Magnetic phase transitions and novel materials for magnetocaloric effect

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Magnetic Phase Transitions and Novel Materials for Magnetocaloric Effect

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

by

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DECLARATION

I, Muhamad Faiz Md Din, 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.

Muhamad Faiz Md Din
October, 2014
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Abstract

The magnetic and structural properties of some selected magnetocaloric materials such as La(Fe, Si)$_{13}$ series compounds, RMn$_2$X$_2$ series (R=rare earth and X=Si or Ge) compounds and typical MM’X series (M, M’= transition metal, X = Si, Ge, Sn) have been systematically investigated in this thesis with total 7 chapters being included. After a general introduction in Chapter 1, the description of theoretical aspects of the research and experimental techniques are given in Chapters 2 and 3, respectively.

In Chapter 4, the investigation on structure and magnetic properties of the La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ and La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cr$_x$Si$_{1.6}$ compounds is presented. Cu substitution for Fe in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ ($x = 0$, 0.06, 0.12, 0.23, 0.34) leads to a reduction in hysteresis loss, a decrease in magnetic entropy change but an increase in Curie temperature ($T_C$). The influences of annealing processes at different temperatures on $T_C$, magnetic hysteresis, and the magnetocaloric effect (MCE) of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ are also investigated in detail. It has been found that a short-time and high temperature annealing process has benefits for the formation of the NaZn$_{13}$ types as phase compared to a long-time and low temperature annealing process.

Furthermore, the effects of substitution Fe by Cr in NaZn$_{13}$-type La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cr$_x$Si$_{1.6}$ ($x=0$, 0.06, 0.12, 0.26, and 0.34) compounds have been investigated by high intensity of X-ray and neutron diffraction, scanning electron microscopy, specific heat, and magnetization measurement. It has been found that a substitution of Cr for Fe in this compounds leads to a decrease in the lattice parameter $a$ at room temperature and a variation on $T_C$. While the first order nature of magnetic phase transition around $T_C$ does not change with increasing Cr.
content up to \(x=0.34\). High intensity X-ray and neutron diffraction study at variable temperatures for highest Cr concentration \(x=0.34\) confirmed the presence of strong magneto-volume effect around \(T_C\) and indicated the direct evidence of coexistence of two magnetic phases across magnetic transition as characteristic of first order nature. The values of \(-\Delta S_M\) around \(T_C\) found to decrease from 17 J kg\(^{-1}\)K\(^{-1}\) for \(x=0\) to 12 J kg\(^{-1}\)K\(^{-1}\) for \(x=0.06\) and then increases with further increasing Cr content up to 17.5 J kg\(^{-1}\)K\(^{-1}\) for \(x=0.34\) under a change of 0–5 T magnetic field. The relative cooling power (RCP) also indicated the similar behaviour which is decrease from 390 J kg\(^{-1}\) for \(x=0\) to 365 J kg\(^{-1}\) for \(x=0.06\) at the beginning and then increases up to 400 J kg\(^{-1}\) for \(x=0.34\) at the same field applied.

Chapter 5 describes the investigation on magnetic behaviour and magnetocaloric effects of RMn\(_2\)X\(_2\)-based materials (R=rare earth and X=Si or Ge). The RMn\(_2\)X\(_2\) series has attracted significant interest in recent years due primarily to their natural layered structure in which R and Mn atoms lie in alternate layers, separated by layers of X atoms. The strong dependence of the Mn–Mn magnetic exchange interaction on the intralayer near neighbour distance, and the interplay between the magnetism of the Mn and R layers lead to a fascinating arrangement of magnetic phases for these compounds. Firstly, in order to clarify the effect of substitution Mn with other transition metal (T) in NdMn\(_2\)Si\(_2\) compound, structural and magnetic properties of the intermetallic compounds NdMn\(_{2-x}\)Ti\(_x\)Si\(_2\) (T=Ti, Cr, Cu and V) have been studied.

The Curie temperature and N’eel temperature of NdMn\(_2\)Si\(_2\) decrease from \(T_C = 36\) K and \(T_N = 380\) K to \(T_C = 14\) K and \(T_N = 360\) K, respectively, on substitution of Ti (\(x = 0.3\)) for Mn. The magnetocaloric effect around \(T_C\) has been investigated in detail. Under a change of magnetic field of 0–5 T, the maximum value of the magnetic entropy change is 27 J kg\(^{-1}\)K\(^{-1}\)
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In substitution Mn with Cr in NdMn\(_{2-x}\)Cr\(_x\)Si\(_2\) compound, a giant magnetocaloric effect has been observed around Curie temperature, \( T_C \approx 42 \) K, in NdMn\(_{1.7}\)Cr\(_{0.3}\)Si\(_2\) with no discernible thermal and magnetic hysteresis losses. Detailed study shown that below 400 K, three magnetic phase transitions take place around 380 K, 320 K and 42 K. High resolution synchrotron and neutron powder diffraction (10–400 K) analysis confirmed the magnetic phases transitions as follows: \( T_N^{\text{intra}} \approx 380 \) K denotes the transition from paramagnetism to intralayer antiferromagnetism (AFl), \( T_N^{\text{inter}} \approx 320 \) K represents the transition from the AFl structure to the canted antiferromagnetic spin structure (AFmc), while \( T_C \approx 42 \) K denotes the first order magnetic transition from AFmc to canted ferromagnetism (Fmc+F(Nd)) due to ordering of the Mn and Nd sub-lattices. The maximum values of the magnetic entropy change and the adiabatic temperature change, around \( T_C \) for a field change of 5 T are evaluated to be \(-\Delta S_M \approx 15.9 \) J kg\(^{-1}\)K\(^{-1}\) and \( \Delta T_{ad} \approx 5 \) K, respectively. The first order magnetic transition associated with the low levels of hysteresis losses (thermal \(< ~0.8 \) K; magnetic field \(< ~0.1 \) T) in NdMn\(_{1.7}\)Cr\(_{0.3}\)Si\(_2\) offers potential as a candidate for magnetic refrigerator applications in the temperature region below 45 K.

Furthermore, the structural and magnetic properties of NdMn\(_{2-x}\)Cu\(_x\)Si\(_2\) compounds (x=0–1.0) also have been investigated. Substitution of Cu for Mn leads to an increase in the lattice parameter \( a \) but a decrease in \( c \) at room temperature. Two magnetic phase transitions have
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Secondly, we carry out investigations of the Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ magnetic phase diagram as functions of both composition and Mn–Mn spacing using X-ray and neutron diffraction, magnetization and differential scanning calorimetry measurements. Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ exhibits an extended region of re-entrant ferromagnetism around $x=0.5$ with re-entrant ferromagnetism at $T_C^{Pr} \sim 50$ K for Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$. The entropy values $-\Delta S_M$ around the ferromagnetic transition temperatures $T_C^{inter}$ from the layered antiferromagnetic AFl structure to the canted ferromagnetic structure Fmc (typically $T_C^{inter} \sim 330$–340 K) have been derived for Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ with $x=0.0$, 0.2, and 0.5 for $\Delta B=0$–5 T. The changes in magnetic states due to Y substitution for Pr are also discussed in terms of chemical pressure, external pressure, and electronic effects.
Thirdly, the structural and magnetic properties of CeMn$_2$Ge$_{2-x}$Si$_x$ compounds with Si concentrations in the range $x = 0.0$–2.0 have been investigated. Substitution of Ge with Si leads to a monotonic decrease of both $a$ and $c$ along with concomitant contraction of the unit cell volume and significant modifications to the magnetic states - a crossover from ferromagnetism at room temperature for Ge-rich compounds to antiferromagnetism for Si-rich compounds. The magnetic phase diagram has been constructed over the full range of CeMn$_2$Ge$_{2-x}$Si$_x$ compositions and co-existence of ferromagnetism and antiferromagnetism has been observed in both CeMn$_2$Ge$_{1.0}$Si$_{1.0}$ and CeMn$_2$Ge$_{0.8}$Si$_{1.2}$ compounds with novel insight provided by high resolution X-ray synchrotron radiation studies. This study has enabled the large variety of magnetic structures and magnetic phase transitions of CeMn$_2$Ge$_{2-x}$Si$_x$ compounds and their related magnetic properties to be determined by controlling chemical concentration.

Finally in Chapter 6, the MnCoGe-based materials, as a typical MM’X (M, M’ = transition metal, X = Si, Ge, Sn) compound which undergoes a second-order phase transition as well as a crystallographic phase transition from the low temperature orthorhombic TiNiSi-type to the high temperature hexagonal Ni$_2$In-type structure have been studied. An investigation on substituting Ge by other metalloids in MnCoGe$_{1-x}$T$_x$ compounds ($T = $ Al and Si) has been implemented in this thesis and it was found that an appropriate $T$ concentration successfully shifted the structural change and magnetic phase transition into the temperature range of interest, leading to the attainment of a high contribution to the giant magnetocaloric effect (GMCE). MnCoGe$_{1-x}$T$_x$ provides the best example for control of the temperature window in order to investigate the effects of the structural and magnetic transition on the total entropy change, providing an excellent vehicle for investigation of the field-induced martensitic transformation in GMCE materials. Thus, in an effort to understand the nature of the
magnetic transition in MnTiGe$_{0.97}$Al$_{0.03}$, critical exponent analysis in the vicinity of the ferromagnetic (FM)–paramagnetic (PM) region has been performed. The outcomes revealed that this material undergoes a structural transition at ~ 420 K as well as a second-order ferromagnetic–paramagnetic transition at ~ 350 K. Finally, a temperature dependent neutron diffraction experiment has been performed and confirmed that there is a coupling of the structural transition and the magnetic phase transition.

Structural, magnetic and magnetocaloric properties of the Mn$_{1-x}$Ti$_x$CoGe also have been investigated using X-ray diffraction, DC magnetization and neutron diffraction measurements in order to define the effect of substitution Mn with Ti in MnCoGe compound. Substitution of Ti for Mn in the parent MnCoGe compound leads to a significant reduction in both structure change temperature, $T_{str}$ (from ~ 645 K for MnCoGe to ~ 235 K for Mn$_{0.94}$Ti$_{0.06}$CoGe and ~ 178 K for Mn$_{0.9}$Ti$_{0.1}$CoGe) and Curie temperature, $T_C$ (from ~ 345 K for MnCoGe to ~ 270 K for Mn$_{0.94}$Ti$_{0.06}$CoGe and ~ 280 K for Mn$_{0.9}$Ti$_{0.1}$CoGe). Moreover, all the critical exponents for Mn$_{0.94}$Ti$_{0.06}$CoGe and Mn$_{0.9}$Ti$_{0.1}$CoGe fulfil the Widom scaling law. The validity of the calculated critical exponents was confirmed by the scaling equation, with the magnetization, field, and temperature data obtained below and above $T_C$ collapsing onto two different curves. Thus, the scaling of the magnetization data above and below $T_C$ was obtained using the respective critical exponents, and the consistency of the values of the critical exponents determined by different methods confirm that the calculated exponents are unambiguous and intrinsic. The critical exponents determined are close to those predicted by the mean-field theory for long range interactions.
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Chapter 1

INTRODUCTION

1.1 General Introduction

Modern society relies on cooling technology for food safety, comfort, and medical applications. For example, in the US about 34% of the electricity is consumed by cooling appliances [1], and 15% of total worldwide energy consumption involves the use of refrigeration (air conditioning, refrigeration, freezing, chilling, etc.) [2]. Nowadays, most cooling devices are based on vapour-compression technology, which was originally developed in the 19th century. As this technique uses strong greenhouse gases and the energy efficiency has reached its limit, rising international concerns about global warming due to ever increasing energy consumption call for a change. Recently, several solid-state cooling technologies, such as optical refrigeration [3], thermoelectric refrigeration [4]-[5], electric refrigeration [6]-[7], and magnetic refrigeration [8]-[9], have been considered as viable alternative techniques because they are becoming increasingly efficient and affordable. For a technique to become a fully mature alternative, however, clever engineering and more detailed studies on the fundamental physical properties are needed.

Conventional refrigerators have become omnipresent in a large number of cooling applications, but the use of chlorofluorocarbons (CFCs) and hydro chlorofluorocarbons (HCFCs) as working fluids has raised serious environmental concerns, mainly because of their contributions to destruction of the ozone layer and global warming [10, 11].
Replacement by fluid HFCs which contain no chlorine and therefore have no ozone depletion potential, is not without problems because HFCs are greenhouse gases \([12]\) with higher global warming potential than \(\text{CO}_2\). Thus, due to serious concerns for the environment, alternative technology should be a more attractive solution to the environmental problems.

By using solid magnetic materials as coolants instead of conventional gases, magnetic refrigeration avoids all harmful gases, including ozone-depleting gases, greenhouse-effect gases that contribute to global warming, and other hazardous gaseous refrigerants. A solid coolant can easily be recycled. Furthermore, it has been demonstrated that magnetic cooling is energetically more energy efficient than conventional gas-compression cooling. This is of particular interest in view of the global energy problems \([13]\). In addition, magnetic refrigerators make very little noise and may be built to be very compact. Therefore, magnetic refrigeration has attracted attention in recent years as a promising environmentally-friendly alternative to conventional gas-compression cooling.

### 1.2 The Magnetocaloric Effect

Magnetic refrigeration is based on the magnetocaloric effect (MCE), which was discovered by Warburg in 1881 \([14]\). In magnetic materials, a change in the degrees of freedom of the spins induces thermal effects. If the magnetic field is applied adiabatically, the material temperature rises, and when the field is removed, the material temperature is consequently decreased. These warming and cooling phenomena in response of an external magnetic field define the magnetocaloric effect (MCE), which can be used in refrigeration technology. The magnitude of the MCE in a magnetic material is defined by the isothermal magnetic entropy change \(\Delta S_M\) or by the adiabatic temperature change \(\Delta T_{ad}\) as the magnetic field is applied.
or removed. Both of these points are very important factors for ideal magnetic material selection to produce a high performance magnetic refrigerator.

Figure 1.1 Gadolinium alloys heats up inside the magnetic field and loses thermal energy by irradiation, so that it is cooler than when it entered the field. This is a magneto-thermodynamic phenomenon, in which a reversible change in temperature of a suitable material is caused by exposing the material to a changing magnetic field [15].

Magnetic materials can order their magnetic moments in a variety of ways, such as ferromagnetic, ferromagnetic, and antiferromagnetic orderings, depending on the characteristics of the material. The moments of a magnetic material are aligned parallel to the magnetic field, as shown in Figure 1.1, when a magnetic field is applied to a magnetic material and affects the spin ordering, leading to lower entropy of the system as disorder decreases. To compensate for the aligned spins, the atoms of the material start to vibrate in an attempt to randomize the spin and lower the entropy of the system again, which contributes to increasing the temperature of the magnetic material. The opposite behaviour occurs when the material is removed from the magnetic field, which decreases the temperature of the magnetic
material. All the moments may be aligned, and increasing the applied field will not yield a further increase in the magnetization at very low temperature and very high field. Magnetization is defined by how much the magnetic moment is aligned, and this behaviour occurs around the phase transition temperature of the material.

1.3 The Magnetic Refrigerator

The magnetic refrigerator (MR) is based on the magnetocaloric effect (MCE), which occurs due to the coupling of a magnetic sublattice with an external magnetic field. With the magnetic spin system aligned by magnetic field, the magnetic entropy changes by $\Delta S_M$ as a result of isothermal magnetization of a material. On the other hand, the sum of the lattice and electronic entropies of a solid must be changed by $\Delta S_M$ as a result of adiabatically magnetizing the material, thus resulting in an increase in the lattice vibrations and the adiabatic temperature change, $\Delta T_{ad}$. Both the isothermal entropy change $\Delta S_M$ and the adiabatic temperature change $\Delta T_{ad}$ are important parameters in quantifying the MCE and the performance of magnetocaloric materials (MCM).

In general, $\Delta S_M$ and $\Delta T_{ad}$ are obtained by using magnetization and heat capacity data in conjunction with the Maxwell equations. Although the Maxwell equations can be used to calculate MCE for first order magnetic transition (FOMT) materials due to the fact that the transition is not truly discontinuous, there can be some errors depending on the numerical integration method used. Thus, direct measurements of $\Delta T_{ad}$ are both useful and required to better understand the nature of the giant magnetocaloric effect (GMCE). Moreover, the direct measurements of $\Delta T_{ad}$ allow investigation of the dynamic performance of FOMT materials experiencing repeated magnetization/demagnetization cycles.
In the magnetic-refrigeration cycle depicted in Figure 1.2, initially randomly (or nearly randomly)-oriented magnetic moments are aligned by a magnetic field, resulting in heating of the magnetic material. This implies a reduction of the entropy of the spin system. The entropy is transferred via the spin-lattice coupling to the lattice, resulting in heating of the magnetic material. The heat is removed from the material to the ambient environment by a heat transfer fluid. In a conventional vapour refrigeration system, the gas medium is compressed, thereby increasing its pressure and temperature, which is followed by a condensation process to transfer the heat to the ambient environment. Upon the removal of the field, as shown in step 3 of Figure 1.2, the magnetic moments randomize, which leads via spin-lattice coupling to cooling of the material below the ambient temperature. Heat from the system to be cooled can then be extracted by using a heat transfer medium. In a conventional refrigeration system, a
high pressure liquid expands and absorbs heat from the space to be cooled. When the magnetic field is generated by superconducting solenoids or permanent magnets, high-energy efficiency can be achieved as entropy is transferred to and from the quantum spin system.

Simultaneous occurrence of changes in degrees of freedom of the spins, magnetovolume effects, and changes in valence may bring about a giant MCE and thus a much more efficient magnetocaloric refrigeration system. Magnetic refrigeration (MR) is potentially a high efficiency, low-cost, and greenhouse-gas-free refrigeration technology, and with the looming phase out of HCFC and hydrofluorocarbon (HFC) refrigerants, is drawing more attention as an alternative to the existing vapour compression refrigeration.

1.4 Objectives of Research

The objective of the present thesis is to explore novel magnetic materials that possess a considerable MCE for real application in magnetic refrigerators. It is the aim of this work to contribute to a better understanding of their fundamental material characteristics, with an emphasis on understanding the relationships between the defined structure, the crystallographic phase, and the magnetic phase structure. The specific objectives are:

1. Study the effects of stoichiometric modifications or atomic substitutions to tune the transition temperature, $T_C$, for phase transitions in order to produce the giant MCE.

2. Develop new MCE material compositions and fabrication conditions for the different types of magnetic phase transitions and the related magneto-structural coupling.
3. Explore the properties of these systems, by quantifying the MCE using magnetic measurements to determine the magnetic entropy change ($\Delta S_M$) and conduct magnetic thermal measurements to determine the adiabatic temperature change ($\Delta T_{ad}$).

