it has been reported that this magnetostructural coupling in the MnCoGe-based materials can lead to a large magnetocaloric effect (MCE) around room temperature [4 – 5]. Thus, the MnCoGe-related systems exhibit great potential to be used as refrigerants in magnetic refrigeration (MR). MR is regarded as a promising, environmentally friendly and more efficient alternative to the currently used conventional gas-compression based refrigeration [6]. Up to now, a lot of studies have been done on the tuning of the magnetostructural coupling in the MnCoGe system [4, 5, 7]. The parent MnCoGe compound is a ferromagnet with a Curie temperature $T_C \sim 345$ K which crystallizes in the orthorhombic TiNiSi-type crystal structure (space group $Pnma$) at room temperature and undergoes a diffusionless crystallographic phase transition to the high temperature hexagonal Ni$_2$In-type structure (space group $P63/mmc$) on heating at the structural transition temperature, $T_{str} \sim 650$ K [5, 8 – 11]. In order to modify the interatomic distances resulting in the tuning of the magnetostructural coupling in MnCoGe compound, several different ways such as substitutions, dopings and the application of physical pressure have been used [4, 5, 7].

We have investigated the substitution of Ti into Mn$_{1-x}$Ti$_x$CoGe compounds with $x = 0.02, 0.04$ and $0.06$ and we found that for the, $x = 0.06$ substitution most successfully shifted the
structural change and magnetic phase transition into our interested temperature range leading to the attainment of a giant magnetocaloric effect. In this chapter, we focus on the magnetic and structural properties as well as the critical behaviour of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy. Thus in an effort to understand the nature of the magnetic transition in Mn$_{0.94}$Ti$_{0.06}$CoGe, we performed a critical exponent analysis in the vicinity of the ferromagnetic (FM) - paramagnetic (PM) region [12 – 14]. In order to probe further the magnetostructural coupling and fully understand the role of structural and magnetic transformation in enhancing the magnetic entropy change, we performed a temperature dependent neutron diffraction experiment over the temperature range 5 – 350 K.

### 7.2 Experimental details

Polycrystalline Mn$_{1-x}$Ti$_x$CoGe (x = 0, 0.02, 0.04 and 0.06) ingots were prepared by arc melting the appropriate amounts of Mn (99.9%), Ti (99.999%) powder, Co (99.9%) and Ge (99.999%) chips in an argon atmosphere. During arc melting, a 3% excess Mn over the stoichiometric amount was added to compensate the weight loss of Mn. The polycrystalline ingots were melted five times to achieve good homogeneity. The ingots were then wrapped in tantalum foil, sealed in a quartz ampoule and subsequently annealed at 850 °C for 120 hours and then quenched in water at room temperature. The magnetization measurements were carried out using the vibration sample magnetometer option of a Quantum Design 14 T Physical Property Measurement System (PPMS) and a Quantum Design Physical Property Measurement System (MPMS) in the temperature range of 100 – 340 K at applied fields of up to 5 T. For critical exponent study, magnetization isotherms were measured in the temperature range 249 – 299 K with an interval of 2 K at applied fields of up to 5 T. Around 1 gram powder sample of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy was placed in a vanadium sample
holder, which was then fitted inside a cryocooler and then mounted on the sample stage of the diffractometer for the neutron diffraction measurements. The neutron data was collected in the temperature range 5 - 350 K at the high intensity powder diffractometer, *Wombat* at OPAL with an incident neutron wavelength of \( \lambda = 2.4177 \) Å. To determine the structural parameters the neutron diffraction patterns were analysed using Rietveld [15 – 16] refinements with the Fullprof package.

7.3 Results and Discussion

7.3.1 Magnetic phase transitions

Temperature dependence [100 K to 340 K] of the magnetization of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy measured in a magnetic field of \( \mu_0 H = 0.01 \) T is shown in Figure 7.1. The sample was measured on warming in a field of \( \mu_0 H = 0.01 \) T after first cooling in zero field (marked as ZFC). The field-cooled cooling magnetization curve, FC, was then recorded on cooling from 340 K to 5 K in an applied field of \( \mu_0 H = 0.01 \) T. A decoupling of the structural and magnetic transitions is clearly observed in the M-T curve as a two-step transition, which was later confirmed by neutron experiment. Bayreuther *et al.* showed that \( T_C \) determined from the linear extrapolation of \( M^2 \) (T) to \( M = 0 \) as suggested by the molecular field theory yields a value closer to the true transition temperature as opposed to the \( T_C \) determined from the minimum of \( dM/dT \) [17]. The inset shows a plot of \( M^2 \) vs T, which reveals a magnetic transition from FM to PM at the ordering temperature, \( T_C \approx 270 \) K as well as a plot of \( dM/dT \) showing the structural transition at \( T_{str} \approx 235 \) K. The absence of thermal hysteresis in the vicinity of the magnetic PM to FM transition is a clear evidence of the second order nature
Figure 7.1 Temperature dependence of magnetization. The inset shows dM/dT vs T used for the determination of T$_{str}$ as well as $M^2$ vs T used for the determination of T$_C$ of this transition. However, a notable thermal hysteresis is observed in the vicinity of the magneto-structural transition from the antiferromagnetic TiNiSi-type to the ferromagnetic Ni$_2$In-type structure confirming its first order nature. It has been previously established that the presence of a small hysteresis at T$_{str}$ is indicative of a magnetoelastic character at the FM to AFM transition [4].

7.3.2 Magnetocaloric effect

In an isothermal process, the magnetic entropy change of the materials can be derived from the Maxwell relation as shown below:
The magnetic entropy changes, $\Delta S_M$ of materials have been calculated using the Maxwell relation [18] and shown in Figure 7.2 (a) as a function of temperature and field. Although the use of Maxwell’s relation for 1st order systems is still questionable, Caron et al. successfully established a method of determining the magnetic entropy change of 1st order systems by using the decreasing field [19]. In our work, we have also evaluated the magnetic entropy change, $\Delta S_M$ in the decreasing field mode, which is shown by the dotted curves in Figure 7.2(a). A comparison of the $\Delta S_M$ values calculated using increasing and decreasing fields respectively shows that the difference between these values is very small, which confirms that there is negligible hysteresis loss occurring in the vicinity of the structural transition thus demonstrating the applicability of the Maxwell relation. As expected, $-\Delta S_M$ increases with the increase in the applied magnetic field. The inset showing the variation of the magnetic entropy with temperature at 1 T, clearly displays two maxima, one occurring at the structural transition and the other at the magnetic transition. Interestingly, the maximum magnetic entropy change is found to be in the vicinity of $T_{str}$ and is about -11.3 Jkg$^{-1}$K$^{-1}$ for a magnetic field change $\Delta B$ of 5 T, which is about one order of magnitude higher than that found in the undoped MnCoGe ($\approx 4.8$ Jkg$^{-1}$K$^{-1}$ at 5 T) [4]. Around the FM to PM transition temperature $T_C$, $-\Delta S_M$ is found to be about 3 Jkg$^{-1}$K$^{-1}$ for a magnetic field change $\Delta B$ of 5 T. The difference of $-\Delta S_M$ at $T_{str}$ and $T_C$ can be understood in the terms of the difference in the order of phase transitions. Compared with some alloys with second order magnetic transition, the $-\Delta S_M$ peak in Mn$_{0.94}$Ti$_{0.06}$CoGe is comparable to that in Gd [20] ($\approx 10.2$ Jkg$^{-1}$K$^{-1}$ at 5 T).

\[
\Delta S_M(T, p, \Delta H)_{\Delta H, p} = \frac{\partial M(T, p, H)}{\partial T} \bigg|_{H, p} dH
\]
(7.1)
Figure 7.2 (a) Temperature dependence of the isothermal magnetic entropy change $-\Delta S_M (T, H)$ for Mn$_{0.94}$Ti$_{0.06}$CoGe calculated from magnetization isotherms; (b) Dependence of the magnetic entropy change on the parameter $(\mu_0 H/T_C)^{2/3}$. The solid line represents a linear fit to the data.

Figure 7.2 (b) shows the dependence of the magnetic entropy change on the parameter $(\mu_0 H/T_C)^{2/3}$. The mean field theory predicts that in the vicinity of second-order phase
transitions, $\Delta S_M$ is proportional to $(\mu_0 H/T_C)^{2/3}$ [21 – 22]. The linear fit to the data in Figure 2(b) clearly demonstrates that the relationship $\Delta S_M \propto (\mu_0 H/T_C)^{2/3}$ is valid around $T_C$.

As shown by neutron diffraction study (Figure 7.3), the phase transition at $T_{str}$ includes the changes in both the crystal symmetry and magnetic properties. The change of symmetry is from the low-temperature orthorhombic TiNiSi-type structure (space group $Pnma$) to the high-temperature hexagonal Ni$_2$In-type structure (space group $P63/mmc$) while the change of magnetic properties are related to the difference of the magnetic moment for these two phases. For the parent MnCoGe compound it was found that in the hexagonal structure, the values of the saturation moment, $M_S$ is 2.76 $\mu_B$ while in the orthorhombic structure with a

![Figure 7.3 Neutron diffraction patterns over the temperature range 10-340 K at 10 K intervals. Below $T_{str}$ and above $T_C$, the neutron pattern can be indexed well with the space group Pnma (orthorhombic structure-hkl Miller indices without*) and space group P63/mmc.](image)
(hexagonal - hkl Miller indices with*), respectively. Between \( T_{\text{str}} \) and \( T_C \), the pattern indicates the coexistence of the orth. phase and the hex. phase.

higher \( M_S = 4.13 \ \mu_B \) [23]. Therefore, the entropy changes around \( T_{\text{str}} \) includes both magnetic and structural contribution while the \( \Delta S_M \) around \( T_C \) only includes the magnetic entropy change.

Moreover, it was found from Figure 7.3 that the structural transition around \( T_{\text{str}} \) is not complete. There is a coexistence of the orthorhombic and hexagonal structures below \( T_C \). The phase fraction is shown as an inset in Figure 7.3. The details of refinement for neutron patterns will be presented in the ensuing section. From the crystallographic point of view, the TiNiSi-type unit-cell can be considered as an orthorhombic distortion of the hexagonal Ni\(_2\)In-type unit-cell. However, the chemical environment has a significant change after the structure change. For example, at \( T = 235 \) K where the phase fraction is 65.3\% for Pnma and 34.7 \% for P63/mmc. In the TiNiSi-type unit-cell, the closest distance between Mn-Mn is 2.985 Å while in the Ni\(_2\)In-type unit-cell it changes to 2.651 Å.

### 7.3.3 Critical exponent analysis

In an effort to further clarify the nature of the FM – PM phase transition, we performed an analysis of the critical behaviour near \( T_C \). We measured the isothermal magnetization versus the applied field around \( T_C \) using an interval of 2 K as shown in Figure 7.4. A plot of \( H/M \) versus \( M^2 \), known as the standard Arrott plot, is shown in Figure 7.5 for the temperatures in the vicinity of \( T_C \). According to the criterion proposed by Banerjee [24], the order of
magnetic transition can be determined from the slope of the isotherm plot. If the H/M versus $M^2$ curves show a negative slope, the transition is first order while a positive slope corresponds to a second order transition. For the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy, the positive slope of the H/M versus $M^2$ curves throughout the transition temperature indicates that the phase transition is second order. This result is consistent with the absence of thermal hysteresis in the vicinity of the PM – FM transition as shown in Figure 7.1, thereby confirming the second order nature of this transition. However, a close inspection of the $H^2$ versus $M^2$ curves reveals that all the curves are not parallel to each other (see the parallel dashed lines in Figure 7.5), indicating that the critical exponents of $\beta = 0.5$ and $\gamma = 1$ are not satisfied.

Figure 7.4 Isothermal magnetization curves for Mn$_{0.94}$Ti$_{0.06}$CoGe in the vicinity of $T_C$. 
Figure 7.5 Arrott plot of $M^2$ vs $H/M$ at temperatures in the vicinity of $T_C$.

The scaling hypothesis postulates that a second order magnetic phase transition near $T_C$ is characterized by a set of critical exponents namely, $\beta$, $\gamma$ and $\delta$ [25]. In this work, we have used different methods to investigate the critical behaviour of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy, namely the modified Arrott plots (MAPs), Kouvel-Fisher method, critical isotherm analysis and the Widom scaling relation. The first method used to calculate the critical exponents is the MAPs method, which is based on the Arrott-Noakes equation of state [26]. Quantitative fits are made to the Arrott plots using the following equations [27].

$$M_S(T) = \lim_{H \to 0}(M) = M_0 (-\epsilon)^\beta, \epsilon < 0$$

(7.2)
Figure 7.6 Temperature dependence of the spontaneous magnetization $M_S$ and inverse initial susceptibility $\chi_0^{-1}$ (solid lines are fitted to equations (7.2) and (7.3)).

\[
\chi_0^{-1}(T) = \lim_{H \to 0} (H/M) = (h_0/M_0)\varepsilon^\gamma, \varepsilon > 0
\]  

(7.3)

where $M_0$ and $h_0$ are constants and $\varepsilon = (T-T_C)/T_C$ is the reduced temperature. Initial values of $\beta$ and $\gamma$ are selected, then a plot of $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$ is obtained. $M_S$ is then determined from the intersection of the linearly extrapolated curve with the $M^{1/\beta}$ axis. It is imperative to note that only the high field linear region is used for the analysis because MAPs tend to deviate from linearity at low field due to the mutually misaligned magnetic domains [28]. Next, $M_S$ is plotted as a function of temperature. To determine $\chi_0^{-1}(T)$ a similar procedure is used in conjunction with the $(H/M)^{1/\gamma}$ axis. The values of $\chi_0^{-1}(T)$ and $M_S(T)$ are plotted as a function of temperature in Figure 7.6 and these plots are then fitted with equations (7.2) and
Figure 7.7 Modified arrott plot obtained by the Kouvel - Fisher method showing isotherms of $M^{1/\beta}$ vs $(\frac{H}{M})^{1/\gamma}$ with the calculated $\beta = 0.61$ and $\gamma = 0.91$.