4. Study the behaviour of the lattice structure and magnetic moment using high technology neutron and synchrotron diffraction equipment.

5. The ultimate aim of the study is to synthesize high quality magnetocaloric materials suitable for use in magnetic refrigeration and to achieve a deep understanding of how to produce novel materials for MCE.

1.5 Organization of Thesis

The present study aims to provide guidance on the optimization of novel magnetic materials for MCE in order to implement them in real applications in magnetic refrigeration. This thesis is organised as follows:

The general introduction with an explanation of the magnetocaloric effect and magnetic refrigeration related to this research study, as well as the specific objectives of the work, are outlined in Chapter 1. A literature review of the variation in the magnetocaloric effect from theoretical aspects, especially in terms of the Gibbs free energy, magnetic entropy, specific heat, chemical pressure, and critical exponent analysis, is presented in Chapter 2.

Chapter 3 is devoted the synthesis procedures for the various material systems investigated in this study and the main characterization techniques to determine the structure and physical properties of the materials. A detailed study of the the effects on the magnetic properties and
magnetocaloric effect of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ compound by partial substitution of Cu and Cr for Fe at specific concentrations is outlined in Chapter 4.

Chapter 5 details the results of an intensive research study on the effects of other metal transition elements (Cu, Cr, Ti, and V) when substituted for Mn in the NdMn$_2$Si$_2$ interlayer compound. This study proposes a new fundamental idea on the role of other metal transition elements in tuning the giant magnetocaloric effect properties of NdMn$_2$Si$_2$ compound, as this layered structure is very significantly sensitive to the Mn-Mn distance. A significant enhancement of the Curie temperature, $T_C$, and the refrigerant capacity was achieved in NdMn$_2$Si$_2$ due to the replacement of Mn with other metal transition elements. Furthermore, the effects of partially replacing Pr with Y in PrMn$_2$Ge$_2$ compound are also investigated in this Chapter. An intensively study of the effects of external pressure accompanied by a high applied magnetic field produced significant outcomes, which are also discussed. Finally, the effects of replacement of Ge by another metalloid (Si) in CeMn$_2$Ge$_2$ compound are included to complete the whole story of ternary intermetallic compounds of the RT$_2$X$_2$ series (R = rare earth, T = transition metal, X = Si or Ge). This study demonstrates the variety of magnetic transition and chemical pressure effects with different substitutions in the composition.

In Chapter 6, the results on the magnetic properties and the critical behaviour analysis of Mn$_{0.94}$Ti$_{0.06}$CoGe and Mn$_{0.9}$Ti$_{0.1}$CoGe alloys are presented. The results of a temperature dependent neutron diffraction study of both Mn$_{0.94}$Ti$_{0.06}$CoGe and Mn$_{0.9}$Ti$_{0.1}$CoGe alloys are also presented in this Chapter so as to elucidate the existence of a coupling in the magneto-structural transition. Moreover, variations in the lattice parameters and phase fractions with temperature change also were detected from the neutron diffraction patterns based on Fullprof refinement.
Finally, Chapter 7 describes the conclusions drawn and outlook based on this study, as well as recommendations regarding future work.

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THEORETICAL ASPECTS

2.1 Magnetic Entropy

The magnetocaloric effect (MCE) is the response of a magnetic solid to a changing magnetic field, which manifests itself by a change in the temperature of the solid [1, 2]. 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 (PM) or soft ferromagnetic (FM) materials absorb heat, and their magnetic entropy decreases when the magnetic field is applied isothermally or heat is otherwise expelled, and their magnetic entropy increases when the magnetic field is reduced isothermally. In order to understand the physics behind the magnetocaloric effect, it is important to gain insight into the behaviour of magnetic materials under the influence of a magnetic field.

The MCE is quantified through the 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 shown 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 2.1 is an $S$-$T$ diagram for a ferromagnetic solid, showing the total entropy in magnetic fields $H_F$ and $H_1$ ($H_1 < H_F$). 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, $\Delta T_{ad}$ [3]. These arrows represent two different transformations, described in the preceding paragraph, which elucidate further the thermodynamics of the magnetocaloric effect [3].

![Diagram](image)

**Figure 2.1** $S$ - $T$ diagram demonstrating the magnetocaloric effect [3].
2.2 Gibbs Free Energy

The MCE is essentially the application of the first and second laws of thermodynamics to a magnetic system. A description of the MCE in a magnetic system involves the use of thermodynamic functions such as the Gibbs free energy, which is a function of $T, H$, and the pressure, $p$, and is used for systems with constant pressure. It can be expressed as:

$$ G = U - TS + pV - \mu_0 MH $$

Here, $U$ is the internal energy and $V$ is the volume. Equation (2.2) is a very important expression, as it is possible to define the first order and second order phase 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.

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.

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

$$ dU = TdS - pdV - \mu_0 HdM $$

$$ dS = -SdT - pdV - \mu_0 HdM $$

$$ dG = Vdp - SdT - \mu_0 MdH $$

Considering the free energy, $F$, the following equations determine the internal parameters $S, p, \text{ and } H$. 
Considering the Gibbs free energy, the following equations determine the internal parameters $S, M, V$:

\[ S(T, H, V) = -\left( \frac{\partial F}{\partial T} \right)_{H, V} \]  

(2.6)

\[ H(T, M, V) = -\left( \frac{\partial F}{\partial M} \right)_{V, T} \]  

(2.7)

\[ p(T, H, V) = -\left( \frac{\partial F}{\partial V} \right)_{H, T} \]  

(2.8)

Replacing the magnetic field $H$ with the magnetic moment $M$ as the external variable we get:

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

(2.12)

Deriving the Maxwell equations using Equations (2.9) and (2.10), (2.9) and (2.11), and (2.9) and (2.12) we get:

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

(2.13)

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

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

(2.15)

### 2.3 Specific Heat

From the second law of thermodynamics, the enthalpy variation of a reversible process can be expressed as
\[\partial S = \left( \frac{\partial Q}{T} \right)\]  

(2.16)

Accordingly, the heat capacity \( C_x \) of a system at constant parameter \( x \) is defined by:
\[ C_x = \left( \frac{\partial Q}{\partial T} \right)_x \]  

(2.17)

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:
\[ C_x = T \left( \frac{\partial S}{\partial T} \right)_x \]  

(2.18)

From Equation (2.20), the differential of the total entropy can be expressed as:
\[ dS(T)_x = \frac{C(T)_x}{T} dT \]  

(2.19)

The total differential of the total entropy of a magnetic system as a function of \( T, p, \) and \( H \) can be written as:
\[ dS = \left( \frac{\partial S}{\partial T} \right)_{H,p} dT + \left( \frac{\partial S}{\partial H} \right)_{T,p} dH + \left( \frac{\partial S}{\partial p} \right)_{T,H} dp \]  

(2.20)
Considering an adiabatic \( (dS = 0) \) and isobaric \( (dp = 0) \) process and using the Maxwell relations (2.13) and (2.18), the temperature change due to a change in the magnetic field is expressed as:

\[
dT = -\frac{T}{C_{H,p}} \left( \frac{\partial M}{\partial T} \right)_{H,p} dH \tag{2.21}
\]

Using Equations (2.15) and (2.19) the temperature change caused by an adiabatic and isobaric change of magnetization is given by:

\[
\partial T = -\frac{T}{C_{M,p}} \left( \frac{\partial H}{\partial T} \right)_{M,p} dM \tag{2.22}
\]

\( C_{H,p} \) and \( C_{M,p} \) are the heat capacity of the material at constant pressure and constant field or constant 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:

\[
dS = \left( \frac{\partial S}{\partial T} \right)_{M,p} dT + \left( \frac{\partial S}{\partial M} \right)_{T,p} dM + \left( \frac{\partial S}{\partial p} \right)_{T,M} dp \tag{2.23}
\]

To obtain the finite temperature change \( \Delta T_{ad} \) for an adiabatic magnetization, Equations (2.21) and (2.22) are integrated as shown below:

\[
\Delta T_{ad}(T,\Delta H) = -\int_{H_1}^{H_2} \left( \frac{T}{C(T,H)} \right)_{H} \left( \frac{\partial M(T,H)}{\partial T} \right)_{H} dH \tag{2.24}
\]

\[
\Delta T_{ad}(T,\Delta M) = -\int_{M_1}^{M_2} \left( \frac{T}{C(T,M)} \right)_{M} \left( \frac{\partial H(T,M)}{\partial T} \right)_{M} dM \tag{2.25}
\]
The integration of the Maxwell relation, Equation (2.13), to give the finite entropy change under isothermal and isobaric conditions is expressed below:

$$\Delta S_M(T, \Delta H) = \int_{H_i}^{H_f} \left( \frac{\partial M}{\partial T} \right)_{H} dH$$  \hspace{1cm} (2.26)

From these equations, it follows that the MCE (absolute value 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.

### 2.4 Critical Exponent Analysis

Analysis of the critical behaviour is one of the methods used to clarify the nature of the FM – PM phase transition. According to the criterion proposed by Banerjee [4], the order of a magnetic transition can be determined from the slope of the isothermal plot. If the $H/M$ versus $M^2$ curve shows a negative slope, the transition is first order, while a positive slope corresponds to a second order transition. 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 $\delta$ [5]. The modified Arrott plots (MAPs), Kouvel-Fisher method, critical isotherm analysis and the Widom scaling relation are the commonly used methods for determining the critical exponents. The first method used to calculate the critical exponents is the MAP method, which is based on the Arrott-Noakes equation of state [6]. Quantitative fits are made to the Arrott plots using the following equations [7]:

$$M_s(T) = \lim_{H \to 0} (M) = M_0 (-\varepsilon)^\beta, \varepsilon < 0$$  \hspace{1cm} (2.27)
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.

$$x_0^{-1}(T) = \lim_{H \to 0} (H/M) = (h_0/M_0)\varepsilon^{\gamma}, \varepsilon > 0 \quad (2.28)$$

Here, $x_0$ is the limit of the susceptibility at zero magnetic field. 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 [8]. Next, $M_S$ is plotted as a function of temperature. To determine $x_0^{-1}(T)$, a similar procedure is used in conjunction with the $(H/M)^{1/\gamma}$ axis. 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.

The Kouvel-Fisher (KF) method, which makes use of Equations (2.29) and (2.30) shown below, is a more accurate way of determining the critical exponents $\beta$ and $\gamma$ [9].

$$\frac{M_S(T)}{dM_S(T)/dT} = \frac{T-T_C}{\beta} \quad (2.29)$$

$$\frac{x_0^{-1}(T)}{d x_0^{-1}(T)/dT} = \frac{T-T_C}{\gamma} \quad (2.30)$$

According to Equations (2.29) and (2.30), plotting $M_S(T)[dM_S/dT]^{-1}$ and $x_0^{-1}(T)[dx_0^{-1}/dT]^{-1}$ versus temperature yields straight lines with slopes of $1/\beta$ and $1/\gamma$, respectively. The value of $T_C$ is obtained from the intercepts on the $x$-axis. 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 (2.31) below as $D$ is the critical amplitudes.

$$M_{T_c} = DH^{1/\delta}, \varepsilon = 0, T = T_C$$  \hspace{1cm} (2.31)

From Equation (2.31), a plot of $\log(M)$ versus $\log(H)$ is expected be a straight line with slope $1/\delta$. Another way of obtaining the critical component $\delta$ is by using the Widom scaling relation shown in Equation (2.32):

$$\delta = 1 + \frac{\varepsilon}{\beta}$$  \hspace{1cm} (2.32)

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:

$$M (H, \varepsilon) = \varepsilon^\beta f_\pm (H / \varepsilon^{\beta+\gamma})$$  \hspace{1cm} (2.33)

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 $H / \varepsilon^{(\beta+\gamma)}$ 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 exponents as well as the $T_C$ are reliable and in agreement with the scaling hypothesis.
2.5 Recent International Progress on Magnetocaloric Materials

The discovery of the giant MCE (GMCE) in Gd$_5$(Si,Ge)$_4$ compounds has triggered vast interest in magnetic cooling. In addition, in 1997 the first near-room-temperature magnetic refrigerator was demonstrated by Zimm et al. at the Astronautics Corporation of America [10]. These two events attracted interest from both scientists and private companies, which started developing new kinds of room-temperature materials and magnetic-refrigerator designs. Figure 2.2 shows the number of publications on magnetic cooling since 1992 to 2010 and Figure 2.3 presents the number of magnetic refrigerators developed per year since 1970.

![Graph showing number of publications on magnetic refrigeration and number of magnetic refrigerators developed per year.](image)

**Figure 2.2** Publications on magnetic refrigeration since 1992 (Source: ISI web, *Science*, May 5, 2010).
For room-temperature applications such as refrigerators and air-conditioners, compounds containing manganese or iron should be a good alternative. Manganese and iron are transition metals with high abundance. Also, in contrast to rare-earth compounds, there exist an almost unlimited number of manganese and iron compounds with critical temperatures near room temperature. The magnetic moment of manganese generally is only about half the size of those for heavy rare-earth elements and the magnetic moment of iron is even less. Enhancement of the caloric effects associated with magnetic moment alignment may be achieved through the induction of a first order phase-transition, or better, a very rapid change of magnetisation at the critical temperature, which will lead to much higher efficiency of the magnetic refrigerator.

In combination with currently available permanent magnets [12], based on modern rare-earth transition-metal compounds [13], this opens the path to the development of small-scale
magnetic refrigerators, which need no longer rely on rather costly and service-intensive superconducting magnets. Another prominent advantage of magnetocaloric refrigerators is that the cooling power can be varied by scaling from miliwatts to a few hundred watts or even kilowatts. To increases the temperature span of the refrigerator, in comparison with the temperature change in a single cycle, all demonstrator models or prototypes nowadays are based on active magnetic regenerator design [14].

![Diagram](image)

**Figure 2.4** Comparison between GMCE materials and conventional MCE materials at $\mu_0\Delta H = 5$ T [14]

### 2.5.1 Gd$_5$Ge$_2$Si$_2$ type compounds

Following the discovery of a sub-room-temperature giant-MCE in the ternary compound Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ ($0.3 \leq x \leq 0.5$) [15], as shown in Figure 2.4, there has been strongly increased interest from both fundamental and practical points of view in studying the MCE in these materials [16-17]. The most prominent feature of these compounds is that they undergo a
first-order structural and magnetic phase transition, which leads to a giant magnetic field-induced entropy change across their ordering temperature. We now therefore will discuss to some extent the structural properties of these compounds. At low temperatures for all $x$, Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ adopts an orthorhombic Gd$_5$Si$_4$-type structure (Pnma), and the ground state is ferromagnetic[18].

At room temperature, however, depending on $x$, three different crystallographic phases are observed. For $x > 0.55$, the aforementioned Gd$_5$Si$_4$ structure is stable, while for $x < 0.3$, the materials adopt the Sm$_5$Ge$_4$-type structure with the same space group (Pnma) but a different atomic arrangement and a somewhat larger volume, and finally, in between these two types of structure, the monoclinic Gd$_5$Si$_2$Ge$_2$ type with space group P1121/a is formed, which has an intermediate volume. The latter structure type is stable only below about 570 K, where again, the orthorhombic Gd$_5$Si$_4$-type structure is formed in a first-order phase transition [19].

As one may guess, the three structure types are closely related; the unit cells contain four formula units and essentially only differ in the mutual arrangement of identical building blocks, which are either connected by two, one, or no covalent-like Si-Ge bonds, resulting in successively increasing unit-cell volumes. The giant magnetocaloric effect is observed for the compounds that exhibit a simultaneous paramagnetic to ferromagnetic and structural phase transition that can be induced by a change in temperature, applied magnetic field, or applied pressure [20-21].

In contrast to most magnetic systems, the ferromagnetic phase has a 0.4% smaller volume than the paramagnetic phase, which results in an increase in $T_C$ on application of pressure of about 3 K/kbar. The structural change at the phase transition also leads to a very large
magneto-elastic effect, and the electrical resistivity behaves anomalously. The strong coupling between the lattice degrees of freedom and the magnetic and electronic properties is rather unexpected, because the magnetic moment in Gd originates from spherical symmetric s-states that, in contrast to other rare-earth elements, hardly couple with the lattice. First principles electronic structure calculations on the atomic level and local-density approximation calculations with spin-orbit coupling added variationally could reproduce some distinct features of the phase transition [22].

Total energy calculations for the monoclinic and orthorhombic phases show different temperature dependences and the structural change occurs at the temperature where the energies are equal. A distinct difference appears in the effective exchange-coupling parameter for the monoclinic and orthorhombic phases, respectively. This difference could be directly related to the change in the Fermi level in the structural transition. Thus, the fact that the structural and magnetic transitions are simultaneous is somewhat accidental, as the exchange energy is of the same order of magnitude as the thermal energy at the structural phase-transition. The electrical resistivity and magnetoresistance of Gd$_5$Ge$_2$Si$_2$ also shows unusual behaviour, indicating a strong coupling between the electronic structure and the lattice.

For several compounds in the series, a very large magnetoresistance effect is reported next to a cusp-like anomaly in the temperature dependence of the resistivity [23-26]. From the point of view of building a refrigerator based on Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$, there are a few points to consider. The largest magnetocaloric effect is observed considerably below room temperature, while a real refrigerator should expel heat at least at about 320 K. Because the structural transition is connected with sliding of the building blocks, impurities can play an important role, especially at the sliding interface. The thermal hysteresis and the size of the magnetocaloric
effect connected with the first-order phase transition strongly depend on the quality of the starting materials and the sample preparation [27].

For the Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ compounds with $x$ around 0.5, small amounts of impurities may suppress the formation of the monoclinic structure near room temperature. These alloys then show only a second order phase transition at a somewhat higher temperature, but with a lower magnetocaloric effect [19],[28-29]. This sensitivity to impurities such as carbon, oxygen and iron strongly influences the production costs of the materials, which may hamper broad-scale application. Next to the thermal and field hysteresis, the magneto-structural transition in Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ appears to be rather sluggish [30, 31]. This will also influence the optimal operation frequency of a magnetic refrigerator and its efficiency.

### 2.5.2 La(Fe,Si)$_{13}$ and related compounds

Another interesting type of material is the rare-earth - transition-metal compounds crystallizing in the cubic NaZn$_{13}$ type of structure. LaCo$_{13}$ is the only binary compound, from the 45 possible combinations of a rare-earth and iron, cobalt, or nickel, that exists in this structure. It has been shown that with an addition of at least 10% Si or Al this structure can also be stabilized with iron and nickel [32].