(7.3), thus obtaining values of $\beta$ and $\gamma$. These new critical exponent values are then used to construct new MAPs. These steps are repeated until the iterations converge to the optimum $\beta$, $\gamma$ and $T_C$ values. Using equations (7.2) and (7.3), the MAPs shown in Figure 7.6 yielded critical parameters, $\beta = 0.61 \pm 0.04$ and $\gamma = 0.91 \pm 0.02$. The modified Arrott plots are drawn in Figure 7.7 which shows clearly that all lines are parallel to each other (dashed lines as an eye guide).
The Kouvel-Fisher method which makes use of the equations (7.4) and (7.5) shown below, is a more accurate way of determining the critical exponents $\beta$ and $\gamma$ [29].

\[
\frac{M_S(T)}{dM_S(T)/dT} = \frac{T-T_C}{\beta} \quad (7.4)
\]

\[
\frac{\chi_0^{-1}(T)}{d\chi_0^{-1}(T)/dT} = \frac{T-T_C}{\gamma} \quad (7.5)
\]

According to the equations (7.4) and (7.5), plotting $M_S(T)[dM_S/dT]^{-1}$ and $\chi_0^{-1}(T)[d\chi_0^{-1}/dT]^{-1}$ versus temperature yields straight lines with slopes of $1/\beta$ and $1/\gamma$ respectively as shown in Figure 7.8. The value of $T_C$ is obtained from the intercepts on the $x$-axis. The critical exponents $\beta$ and $\gamma$ as well as $T_C$ obtained using the Kouvel-Fisher method are $\beta = 0.61 \pm 0.04$, $T_C = 276$ K and $\gamma = 0.91 \pm 0.03$, $T_C = 275$ K. A comparison of the critical exponents $\beta$ and $\gamma$ obtained using the MAPs and those obtained using the KF method reveals that these values match extremely well. The value of the critical component $\delta$ can be determined directly from the critical isotherm $M(T_C, H)$ according to equation (7.6) below.

\[
M_{t_c} = DH^{1/\delta}, \epsilon = 0, T = T_c \quad (7.6)
\]

Figure 7.9 shows the magnetic field dependence of magnetization at $T_C = 275$ K for the
**Figure 7.8** Kouvel-Fisher plot for the spontaneous magnetization $M_S(T)$ and the inverse initial susceptibility $\chi_0^{-1}(T)$ (solid lines are fitted to equations (7.4) and (7.5)).

**Figure 7.9** The critical isotherm analysis at $T_C$. The inset shows the same plots on the log–log scale (solid line is a linear fit to Equation (7.6)).
\( \text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe} \) alloy. The insert shows the critical isotherm on a log – log scale. From equation (7.6) a plot of \( \log (M) \) versus \( \log (H) \) is expected to be a straight line with slope \( 1/\delta \). The obtained \( \delta \) value from the critical isotherm is 2.59. Another way of obtaining the critical component \( \delta \) is by using the Widom scaling relation shown in equation (7.7):

\[
\delta = 1 + \frac{\gamma}{\beta}
\]  

Using equation (7.6) and the critical parameters \( \beta \) and \( \gamma \) obtained using the MAPs and those obtained using the Kouvel-Fisher method, the deduced \( \delta \) values are 2.52 and 2.49 respectively. Thus, the Widom scaling relation has confirmed the reliability of the critical exponents deduced from the experimental data. The reliability of the calculated exponents \( \beta \) and \( \gamma \) can be confirmed by using the scaling theory. In the critical region, according to the scaling theory, the magnetic equation of state can be written as:

\[
M (H, \varepsilon) = \varepsilon^\beta f_\pm (H / \varepsilon^{(\beta+\gamma)})
\]  

Where \( \varepsilon \) is the reduced temperature \( (T - T_C) / T_C \) and \( f_+ \) and \( f_- \) are regular analytical functions above and below \( T_C \) respectively. Using \( \beta \) and \( \gamma \) obtained from the Kouvel-Fisher method, the plots of \( M / \varepsilon^\beta \) versus \( H / \varepsilon^{(\beta+\gamma)} \) (shown in Figure 7.10) yield two universal curves, one for temperatures above \( T_C \) and the other one for temperatures below \( T_C \), in agreement with the scaling theory. This therefore confirms that the obtained values of the critical components as well as the \( T_C \) are reliable and in agreement with the scaling hypothesis.
Figure 7.10 Scaling plots indicating universal curves below and above $T_C$ for the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy.

It is well accepted that the order parameter of phase transition around magnetic transition temperature is fluctuating on all available length scales and those fluctuations smear out the microscopic details of the interactions in the continuous phase transition system [30]. The mean field interaction model for long range ordering has theoretical critical exponents of $\beta = 0.5$, $\gamma = 1.0$ and $\delta = 3.0$ [31] while the theoretical values based on the three dimensional Heisenberg model corresponding to short range interactions are $\beta = 0.365$, $\gamma = 1.386$ and $\delta = 4.80$ [32]. The $\delta$, $\beta$, $\gamma$ values derived for the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy are close to the mean field values, thus indicating that long range interactions dominate the critical behavior around $T_C$ in this compound. Thus, the critical behaviour analysis in the vicinity of $T_C$ determined that the magnetism of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy is governed by long range interactions,
which is in agreement with the linear fit to the data in Figure 7.2 (b) which clearly demonstrates that the relationship $\Delta S_m \propto (\mu_0 H/T_C)^{2/3}$ is valid around $T_C$.

### 7.3.4 Neutron diffraction

A temperature dependent neutron diffraction image for selected 20 region is shown in Figure 7.11 with the orthorhombic phase $(hkl)$ Miller indices (space group $Pnma$) being marked without * and the hexagonal phase $(hkl)$ Miller indices (space group $P6_3/mmc$) with *. It can be seen clearly that with increasing temperature one structure transition takes place starting from around 220 K and completing at 270 K, which agrees well with our magnetic study measurements (discussed above) revealing a phase transition at approximately 235 K.

![Neutron diffraction image](image)

**Figure 7.11** Neutron diffraction image for Mn$_{0.94}$Ti$_{0.06}$CoGe taken at 5 K steps over the temperature range 5 - 350 K.
Compared with the parent MnCoGe compound where the structure change occurring at $T_{\text{str}} \sim 650$ K, the substitution of 6 percent Ti for Mn leads to a significant reduction in $T_{\text{str}}$. In order to show the transition clearly, we draw the neutron diffraction patterns at selected temperatures ($T = 200$ K, 245 K and 350 K) in Figure 7.12.