The NaZn$_{13}$ structure contains two different Zn sites. The Na atoms at 8$a$ and Zn atoms at 8$b$ form a simple CsCl type of structure. Each ZnI atom is surrounded by icosahedra composed of 12 ZnII atoms at the 96$i$ site. In La(Fe,Si)$_{13}$, La occupies the 8$a$ site, while the 8$b$ site is fully occupied by Fe and the 96$i$ site is shared by Fe and Si. The iron rich compounds La(Fe,Si)$_{13}$ show typical Invar behaviour, with magnetic ordering temperatures around 200 K
that increase to 262 K with lower iron content [33]. Thus, although the magnetic moment is diluted and also decreases per Fe atom, the magnetic ordering temperature increases. Around 200 K, the magnetic ordering transition is found to be also distinctly visible in the electrical resistivity, where a chromium-like cusp in the temperature dependence is observed. In contrast to Gd$_5$Ge$_2$Si$_2$, this phase transition is not accompanied by a structural change, and thus, above and below $T_C$, the material is cubic.

Recently, because of the extremely sharp magnetic ordering transition, the (La,Fe,Si,Al) system was reinvestigated by several research groups, and a large magnetocaloric effect was reported [34-36]. The largest effects are observed for the compounds that show a field- or temperature-induced phase transition of first order. Unfortunately, these large effects only occur up to about 210 K, as the magnetic sublattice becomes more and more diluted. When using standard melting techniques, preparation of homogeneous single-phase samples appears to be rather difficult, especially for alloys with high transition metal content. Almost single phase samples are reported when, instead of normal arc melting, rapid quenching by melt spinning and subsequent annealing is employed [37-39]. Samples prepared in this way also show a very large magnetocaloric effect.

To increase the magnetic ordering temperature without losing too much magnetic moment, one may replace some Fe by other magnetic transition metals. Because the isostructural compound LaCo$_{13}$ has a very high critical temperature, substitution of Co for Fe has been widely studied. The compounds La(Fe,Co)$_{13-x}$Al$_x$ and La(Fe,Co)$_{13-x}$Si$_x$ with $x \approx 1.1$ and thus a very high transition-metal content, show a considerable magnetocaloric effect near room temperature [40-43]. This is achieved with only a few percent Co, and the Co content can
easily be varied to tune the critical temperature to the desired value. It should be mentioned, however, that near room temperature, the values for the entropy change drop steeply.

Hydrogen is the most promising interstitial element. In contrast to other interstitial atoms, interstitial hydrogen not only increases the critical temperature, but also leads to an increase in magnetic moment \([35], [44-48]\). The lattice expansion due to the addition of three hydrogen atoms per formula unit is about 4.5%. The critical temperature can be increased up to 450 K, as the average magnetic moment per Fe increases from 2.0 \(\mu B\) up to 2.2 \(\mu B\) and the field- or temperature-induced phase transition is found to be of first order for all hydrogen concentrations.

For a certain Si percentage, this all results in an almost constant value of the magnetic entropy change per mass unit over a broad temperature span. From the materials cost point of view, the La(Fe,Si)\(_{13}\) type alloys appear to be very attractive. La is the cheapest from the rare-earth series, and both Fe and Si are available in large amounts. The processing will be a little more elaborate than for a simple metal alloy, but this can be optimized. For use in a magnetic refrigerator, next to the magnetocaloric properties, the mechanical properties and chemical stability may also be of importance.

The hydrogenation process in rare-earth transition-metal compounds almost always produces granular material due to the strong lattice expansion. In the case of the cubic NaZn\(_{13}\) type of structure, however, this does not seem to be the case. At the phase transition in La(Fe,Si)\(_{13}\) type alloys, a volume change of 1.5% is also observed \([49]\). If this volume change is performed very frequently, the material will definitely become very brittle and probably break into even smaller grains. This can have a distinct influence on the corrosion resistance
of the material and thus on the lifetime of a refrigerator. The suitability of this material definitely needs to be tested.

2.5.3 RT$_2$X$_2$ interlayer compounds

Ternary rare-earth (R) compounds of the type RT$_2$X$_2$, where T = transition metal and X = Si, Ge, exhibit a large variety of structural and physical properties (Refs.[50-52]) and as such continue to attract interest. The interplay between the R-T and T-T exchange interactions in these RT$_2$X$_2$ compounds, combined with the extensive ranges of solubility of the R, T and X elements, enables structural and magnetic behaviours to be controlled through elemental substitution [53-56]. Given this scope to tune their physical and magnetic properties and related magnetic phase transitions, RT$_2$X$_2$-based compounds have attracted attention in exploring their magnetocaloric effect behaviour [57-59].

The ternary intermetallic compounds of the RT$_2$X$_2$ series have attracted considerable attention because of the rich variety of interesting phenomena, including superconductivity, magnetism, mixed valence, heavy fermions, and Kondo behaviour [60, 61]. RT$_2$X$_2$ compounds form mainly in the ThCr$_2$Si$_2$ structure (space group $I4/mmm$), with the layered nature of this crystal structure leading to strong dependence of the magnetic interactions on the interplanar and intraplanar interatomic distances [53]. From this point of view, RMn$_2$X$_2$ compounds with X= Si or Ge have attracted special attention, due mainly to the interesting interplay between the magnetism of the layers of 3$d$ and 4$f$ atoms and the strong dependence of the magnitude of the Mn moment and the magnetic state of the Mn sublattice on the Mn-Mn interatomic distances [57, 61-66].
As a general guide, for intraplanar distance, \(d_{\text{Mn-Mn}}\) below \(~2.87\ \text{Å}\), the coupling between Mn layers is antiferromagnetic while above this value, the coupling is ferromagnetic [67-69]. In NdMn\(_2\)Si\(_2\), below \(T_N\sim 380\ \text{K}\) the Mn sublattice orders antiferromagnetically, while below \(T_C\sim 36\ \text{K}\) the compound is ferromagnetic with ordered moments at both the Nd and the Mn sublattices [70, 71]. These magnetic behaviours with different temperature dependences reflect different types of exchange interactions with different mechanisms with both the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction \textit{via} conduction electrons, and super exchange between magnetic atoms \textit{via} the Si or Ge atoms contributing. Generally, the exchange interactions in RMn\(_2\)X\(_2\) compounds can be divided into four classes: Mn–Mn within the Mn layers, Mn–Mn between the Mn layers, and Mn–R and R–R interactions [72].

Investigations of the RMn\(_2\)X\(_2\) magnetic phase diagram as functions of both composition and Mn–Mn spacing using x-ray and neutron diffraction, magnetisation and differential scanning calorimetry measurements. For example, Pr\(_{1-x}\)Y\(_x\)Mn\(_2\)Ge\(_2\) exhibits an extended region of re-entrant ferromagnetism around \(x\sim0.5\) with re-entrant ferromagnetism at \(T_{c}\text{Pr}\sim 50\ \text{K}\) for Pr\(_{0.5}\)Y\(_{0.5}\)Mn\(_2\)Ge\(_2\). The entropy values \(-\Delta S_M\) around the ferromagnetic transition temperatures \(T_{c}\text{inter}\) from the layered antiferromagnetic AF\(_l\) structure to the canted ferromagnetic structure \(Fmc\) (typically \(T_{c}\text{inter}\sim 330-340\ \text{K}\)) have been derived for Pr\(_{1-x}\)Y\(_x\)Mn\(_2\)Ge\(_2\) with \(x=0.0, 0.2\) and 0.5 for \(\Delta B=0-5\ \text{T}\). The changes in magnetic states due to Y substitution for Pr are discussed in terms of chemical pressure, external pressure and electronic effects.

2.5.4 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
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 [75].

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 [76]. 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 [77]. It has been established that for the MnCoGe compound, the structural transition temperature, $T_{str}$ between the orthorhombic and hexagonal phase can be changed by either changing the composition [78], or applying an external pressure [79, 80].

Kanomata et al. [75] clearly point out that the structural transition in MnCoGe, as shown in Figure 2.7, is accompanied by strong thermal hysteresis ($\Delta T_{hys}$ ~ 40 K) and a large volume change ($\Delta V/V$ ~ 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 [81, 82].

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 $ab$ $initio$ 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.

![Figure 2.5](image)

**Figure 2.5** Volume and lattice parameters of the MnCoGe alloy as a function of temperature [45].

Markin *et al.* studied the concentrational 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 [83]. 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.* [76], 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 $-5.6 \text{ J kg}^{-1} \text{K}^{-1}$ for a magnetic field change $\Delta B = 0.5 \text{ T}$. Meanwhile, an enhanced $\Delta S_M$ value up to $-9 \text{ J kg}^{-1} \text{K}^{-1}$ 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 [84, 85].

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 [86].

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.

Caron et al. [87] 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 [82].
2.5.5 MnAs based compounds

MnAs is similar to Gd$_5$Ge$_2$Si$_2$ in having two distinct crystallographic structures [88]. At low and high temperature the hexagonal NiAs structure is found, and for the narrow temperature range of 307 K to 393 K, the orthorhombic MnP structure exists. The high temperature transition in the paramagnetic region is of second order. The low temperature transition is a combined structural and ferro-paramagnetic transition of first order with large thermal hysteresis.

The change in volume at this transition amounts to 2.2% [89]. The transition from paramagnetic to ferromagnetic occurs at 307 K, and the reverse transition from ferromagnetic to paramagnetic occurs at 317 K. Very large magnetic entropy changes are observed in this transition [90, 91]. Similar to the application of pressure [92, 93], substitution of Sb for As leads to lowering of $T_C$ [94, 95], and 25% Sb gives a transition temperature of 225 K. The thermal hysteresis, however, is affected quite differently by hydrostatic pressure or Sb substitution.

In Mn(As,Sb), the hysteresis is strongly reduced, and at 5% Sb, it is reduced to about 1 K. In the concentration range of 5 to 40% of Sb, $T_C$ can be tuned between 220 and 320 K without losing much of the magnetic entropy change [96, 97]. Direct measurements of the temperature change confirm a $\Delta T$ of 2 K/T [98]. On the other hand, MnAs under pressure shows an extremely large magnetic entropy change [99] in conjunction with large hysteresis.

The materials costs of MnAs are quite low, but processing of As containing alloys is complicated due to the biological activity of As. In the MnAs alloy, the As is covalently
bound to the Mn and would not be easily released into the environment. This should be experimentally verified, however, especially because second phases frequently form in an alloy that may be less stable. The change in volume in Mn(As,Sb) is still 0.7%, which may result in aging after frequent cycling of the material.

2.5.6 Heusler Alloys

Heusler alloys frequently undergo a martensitic transition between the martensitic and the austenitic phase, which is generally temperature induced and of first order. Ni$_2$MnGa orders ferromagnetically, with a Curie temperature of 376 K and a magnetic moment of 4.17 μB, which is largely confined to the Mn atoms, with only a small moment of about 0.3 μB associated with the Ni atoms [100]. As may be expected from its cubic structure, the parent phase has a low magnetocrystalline anisotropy energy ($H = 0.15$ T). In its martensitic phase, however, the compound exhibits a much larger anisotropy ($H = 0.8$ T). The martensitic transformation temperature is near 220 K.

This martensitic transformation temperature can be easily varied to around room temperature by modifying the composition of the alloy from the stoichiometric one. The low temperature phase evolves from the parent phase by a diffusionless, displacive transformation leading to a tetragonal structure, $a = b = 5.90$ Å, $c = 5.44$ Å. The martensitic phase generally accommodates the strain associated with the transformation (6.56% along the $c$-axis for Ni$_2$MnGa) by the formation of twin variants. This means that a cubic crystallite splits up into two tetragonal crystallites sharing one contact plane. These twins pack together in compatible orientations to minimize the strain energy (in much the same way as the magnetization of a
ferromagnet may take on different orientations by breaking up into domains to minimize the magnetostatic energy).

Alignment of these twin variants by the motion of twin boundaries can result in large macroscopic strains. In the tetragonal phase with its much higher magnetic anisotropy, an applied magnetic field can induce a change in strain, which is why these materials may be used as actuators. Next to this ferromagnetic shape memory effect, very close to the martensitic transition temperature, one observes a large change in magnetization for low applied magnetic fields. This change in magnetization is also related to the magnetocrystalline anisotropy. This change in magnetization results in a moderate magnetic entropy change of a few J/mol K, which is enhanced when measured on a single crystal [101, 102]. When the composition in this material is tuned in such a way that the magnetic and structural transformations occur at the same temperature, the largest magnetic entropy changes are observed [103-105].

For magnetocaloric applications, the extremely large length changes in the martensitic transition will definitely result in aging effects. It is well known for the magnetic shape-memory alloys that only single crystals can be frequently cycled, while polycrystalline materials spontaneously powderize after several cycles.

### 2.5.7 Fe$_2$P based compounds

The binary intermetallic compound Fe$_2$P can be considered as the parent alloy for an interesting class of materials. This compound crystallizes in the hexagonal non-centrosymmetric Fe$_2$P type structure with space group P 6 2 m. In this structure, Fe and P
occupy four different crystallographic sites, Fe occupies the 3g and 3f sites, and P occupies the 1b and 2c sites. Thus, one has a stacking of alternating P-rich and P-poor layers. Neutron diffraction has revealed that the magnetic moment of Fe on the 3g sites is about 2 μB, whereas the moment on the 3f sites is about 1 μB [106]. The Curie temperature of this compound is 216 K, and the magnetic transition is of first order [107].

The magnetic-ordering transition from the paramagnetic state to the ferromagnetic state is accompanied by a discontinuous change in the volume of 0.05%. Thus, the ferromagnetic state has a bigger volume than the paramagnetic one. This phase transition is found to be extremely sensitive to changes in pressure or magnetic field. Application of pressure first reduces the Curie temperature, and at pressures exceeding 5 kbar, antiferromagnetic ordering preceding the ferromagnetic ordering is observed [108]. Substitution of As, B, or Si into the P sublattice results in an increase in the Curie temperature [109], which can easily be lifted to above room temperature for As or Si concentrations of 10% or by 4% for B. Substitution of Mn for Fe on the 3g sites further increases the magnetic moment to about 4 μB.

To stabilize the Fe₂P-type of structure, simultaneously with the Mn substitution, part of the P should also be replaced. The most extensively studied series of alloys is of the MnFe(P,As) type. The magnetic phase diagram for the MnFeP-MnFeAs system [110] shows a rich variety of crystallographic and magnetic phases. The most striking feature is the fact that for As concentrations between 30 and 65% the hexagonal Fe₂P type of structure is stable, and the ferromagnetic order is accompanied by a discontinuous change in the volume. While the total magnetic moment is not affected by changes in the composition, the Curie temperature increases from about 150 K to well above room temperature. We reinvestigated this part of
the phase diagram [111, 112] and investigated possibilities for partially replacing the As [113-115].

The large MCE observed in Fe$_2$P based compounds originates from a field-induced first order magnetic phase transition. The magnetisation is reversible depending on the temperature and in alternating magnetic field. The magnetic ordering temperature of these compounds is tuneable over a wide temperature interval (200 K to 450 K). The excellent magnetocaloric features of the compounds of the MnFe (P,Si,Ge,As) type, in addition to the very low material costs, make it an attractive candidate material for a commercial magnetic refrigerator. In the same way as for MnAs alloys, however, it should be verified that materials containing as do not release it to the environment. The fact that the magnetoelastic phase-transition is rather a change of \( c/a \) than a change of volume, makes it feasible that this alloy, even in polycrystalline form, will not experience severe aging effects after frequent magnetic cycling [81].
References


Chapter 3

EXPERIMENTAL METHODS AND PROCEDURES

3.1 Sample Preparation

The basic principles of the equipment used to prepare the materials presented in this thesis are outlined in this chapter. All the materials used for measurement in this thesis are polycrystalline and were prepared using the arc melting method at UNSW@ADFA, Canberra and the ball-milling method at ISEM, University of Wollongong.

3.1.1 Bulk sample Preparation – Arc melting

Stoichiometric amounts of the starting elements, typically with purity greater than 99.9%, were melted using an argon arc furnace with a tungsten electrode and water cooled copper hearth. The furnace was flushed 3-4 times with high purity argon gas to minimise the amount of oxygen in the tube and hence prevent oxidation during the melting process. The gas pressure was initially set slightly lower than ambient pressure to allow for its increase due to the high temperatures experienced during melting. The process commenced with the melting of a titanium getter, for further reduction of the residual oxygen in the furnace, before proceeding to the actual starting materials. The preparations were carried out with sets of smaller masses (approximately 1 - 2.5 g), and each specimen was melted, turned, and remelted at least 6 times to ensure homogeneity of the specimens. Due to the sensitivity of all specimens, it was found that vacuum annealing was required to obtain a good quality
structure. To do this, the specimens were wrapped in Ta foil, sealed in an evacuated quartz tube, and annealed at a specific temperature and time before quenching in water.

3.1.2 Bulk sample Preparation – Ball milling

In order to investigate which method is most beneficial to produce the desired structure in Mn$_{1-x}$Co$_x$Ge alloys, ball milling was performed as a comparison with arc melting. All the powders, which were of high purity (> 99.9%), were mixed in an agate mortar and loaded into a stainless steel vial under high purity Ar atmosphere inside a glove box. Before sealing the vial, stainless steel balls 5 mm in diameter were added, with a powder-to-ball ratio of 1:10. The ball milling was performed in a planetary crushing Fritsch Pulverisette 7. A low energy ball milling at 200 rpm for 30 minutes was conducted before high energy ball milling at 500 rpm for 6 hours. The fine powder was then pressed into pellets and sealed in quartz ampoules in an Ar atmosphere of 200 mbar. Finally, the as-milled alloy was annealed at 1423 K for 1 hour before a quenching in water.

3.2 Structural and Characterization Analysis of the Samples

In order to determine the structural properties as well as the quantification of the phases and impurities therein, X-ray diffraction (XRD), neutron diffraction, and scanning electron microscopy (SEM) were carried out. These characterizations needed to be done as a first step before measuring the physical properties of the samples, as if the impurity content is more than 5%, it means that the sample is not suitable for further investigation. All these techniques are elaborated in detail below.
3.2.1 Neutron and Synchrotron (X-ray) Diffraction

The neutron diffraction technique is used not only for the determination of the atomic structure, but also for the magnetic structure and moment of a material as well. 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 that direct them to targets in a series of instruments. The Echidna and Wombat neutron beam instruments were used in this study for a few selected materials, as this equipment offers very limited beam time. A schematic diagram of the Echidna and Wombat neutron diffractometers is shown in Figure 3.1.