It can be seen from Figure 7.12 that at 200 K the compound crystallizes in the orthorhombic TiNiSi-type structure (space group $Pnma$) while at 350 K the crystal structure changes to the hexagonal Ni$_2$In-type (space group $P6_3/mmc$). At 245 K, there is a co-existence of both phases, thus confirming our expectations from magnetic measurements. Further analysis of the neutron diffraction data using the Rietveld refinement resulted in the determination of the lattice parameters as well as the volume phase fractions for the orthorhombic and hexagonal phases. Figure 7.13 shows the evolution of the orthorhombic and hexagonal phase fractions as a function of temperature. The volume phase fractions as a function of temperature have been fitted using the sigmoidal Boltzmann equation shown in Equation (7.91) below:

$$F(T) = \frac{(F(T_1) - F(T_2))}{1 + \exp\left[\frac{T - T_{\text{str}}}{dT}\right]} + F(T_2), \quad (7.9)$$

where $F(T)$ represents the temperature dependence of the orthorhombic or hexagonal phase fraction with $T_1 = 0$ K and $T_2 = +\infty$, $T_{\text{str}}$ is the transition temperature and $dT$ is the temperature width of the transition.
Figure 7.12 Measured and calculated neutron diffraction patterns for the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy at 200 K, 245 K and 350 K. The points (marked by crosses) are the experimental data while the solid lines are the calculated results. The vertical bars indicate the peak positions that are calculated by the refinement and the bottom solid line indicates the difference between the experimental and the calculated results.
Figure 7.13 Quantitative phase analysis of the orthorhombic TiNiSi-type phase (space group \textit{Pnma}) and the hexagonal Ni$_2$In-type phase (space group \textit{P6$_3$/mmc}).

Table 7.1 Tabulated values of the numerical coefficients $F(T_1)$ and $F(T_2)$ representing the fitted orthorhombic and hexagonal phase fractions at $T_1 = 0$ K and $T_2 = +\infty$ determined from the sigmoidal Boltzmann fit.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$F(T_1)$</th>
<th>$F(T_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{Pnma}</td>
<td>$98.8 \pm 1.59$</td>
<td>$6.99 \pm 1.87$</td>
</tr>
<tr>
<td>\textit{P6$_3$/mmc}</td>
<td>$1.2 \pm 1.59$</td>
<td>$93.01 \pm 1.87$</td>
</tr>
</tbody>
</table>
The peak intensity as a function of temperature for the (002)* and (011) peaks.

The numerical coefficients $F(T_1)$ and $F(T_2)$ representing the fitted orthorhombic and hexagonal phase fractions at $T_1$ and $T_2$ are listed in Table 7.1. The orthorhombic and hexagonal phase fractions represented by the fitting coefficients $F(T_1)$ and $F(T_2)$ are 98.8 and 6.99 as well as 1.2 and 93.01 vol. % respectively. The orthorhombic phase fraction determined from the neutron diffraction pattern measured at 5 K is approximately 100 vol. % which is in excellent agreement to the $F(T_1)$ value of 98.8 ± 1.59 determined from the sigmoidal Boltzmann fit.

The peak intensities of the selected reflections (002)* (for P6$_3$/mmc) and the (011) (for Pnma) as a function of temperature are shown in Figure 7.14. The peak intensity of the (011) reflection which decreases with an increase in temperature corresponds to the decrease of the
*Pnma* phase fraction whilst the peak intensity of the (002)* reflection which increases with an increase in temperature corresponds to the increase of the P6₃/mmc phase fraction with temperature. Figure 7.15 shows the refined structural parameters of the Mn₀.⁹₄Ti₀.⁰₆CoGe compound as a function of temperature from neutron diffraction data. The lattice parameters and volumes between these two structures can be described by \( a = a_{\text{ortho}} = c_{\text{hex}}, b = b_{\text{ortho}} = a_{\text{hex}}, c = c_{\text{ortho}} = \sqrt{3}a_{\text{hex}}, \) and \( V = V_{\text{ortho}} = 2V_{\text{hex}} \) [33 - 34]. The lattice parameter \( b \), indicates the exchange interaction between the Mn-Mn moments along this axis and a change in this parameter strongly influences the Curie temperature. Around the structural transition temperature, \( T_{\text{str}} \approx 235 \) K, it is clearly evident in Figure 7.15 that when the symmetry changes from orthorhombic to hexagonal, there is a large volume change (\( \Delta V = \frac{1}{2}V_{\text{orth}} - V_{\text{hex}} = 2.65 \ \text{Å}^3 \) so approximately \( \Delta V/V = 3.45\% \)). By comparison, Kanomata *et al.* [9] estimated the difference in the unit cell volume at \( T_{\text{str}} \Delta V \approx 3 \ \text{Å}^3 \) for the MnCoGe alloy. For first order magnetic phase transitions it is assumed that the total field-induced magnetic entropy change \( \Delta S_{\text{tot}} \) can be expressed as the sum of the conventional second-order magnetic entropy change \( \Delta S_M \) and the entropy differences of the two different crystallographic polymorphs \( \Delta S_{\text{st}} \), i.e. \( \Delta S_{\text{tot}} = \Delta S_M + \Delta S_{\text{st}} \). It was reported that the structural entropies are proportional to the volume differences of the phases involved in the transition [35]. Such a difference in the volume change around \( T_{\text{str}} \) for Mn₀.⁹₄Ti₀.⁰₆CoGe will lead to a significant structural entropy change then resulting in the total magnetic entropy change.
Figure 7.15 Volume and lattice parameters as a function of temperature. Open symbols denote the orthorhombic phase, closed symbols denote the hexagonal phase and half-filled symbols denote the corresponding phases in the mixed phase region.
Moreover, around $T_{str}$ the closest distance between Mn-Mn is determined to be 2.985 Å in the 
TiNiSi-type unit-cell while it changes to 2.651 Å in the Ni$_2$In-type unit-cell. The bond lengths 
were calculated using the BLOKJE program [36]. According to Goodenough’s theory which 
explains the localized character of the magnetic moment in alloys, in the Mn$_{0.94}$Ti$_{0.06}$CoGe 
compound, the moment is carried by the Mn and Co atoms [37]. At 5 K the calculated 
saturation moments $\mu_{\text{Mn}}$ and $\mu_{\text{Co}}$ are 2.86 and 1.63 $\mu_B$ respectively with $\mu_{\text{Mn}}=2.76$ and 
$\mu_{\text{Co}}=1.68 \mu_B$ at 200 K. At 245 K we have two phases co-existing and too many parameters 
causing the refinement to become unstable so we have to make assumption. If we assume that 
the magnetic moments for Mn and Co atoms for the Pnma phase do not change between 200 
K and 245 K, then the derived values of $\mu_{\text{Mn}}$ and $\mu_{\text{Co}}$ for P6$_3$/mmc at 245 K are 1.0 and 1.3 
$\mu_B$, respectively.

At 200 K in the TiNiSi-type unit-cell, the closest distance between Mn-Mn is 2.984 Å while 
at 345 K in the Ni$_2$In-type unit-cell the closest distance between Mn-Mn changes to 2.658 Å. 
In this work, the quality of the obtained neutron data was such that the calculated magnetic 
moment for the hexagonal phase was unreliable. If we assume that the magnetic moments for 
Mn and Co atoms for the Pnma phase do not change between 200 K and 245 K, the derived 
values of $\mu_{\text{Mn}}$ and $\mu_{\text{Co}}$ for P6$_3$/mmc at 245 K are 1.0 and 1.3 $\mu_B$, respectively. The reduction 
of the saturation moment is expected in the hexagonal phase compared with the orthorhombic 
phase [38]. Fig. 7.16 (a) shows the isothermal magnetization curves measured in the vicinity 
of $T_{str}$ and $T_C$ for the Mn$_{0.94}$Ti$_{0.06}$CoGe compound in increasing field up to 8T. The figure 
clearly displays two transitions as marked by arrows and a significant hysteresis in the 
vicinity of $T_{str}$. Also, it can be clearly seen that there is a gradual drop in magnetization 
around $T_{str}$ with temperature. This large change in magnetization in the vicinity of $T_{str}$ implies 
that the magnetic state also significantly changes when the structure changes, which is
Figure 7.16 (a) Field dependences of magnetization of the Mn$_{0.94}$Ti$_{0.06}$CoGe compound measured in the vicinity of $T_{\text{str}}$ and $T_C$ with increasing field up to 8T. (b) Dependence of the magnetic entropy change at the structural transition temperature $T_{\text{str}}$ and magnetic phase transition temperature $T_C$ on the parameter $(\mu_0 H/T_C)^{2/3}$. The solid line represents a linear fit to the data.

expected to contribute to the large magnetic entropy change near this transition. It is clear that the structural transition at $T_{\text{str}} \sim 235$ K, $T_{\text{str}}$ accompanied with the modification of magnetic properties indicates the existence of strong magneto-structural coupling, similar to what was observed by Samanta et. al.[39]. It is clearly evident in Figure 7.16 (b), that the change of the peak of the magnetic entropy change is steep at $T_{\text{str}}$, whilst that at $T_C$ is gradual, meaning that a prominent peak in $\Delta S_M$ would be expected in the vicinity of $T_{\text{str}}$. The transition at $T_{\text{str}}$ is 1$^{\text{st}}$ order whilst that at $T_C$ is 2$^{\text{nd}}$ order and the entropy changes around $T_{\text{str}}$ includes both magnetic and structural contribution while the $\Delta S_M$ around $T_C$ only includes the magnetic contribution. Also, the difference of $-\Delta S_M$ at $T_{\text{str}}$ and $T_C$ can be understood in the terms of the difference in the order of phase transitions.
So, the observed giant MCE around $T_{sl}$ (approximately 18 J/kg K for $\Delta B = 8$ T) in the Mn$_{0.94}$Ti$_{0.06}$CoGe compound can be attributed to the combined effect of an abrupt change in magnetization as well as volume in the vicinity of the structural transition (structural entropy change).

7.4. Conclusions

A giant MCE associated around 235 K has been observed for Mn$_{0.94}$Ti$_{0.06}$CoGe alloy which has been found to be related to a first-order structural transformation. The giant MCE values are comparable with those reported for materials that exhibit a giant MCE in this temperature range. An excellent agreement of the critical exponents of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy determined using the isothermal magnetization in the vicinity of $T_C$ based on various techniques such as the Kouvel-Fisher method, the modified Arrott plot as well as the critical isotherm was obtained. Moreover, all critical exponents fulfil the Widom scaling law. The validity of the calculated critical components was confirmed by the scaling equation with the obtained magnetization, field and temperature data below and above $T_C$ collapsing into two different curves. Thus, the scaling of the magnetization data above and below $T_C$ obtained using the respective critical exponents and the consistency in the values of the critical exponents determined by different methods confirm that our calculated exponents are unambiguous and intrinsic. The determined critical exponents are close to those predicted by the mean-field theory, with long range interactions.

The lattice parameters as well as volume phase fractions for the orthorhombic and hexagonal phases of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy have been determined from neutron powder diffraction data measured in the temperature range 5 – 350 K using Rietveld refinement. The volume
phase fractions as a function of temperature were fitted using the sigmoidal Boltzmann equation and the numerical coefficients $F(T_1)$ and $F(T_2)$ representing the fitted orthorhombic and hexagonal phase fractions at $T_1 = 0$ K and $T_2 = +\infty$ were determined. A large volume change $\Delta V/V = 3.45\%$ was detected at the structural transition $T_{str} \sim 235$ K with a significant drop in magnetization being observed. Both changes in crystal structure and magnetization around $T_{str}$ are found to contribute to the larger magnetocaloric effects determined.
References


CHAPTER 8

HIGH PRESSURE SYNCHROTRON X-RAY DIFFRACTION

STUDY OF THE Mn$_{0.94}$Ti$_{0.06}$CoGe ALLOY

8.1 Introduction

Normally, chemical pressure is used to simultaneously tune separate magnetic and crystallographic transitions to coincide, to give rise to a coupled first order magnetic transition. Unlike, the chemical pressure, physical pressure does not suffer from parasitic effects originating in the substitution itself, since it retains the composition and purity of the sample. Thus hydrostatic pressure provides a clean way of probing the spin-lattice coupling and is useful in elucidating the effects of chemical pressure. Previous studies have demonstrated successfully that the pressure tuning of MCE in certain magnetocaloric materials is an effective way of improving magnetic refrigeration [1 - 2]. The major aim of this work, however, is to study the stability of the different crystallographic structures under an applied hydrostatic pressure. In this work, we intend to probe the response of the structural transition to the applied hydrostatic pressure. A thorough understanding of this response will enable us to determine the exact pressure which gives us a structural transition occurring at the same temperature as the magnetic phase transition. Hence this will be of paramount importance in the design of novel magnetic refrigerants with magnetostructural couplings.

Generally, in high pressure experiments the investigated sample sizes are normally very small since high pressure can only be generated within small anvil cells. However, a small sample volume results in a low count rate in an x-ray scattering experiment. Therefore, in this work
synchrotron radiation has been essential in obtaining high resolution powder diffraction data using the diamond-anvil cell, which is impossible using typical laboratory diffractometers. Thus, it is has been efficient to perform this high pressure x-ray diffraction experiment at the Australian Synchrotron light source where the incoming photon flux is orders of magnitude higher than that of a typical laboratory diffractometer.

![Diagram](image)

**Figure 8.1** Experimental set-up of the high pressure x-ray powder diffraction experiment.

### 8.2 Experimental details

High-pressure X-ray diffraction was performed at the Powder Diffraction beamline at the Australian Synchrotron using a gasketed diamond anvil cell (DAC). The experimental set-up for a high-pressure X-ray powder diffraction experiment is represented in Figure 8.1. The DAC utilised in this work was based on developments by Merrill and Bassett in 1974 [3]. A photograph of the Merrill-Bassett diamond-anvil cell is shown in Figure 8.2. The DAC is small in size (~ 5 cm in diameter) and operates on a simple principle. A metallic gasket, with a hole in the middle, is compressed between the two small flat faces of the diamond anvils. When a force (generated by tightening the screws shown in Figure 8.2) is applied over this small area, high pressures are generated within the gasket hole, which is filled with a 4:1 methanol-ethanol mixture acting as a pressure transmitting medium. The limit of the pressure one can produce depends on many factors such as the strength and shape of the diamonds, the
type of gasket used and the ability of the cell to withstand the applied stress. The Merrill-Bassett diamond anvil cell is small enough to fit on a standard goniometer head, and it can be used on a normal diffractometer.