![Figure 3.1](image.jpg)  
**Figure 3.1** Schematic diagrams of the (a) Echidna and (b) Wombat diffractometers as cited from ANSTO website.
As mentioned previously, an intense beam of neutrons is produced at the nuclear reactor, and this neutron beam is channelled through a collimator that narrows the beam so that only neutrons travelling normal to the reactor surface are used. The neutron beam is then targeted on a monochromator (usually graphite), which will reflect neutrons with a wavelength close to a value determined by the angular setting of the 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 the researchers. The Echidna provided high resolution diffraction patterns and Wombat has high intensity. These are among the most powerful diffractometers in the world, promising high quality outcomes for the present research study.

Synchrotron X-ray diffraction equipment located at the Australian Synchrotron was used in order to identify change of structure of samples, especially with regards to strain, the magnetic contribution, and valence effects. Because it provides high resolution and a sophisticated facility for powder diffraction, all the physical and chemical behaviour that takes place at critical transitions can be explored and efficiently clarified.

The powder diffraction beamline as shown in Figure 3.2 is located on a bending magnet source and has been designed to operate over the energy range of 5-30 keV. The beamline consists of three hutches and a user cabin. The first hutch contains the optics, including mirrors and a double crystal monochromator. The centre hutch houses the primary end station where the majority of powder diffraction experiments are undertaken. Finally, the third hutch contains a large optical table which allows a variety of alternative configurations, primarily centred on engineering applications.
3.2.2 Scanning Electron Microscopy

The scanning electron microscope (SEM) generates a variety of signals at the surface of solid specimens by using a focused beam of high energy electrons. Electron and sample interactions generate a signal which reveals information about the sample, such as the morphology, chemical composition, and crystalline structure, for in this study.

A precise measurement of very small features of the sample down to the nanometer (nm) size was possible using SEM (JEOL Model JSM-6490) for this study, and the basic operation is shown in Figure 3.3. 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.
Figure 3.3 (a) Basic construction of SEM and (b) construction of an electron gun.

3.2.3 Diffraction Analysis

In order to analyse all the diffraction patterns collected from X-rays and neutrons in this study, refinement with the FullProf program was performed as this software package is very efficient and user-friendly. The FullProf program has been mainly developed for Rietveld analysis (structure profile refinement) of neutron (constant wavelength, time-of-flight, nuclear and magnetic scattering) or X-ray powder diffraction data collected with constant or variable steps at scattering angle $2\theta$.

The program can be also used as a profile matching (or pattern decomposition using the Le Bail method) tool, without detailed knowledge of the structure as in Figure 3.4. Single crystal refinement can also be performed alone or in combination with powder data. Time-of-flight (TOF) neutron data analysis is also available. Energy dispersive X-ray data can also be treated, but only for profile matching.
3.3 Physical Properties Measurement System (PPMS)

Physical properties measurement has an important role in verifying the behaviour and characteristics of every single sample in this study. Furthermore, the effects of the doping concentration in the parent compound are clearly shown using this method.

3.3.1 Vibrating Sample Magnetometer (VSM)

The vibrating sample magnetometer (VSM) measurement system for the PPMS is a fast, sensitive, and fully automated DC magnetometer. The sensitivity of the VSM detection coils is not significantly affected by large magnetic fields, so the PPMS VSM can perform sensitive measurements up to the maximum field of 14 T that is available from PPMS magnet equipment. The VSM detection coil is inserted into the PPMS sample chamber by using the standard PPMS sample interface design. This procedure will make it easy to reconfigure the VSM option with alternate pick-up coil designs in the future. If the temperature range is over
360 K, the oven chamber is inserted, with the VSM oven allowing measurements up to the 1000 K temperature limit.

### 3.3.2 Superconducting Quantum Interference Device (SQUID)

The Quantum Design MPMS 5XL SQUID uses a superconducting quantum interference device (SQUID) magnetometer to monitor very small changes in magnetic flux and so discover the magnetic properties of the samples in this study. It is extremely sensitive for all kinds of AC and DC magnetic measurements. The SQUID detects and measures the magnetic moment of a sample. From this, the magnetization and magnetic susceptibility can be determined. Applications of the SQUID magnetometer include measurements of small quantities of paramagnetic ions, characterization of all kinds of magnetic materials, and quantitative determination of the number of unpaired electrons in samples. The MPMS-XL provides solutions for a unique class of sensitive magnetic measurements in key areas such as high-temperature superconductivity, biochemistry, and magnetic recording media.

### 3.3.3 Specific Heat Measurements

This type of measurement is very essential in this study, as the physics of various types of behaviour at some stages will need to be explained in detail, for example, adiabatic temperature, Debye temperature, phonon and electron contributions, and other unexpected outcomes. Unprecedented ease of use is the first feature of the PPMS Heat Capacity system (Model P650) that has been implemented during this study. Following a simple sample-mounting procedure, the sample mount is inserted into the PPMS sample chamber, the measurement parameters are entered into the software package and the measurement is
initiated. The system automatically accommodates all the necessary temperature, field, and vacuum settings; the data acquisition and analysis; and the data plotting. The option uses a hybrid adiabatic relaxation method that combines excellent measurement accuracy with robust error analysis. The PPMS Heat Capacity option uses the basic PPMS to control environmental variables, such as the temperature and magnetic field, while specialized components perform the heat capacity measurements. The Heat Capacity option includes hardware and software that allow fully automated high-sensitivity heat capacity measurements to be routinely performed between 1.9 K and 400 K (< 0.4 K to 350 K with the Helium-3 System) in magnetic fields up to 14 T.

### 3.3.4 Resistivity Measurements

Resistivity measurement is an additional method applied in order to confirm that something has happened at a transition temperature or some special stage and can be used to calculated magnetocaloric effect (MCE) values as well. The DC resistivity measurement option to the PPMS used in this study adds resistance bridge capability to the Model 6000 PPMS Controller, featuring a current range of 5 nA to 5 mA, and with voltage sensitivity as low as 20 nV. This bridge provides four independent channels that can be used for measuring up to four samples at one time, which is a very advantage for saving time.

### 3.3.5 Differential scanning calorimetry (DSC)

Differential scanning calorimeters (DSC) measure the temperatures and heat flows associated with thermal transitions in a material. This method is particularly valuable, as it is not influenced by magnetic field. This type of measurement includes the investigation, selection,
comparison, and end-use performance evaluation of materials in this research, with a view to real applications. TA Instruments Q100 DSC technology was used in this study as a more accurate way of measuring heat flow. It provides significant improvements in baseline flatness, transition resolution, and sensitivity. This advanced equipment allows direct measurement of heat capacity and makes Modulated® DSC experiments both faster and more accurate in the temperature range from 77 K to 550 K.
Chapter 4

MAGNETIC PROPERTIES AND MAGNETOCALORIC EFFECT OF La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$

4.1 Effect of Substitution on Fe with Others Metal Transition in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$

The La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ compound which formed in NaZn$_{13}$ type structure attracted many researchers to further investigate regarding to how interesting its behaviour is with tuning or substitution effect. Investigation on how the replacement of transition metal (Fe) in this compound with another transition metal modifies the physical properties and the limitation in the NaZn$_{13}$ type structure with substitution has been reported in this study.

4.1.1 Introduction

Magnetic refrigeration is becoming more reliable, which will enable it to replace conventional refrigeration systems, a change which is desirable because of the advantages of using the magnetocaloric effect (MCE) for applications. This technology has significant advantages - high refrigeration efficiency, environmental friendliness, small volume requirement, low cost, lack of toxicity, and no noise pollution, which makes it attractive for further research, compared with the widely used gas compression refrigeration technology. The MCE was originally discovered by Warburg [1] in 1881, and since the discovery of the giant magnetocaloric effect at room temperature in 1997 [2], magnetic materials with large MCE have been extensively studied experimentally and theoretically, especially over the past
two decades. Up to the present time, a number of materials with giant magnetic entropy changes have been discovered, such as MnFe(As, P) [3], MnCoGeB [4], MnNiGe:Fe [5], Gd₅Si₂Ge₂ [2], (Mn, Fe)₂(P, Ge) [6], MnAs₁₋ₓSbₓ [7], and La(Fe, Si)₁₃ [8-10].

Cubic NaZn₁₃-type La(Fe, Si)₁₃ has become one of the most interesting systems for exploring large MCE because its magnetic properties are strongly doping dependent, and it shows large enough spontaneous magnetization for applications, as well as soft ferromagnetism [11-13]. These effects can be ascribed to the itinerant-electron metamagnetic (IEM) transition in the vicinity of the first order transition temperature. Doping other magnetic rare-earth elements, such as Pr, Nd, Ce, Er, and Gd, into the La site has been used to change the temperature and to reduce the critical field of the 3d-metamagnetic transition in La(Fe, Si)₁₃ compound [14-16] because the rare earth-Fe magnetic coupling displays a strong dependence on the type rare earth. The cubic NaZn₁₃-type compound is hard to form by the common solidification process due to the intrinsic incompleteness of the peritectic reaction, γ-Fe+L → La(Fe, Si)₁₃(τ₁₄), which often results in a mixed microstructure of α-Fe + La(Fe, Si)₁₃(τ₁₄) + LaFeSi(τ₄) [17]. Recent study indicated that silicon (Si) concentration also plays the role to form NaZn₁₃ type structure [18]. Moreover stability of La(FeₓSi₁₋ₓ)₁₃ is governed by reaction diffusion according to magnetic and electronic states contribution [19]. Many groups have prepared this compound through annealing at temperatures in the range of 1173-1323 K for ten or more days to form the NaZn₁₃-type structure [20-22]. However the peritectic reaction temperature in La(Fe, Si)₁₃ is around 1673 K, according to the La-Fe quasi binary diagram [23], and the temperature was found to have an effective role in shortening the phase transformation process [24], as demonstrated by Liu et al. [25] and Chen et al. [26]. Both groups reported that preparation in the temperature range of 1323-1623 K can produce the greatest phase fraction of the NaZn₁₃-type structure.
According to Shen et al. [27], the replacement of La by other rare earth elements can lead to remarkable enhancements in the magnetic entropy change. However these phenomena always are accompanied by an increased hysteresis loss because of the features of the first order transition. In the LaFe$_{13-x}$Si$_x$ structure there are 3 in equivalent atomic sites: (8$a$) occupied by La, (8$b$) occupied by Fe1 and (96$i$) occupied by Fe2 and Si [31]. It was reported that the substitution of Cu for Si can lead to a remarkable reduction in both thermal and magnetic hysteresis in LaFe$_{11.7}$(Si$_{1-x}$Cu$_x$)$_{1.3}$ with reduction the lattice parameter [28]. This present study investigates how the replacement of transition metal (Fe) with another transition metal (Cu and Cr) modifies the physical properties and the limitation of substitution content in the NaZn$_{13}$ type structure. The effects of annealing at different temperatures on the structure and magnetic properties of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ were also investigated.

4.1.2 Experimental and Procedures

Samples polycrystalline with the nominal compositions La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ and La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cr$_x$Si$_{1.6}$ (x = 0, 0.06, 0.12, 0.23, 0.34) were prepared by arc melting appropriate amounts of high purity constituent elements under a high purity argon atmosphere in a water-cooled copper crucible. The starting materials were pure elements (≥ 99.9%), and excesses of 10 at. % for La were used to compensate for the weight loss during the arc melting [29]. The ingots were turned over and re-melted several time to ensure their homogeneity. The resulting ingots were wrapped in tantalum foil and sealed under vacuum in a quartz tube, then annealed by the following processes: a La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ sample was annealed at 1323 K for 14 days, while La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ and La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cr$_x$Si$_{1.6}$ samples with x = 0, 0.06, 0.12, 0.23, 0.34 were annealed at 1523 K for 4 hours, respectively, to improve crystallization of the samples. Afterwards, the samples were quenched in water.
Room temperature powder x-ray diffraction (XRD) measurements were performed using Cu Kα1 radiation to identify phase purity. The crystal structures of the samples were checked by room temperature powder XRD with the diffraction patterns refined using the Fullprof software package [30], scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). The vibrating sample magnetometer option of a Quantum Design 14 T physical property measurement system (PPMS) and an MPMS XL magnetic property measurement system (MPMS) were used to determine the magnetic and MCE properties. The crystallographic and magnetic structural behaviors of the set of La$_{0.7}$Pr$_{0.3}$Fe$_{11.06}$Cr$_{0.34}$Si$_{1.6}$ samples were investigated over the temperature range 3-450 K by neutron powder diffraction experiments using the high intensity powder diffractometer Wombat (2.4205(2) Å) at OPAL, and high intensity x-ray diffraction (λ = 0.8265(8) Å) at Australian Synchrotron.

4.1.3 Result and Discussion

4.1.3.1 La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$

It is well accepted that the phase percentage of impurity phases in the NaZn$_{13}$-type compounds is particularly related to the preparation process [25, 26]. Recently systematic study on phase stability of NaZn$_{13}$-type was carried out on the basis of various cross section of the ternary phase diagram [18]. From this point of view, La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ was selected to be prepared by two different annealing treatments to clarify which method is more practical and produces better quality samples. Results from the XRD data (as shown in Figure 4.1) indicate that high temperature annealing (HTA) over a short time can form more NaZn$_{13}$-type phase than low temperature annealing (LTA) over a longer time. LTA produces much more LaFeSi and the α-Fe phase in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$. It is clearly shown in Table 4.1 that
Figure 4.1 Room temperature x-ray diffraction patterns of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Cu$_x$Si$_{1.6}$ (x = 0, 0.06, 0.12) produced by the HTA and LTA processes. Rietveld refinements to the experimental diffraction patterns for x=0 sample by the HTA are shown as a typical example. The lines show the calculated profiles through the experimental data and the residuals. The markers for the crystallographic structures (top for NaZn$_{13}$ phase, middle for α-Fe and bottom for LaFeSi) are indicated.

The LTA process results in smaller amounts of the NaZn$_{13}$ phase through a peritectic reaction. (The results refer to the refined composition). This phenomenon regarding non-equilibrium solidification behaviour is the result of an incomplete peritectic reaction, γ-Fe+L $\rightarrow$ La(Fe, Si)$_{13}(\tau_{1a})$ [17]. This behaviour similar to Niitsu et al. [18] where below 1373 K the NaZn$_{13}$-type phase is difficult to be formed even being annealed after 45 days. When the annealing temperature is higher, the speed of diffusion of atoms is higher during the high temperature and solid phase diffusion reaction process. Thus, on increasing the annealing
temperature to 1523 K and annealing for 4 hours (HTA), the amount of the NaZn$_{13}$ phase gradually increases, eliminating almost all of the LaFeSi phase and decreasing the amount of the α-Fe phase. The Rietveld refinement results are listed in Table 4.1, and it can be clearly seen that the weight fraction of the NaZn$_{13}$ phase increases from 69 % for LTA to 96 %, while the weight fractions of LaFeSi and α-Fe phase for HTA are reduced. Indicated to obtain single NaZn$_{13}$–type phase by a peritectic reaction is quite difficult using conventional melting [18] and substitution of Fe by Cu in NaZn$_{13}$–type phase contribute to change stability of metallic, magnetic and electronic state [19]. The constituents of the NaZn$_{13}$ phase obtained at 1523 K after 4 hours annealing are in agreement with reports from other groups [25, 26].

La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ (x = 0, 0.06, 0.12, 0.23, 0.34) compounds were prepared using HTA at 1523 K for 4 hours. The XRD patterns in Figure 4.1 clearly show that Cu doping contributes to an increased amount of α-Fe and LaFeSi phases in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$. It was been found when the amount of Cu in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ increases, the peak intensities of the α-Fe and LaFeSi phases gradually start to increase. We suggest that this behaviour is related to bulk diffusion rate controlling factor of homogenization in NaZn$_{13}$–type phase by substitution Cu for Fe. From Table 4.1, it can be seen that the weight fraction of the NaZn$_{13}$ phase decreases from 96 % at x = 0 to 85 % at x = 0.34, while the LaFeSi and α-Fe phase fractions in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ increase with the increasing Cu substitution.

In the La-Fe-Si ternary system, the chemical affinity is very strong for La-Si, while it is just moderate for Fe-Si. The enthalpy of mixing for La-Fe is positive, which means no formation of binary La-Fe phase [31]. The introduction of Cu into La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ starts to produce large differences in affinity between the La-Si and the La-Fe pairs, gradually changing the interatomic distances of the pairs, while the structural stability of clusters (domains of NaZn$_{13}$ structure) will be lowered. Recently the study by Fujita et al. [19] shown...
that diffusion is also sensitive to modification of both the electronic structure and lattice spacing which agrees with the fact that Cu atomic radius (1.28 Å) is larger than Fe atomic radius (1.24 Å) in this study. If the amount of replacement of Fe by Cu further increases, it contributes to an increased amount of α-Fe and LaFeSi, making it impossible to form the NaZn$_{13}$ phase structure. This situation is proved by the high magnification SEM image in Figure 4.2, which shows that the percentage of NaZn$_{13}$ phase starts to decrease with increasing Cu content in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_{x}$Si$_{1.6}$. Figure 4.2(b) with the highest Cu concentration shows clearly how the substitution of Cu into the Fe site reduces the weight fraction of NaZn$_{13}$ phase indicating the presence of the limitations of Cu substitution for the structural stability of NaZn$_{13}$ phase.

### Table 4.1 Synthesis conditions (heat treatment process) and results of the structural characterization (phase observed, analysed compositions, lattice parameter of the NaZn$_{13}$, α-Fe, and LaFeSi phases; and atomic distances (Fe1-Fe2 and Fe2-Fe2) of NaZn$_{13}$) from XRD. (Statistical uncertainties are given in parentheses)

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>Heat treatment (T(K)/t)</th>
<th>Phase</th>
<th>Wt%</th>
<th>Refined composition</th>
<th>Lattice parameter, a (Å) for Fe1-Fe2</th>
<th>Atomic Distance (Å) for Fe2-Fe2</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.4}$Si$</em>{1.6}$</td>
<td>1323K/14 days</td>
<td>NaZn$_{13}$, α-Fe, LaFeSi</td>
<td>69.1(1)</td>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{14.1(2)}$Si$</em>{2.1(2)}$</td>
<td>11.4510(3)</td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.4}$Si$</em>{1.6}$</td>
<td>1523K/4 hours</td>
<td>NaZn$_{13}$, α-Fe, LaFeSi</td>
<td>96.1(2)</td>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.6(2)}$Si$</em>{1.6(2)}$</td>
<td>11.4585(5)</td>
<td>2.4508(2)</td>
</tr>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.3}$Cu$</em>{0.06}$Si$_{1.6}$</td>
<td>1523K/4 hours</td>
<td>NaZn$_{13}$, α-Fe, LaFeSi</td>
<td>91.7(2)</td>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.0}$Cu$</em>{0.06}$Si$_{1.6}$</td>
<td>11.4604(3)</td>
<td>2.4512(3)</td>
</tr>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.2}$Cu$</em>{0.12}$Si$_{1.6}$</td>
<td>1523K/4 hours</td>
<td>NaZn$_{13}$, α-Fe, LaFeSi</td>
<td>88.2(2)</td>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.0}$Cu$</em>{0.12}$Si$_{1.6}$</td>
<td>11.4627(4)</td>
<td>2.4517(2)</td>
</tr>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.1}$Cu$</em>{0.23}$Si$_{1.6}$</td>
<td>1523K/4 hours</td>
<td>NaZn$_{13}$, α-Fe, LaFeSi</td>
<td>86.8(1)</td>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.0}$Cu$</em>{0.23}$Si$_{1.6}$</td>
<td>11.4650(4)</td>
<td>2.4521(2)</td>
</tr>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.0}$Cu$</em>{0.34}$Si$_{1.6}$</td>
<td>1523K/4 hours</td>
<td>NaZn$_{13}$, α-Fe, LaFeSi</td>
<td>85.2(8)</td>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.1}$Cu$</em>{0.34}$Si$_{1.71}$</td>
<td>11.4662(4)</td>
<td>2.4525(2)</td>
</tr>
</tbody>
</table>
Figure 4.2 High magnification backscattered SEM images of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ samples: (a) $x = 0$ and (b) $x = 0.34$.

Figure 4.3 shows the temperature dependence of the magnetization of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ for $x = 0$, with preparation by LTA and HTA, and the lowest level of Cu substitution, $x = 0.06$, with preparation by HTA, measured under the low magnetic field of 0.01 T in the temperature range from 100-300 K. The $T_C$ shown in the inset was defined by the minimum of $dM/dT$. $T_C$ of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ produced by the LTA method is 10 K higher than by HTA and has different magnetic phase transition characteristics because of the different Si concentration in the NaZn$_{13}$ phase, which is that the LTA method forms higher Si composition and contributes to increase $T_C$ and changes the nature of transition from first to
Figure 4.3 Temperature dependence of magnetization of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ for $x = 0$ with LTA, and $x = 0$, $x = 0.06$ with HTA, measured in a field of 0.01 T. The inset shows the values of the Curie temperature ($T_C$) for the different samples.

second order characteristic [12]. We assume the LTA treatment interacts to form more α-Fe and LaFeSi phase but decreases NaZn$_{13}$ phase content regarding to temperature and time during annealing process difficulty in solution treatment at low temperature contribute to increase Si composition. In Table 4.1, it is indicated from XRD data refinement that the proportion of Si in the NaZn$_{13}$ phase for LTA is higher than for HTA. In terms of the effects of increasing the Si concentration in NaZn$_{13}$ phase, we assume that this phenomenon contributes to increasing the value of $T_C$ and changes the phase transition behaviour. Similar behaviour has also been reported by Bo Liu et al. [31] where the effects of Cu doping were found to increase the $T_C$ and change the magnetic phase transition from first to second order type. It was accepted that two types of exchange interactions exist between Fe-Fe in the Fe-rich rare earth intermetallic compounds: when the separation of the Fe–Fe pair is smaller than 2.45 Å, the exchange interaction is negative, while the interaction is positive at larger Fe–Fe
Figure 4.4 Curie temperature and lattice parameter for La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ samples as functions of copper concentration.

distances. It was reported [31] that in the La(Fe,Si)$_{13}$ structure, there exist one La site (8$a$ site), two Fe sites Fe1 (8$b$ site) and Fe2 (96$i$ site). It was reported that in the LaFe$_{13-x}$Si$_x$ compounds the La atom (8$a$) has 24 near neighbours of Fe2 (Fe or Si) atoms (96$i$), but no near neighbours of Fe1 atoms (8$b$) while the Fe2 atom has nine near neighbours of Fe2 in addition to two neighbours of La and one neighbour of Fe1. The Fe1 is surrounded by 12 near neighbours of Fe2 (Fe or Si) atoms. The interatomic distances of Fe-Fe between the near neighbours Fe1–Fe2 and Fe2–Fe2 can be directly derived from Wigner–Seitz calculations. For LaFe$_{11.4}$Si$_{1.6}$, it was found that the Fe1–Fe2 atomic distance, is 2.443 Å and the Fe2-Fe2 being about 2.53 Å [31]. Based on the fact that the atomic radius of Cu (1.28 Å) is bigger than that of Fe (1.24 Å), Cu doping will lead to an increase in the lattice parameter and the Fe-Fe distance, which will enhance the positive interactions, thus increasing $T_C$. The composition dependences of $T_C$ and the lattice parameter are shown in Figure 4.4. The Fe1-Fe2 and Fe2-Fe2 distances have been obtained with the BLOKJE program [32] using the
structural and positional parameters and listed in Table 4.1. It can be seen clearly that the substitution of Cu for Fe leads to a monotonic increase in both $T_C$ and lattice parameter resulting in an increment of Fe1-Fe2 and Fe2-Fe2 distance even though the Cu substitution for Fe results in a dilution of magnetic atom (Fe) content.

![Figure 4.5 Magnetization (M) as a function of a magnetic field (H) for La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ samples with $x = 0, 0.06, 0.12, 0.23$ at $T = 10$ K.](image)

Figure 4.5 shows the magnetization versus magnetic field from 0-5 T for La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ ($x = 0, 0.06, 0.12, 0.23$) at 5 K. All the compounds were found to exhibit ferromagnetic behaviour with a magnetization below 24 µB/f.u. at field applied less than 2 T. According to the characteristics of Cu as a diamagnetic element, the replacement of Fe by Cu will reduce the saturation magnetization field in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ compound as clearly shown in Table 4.2. If we assume that the Pr moment contribution does not change with increasing Cu content, the average moment of the Fe can be derived from the total moment. It is found that the replacement of Fe by Cu leads to a decrease in the average moment of the Fe in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$. For the sample with $x = 0.34$, the value of the saturation
Figure 4.6 Isothermal magnetization curves $M(H)$ in the vicinity of $T_C$ for (a) $\text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.4}\text{Si}_{1.6}$ and (b) $\text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.34}\text{Cu}_{0.06}\text{Si}_{1.6}$, both produced by the HTA process. (c) Magnetic hysteresis loss for both at 5 T field applied.
magnetization is higher than expected, which can be ascribed to the contribution from the large amount of α-Fe moment in La$_{0.7}$Pr$_{0.3}$Fe$_{11.06}$Cu$_{0.34}$Si$_{1.6}$.

Table 4.2 Results of the magnetic characterization of HTA La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ (x = 0, 0.06, 0.12, 0.23, 0.34) and of LTA x = 0 compound. The Curie temperature is given for a magnetic field of 0.01 T, order of magnetic transition, the saturation magnetization is given at 10 K, and the magnetic entropy change and the relative cooling power are given for a field of 0-5 T. (Statistical uncertainties are given in parentheses)

<table>
<thead>
<tr>
<th>Refined composition</th>
<th>$T_C$ (K)</th>
<th>Order of Transition</th>
<th>$M_s$ ($\mu_B$/f.u.) at 5K</th>
<th>$\Delta S_M$ (J/kg K) for 5T</th>
<th>RCP (J/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{14.10}$Si$</em>{2.10}$LTA</td>
<td>210</td>
<td>Second</td>
<td>-</td>
<td>7(2)</td>
<td>220(1)</td>
</tr>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.0}$Si$</em>{1.60}$HTA</td>
<td>197</td>
<td>First</td>
<td>22.8(3)</td>
<td>17(2)</td>
<td>400(2)</td>
</tr>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.03}$Cu$</em>{0.06}$Si$_{1.62}$HTA</td>
<td>210</td>
<td>Second</td>
<td>22(2)</td>
<td>12(1)</td>
<td>330(2)</td>
</tr>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.05}$Cu$</em>{0.12}$Si$_{1.67}$HTA</td>
<td>218</td>
<td>Second</td>
<td>21.6(2)</td>
<td>9(2)</td>
<td>300(1)</td>
</tr>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.08}$Cu$</em>{0.22}$Si$_{1.68}$HTA</td>
<td>224</td>
<td>Second</td>
<td>21(1)</td>
<td>7(2)</td>
<td>280(1)</td>
</tr>
<tr>
<td>La$<em>{0.7}$Pr$</em>{0.3}$Fe$<em>{11.12}$Cu$</em>{0.34}$Si$_{1.71}$HTA</td>
<td>230</td>
<td>Second</td>
<td>21.4(2)</td>
<td>5(1)</td>
<td>245(2)</td>
</tr>
</tbody>
</table>

The corresponding Arrott plots ($M^2$ versus B/M) are drawn in Figure 4.7. It was well accepted that the positive slopes in the isotherm Arrott plots indicate the second-order nature of the phase transition around $T_C$ while negative aslope for first order transition according to I-S model [26]. It can be seen from Figure 4.7 that the replacement of Fe by Cu in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ has changed the slope from negative to positive and reduced the characteristics of the IEM transition above $T_C$ [12] (summary in Table 4.2).

Magnetic entropy change, $\Delta S_M$, is defined from the magnetization curve by the Maxwell relation [33, 34]:

$$\Delta S_M(T, H) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH \quad (4.1)$$

The values of $\Delta S_M$ around $T_C$ have been derived from the magnetic data and are shown in Figure 4.8 (a) as a function of temperature with a 0-5 T change in field for La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$. 

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Figure 4.7 Arrott plots for La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ (x = 0 and 0.06) compounds.

$\chi_{Cu_xSi_{1.6}}$ (x = 0, 0.06, 0.34) for HTA and (x = 0) for LTA compounds. It can be seen clearly that the $-\Delta S_M$ peak gradually becomes broader at higher temperature with increasing magnetic field from 1 to 5 T, which is a characteristic of the field induced IEM transition from the paramagnetic to the ferromagnetic state at temperatures above $T_C$. This is clearly evident for the HTA compound with x = 0 in Figure 4.8 (b). The value of $-\Delta S_M$ for the LTA x = 0 compound is very small, around 7 J/kgK compared to 17 J/kgK for the HTA x = 0 sample,
Figure 4.8 Magnetic entropy change, $-\Delta S_M$, (a) for a 0-5 T change in field of $\text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.4-x}\text{Cu}_x\text{Si}_{1.6}$ ($x = 0, 0.06, 0.34$) for HTA and $x = 0$ for LTA compounds and (b) from 0 to 1, 2, 3, 4 and 5 T change in field of $\text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.4}\text{Si}_{1.6}$ compound for HTA as a function of temperature.

which is larger than that observed in Gd (10.2 J/kgK). We ascribe this effect to the lower percentage of the NaZn$_{13}$ type phase in the LTA sample with $x = 0$. Moreover, it has been
found that the replacement of Fe by Cu decreases $-\Delta S_M$ from 12 J/kgK for $x = 0.06$ to 5 J/kgK for $x = 0.34$.

The relative cooling power (RCP) is a very important aspect of the MCE, and it is directly related to the magnetic refrigerator application. Using the maximum of the entropy variation $-\Delta S_M^{\text{max}}$ and the full width at half maximum of the peak in the temperature dependence of the magnetic entropy change $-\Delta S_M$, one can derive the value of RCP as defined by the following formula [22, 35]:

$$\text{RCP} = -\Delta S_M^{\text{max}} \delta T_{\text{FWHM}}$$

(4.2)

A summary of RCP values and other magnetic characterization parameters for HTA $\text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.4-x}\text{Cu}_x\text{Si}_{1.6}$ ($x = 0, 0.06, 0.12, 0.23, 0.34$) and LTA $x = 0$ compounds are listed in Table 4.2. It can be seen that the HTA process yields a significant improvement in sample quality compared to LTA, considering the superior values of $-\Delta S_M$ and RCP. However, the value of the saturation magnetization was reduced by increasing the Cu content. This lead to a decrease in the magnetic entropy change when the concentration of Cu increases from $x = 0$ to $x = 0.34$. The RCP shows the same behaviour with MCE, even though an increase in Cu content changes the type of magnetic phase transition from first order to second order and increases the temperature span. It was found that the RCP decreases from 400 J/kg for $x = 0$ to 245 J/kg for $x = 0.34$ on application of a 0 to 5 Tesla magnetic field change.
4.1.3.2 \( \text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.4-x}\text{Cr}_x\text{Si}_{1.6} \)

The room temperature diffraction analysis in Table 4.3 shown that the Cr substitution first contributes to an increase the amount of \( \alpha\)-Fe and LaFeSi phases from beginning to \( x=0.06 \) then decrease until \( x=0.34 \) in \( \text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.4-x}\text{Cr}_x\text{Si}_{1.6} \) compounds. We suggest this behavior may be related to bulk diffusion rate controlling factor of homogenization in cubic \( \text{NaZn}_{13} \)-type phase structure (space group \( Fm\overline{3}c \)) by substitution Cr for Fe. From Table 4.3, it can be seen that the weight fraction of the \( \text{NaZn}_{13} \) structure decreases from 96 % at \( x = 0 \) to 85 % at \( x = 0.06 \) then increase to 97 % with increasing Cr content till \( x=0.34 \).

**Table 4.3** Results of the structural characterization (type and weight of phase observed, lattice parameter of the \( \text{NaZn}_{13} \), \( \alpha\)-Fe, and LaFeSi phases; and atomic distances (Fe1-Fe2 and Fe2-Fe2) of \( \text{NaZn}_{13} \)) from room temperature x-ray diffraction analysis and Curie temperature, \( T_C \) for \( \text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.4-x}\text{Cr}_x\text{Si}_{1.6} \) compounds.

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>Phase</th>
<th>Wt%</th>
<th>Lattice parameter, ( a (\text{Å}) )</th>
<th>Atomic Distance (Å) for Fe1-Fe2</th>
<th>Fe2-Fe2</th>
<th>( T_C ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}<em>{0.7}\text{Pr}</em>{0.3}\text{Fe}<em>{11.4}\text{Si}</em>{1.6} )</td>
<td>( \text{NaZn}_{13} )</td>
<td>96.1(2)</td>
<td>11.4585(5)</td>
<td>2.4508(2)</td>
<td>2.5522(3)</td>
<td>197</td>
</tr>
<tr>
<td></td>
<td>( \alpha)-Fe</td>
<td>3.5(6)</td>
<td>11.4585(5)</td>
<td>2.4508(2)</td>
<td>2.5522(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LaFeSi</td>
<td>0.4(5)</td>
<td>11.4585(5)</td>
<td>2.4508(2)</td>
<td>2.5522(3)</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.7}\text{Pr}</em>{0.3}\text{Fe}<em>{11.34}\text{Cr}</em>{0.06}\text{Si}_{1.6} )</td>
<td>( \text{NaZn}_{13} )</td>
<td>85.9(1)</td>
<td>11.4556(4)</td>
<td>2.4506(3)</td>
<td>2.5521(2)</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>( \alpha)-Fe</td>
<td>10.6(6)</td>
<td>11.4556(4)</td>
<td>2.4506(3)</td>
<td>2.5521(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LaFeSi</td>
<td>3.5(3)</td>
<td>11.4556(4)</td>
<td>2.4506(3)</td>
<td>2.5521(2)</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.7}\text{Pr}</em>{0.3}\text{Fe}<em>{11.28}\text{Cr}</em>{0.12}\text{Si}_{1.6} )</td>
<td>( \text{NaZn}_{13} )</td>
<td>92.6(1)</td>
<td>11.4540(3)</td>
<td>2.4505(4)</td>
<td>2.5517(2)</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>( \alpha)-Fe</td>
<td>6.0(3)</td>
<td>11.4540(3)</td>
<td>2.4505(4)</td>
<td>2.5517(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LaFeSi</td>
<td>1.4(6)</td>
<td>11.4540(3)</td>
<td>2.4505(4)</td>
<td>2.5517(2)</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.7}\text{Pr}</em>{0.3}\text{Fe}<em>{11.17}\text{Cr}</em>{0.23}\text{Si}_{1.6} )</td>
<td>( \text{NaZn}_{13} )</td>
<td>94.0(1)</td>
<td>11.4524(3)</td>
<td>2.4501(3)</td>
<td>2.5515(2)</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>( \alpha)-Fe</td>
<td>4.7(6)</td>
<td>11.4524(3)</td>
<td>2.4501(3)</td>
<td>2.5515(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LaFeSi</td>
<td>1.3(2)</td>
<td>11.4524(3)</td>
<td>2.4501(3)</td>
<td>2.5515(2)</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.7}\text{Pr}</em>{0.3}\text{Fe}<em>{11.06}\text{Cr}</em>{0.34}\text{Si}_{1.6} )</td>
<td>( \text{NaZn}_{13} )</td>
<td>97.6(6)</td>
<td>11.4518(2)</td>
<td>2.4996(3)</td>
<td>2.5511(1)</td>
<td>195</td>
</tr>
<tr>
<td></td>
<td>( \alpha)-Fe</td>
<td>2.3(3)</td>
<td>11.4518(2)</td>
<td>2.4996(3)</td>
<td>2.5511(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LaFeSi</td>
<td>0.2(4)</td>
<td>11.4518(2)</td>
<td>2.4996(3)</td>
<td>2.5511(1)</td>
<td></td>
</tr>
</tbody>
</table>

As mentioned by Liu Xu et al.,[31] in the La-Fe-Si ternary system, the chemical affinity is very strong for La-Si, while it is just moderate for Fe-Si. The enthalpy of mixing for La-Fe is
positive, which means no formation of binary La-Fe phase. The introduction of Cr into La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cr$_x$Si$_{1.6}$ starts to produce large differences in affinity between the La-Si and the La-Fe pairs, gradually changing the interatomic distances of the pairs, while the structural stability of clusters (domains of NaZn$_{13}$ structure) will be lowered. That diffusion also sensitive to modification of both the electronic structure and lattice spacing [19] agree with phenomena of lattice parameter $a$, which decreases from 11.458(3) Å at $x=0$ to 11.451(5) Å at $x=0.34$ even Cr atomic radius (1.3 Å) is larger than Fe atomic radius (1.26 Å) and different electronic environment (Fe ~ $3d^64s^2$ and Cr ~ $3d^54s^1$) in this study. This situation is proved by the high magnification SEM image in Figure 4.9(a) and (b), which shows that the percentage of NaZn$_{13}$ phase for $x=0.34$ are higher than $x=0.06$ presence of the advantage in increasing Cr concentration. In order to justify if the Cr entered in the NaZn$_{13}$ phase structure, EDS analysis has been performed and proved that Cr exists in the NaZn$_{13}$ phase structure as expected by using comparison for $x=0$ and highest Cr concentration $x=0.34$.