Figure 8.2 Merrill-Basset Diamond Anvil Cell.

8.2.1 Diamond Anvil Cell

A schematic diagram of the diamond anvil cell is shown in Figure 8.3. The DAC consists of four (4) main components:

1. **The force generating device**

   The Merrill-Bassett diamond anvil cell has a casing with the screws. Tightening of these screws moves the casings and the diamonds closer together and builds pressure.

2. **The two opposing diamonds in between which the pressure is created**

   The diamonds used are high quality flawless diamonds whose tips are cut and polished. They are placed perfectly parallel to each other in order to produce uniform pressure.
The gasket which is made of a thin tungsten foil (~0.2 mm thickness at ambient pressure) separates the diamonds. A photograph of a gasket similar to the one used in this experiment is shown in Figure 8.4. The main role of the gasket is to contain the sample,
ruby pieces (acting as pressure calibrants) and the pressure transmitting medium in the drilled hole.

4. **Pressure transmitting medium**

A 4:1 methanol-ethanol mixture was loaded additionally into the cavity to act as pressure transmitting medium. It should be noted in Figure 8.3 that the sample and ruby piece are completely immersed in the pressure transmitting medium.

8.2.2 Sample preparation and Loading

For the sample preparation, three elements are needed which are, the pressure transmitting medium, the pressure calibrant (small ruby chips) and the material of interest which in this case, is the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy. The samples used in these high pressure measurements are very small in size usually less than 1 µm in diameter. The tiny sample is initially loaded into the gasket hole along with two small chips of ruby. Great care must be taken in order to avoid flushing out either the sample or the ruby chips during the subsequent flooding of the sample chamber with the pressure transmitting medium. Also, it is imperative to ensure that the gasket does not impinge on the sample or the ruby pieces so as to avoid additional stresses being applied either to the sample or ruby pieces upon gasket extrusion, which would result in sample destruction or “pinching” of ruby chips which introduces uncertainty in the pressure calibration.

8.2.3 Pressure Determination

The ruby fluorescence method is the most commonly used method for the determination of pressure in DACs. This method uses the known pressure dependence of the wavelengths of the $R_1$ and $R_2$ lines of ruby. Small ruby chips are enclosed in the sample chamber during the
sample preparation as described above. These ruby chips are excited by an Ar+ laser. One of the ruby chips in the sample chamber is focused under a microscope and the laser light is injected. The signal coming from the ruby is sent through a fibre optic cable to a grating spectrometer where it is spectrally analyzed and amplified by a photo multiplier. The signal is then recorded by a computer. At ambient pressure, the R₁ and R₂ lines of ruby are found at 694.25 and 692.70 nm respectively. With increasing pressure they are shifted to higher wavelengths. Since the intensity of the R₁ line is much higher than that of the R₂ line the R₁ line is used for pressure determination. This is done by determination of its wavelength and calculation of the pressure using equation 8.1 below:

\[
p = \left(\left(\frac{\Delta \lambda}{\lambda_0} + 1\right)^5 - 1\right)
\]

where \(\Delta \lambda = \lambda - \lambda_0\) is the difference between the determined wave length \(\lambda\) under pressure and the wave length \(\lambda_0\) at ambient pressure. Mao et al. were able to derive the pressure dependence (Equation 8.1) of the wave length of the R₁ line of ruby by performing x-ray diffraction on Ag, Co, Mo, and Pd and measuring the volumes of the unit cells of these metals and by using their compressibility[4–6].

### 8.3 Results and Discussion

The data presented herein was collected at the high resolution Powder Diffraction beamline (PD) at the Australian Synchrotron. Data is collected on an image plate detector (Mar345) and is processed according to the procedure outlined in the ensuing section.
8.3.1 Data Reduction of Image Plate Data Using FIT2D

The powder diffraction data was recorded using a 2-dimensional (2D) Mar345 detector. 2D powder diffraction image data were generated during the experiment and are shown in Figure 8.5.

![Image of powder diffraction data recorded using a 2D Mar345 detector.]

**Figure 8.5** Powder diffraction image data recorded using a 2D Mar345 detector.
Figure 8.5 Powder diffraction image data recorded using a 2D Mar345 detector.
In order to perform Rietveld refinements of the powder diffraction data using the Fullprof software to obtain the lattice parameters, the 2D powder diffraction data must be converted to a series of one-dimensional (1D) powder patterns. For this process, the Fit2D software program was used [7]. This program allowed for the detector calibration and integration of powder diffraction data from 2D to 1D 2θ scans. The data reduction is performed by first loading the image plate data using Fit2D. The z-scaling is set to weak peaks in order to make the image plate data more visible in order to see enough details. Finally, the masking of the beam mask and other intense single-crystal reflections from the diamond and ruby. A schematic illustrating the stages of data reduction is shown in Figure 8.6. The raw image collected on the Mar345 detector is shown in (a). The concentric rings correspond to the diffracted intensities from the sample; the several dark spots in the image are intense diamond reflections from the DAC. This can be masked to avoid contamination of the sample diffraction pattern. The masking process is shown in Figure 8.6 (b) with the red regions being the masked regions. Figure 8.6 (c) shows the integrated 1D data. The large background

**Figure 8.5** Powder diffraction image data recorded using a 2D Mar345 detector.
common to such data collections is due to the inelastic Compton scattering from the diamonds and is subtracted prior to data refinement.

Figure 8.6 A schematic illustrating stages of data reduction.
8.3.2 Effect of Pressure on Structural Properties

**Figure 8.7** Evolution of powder diffraction patterns for the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy at selected pressures.

Figure 8.7 shows a series of diffraction patterns of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy collected at different pressures. At ambient pressure all peaks can be indexed according to the hexagonal Ni$_2$In-type structure (space group P63/mmc). As can be seen in Figure 8.7, with increasing pressure, the peaks shift to the right due to contraction of the lattice. On closer inspection, the peaks appear to start broadening with an increase in pressure. There are no indications of a phase transition and the signatures of the orthorhombic phase persist in the entire range of our measurements.
Figure 8.8 Evolution of structural parameters for the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy with pressure.

The dashed line through the data points is a guide to the eye.