![Figure 4.9](image)

**Figure 4.9** High magnification backscattered SEM images of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cr$_x$Si$_{1.6}$ samples: (a) $x = 0.34$ and (b) $x = 0.06$.

The temperature dependence of the magnetization of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cr$_x$Si$_{1.6}$ compound is measured under the low magnetic field of 0.01 T. The $T_C$ shown in Table 4.3 was defined by
the minimum of \( dM/dT \). \( T_C \) was found to decrease first from 197 K at \( x=0 \) to 180 K at \( x=0.06 \) but start to increase to 185 K at \( x=0.12 \) until 195 K at higher Cr concentration \( x=0.34 \). We assume more presence of \( \alpha \)-Fe and LaFeSi phase at lower Cr concentration is responsible for the variation in value of \( T_C \) as both of these phases are impurity. However, both of these phases are not critical to the nature of magnetic phase transition as we found that the first order phase transition behaviour did not change compared to other study [36]. The variation of the \( T_C \) values with the Cr content in these compounds happen accordingly to two types of exchange interactions exist between Fe-Fe in the Fe-rich rare earth intermetallic compounds: when the separation of the Fe–Fe pair is smaller than 2.45 Å, the exchange interaction is negative, while the interaction is positive at larger Fe–Fe distances. The Fe1-Fe2 and Fe2-Fe2 distances have been obtained with the BLOKJE program [32] using the structural and positional parameters and listed in Table 4.3. It can be seen clearly that the substitution of Cr for Fe leads to a decrease lattice parameter \( a \), resulting in an decrement of Fe1-Fe2 and Fe2-Fe2 distance as confirmed the replacement Fe by Cr results in a dilution of magnetic atom (Fe) content.

Magnetization curves as a function of magnetic field up to 5 T for La\(_{0.7}\)Pr\(_{0.3}\)Fe\(_{11.4-x}\)Cr\(_x\)Si\(_{1.6}\) (\( x = 0 \) and 0.34) have been measured under increasing and decreasing field at various temperatures and are shown in Figure 4.10 (a) and (b). The measurements were performed over a wide range of temperature around \( T_C \). Magnetic hysteresis is one characteristic of the first order magnetic transition, which is defined as the enclosed area between the ascending and descending branches of the magnetization curve. It can be seen that the M-B curves exhibit almost no magnetic hysteresis for \( x = 0.34 \) which is found same of the characteristic at \( x = 0 \). Furthermore it indicates that the field induced first order transition from
paramagnetic to ferromagnetic notably slightly increases by the introduction of Cr. The advantage of the sample with higher itinerant-electron metamagnetic (IEM) transition will contribute to enhance the value of magnetic entropy change. The corresponding Arrott plots ($M^2$ versus $B/M$) are drawn in Figure 4.10 (c) depicted the negative slopes in the isotherm Arrott plots indicate the first-order nature of the phase transition around $T_C$ according to I-S model for highest concentration $x=0.34$ [12, 26]. It has been reconfirmed that the first order nature consistent by others method (heat capacity measurement those that involve a latent heat) as shown in Figure 4.10 (d) and mixed peaks appear around $T_C$ indicating the

**Figure 4.10** Isothermal magnetization curves in the vicinity of the ferromagnetic ordering temperatures for: (a) La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ and (b) La$_{0.7}$Pr$_{0.3}$Fe$_{11.06}$Cr$_{0.34}$Si$_{1.6}$; (c) Arrott plots of $M^2$ versus $B/M$ and (d) heat capacity measurement for the set of La$_{0.7}$Pr$_{0.3}$Fe$_{11.06}$Cr$_{0.34}$Si$_{1.6}$.
coexistence of phases across magnetic transition defined by high intensity x-ray diffraction as will discuss later.

In order to satisfy the suitability of different experimental and related analytical approaches to establish the isothermal entropy change, $-\Delta S_M$, is defined from the magnetization curve by the Maxwell relation in equation 4.1 [33, 34]. The values of $-\Delta S_M$ around $T_C$ have been derived from the magnetic data and are shown in Figure 4.11 (a) as a function of temperature with a 0-5 T change in field for La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cr$_x$Si$_{1.6}$ ($x = 0, 0.06, 0.12, 0.23$ and $0.34$) compounds. $-\Delta S_M$ found to decrease from $17$ J kg$^{-1}$ K$^{-1}$ at $x=0$ to $12$ J kg$^{-1}$ K$^{-1}$ at $x=0.06$ then begin to increase to $14.2$ J kg$^{-1}$ K$^{-1}$ at $x=0.12$ until reach $17.5$ J kg$^{-1}$ K$^{-1}$ at $x=0.34$ which is larger than Gd ($10.2$ J kg$^{-1}$ K$^{-1}$). It can be seen clearly that the $-\Delta S_M$ peak gradually becomes broader at higher temperature with increasing magnetic field from 2 to 5 T, which is a characteristic of the field induced IEM transition from the paramagnetic to the ferromagnetic state at temperatures above $T_C$ as shown for $x = 0.34$ in Figure 4.11 (b) and agree well with the $-\Delta S_M$ values which are determined from heat capacity measurement. The peak value of the adiabatic temperature change is derived to be $\Delta T^{\text{max}}_{ad} = 8.4$ K for $\Delta B = 0-5$ T and $5.5$ K for $\Delta B = 0-2$ T as can be evaluated from $-\Delta S_M(T, B)$ and the heat capacity data as:

$$\Delta T_{ad}(T, B) = \int_0^B \frac{T}{c_{B,P}} \left( \frac{\partial M}{\partial T} \right)_B dB$$  \hspace{1cm} (4.3)$$

The relative cooling power (RCP) is directly related to the magnetic refrigerator application. Using the maximum of the entropy variation $-\Delta S^{\text{max}}_M$ and the full width at half maximum of the peak in the temperature dependence of the magnetic entropy change $-\Delta S_M$, one can derive the value of RCP as defined by the equation 4.2 [22, 35]. It can be seen at Figure 4.11 (a) that the RCP values increase from $365$ J kg$^{-1}$ at $x=0.06$; $372$ J kg$^{-1}$ at $x=0.12$; $384$ J kg$^{-1}$ at $x=0.23$ and $420$ J kg$^{-1}$ at $x=0.34$ under 0-5 T field applied. The RCP value at $x=0.34$ is slightly
higher than parent compound as indicated the promising material of La$_{0.7}$Pr$_{0.3}$Fe$_{11.06}$Cr$_{0.34}$Si$_{1.6}$ compound.

Figure 4.11 (a) The relative cooling power, RCP and the temperature dependence of the isothermal magnetic entropy change, -$\Delta S_M$, for La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cr$_x$Si$_{1.6}$ compounds with $x = 0$, 0.06, 0.12, 0.23 and 0.34 as measured from magnetization isotherms ($\Delta B = 0$-5 T from decreasing field curves). (b) The magnetic entropy change, -$\Delta S_M$, determined from magnetization and the heat capacity measurements for La$_{0.7}$Pr$_{0.3}$Fe$_{11.06}$Cr$_{0.34}$Si$_{1.6}$ ($\Delta B = 0$-5 and 0-2 T). (c) The adiabatic temperature change, $\Delta T_{ad}$, for La$_{0.7}$Pr$_{0.3}$Fe$_{11.06}$Cr$_{0.34}$Si$_{1.6}$ as determined from the heat capacity measurements.

The high intensity of neutron and x-ray diffraction over 10-300 K has been studied for La$_{0.7}$Pr$_{0.3}$Fe$_{11.06}$Cr$_{0.34}$Si$_{1.6}$ compound in order to investigate the magneto-volume effect producing large magnetic entropy change, MCE. Neutron diffraction patterns indicated the shift of the peaks position to higher angle around $T_C$ confirm the contraction of unit cell volume as shown in Figure 4.12 (a) and agree well with the x-ray diffraction analysis in Figure 4.12 (b) together with coexistence of two phases (paramagnetic and ferromagnetic phases) across magnetic transition as indicator for first order magnetic behaviour. The
Figure 4.12 (a) Neutron diffraction patterns for La$_{0.7}$Pr$_{0.3}$Fe$_{11.06}$Cr$_{0.34}$Si$_{1.6}$ over temperature range 10-250 K (wavelength $\lambda = 2.4205(2)$ Å) respectively. (b) High intensity x-ray diffraction pattern at selected temperature range 170-300 K (wavelength $\lambda = 0.866(1)$ Å). The coexistence peaks appear as shown by arrow; (c) The lattice parameters change around $T_C$ of La$_{0.7}$Pr$_{0.3}$Fe$_{11.06}$Cr$_{0.34}$Si$_{1.6}$ compound as a function of temperature.

Variation in decrease of the lattice parameter, $a$ has been found from 11.5148(3) Å at 170 K to 11.4608(2) Å at 200 K as depict in Figure 4.12 (c). The changes in lattice parameter at $T_C$
~ 195 K according to magnetic state changes from ferromagnetic to paramagnetic structure [37], indicates the presence of strong magneto-volume behaviour as contribute to the increase of the total of entropy change around T_C. It been found that around \( -\Delta S_{\text{structural}} \approx 3.15 \text{ J kg}^{-1} \text{ K}^{-1} \) is estimated using the method from Gschneidner et al. [38] under \( \Delta B = 0-5 \text{ T} \).

4.1.4 Conclusion

A systematic investigation of the structural and magnetic characterization of La\(_{0.7}\)Pr\(_{0.3}\)Fe\(_{11.4}\)-\(x\)Cu\(_x\)Si\(_{1.6}\) (\(x = 0, 0.06, 0.12, 0.23, 0.34\)) for HTA and \(x = 0\) for LTA samples has been carried out. The results show that the HTA process resolves the problem of non-equilibrium solidification behaviour due to the incomplete peritectic reaction \(\gamma\)-Fe+L → La(Fe,Si)\(_{13}\)(\(\tau_{1a}\)) that occurs in the LTA process. The HTA sample with \(x = 0\) shows promising values of \( -\Delta S_M \) and RCP with very small hysteresis loss. This indicates the elevated temperature in HTA plays an important role to form the NaZn\(_{13}\) type structure in the La\(_{0.7}\)Pr\(_{0.3}\)Fe\(_{11.4}\)Si\(_{1.6}\) compound. However, the substitution of Cu for Fe leads to a decrease in the magnetic entropy change and eliminates hysteresis loss. Increasing the Cu concentration (starting from \(x = 0.06\)) also results in a change in the magnetic phase transition type from first to second order and reduces the characteristics of the IEM transition. The Curie temperature, \(T_C\), increases with increasing Cu content, which can be ascribed to the increase in the lattice parameter and the modification of the composition. The compound with a small amount of Cu substitution shows a promising magnetic performance for magnetic refrigerator application, with no hysteresis loss and reasonable RCP.

Substitution of Cr for Fe La\(_{0.7}\)Pr\(_{0.3}\)Fe\(_{11.4-x}\)Cr\(_x\)Si\(_{1.6}\) compounds leads to decreases in lattice parameter but variation behaviour on temperature transition, \(T_C\). The variation in the value of
$T_C$ with increasing Cr concentration can be understood in terms of sensitive changes of Fe1-Fe2 and Fe2-Fe2 distances. Analysis of the magnetisation data demonstrates that the order of magnetic phase transition around $T_C$ is consistent on first order type even $x=0.34$ for $\text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.4-x}\text{Cr}_x\text{Si}_{1.6}$ compounds. Replacement of Fe by Cr leads to a reduction of the magnetic entropy change from beginning at $x=0$; $(-\Delta S_M = 17 \text{ J kg}^{-1} \text{ K}^{-1})$ to $x=0.06$; $(-\Delta S_M = 12 \text{ J kg}^{-1} \text{ K}^{-1})$, however starts to enhance again when keep increasing Cr concentration until $x=0.34$; $(-\Delta S_M = 17.5 \text{ J kg}^{-1} \text{ K}^{-1})$. High intensity Neutron and X-ray diffraction studies demonstrate that $\text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.06}\text{Cr}_{0.34}\text{Si}_{1.6}$ compound has contraction in unit cell from ferromagnetic to paramagnetic structure which contributes to produce high magnetic entropy change. However this investigation is still incomplete as it will be the platform for us to further study, particularly further increase Cr concentration in this compound in order to confirm the ultimate of the beneficial in Cr substitution.

References


Chapter 5

STRUCTURAL, MAGNETIC PHASE TRANSITION AND ENTROPY CHANGE ON $RT_2X_2$ COMPOUND ($R=$RARE EARTH), ($T=$TRANSITION METAL) AND ($X=$METALLIOD)

5.1 Substitution Mn with Others Transition Metal in NdMn$_2$Si$_2$ Compound

Magnetic materials with first order magnetic transition (FOMT) are found to exhibit large magnetocaloric effect (MCE) compared to second order magnetic transition (SOMT) [1-4]. Among them, the tetragonal intermetallic compounds RMn$_2$X$_2$ ($R=$rare earth; $T=$transition metal and $X=$Si or Ge) attract special attention mainly in interesting interplay between 3$d$ and 4$f$ magnetism and present wide range of magnetic behaviour [5-7]. For example, NdMn$_2$Si$_2$ compound provides the promising prospect for enhanced magnetocaloric effect because of the crystal structure nature in layered allows to control of the intrinsic magnetism via inter and intra planar separations of the Mn atoms with Nd atoms performing the large magnetization due to ferromagnetic coupling between the Mn and Nd sublattices below the Nd ordering temperature [8].

5.1.1 Introduction

Application of the magnetocaloric effect (MCE) for magnetic refrigeration offers advantages that are well known, with increasing prospects as the basis of magnetic cooling to replace conventional refrigeration systems over appropriate temperature regions [9-11]. Given these
promising developments, magnetic materials which exhibit a large magnetocaloric effect have been studied, both experimentally and theoretically, over the past two decades [12, 13]. A number of materials which exhibit giant magnetic entropy changes at magnetic transitions have been investigated, including \( \text{Gd}_{5}\text{Si}_{2}\text{Ge}_{2} \) [14], \((\text{Mn, Fe})_{2}(\text{P, Ge}) \) [15], \( \text{MnAs}_{1-x}\text{Sb}_{x} \) [16], and \( \text{La(Fe, Si)}_{13} \) [17]. All of these materials undergo a first-order magnetic phase transition which, given the rapid change in magnetisation, enhances the scope for a large MCE. However such behaviour is often accompanied by hysteresis. For example, \( \text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.4}\text{Si}_{1.6} \) exhibits thermal hysteresis \( \sim 1.9 \) K and magnetic hysteresis \( \sim 0.2 \) T around \( T_c \sim 188 \) K [17]. The presence of a hysteresis effect in a material will lead to a decrease in efficiency of the energy performance during cooling and heating processes and therefore limit its use in practical applications. As such the search for suitable materials that show both a large MCE and are free from hysteresis continues.

The ternary intermetallic compounds of the \( \text{RT}_2\text{X}_2 \) series (\( R = \text{rare earth}, T = \text{transition metal}, X = \text{Si or Ge} \)) have attracted considerable attention because of the rich variety of interesting phenomena, including superconductivity, magnetism, mixed valence, heavy fermions, and Kondo behaviour [18, 19]. \( \text{RT}_2\text{X}_2 \) compounds form mainly in the \( \text{ThCr}_2\text{Si}_2 \) structure (space group \( I4/mmm \)), with the layered nature of this crystal structure leading to strong dependence of the magnetic interactions on the interplanar and intraplanar interatomic distances [20]. From this point of view, \( \text{RMn}_2\text{X}_2 \) compounds with \( X = \text{Si or Ge} \) have attracted special attention, due mainly to the interesting interplay between the magnetism of the layers of \( 3d \) and \( 4f \) atoms and the strong dependence of the magnitude of the Mn moment and the magnetic state of the Mn sublattice on the Mn-Mn interatomic distances [2, 3, 5, 19, 21-23]. As a general guide, for intraplanar distance, \( d_{\text{Mn-Mn}} \) below \( \sim 2.87 \) Å, the coupling between Mn layers is antiferromagnetic while above this value, the coupling is ferromagnetic [24-26].
NdMn$_2$Si$_2$, below $T_N \sim 380$ K the Mn sublattice orders antiferromagnetically, while below $T_C \sim 36$ K the compound is ferromagnetic with ordered moments at both the Nd and the Mn sublattices [8, 27]. These magnetic behaviours with different temperature dependences reflect different types of exchange interactions with different mechanisms with both the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction via conduction electrons, and super exchange between magnetic atoms via the Si or Ge atoms contributing. Generally, the exchange interactions in RMn$_2$X$_2$ compounds can be divided into four classes: Mn–Mn within the Mn layers, Mn–Mn between the Mn layers, and Mn–R and R–R interactions [28].

Here, the section presents a detailed investigation of the influence of replacing Mn atoms by others transition metal (Ti, Cr, Cu and V) atoms on the magnetic structure and magnetic phase transition in NdMn$_2$Si$_2$ compound. The main interest is to explore the effects of replacing Mn atoms of atomic radius $r$ (Mn) = 1.35 Å and electronic configuration Mn $(3d^54s^2)$ with different others transition metal atoms of atomic radius and electron configuration. In the case of NdMn$_{2-x}$Co$_x$Si$_2$ [29] for example, replacement of Mn by the smaller Co atoms, $r$(Co) = 1.25 Å of electronic configuration Co $(3d^74s^2)$, leads to a decrease in magnetic entropy change from $\sim$ 14.4 J kg$^{-1}$ K$^{-1}$ with $x=0.2$ to 12.4 J kg$^{-1}$ K$^{-1}$ with $x=0.4$ ($\Delta B = 0$- 5 T) but the Curie temperature $T_C \sim 45$ K does not change with increasing Co concentration for NdMn$_{2-x}$Co$_x$Si$_2$ ($x=0.2$, 0.4, 0.8 and 1). In this study, investigation on the effects of others transition metal substitution for Mn in NdMn$_2$Si$_2$ compound on the structural and magnetic properties. Given that others transition metal atoms are significantly different with Mn atoms ($r$(Mn) = 1.35 Å), replacement of Mn by others transition metal in NdMn$_2$Si$_2$ compound is expected to increase or decrease the distance between magnetic atoms, thus modifying the magnetic states of both the Nd and the Mn sublattices.
5.1.2 Experimental and Procedures

Polycrystalline samples with nominal compositions NdMn$_{2-x}$T$_x$Si$_2$ (T = Ti, Cr, Cu and V) were prepared by the arc melting of appropriate amounts of high purity constituent elements under a high purity argon atmosphere in a water-cooled copper crucible. The starting materials were pure elements (≥ 99.9%), and an excess of 3 at. % Mn was used to compensate for the loss during the arc melting and annealing processes. The ingots were turned over and re-melted several times to ensure homogeneity. The resulting ingots were wrapped in Ta foil and sealed under vacuum in a quartz tube, annealed at 900°C for 7 days to improve crystallization of the samples [6], and then quenched into water. The crystal structure of the samples were checked by room temperature powder x-ray diffraction (XRD) measurements using CuK$_\alpha 1$ radiation with the diffraction patterns refined using the Fullprof software package [30]. The magnetic properties were investigated over the temperature 10-300 K using the vibrating sample magnetometer option of a Quantum Design 14 T physical properties measurement system (PPMS) and an MPMS XL magnetic properties measurement system. Differential scanning calorimetry (DSC) measurements were carried out using a TA instrument DSC-Q100 over the range 300-450 K to check for possible phase transitions in the higher temperature range and investigate thermal hysteresis changes at the magnetic transitions. The crystallographic and magnetic structural behaviors of the set of NdMn$_{2-x}$T$_x$Si$_2$ samples were investigated over the temperature range 3-450 K by powder neutron diffraction experiments using the high resolution powder diffractometer Echidna (wavelength $\lambda = 1.622(1)$ Å) and high intensity powder diffractometer Wombat (wavelength $\lambda = 2.4205$ Å; 6-400 K) at the Open Pool Australian Light Water Reactor (OPAL), Lucas Heights, Australia.
5.1.3 Result and Discussion

5.1.3.1 NdMn$_{2-x}$Ti$_x$Si$_2$

Confirmation that all of the NdMn$_{2-x}$Ti$_x$Si$_2$ (x = 0, 0.1, 0.2, 0.3) samples crystallize in the expected ThCr$_2$Si$_2$ type structure with space group I4/mmm [31] was provided by analysis of the x-ray powder diffraction patterns. NdMn$_{2-x}$Ti$_x$Si$_2$ compounds have Nd atoms in the 2a site (0, 0, 0), while Ti and Mn share the position at the 4d site (0, $1/2$, $1/4$), and Si atoms occupy the 4e site (0, 0, z). The measured data from the diffraction patterns were analysed using the Rietveld refinement technique [30], and the distances between neighbouring atoms (Tables 5.1 and 5.3) have been obtained with the BLOKJE program [32], using the structural and positional parameters. Compared with pure NdMn$_2$Si$_2$ [22, 28], substitution of Ti for Mn does not change the crystal structure but leads to an expansion of the unit cell. The lattice constants $a$ and $c$, and correspondingly the unit cell volumes, were found to increase with the Ti content consistent with the larger atomic radius of Ti compared to Mn. As shown in Table 5.1, $d_{\text{Mn-Mn}}$ increases from 2.8312(6) Å for x=0 to 2.8341(6) Å for x=0.3. However $d_{\text{Mn-Mn}}$ remains below $d_{\text{Mn-Mn}}^{\text{crit}} = 2.87$ Å for all compositions. The geometric influence due to the size difference of Ti and Mn can be understood in the term of chemical pressure using the Murnaghan equation of state (see e.g. the case of PrMn$_{2-x}$Fe$_x$Ge$_2$ compounds [6]):

$$p = \left( \frac{B_0}{B_0'} \right) \left[ \left( \frac{V}{V_0} \right)^{-B_0} - 1 \right]$$  \hspace{1cm} (5.1)

where $B_0$ is the isothermal bulk modulus, $B_0'$ is its pressure derivative, and $V_0$ and $V$ are the volume at ambient pressure and pressure $p$, respectively. Using the values of $B_0 = 867$ kbar, $B_0' = 5.1$ for CeNi$_2$Ge$_2$ [33], the corresponding pressure can derived to be -3.35 kbar, -5.3
kbar and -6.05 kbar for the NdMn$_{2-x}$Ti$_x$Si$_2$ samples ($x=0.1$, 0.2 and 0.3) respectively. As discussed below these changes in $d_{\text{Mn-Mn}}$ distances influence the magnetic properties.

Table 5.1 Lattice parameters, unit cell volume, and intralayer Mn-Mn distance of the NdMn$_{2-x}$Ti$_x$Si$_2$ compounds with $x=0$, 0.1, 0.2 and 0.3 as determined from refinement of the room temperature x-ray diffraction patterns. The errors are shown for NdMn$_2$Si$_2$ as a typical example.

<table>
<thead>
<tr>
<th>NdMn$_{2-x}$Ti$_x$Si$_2$</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
<th>c/a</th>
<th>$d_{\text{Mn-Mn}}$ (Å)</th>
<th>$d_{\text{Mn-Nd}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0</td>
<td>4.0039(5)</td>
<td>10.5251(6)</td>
<td>168.73(4)</td>
<td>2.6287(3)</td>
<td>2.8312(6)</td>
<td>3.3063(6)</td>
</tr>
<tr>
<td>x=0.1</td>
<td>4.0067</td>
<td>10.5515</td>
<td>169.39</td>
<td>2.6335</td>
<td>2.8332</td>
<td>3.3124</td>
</tr>
<tr>
<td>x=0.2</td>
<td>4.0073</td>
<td>10.5743</td>
<td>169.81</td>
<td>2.6388</td>
<td>2.8336</td>
<td>3.3171</td>
</tr>
<tr>
<td>x=0.3</td>
<td>4.008</td>
<td>10.5779</td>
<td>169.92</td>
<td>2.6392</td>
<td>2.8341</td>
<td>3.318</td>
</tr>
</tbody>
</table>

The temperature dependence of the magnetization of NdMn$_{2-x}$Ti$_x$Si$_2$ ($x=0$, 0.1, 0.2, 0.3) measured in a magnetic field of $B=0.01$ T over the temperature range $\sim 10$-300 K is shown in Figure 5.1 together with the differential scanning calorimetry (DSC) curves over the temperature range $\sim 300$-450 K. The inset shows the values of the Néel temperature $T_N$ and the Curie temperature $T_C$, for the set of compounds as defined by $1/M$ versus temperature and the maxima of the $dM/dT$ versus temperature graphs respectively. For the DSC measurements, the phase transition temperatures were determined by the maxima of the DSC signals (see figure 5.1). Comparison of results obtained under otherwise identical conditions for cooling and warming revealed almost no thermal hysteresis across all compositions ($\Delta T = 0.3$ K at $x=0$ and $\Delta T = 0$ K at $x = 0.1$, 0.2 and 0.3). Inspection of the insert to Figure 5.1, reveals that $T_N$ decreases from $\sim 380$ K to $\sim 360$ K with increase in Ti concentration from $x=0$ to $x = 0.3$ while $T_C$ decreases from $\sim 36$ K to $\sim 14$ K. As shown in Table 5.1 $d_{\text{Mn-Mn}}$ and $d_{\text{Mn-Nd}}$ are found to increase from $d_{\text{Mn-Mn}} = 2.8312(6)$ Å, $d_{\text{Mn-Nd}} = 3.3063(6)$ Å at $x = 0$ to $d_{\text{Mn-Mn}} = 2.8341(6)$ Å, $d_{\text{Mn-Nd}} = 3.3180(6)$ Å at $x = 0.3$ and this expansion (size effect) will lead to enhancement of the Mn-Mn intralayer exchange interaction. On the other hand, increased Ti
Concentration is also expected to weaken the exchange interactions of Mn-Mn between layers and the Mn-Nd due to the magnetic dilution effect. Moreover, the change in electronic environment on replacing Mn (3d54s2) by Ti (3d24s2) is also expected to influence the magnetic structures and states of the NdMn2-xTi xSi2 compounds. This is supported by Density Functional Theory calculations for RMn2Ge2 (R = Y or Ca) compounds [34] which indicate that to a large extent, the magnetic moment is determined mainly by the interatomic Mn-Mn distances, while the interstitial electron density contributes to the change in magnetic structures. Assuming the expansion of the unit cell volume due to Ti substitution (chemical pressure) to be equivalent to the influence of external pressure [26] and using dTc/dp = -0.6 K/kbar in NdMn2Ge2 [35] (the same crystal structure), as a guide for the modulus values for NdMn2-xTi xSi2, the magnetic transition temperatures, Tc, expected from the pressure effect due to replacement of Mn atoms by the larger Ti atoms have been calculated as shown in Figure 5.2. The analysis based on the Murnagahan relationship indicates a slight increase in Tc.
with Ti concentration from $T_C = 36$ K for $x = 0$ to $T_C = 37$ K for $x = 1$ whereas the experimental data reveal a decrease from $T_C = 36$ K for $x = 0$ to $T_C = 14$ K for $x = 0.3$. These results indicate that for NdMn$_{2-x}$Ti$_x$Si$_2$ compounds over the Ti concentration range $x = 0.0$ to $1.0$, the electronic effects, rather than atomic size effects produce the observed decrease in magnetic transition temperature ($T_C$; Fig 2).

**Figure 5.2** Experimental (squares) and calculated values (circles) of the Curie temperature $T_C$ as a function of Ti concentration for NdMn$_{2-x}$Ti$_x$Si$_2$ ($x = 0, 0.1, 0.2, 0.3$). The $T_C$ values were calculated using the Murnaghan equation and $dT_C/dp = -0.6$ K/kbar as described in the text. The dashed lines act as a guide to the eye with the horizontal dashed line included to emphasise the slight increase in the calculated $T_C$ values, with increasing Ti concentration.

The magnetization versus field curves ($B = 0-5$ T) for NdMn$_{2-x}$Ti$_x$Si$_2$ ($x = 0, 0.1, 0.2, 0.3$) at 10 K are shown in Figure 5.3. The magnetization is not saturated up to 5 T indicating large magnetic anisotropy in these samples. This behaviour is supported by the strong uniaxial magnetic anisotropy observed for NdMn$_2$Si$_2$ [8] with the moment of 4.16 $\mu_B$/f.u. inhibiting saturation in magnetization up to fields of $B = 5$ T. The saturation magnetization values at 10 K were derived from graphs of magnetisation $M$ versus $1/B$ by extrapolation and applying the law of approach to saturation. The saturation magnetization, $M_S$ (at 10 K) is found to decrease with increasing Ti concentration in the NdMn$_{2-x}$Ti$_x$Si$_2$ compounds (Table 5.2). With assume
that the rare earth moment does not change with Ti content, it can be derived that the substitution of Ti atoms for Mn leads to a decrease of around $-4.6 \mu_B$ per Ti atom (from linear fitting), which is much faster than that expected with a simple dilution model (in which the Ti atoms do not carry magnetic moment). This behaviour is similar to that observed in NdMn$_{2-x}$Co$_x$Si$_2$ ($-2.1 \mu_B$ per Co atom decrease of $M_s$ at 5 K) [29], NdMn$_{2-x}$Cr$_x$Si$_2$ ($-2.8 \mu_B$ per Cr atom decrease of $M_s$ at 4.2 K) [36] and NdMn$_{2-x}$Fe$_x$Si$_2$ [37] compounds.

![Figure 5.3](image.png)

**Figure 5.3** Magnetization curves ($B = 0 - 5$ T) for NdMn$_{2-x}$Ti$_x$Si$_2$ compounds ($x = 0, 0.1, 0.2, 0.3$) at $T = 10$ K (closed symbols denote field increasing and open symbols field decreasing).

The magnetization curves obtained for NdMn$_2$Si$_2$ and NdMn$_{1.9}$Ti$_{0.1}$Si for fields in the range $B = 0 - 8$ T and $B = 0 - 5$ T around their ferromagnetic ordering temperatures are shown in Figures 5.4(a) and 5.4(b), respectively. These data were obtained for increasing and decreasing fields at 2 K intervals spanning a range of about 45 K around $T_C$, thus providing information about magnetic hysteresis loss effects as discussed below using expression [38]:

$$\text{Magnetic hysteresis loss} = \int_{decrease}^{increase} (\partial M)_H \, dH. \quad (5.2)$$
Figure 5.4 Isothermal magnetization curves in the vicinity of the ferromagnetic ordering temperatures for: (a) NdMn$_2$Si$_2$ ($T_C = 36$ K with $B = 0 - 8$ T) and (b) NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ ($T_C = 22$ K with $B = 0 - 5$ T) (the arrows indicate the direction of the applied fields during magnetisation measurements, and (c) Comparison of the magnetic hysteresis losses for NdMn$_2$Si$_2$ and NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ for magnetic fields over the ranges $B=0$-5 T (the results for $B=0$-2 T are shown in the insert).
Magnetic hysteresis effects (as indicated by the area enclosed between the ascending and descending branches of the magnetization curves) are also characteristic of first order

![Image](image.png)

**Figure 5.5** (a) Magnetic field dependence of the magnetization for applied fields in the range 0-5 T at selected temperatures for NdMn$_2$Si$_2$. $H_C$ corresponds to the field at the onset of the antiferromagnetic to ferromagnetic transition, indicated by arrow; (b) Critical field values, $H_C$, for NdMn$_2$Si$_2$ and NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ at selected temperatures.

magnetic transitions. As demonstrated in Figure 5.4(c), comparison of the magnetisation curves around the ferromagnetic ordering temperatures for NdMn$_2$Si$_2$ (figure 5.4(a)) with those for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ (figure 5.4(b)) reveal pronounced hysteresis losses of up to ~ 28.5 J kg$^{-1}$ (indicated values for B = 0 - 5 T as suitable to comparison) for NdMn$_2$Si$_2$ at $T_C = 36$ K
while negligible hysteresis losses of ~ 0.8 J kg⁻¹ are observed for NdMn₁·₉Ti₀·₁Si₂ around \( T_C = 22 \) K.

Table 5.2 Results of the magnetic characterization of NdMn₂₋ₓTiₓSi₂ compounds with \( x = 0, 0.1, 0.2 \) and 0.3. The magnetic features listed are: Curie temperature \( (T_C; \text{determined by graphs of } \frac{dM}{dT} \text{ versus } T) \) and the order of the magnetic transition around \( T_C \); Néel temperature \( (T_N; \text{determined by graphs of } \frac{1}{M} \text{ versus } T) \) and the saturation magnetization, \( M_S \), as determined at 10 K. The magnetic entropy change \( (-\Delta S_M) \) and the relative cooling power \( (\text{RCP}) \) are given for a field change of 0-5 T. The errors are shown for NdMn₂Si₂ as a typical example.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( T_C ) (K)</th>
<th>Nature of Transition at ( T_C )</th>
<th>( T_N ) (K)</th>
<th>( M_S ) (( \mu_B/\text{f.u.} )) ( (T=10 ) K)</th>
<th>( -\Delta S_M ) (J kg⁻¹ K⁻¹) ( (B=0-5 ) T)</th>
<th>RCP (J kg⁻¹) ( (B=0-5 ) T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdMn₂Si₂</td>
<td>36(3)</td>
<td>First</td>
<td>380(3)</td>
<td>4.4(4)</td>
<td>27(3)</td>
<td>127(3)</td>
</tr>
<tr>
<td>NdMn₁·₉Ti₀·₁Si₂</td>
<td>22</td>
<td>First</td>
<td>374</td>
<td>3.6</td>
<td>15.3</td>
<td>99</td>
</tr>
<tr>
<td>NdMn₁·₈Ti₀·₂Si₂</td>
<td>16</td>
<td>First</td>
<td>365</td>
<td>3.2</td>
<td>13</td>
<td>89</td>
</tr>
<tr>
<td>NdMn₁·₇Ti₀·₃Si₂</td>
<td>14</td>
<td>First</td>
<td>360</td>
<td>3</td>
<td>10</td>
<td>70</td>
</tr>
</tbody>
</table>

It is demonstrated clearly in Figure 5.4(c) that magnetic hysteresis losses decrease significantly on substitution of Ti for Mn. This behaviour indicates that increasing Ti concentration contributes to a weakening of the characteristic field induced metamagnetic transition from the antiferromagnetic to the ferromagnetic state. As shown in Figure 5.5(a) for NdMn₂Si₂, with the applied field below the critical value field (\( H_C \)), the magnetization increases linearly with increasing field applied expected for an antiferromagnetic state. However for applied field greater than \( H_C \), the magnetization initially increases rapidly before tending towards saturation at higher fields (similar behaviour is observed for La₀·₅Pr₀·₅Mn₂Si₂ [19] of the same ThCr₂Si₂ bct crystal structure) i.e. ferromagnetic behaviour. In the present investigation, as shown in Figure 5.5(b) the value of \( H_C \) is found to increase significantly with increasing the temperature and Ti concentration. Welter et al [8] have postulated that the ferromagnetic ordering of Nd sublattice below \( T_C \) drives the change in order of the Mn sublattice from antiferromagnetism to ferromagnetism in NdMn₂Si₂. It can be seen from Figures 5.4(a) and 5.4(b) that the metamagnetic transition occurs at higher temperatures and
lower values of $H_C$ in NdMn$_2$Si$_2$ compared with NdMn$_{0.5}$Ti$_{0.1}$Si$_2$. Therefore the metamagnetic transition is expected to produce a larger magnetocaloric effect for $x = 0$, with a decrease in MCE values for $x = 0.1$, 0.2 and 0.3 as described below in the magnetic entropy section.

As mentioned before, significant MCE values and magnetic entropy changes are usually obtained with a first order magnetic transition due to a large rate of change of magnetisation. Although such materials have this advantage compared with materials that exhibit a second order transition, first order magnetic transitions usually exhibit considerable thermal and magnetic hysteresis. The details of this study have established that hysteresis effects have effectively been eliminated by substitution of Mn with Ti in NdMn$_{2-x}$Ti$_x$Si$_2$ compounds. Figures 5.6(a - d) show the corresponding Arrott plots ($M^2$ versus $B/M$) for the $x = 0$, 0.1, 0.2 and 0.3 samples, respectively. The Arrott plots are found to exhibit features characteristic of a first order transition for all of the samples. In particular the nature of the Arrott plot near $T_C$ denotes a negative order of the sign of the coefficient $c_2(T)$ in the Landau expansion of the magnetic free energy [39], thereby denoting a first order magnetic transition. The present findings demonstrate that the ferromagnetic transition at $T_C$ in NdMn$_{2-x}$Ti$_x$Si$_2$ remains a first order transition on substitution of Ti for Mn to Ti concentration up to $x=0.3$.

The magnetic entropy change, $-\Delta S_M$, has been determined for the set of NdMn$_{2-x}$Ti$_x$Si$_2$ compounds ($x = 0$, 0.1, 0.2 and 0.3) from their magnetization curves for both increasing and decreasing field values as functions of temperature and magnetic field ($\Delta B = 0$-$5$ T). The magnetic entropy change has been derived by applying the standard Maxwell relation [40]:

$$- \Delta S_M(T, B) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_B dB.$$

As shown by the curves of Figure 5.7(a), the $-\Delta S_M$ peak (closed symbols for increasing field values and open symbols for decreasing field values) gradually broadens towards higher
temperatures with increasing magnetic field (from $\Delta B = 0\text{-}5\text{ T}$), behaviour characteristic of a field induced transition from an antiferromagnetic to a ferromagnetic state.