The application of pressure modifies the structural parameters and Figure 8.8 shows the evolution of structural parameters for the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy with pressure. It is clear from Figure 8.8 that the lattice parameters $a$ and $c$, monotonically decrease in the entire range
of our measurements. The fact that both lattice parameters \( a \) and \( c \) exhibit a similar monotonic pressure dependence, indicates the absence of substantial anisotropy in the compressibility along \( a \) and \( c \). The pressure dependence of the volume does not include any discontinuity, confirming that there is no phase transition occurring in the entire range of our measurements. In an effort to probe further the anisotropy, we investigated the pressure dependence of the \( c/a \) ratio, shown in Figure 8.9. This figure shows that there is a decrease of \( c/a \) ratio with pressure in the entire range of our measurements. The absence of a sudden jump in the \( c/a \) ratio with pressure confirms that there is no structural phase transition occurring in the entire range of our measurements.

![Figure 8.9](image-url)

**Figure 8.9** \( c/a \) ratio versus pressure for the \( \text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe} \) alloy. The dashed line through the data points is a guide to the eye.
Unit cell dimensions were derived by Le Bail fitting to the observed powder diffraction patterns by means of the general structure analysis system using FULLPROF [8]. The experimental pressure – volume data for the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy were fitted to a Murnaghan equation of state (EOS) [5]:

\[
P = \frac{B_0}{B'(V_0/V)^{B'} - 1}
\]  

(8.1)

where $V_0$, $B_0$, and $B'$ are the volume, bulk modulus at its first derivative at ambient pressure. The experimental pressure – volume data was also fitted using a third order Birch – Murnaghan EOS shown below:

\[
P = 1.5B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}] \times \{1 + 0.75(B' - 4)[(V/V_0)^{-2/3} - 1]\}
\]  

(8.2)

The bulk modulus ($B_0$) and its pressure derivative ($B'$) were extracted by fitting the experimentally observed pressure versus volume data to:

i. the Murnaghan EOS.

ii. the third order Birch – Murnaghan EOS (using a constrained value of $B'$).

iii. the third order Birch – Murnaghan EOS (using an unconstrained value of $B'$).

In all three cases, the fitting was done using the computer program EOS - FIT V5.2 [9]. As an input to the program, initial values of $V_0 = 68.14$ Å$^3$ as well $B_0 = 140$ GPa were used. It should be noted that the extraction of the EOS parameters using the Murnaghan EOS was for
comparative purposes only. However, the use of the third order Birch – Murnaghan EOS for the determination of the EOS parameters for the Mn_{0.94}Ti_{0.06}CoGe alloy is justified since this equation provides an excellent description of the compression of most solids [10 – 13]. The pressure – volume data has been analysed first by assuming and fixing B’ to be 4, and secondly by allowing B’ to be 4 to vary during the fitting process. The value of B’ = 4 has been experimentally shown to reproduce compression data for a wide variety of substances [14]. The refined values of B₀ and B’ are shown in Table 8.1. In this case, the use of the unconstrained value of B’ determined the bulk modulus to be B₀ = 222.64 ± 36.9. The uncertainty in the determined B₀ is too large, therefore we consider the fit with B’ fixed at 4, to yield the best value for the bulk modulus which is determined to be B₀ = 231.72 ± 7.79. It also worth noting that the EOS parameters determined using the Murnaghan EOS are a close match to those determined using the third order Birch – Murnaghan EOS (using a constrained value of B’).

Table 8.1 Equation of state (EOS) parameters for the Mn_{0.94}Ti_{0.06}CoGe alloy.

<table>
<thead>
<tr>
<th>EOS</th>
<th>B₀ (G Pa)</th>
<th>dB/dP (B’)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Murnaghan</td>
<td>232 ± 7.79</td>
<td>4 (assumed)</td>
<td>B’ constrained</td>
</tr>
<tr>
<td>3rd order Birch - Murnaghan</td>
<td>231.72 ± 7.79</td>
<td>4 (assumed)</td>
<td>B’ constrained</td>
</tr>
<tr>
<td>3rd order Birch - Murnaghan</td>
<td>222.64 ± 36.9</td>
<td>5.79 ± 7.066</td>
<td>B’ unconstrained</td>
</tr>
</tbody>
</table>
Figure 8.10 Relative volume of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy as a function of pressure. The solid line represents the Birch-Murnaghan equation of state using the parameters obtained in this study.

The variation of the relative volume with pressure data shown in Figure 8.10 was fitted using the third order Birch–Murnaghan EOS (using a constrained value of B'). The result of the fit is shown as a solid line in Figure 8.10 demonstrating the excellent agreement between the fitted curve and the experimental data.

The application of pressure modifies the structural parameters such as the Mn-Mn interatomic distance of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy. The bond lengths were calculated using the BLOKJE
program [15]. Figure 8.11 shows that with increasing pressure, the Mn-Mn interatomic distance monotonically decreases up to 10.4 GPa. At ambient pressure the closest distance between Mn-Mn is determined to be 2.644 Å in the TiNiSi-type unit-cell while it changes to 2.552 Å at a pressure of 10.4 GPa. It was reported in MnCoGe related compounds that, for the orthorhombic phase, the larger distance between the dominant Mn–Mn magnetic coupling will lead to the narrower 3d bandwidths and a large exchange splitting between the majority and minority bands then result in the larger moment [16]. On the contrary, the hexagonal phase with shorter Mn-Mn distances has the smaller magnetic moment due to the stronger Mn–Mn coupling and the resulting wider 3d band. In this study, the reduction in the Mn-Mn distance due to the application of pressure will be expected to lead to a further decrease of magnetic moment as detected for Mn$_{1-x}$Cr$_x$CoGe compounds in ref [17].

![Graph showing the pressure dependence of the Mn–Mn interatomic distances in the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy. The line serves as a guide to the eye.](image)

**Figure 8.11** Pressure dependence of the Mn – Mn interatomic distances in the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy. The line serves as a guide to the eye.
8.4 Conclusions

High pressure x-ray diffraction studies were performed on the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy up to a pressure of 10.4 GPa. The hexagonal Ni$_2$In-type structure (space group P63/mmc) structure is stable in the investigated pressure regime and no phase transition is found to occur. Unit cell parameters were determined and the calculated volumes were found to be well reproduced by the third order Birch–Murnaghan equation of state. The bulk modulus $B_0 = 231.72 \pm 7.79$ GPa has been determined from the observed pressure–volume data. The determination of the EOS parameters and the investigation of the phase stability with pressure of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy are useful guidelines that can be used together with theoretical calculations to predict crystallographic phase transitions.
References


CHAPTER 9

CONCLUSIONS AND OUTLOOK

In this thesis, the magnetocaloric materials namely, the $\beta$-Co(OH)$_2$ nanosheets, La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds, La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds and the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy have been systematically investigated with their structural, magnetic and magnetocaloric properties being studied in detail. The aim of this doctoral work was to contribute towards a better understanding of the fundamental material characteristics, with an emphasis on understanding the relationship between a defined structure, the crystallographic phase and magnetic phase structure, and alteration in the magnetocaloric properties. This work has important contributions towards an understanding of the role of atomic substitution in tuning the magnetocaloric properties. The main results of the thesis are summarized as follows:

- $\beta$-Co(OH)$_2$ nanosheets have been successfully prepared by a microwave assisted hydrothermal and conventional chemical reaction method. The material displays a very high magnetic moment of $M_S \sim 110$ emu / g at 3 K, which causes a highly reversible giant MCE of 17 J/kg K at 11 K in a magnetic field change of 5 T thereby indicating the suitability of this material for use in magnetic refrigeration. The study of the magnetism of the $\beta$-Co(OH)$_2$ nanosheets, revealed that the spin-glass-like surface spins may have a significant effect on the MCE of this material system and the sign of the field-induced first order magnetic phase transition is possibly a result
of a competition or coupling of the surface spin, impure phase and the $\beta$-Co(OH)$_2$ bulk magnetic behaviour. Since this material system synthesizes in the nanostructured form, it would be beneficial to carry out an indepth study to elucidate the grain – grain boundary characteristics of this material system in order to gain an insight into the nanomagnetism of this material.

- We have investigated the effect of boron doping on the magnetic and magnetocaloric properties of La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds (with boron doping level, $x = 0$, 0.03, 0.06, 0.2 and 0.3). This study brings new light on the role of boron (B) in tuning the magnetocaloric properties of the La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ compound. We achieved a significant enhancement of the Curie temperature and the refrigerant capacity in La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ due to boron doping. We also demonstrated how boron doping at high levels tunes the magnetic transition from 1$^{st}$ to 2$^{nd}$ order. These results thus support the role of low level boron doping in the enhancement of the magnetocaloric effect in La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ alloys, thus making this material system a promising candidate for magnetic refrigeration near room temperature.

- Results from our study reveal that large $\Delta S_M$ and RC values and a small hysteresis loss can be simultaneously achieved in the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds and the introduction of interstitial boron atoms into the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$ material system could be a promising method of depressing the hysteresis loss whilst maintaining the large MCE. The determination of $\Delta S_M$ for La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_x$ compounds using the Clausius-Clapeyron equation yields reasonable estimates of the MCE in these compounds. Our results demonstrate that the hysteresis behaviour of a material is critical in evaluating its potential as a functional magnetic refrigerant. Also, high
resolution neutron diffraction measurements performed on the La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_{1.6}$B$_{x}$ compounds revealed that, in the vicinity of the FM – PM transition there is a co-existence of a large volume change as well as a spontaneous magnetostriction jump, which gives rise to a first order magnetic transition.

❖ We report the results of the role of titanium (Ti) in tuning the magnetocaloric properties of the MnCoGe compound. We have investigated the substitution of Ti into Mn$_{1-x}$Ti$_{x}$CoGe compounds with $x = 0.02$, 0.04 and 0.06 and we found that the, $x = 0.06$ substitution most successfully shifted the structural change and magnetic phase transition into our interested temperature range leading to the attainment of a giant magnetocaloric effect. A comprehensive neutron diffraction investigation of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy was performed in order to probe further the magnetostructural coupling and fully understand the role of structural and magnetic transformation in enhancing the magnetic entropy change. A large volume change $\Delta V/V = 3.45\%$ was detected at the structural transition $T_{\text{str}} \approx 235$ K with a significant drop in magnetization being observed. Both changes in crystal structure and magnetization around $T_{\text{str}}$ were found to contribute to the larger magnetocaloric effect determined. A giant MCE around 235 K has been observed for the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy which has been found to be related to a first-order structural transformation. An excellent agreement of the critical exponents of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy determined using the isothermal magnetization in the vicinity of $T_C$ based on various techniques such as the Kouvel-Fisher method, the modified Arrott plot as well as the critical isotherm was obtained. Moreover, all critical exponents fulfilled the Widom scaling law. The determined critical exponents are close to those predicted by the mean-field theory, with long range interactions.
High pressure x-ray diffraction studies up to 10.4 GPa were performed on the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy using synchrotron radiation and a diamond anvil cell. No structural phase transitions occurred in the entire range of our measurements. Unit cell parameters were determined up to 10.4 GPa and the calculated unit cell volumes were found to be well represented by a third order Birch-Murnaghan equation of state. The bulk modulus determined from the pressure – volume data was found to be, $B_0 = 231.72 \pm 7.79$ GPa. This study, employing high resolution synchrotron x-rays has helped clarify the behaviour of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy under high pressure.

The work carried in this doctoral study has provided an insight on the effect of atomic substitutions in tuning the magnetocaloric effect as well as the magnetic phase transitions of various magnetocaloric materials. It is my hope that this work may act as a foundation for further research in the development of new materials that can fulfil specific requirements of cooling devices. Future work may include:

- It would be very interesting to tune the surface anisotropy of the $\beta$ - Co(OH)$_2$ nanosheets by coating with various antiferromagnetic material. An in depth study of the effect of tuning the surface anisotropy of the $\beta$ - Co(OH)$_2$ nanosheets on the magnetocaloric properties will provide an insight into an alternative way of tuning the MCE properties.

- There is a need to perform pressure dependent magnetisation measurements of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy in the diamond anvil cell up to a pressure of 15 GPa. Such an experiment will help to explain if at all, its possible to physically tune (by the
application of pressure) the structural and magnetic transitions to enable them to coincide, giving rise to a giant magnetocaloric effect. It is also desirable to investigate the influence of pressure on the critical field $B_C$, hysteresis, $\Delta S_M$ and refrigerant cooling capacity (RCP) for the above mentioned sample as well as other material systems.

- It will be very interesting to perform resistivity measurements as a function of pressure on the $\text{Mn}_{0.04}\text{Ti}_{0.06}\text{CoGe}$ alloy (as well as other material systems) to track magnetic or structural transitions to much high pressures (e.g., routinely to 30 GPa).
Publication List

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2. **P. Shamba**, R. Zeng, J. L. Wang, S. J. Campbell & S. X. Dou “Enhancement of the refrigerant capacity in low level boron doped La$_{0.8}$Gd$_{0.2}$Fe$_{11.4}$Si$_{1.6}$” *(Journal of Magnetism and Magnetic Materials)* 331, 102 (2013)


6. J. C. Debnath, **P. Shamba**, A. M. Strydom, J. L. Wang, S. X. Dou, “Investigation of critical behaviour in Mn$_{0.94}$Nb$_{0.06}$CoGe alloy by using the field dependence of magnetic entropy change”, *(Journal of Applied Physics)* 113, 093902 (2013)

7. M. F. Md Din, J. L. Wang, R. Zeng, **P. Shamba**, J. C. Debnath & S. X. Dou. “Effects of Cu substitution on structural and magnetic properties of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ compounds” *(Intermetallics)* 36, 1 (2013) DOI: http://dx.doi.org/10.1016/j.intermet.2012.12.013


16. **P. Shamba**, R. Zeng, S. Aminorroaya-Yamini, J. L. Wang, J.C Debnath and S. X. Dou, “Modification of hydrogenation and magnetocaloric properties of the La$_{0.8}$Ce$_{0.2}$FeSi compound induced by interstitial boron” *(In preparation)*