The changes in magnetic entropy for the set of NdMn$_{2-x}$Ti$_x$Si$_2$ compounds ($x = 0, 0.1, 0.2$ and $0.3$) around their ferromagnetic ordering temperatures are shown in Figure 5.7(b) as calculated from decreasing applied fields in order to satisfy the suitability of different experimental and related analytical approaches to establish the isothermal entropy change [41]. The entropy values at the respective Curie temperatures are ($\Delta B = 0\text{-}5\text{ T}$): $-\Delta S_M \approx 27\text{ J kg}^{-1}\text{ K}^{-1}$ at $T_C = 36\text{ K}$; $-\Delta S_M \approx 15.3\text{ J kg}^{-1}\text{ K}^{-1}$ at $T_C = 22\text{ K}$; $-\Delta S_M \approx 13\text{ J kg}^{-1}\text{ K}^{-1}$ at $T_C = 16\text{ K}$.
and $-\Delta S_M \sim 10 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T_C = 14 \text{ K}$. The decrease in magnetization on substitution of the non-magnetic Ti for Mn, correspondingly reduces the value of $-\Delta S_M$. Never the less it is noted that the MCE values of $-\Delta S_M \sim 15.3 \text{ J kg}^{-1} \text{ K}^{-1}$ for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ and $-\Delta S_M \sim 13 \text{ J kg}^{-1} \text{ K}^{-1}$ for NdMn$_{1.8}$Ti$_{0.2}$Si$_2$ are comparable with MCE values for other materials with small hysteresis that exhibit transitions in the temperature region below 100 K. These materials include: TbCoC$_2$ [42] ($-\Delta S_M = 15 \text{ J kg}^{-1} \text{ K}^{-1}$ at 28 K), GdCoAl [43] ($-\Delta S_M = 10.4 \text{ J kg}^{-1} \text{ K}^{-1}$ at 100 K) and TbCoAl [43] ($-\Delta S_M = 10.5 \text{ J kg}^{-1} \text{ K}^{-1}$ at 70 K), all of which - in common with NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ and NdMn$_{1.8}$Ti$_{0.2}$Si$_2$ - importantly exhibit no field hysteresis losses.

**Figure 5.7** (a) The temperature dependence of the isothermal magnetic entropy change, $-\Delta S_M$, for NdMn$_{0.9}$Ti$_{0.1}$Si$_2$ as determined from the magnetization isotherms for $\Delta B = 0-1 \text{ T}$, $\Delta B = 0-2 \text{ T}$, $\Delta B = 0-3 \text{ T}$, $\Delta B = 0-4 \text{ T}$ and $\Delta B = 0-5 \text{ T}$ (closed symbols for increasing fields and open symbols for decreasing fields). (b) The temperature dependence of the isothermal magnetic entropy change, $-\Delta S_M$, for NdMn$_{2-x}$Ti$_x$Si$_2$ compounds with $x = 0$, 0.1, 0.2 and 0.3 as measured from magnetization isotherms ($\Delta B = 0-5 \text{ T}$ from decreasing field curves).
The magnetic entropy change, $-\Delta S_M (T, B)$ has also been derived from heat calorimetric measurements of the field dependence of the heat capacity using the expression [10, 44, 45]:

$$-\Delta S_M (T, B) = \int_0^T \left( \frac{C(T,B) - C(T,0)}{T} \right) dT$$  \hspace{1cm} (5.4)

where $C(T,B)$ and $C(T,0)$ are the values of the heat capacity measured in field $B$ and zero field, respectively. The corresponding adiabatic temperature change, $\Delta T_{ad}$ can be evaluated from $-\Delta S_M (T, B)$ and the heat capacity data as:

$$\Delta T_{ad}(T,B) = \int_0^B \frac{T}{C_{B,P} \left( \frac{dM}{dT} \right)_B} dB$$  \hspace{1cm} (5.5)

Figure 5.8(b) shows the set of heat capacity measurement obtained for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ with $B = 0$, 2, and 5 T. The corresponding $-\Delta S_M (T, B)$ values for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ are shown in Figure 5.8(a) with the $\Delta T_{ad}$ values shown in Figure 5.8(c) (open symbols). The peak value of the adiabatic temperature change is $\Delta T_{ad}^{max} = 4.7$ K for $\Delta B = 0$-5 T.

As shown in Figure 5.8(a), the maximum magnetic entropy change for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ as determined from the heat capacity measurements of $-\Delta S_M^{max} \sim 15$ J kg$^{-1}$ K$^{-1}$ and 9.3 J kg$^{-1}$ K$^{-1}$ for $\Delta B = 0$-5 T and 0-2 T are similar to the maximum entropy change $-\Delta S_M^{max} \sim 15.3$ J kg$^{-1}$ K$^{-1}$ and 9.8 J kg$^{-1}$ K$^{-1}$ as determined from the magnetic measurements using the Maxwell relation. The good agreement between the two sets of measurements confirms that the $-\Delta S_M$ values derived for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ from the magnetization measurements represent the MCE behaviour within experimental errors [14, 22, 46]. Similarly, the $\Delta T_{ad}$ values determined by combing the $-\Delta S_M (T, B)$ (derived from magnetic data) and specific heat results are also drawn in Figure 5.8(c) using closed symbols to make a comparison, which are found to be consistent with the values (open symbols) derived from the specific heat only. By comparison, Nikitin et al [47] reported that the value of $\Delta T_{ad}^{max}$ in NdMn$_2$Si$_2$ compound (around $T_C \sim 32$ K) can be up to 8.2 K with a field change of $\Delta B=0$-6 T.
Figure 5.8 (a) The magnetic entropy change, $-\Delta S_M$, determined from the heat capacity measurements of figure 5.8(b) for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ ($\Delta B = 0$ T, $\Delta B = 0$-5 T). (b) The heat capacity of NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ as measured over the temperature range 10-70 K in magnetic fields B = 0 T, 2 T, 5 T. (c) The adiabatic temperature change, $\Delta T_{ad}$, for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ as determined from the heat capacity(open symbol) of figure 5.8(b) and magnetization (closed symbol) measurements.

In general, the relative cooling power (RCP) is an important parameter of the magnetocaloric material, providing an accepted criterion to evaluate the refrigeration efficiency in practical application. The RCP is used to evaluate the cooling power of magnetic refrigerants by measuring how much heat can be transferred between two temperatures (low and high in temperature span range) in one ideal refrigeration cycle. The RCP is defined by the following expression [48]:

$$RCP = -\Delta S^\text{max}_M \delta T_{\text{FWHM}}$$

(5.6)

$-\Delta S^\text{max}_M$ denotes the maximum entropy change and $\delta T$ represents the full width at half maximum (FWHM) of the temperature dependence of the magnetic entropy change $-\Delta S_M$. A summary of the RCP values and other magnetic characterization parameters for NdMn$_2$. 

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$x\text{Ti}_x\text{Si}_2$ ($x = 0, 0.1, 0.2, 0.3$) compounds is listed in Table 5.2. The RCP shows the same trend with Ti concentration as the magnetic entropy change. It is noted that $\delta T$ increases with Ti content: $\delta T = 9.5$ K, $\delta T = 12.0$ K, $\delta T = 12.4$ K and $\delta T = 12.8$ K for $x=0$, 0.1, 0.2 and 0.3 respectively. It was found that the RCP decreases from $\sim 127$ J kg$^{-1}$ for $x = 0$ to $\sim 70$ J kg$^{-1}$ for $x = 0.3$ for a change in magnetic field $\Delta B = 0.5$ T.

The NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ compound was selected for investigation by neutron diffraction measurements over the temperature range 3-450 K as representative of the magnetic behaviour of the NdMn$_{2-x}$Ti$_x$Si$_2$ samples (figure 5.1). The aims were to determine the magnetic structures and to explore structural changes at the transition temperatures. The diffraction patterns ($\lambda = 1.622(1)$ Å) and Rietveld refinements obtained for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ at 450 K, 150 K and 15 K are shown in Figures 5.9(a), 5.9(b) and 5.9(c), respectively. The selected temperatures typify the behaviour of NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ in the three magnetic regions (paramagnetic-antiferromagnetic-ferromagnetic) as indicated from the magnetisation and DSC measurements of Figure 5.1. Rietveld refinements of the neutron diffraction pattern at 450 K (figure 5.9(a)) confirm that NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ has the ThCr$_2$Si$_2$ structure as expected. The absence of magnetic scattering above $T_N \sim 374$ K (figure 5.1) in reflections such as (101), (111) and (112) is consistent with a paramagnetic (PM) state. (cf. e.g. the disordered magnetic states (PM) observed in PrMn$_{1.6}$Fe$_{0.4}$Si$_2$ [6], EuMn$_2$Si$_2$ [49] and LaPrMn$_2$Si$_2$ [50]). Below $T_N \sim 374$ K, NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ is found to exhibit the antiferromagnetic interlayer coupling structure (AFil) down to $T_C \sim 22$ K (see e.g. the 150 K pattern of figure 5.9(b)). The AFil structure – a collinear antiferromagnetic structure between adjacent Mn planes in a + - +
Figure 5.9 (a), (b), and (c) Neutron diffraction patterns for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ at 450 K, 150 K, and 15 K respectively. The star symbols represent the observed patterns and the red solid lines the refined patterns. The blue lines represent the differences between the observed and refined patterns; the vertical bars indicate the Bragg peak positions for the nuclear (top), Fmc magnetic (middle) and AFil magnetic (bottom) structure respectively. (d) The temperature dependence of the integrated intensities of the (101), (112) and (111) reflections for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ over the temperature range 3-450 K. The $T_N \sim 374$ K and $T_C \sim 22$ K transition temperatures that delineate the paramagnetic PM, antiferromagnetic AFil and ferromagnetic Fmc+F(Nd) regions are shown by the dashed lines. The lines through the intensity values act as guides to the eye. (e) The structure of NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ and the antiferromagnetic AFil and ferromagnetic Fmc+F(Nd) structures.

- sequence along the $c$-axis – is indicated by the magnetic scattering observed at the (111), (113) and (201) reflections; (extinction rules $h + k = 2n$ and $h + k + l = 2n+1$) in agreement with Dincer et al [50]. In order to draw out the changes in magnetic structures with temperature, the temperature dependence of the peak intensity for selected magnetic peaks is shown in Figure 5.9(d). Furthermore, the absence of magnetic scattering from the (111), (113) and (201) reflections at 15 K in Figure 5.9(c), combined with the increase in intensity of the
(112) and (101) peaks as in Figure 5.9(d), indicate that the interlayer spin components of the Mn moments align parallel, thus leading to a canted ferromagnetic structure (Fmc) for the Mn sublattice. The presence of the purely magnetic peak (001) below Tc indicates the existence of antiferromagnetic component of Mn moment in the ab-plane \[22\]. At lower temperature (e.g. 3 K; figure 5.9(d)), the increase in the intensities of the (112) (contributions from both Nd- and Mn-sublattices) and (101) (contribution only from Nd-sublattice \[22\]) reflections further indicates an additional contribution from Nd moments coupled parallel to

**Table 5.3** Structural and magnetic parameters of NdMn\(_{1.9}\)Ti\(_{0.1}\)Si\(_2\) as derived from Rietveld refinements of the neutron diffraction patterns and the BLOKJE program. \(\mu_{\text{total}}^{\text{Mn}}\) - the Mn magnetic moment; \(\mu_{\text{c}}^{\text{Mn}}\) - the Mn moment along the c-axis; \(\mu_{\text{ab}}^{\text{Mn}}\) - the Mn moment in (001) Mn layers; \(\mu_{\text{Nd}}\) - the Nd moment along the c-axis; the errors for the data at T=3 K are shown as typical examples.

<table>
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<tr>
<th>T (K)</th>
<th>3 K</th>
<th>15 K</th>
<th>25 K</th>
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<th>50 K</th>
<th>150 K</th>
<th>200 K</th>
<th>300 K</th>
<th>450 K</th>
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<tr>
<td>(a(\text{Å}))</td>
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<td>4</td>
<td>3.999</td>
<td>3.998</td>
<td>3.997</td>
<td>4.001</td>
<td>4.003</td>
<td>4.009</td>
<td>4.022</td>
</tr>
<tr>
<td>(V(\text{Å}^3))</td>
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<td>168.38</td>
<td>168.43</td>
<td>168.44</td>
<td>168.42</td>
<td>168.74</td>
<td>169.04</td>
<td>169.73</td>
<td>171.13</td>
</tr>
<tr>
<td>(d_{\text{Mn-Mn}}(\text{Å}))</td>
<td>2.8286(9)</td>
<td>2.8285</td>
<td>2.8273</td>
<td>2.8272</td>
<td>2.8271</td>
<td>2.8271</td>
<td>2.8288</td>
<td>2.8307</td>
<td>2.8351</td>
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<tr>
<td>(Z_{\text{Si}})</td>
<td>0.3793(6)</td>
<td>0.3813</td>
<td>0.3807</td>
<td>0.3812</td>
<td>0.3813</td>
<td>0.3789</td>
<td>0.3786</td>
<td>0.3809</td>
<td>0.381</td>
</tr>
<tr>
<td>(\mu_{\text{total}}^{\text{Mn}})</td>
<td>1.56(4)</td>
<td>1.54</td>
<td>1.67</td>
<td>1.98</td>
<td>2.1</td>
<td>1.91</td>
<td>1.85</td>
<td>1.53</td>
<td>-</td>
</tr>
<tr>
<td>(\mu_{\text{c}}^{\text{Mn}})</td>
<td>1.30(6)</td>
<td>1.26</td>
<td>1.17</td>
<td>1.98</td>
<td>2.1</td>
<td>1.91</td>
<td>1.85</td>
<td>1.53</td>
<td>-</td>
</tr>
<tr>
<td>(\mu_{\text{ab}}^{\text{Mn}})</td>
<td>0.86(2)</td>
<td>0.89</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\mu_{\text{Nd}})</td>
<td>2.56(5)</td>
<td>2.77</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>(R_{\text{wp}})</td>
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<td>5.87</td>
<td>5.99</td>
<td>6.21</td>
<td>6.59</td>
<td>6.93</td>
<td>7.35</td>
<td>7.75</td>
<td>8.05</td>
</tr>
<tr>
<td>(R_{\text{exp}})</td>
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<td>3.95</td>
<td>4.67</td>
<td>4.89</td>
<td>5.04</td>
<td>5.25</td>
<td>5.65</td>
<td>5.78</td>
</tr>
</tbody>
</table>

the Mn moments along \(c\)-axis thereby leading to the formation of Fmc+F(Nd) magnetic structure as depicted in Figures 5.9(e). This behavior agrees well with the results of Welter et al \[51\] who demonstrated that in the RMn\(_2\)Ge\(_2\) compounds with R= Pr and Nd rare earth moments ferromagnetically coupled with the Mn sublattice at low temperatures. This behaviour, also applicable to NdMn\(_2\)Si\(_2\) \[8\] and NdMn\(_2\)Si\(_{1.6}\)Ge\(_{0.4}\) \[22\] compounds, is due to the exchange interaction between the light rare earth elements and 3\textit{d} transition metal as
reported by Coey [52]. Ordering of the Nd sublattice in NdMn$_2$Si$_2$ below T$_C$ has also been confirmed by Chatterji et al [53] from inelastic neutron scattering.

![Figure 5.10](image.png)

**Figure 5.10** (a) The lattice parameters of NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ as a function of temperature and (b) temperature dependence of the Mn magnetic moment (3-450 K). The Néel temperature T$_N$ and Curie temperature T$_C$ are denoted by arrows with the dotted lines delineating the paramagnetic (PM), antiferromagnetic (AFil-type) and ferromagnetic (Fmc+F(Nd)) regions. The line through the moment values act as a guide to the eye.

The variation in the $a$ and $c$ lattice parameters with temperature are plotted in Figure 5.10(a). Both the $a$ and $c$ values exhibit a monotonic decrease with temperature in the region of the antiferromagnetic transition between T$_N$ = 374 K and T$_C$ = 22 K, while below T$_C$ = 22 K, the $a$ lattice parameter expands slightly from 3.998 Å at 35 K to 4.001 Å at 3 K whereas the $c$ lattice parameter decreases from 10.536 Å at 35 K to 10.523 Å at 3 K. The variation in lattice parameters $a$ and $c$ shown in Figure 5.10(a) for the PM, AFil, and Fmc+F(Nd) states is comparable with the behaviour in NdMn$_2$Si$_2$ [8]. The changes in lattice parameter at T$_C$ ~ 22 K when the magnetic state changes from AFil to Fmc+F(Nd) structure, indicates the presence
of strong magnetostructural coupling around $T_C$. As discussed recently [7, 54], the strong magnetostructural coupling leads to a large structural entropy change around the magnetic phase transition, thereby contributing to the total entropy change around $T_C$.

Figure 5.10(b) is a plot of the temperature dependence of the Mn magnetic moments as derived from the refinements. Within the AF il state region ($T_N \sim 374 \, \text{K} > T > T_C \sim 22 \, \text{K}$), the Mn moment increases to $\mu^{\text{Mn}} = 2.1 \, (1) \, \mu_B$ at 50 K with both Nd and Mn ordering magnetically below $T_C \sim 22 \, \text{K}$. The magnetic moments for Mn and Nd have been derived to be $\mu^{\text{total Mn}} = 1.56 \, (4) \, \mu_B$ (of basal plane and axial components $\mu^{\text{ab Mn}} = 0.86(2) \, \mu_B$ and $\mu^{\text{c Mn}} = 1.30(6) \, \mu_B$ respectively) and $\mu^{\text{Nd}} = 2.56(5) \, \mu_B$ at 3 K. The Nd moment and the ferromagnetic component of the Mn moment along the $c$-axis for $\text{NdMn}_{1.9}\text{Ti}_{0.1}\text{Si}_2$ are found to be $2.56(1) \, \mu_B$ and $1.30(1) \, \mu_B$ respectively. The resultant total moment is $3.86(1) \, \mu_B$ per formula unit at 3 K which is slightly higher than that obtained from DC magnetization measurement at 10 K (3.6 $\mu_B$ per formula unit). This different value of magnetic moment is related to the non-saturation behavior shown by the magnetisation curve from DC measurements at 10 K even for a field applied of 5 T.

5.1.3.2 NdMn$_{2-x}$Cr$_x$Si$_2$

As shown by the series of x-ray diffraction patterns in Figure 5.11(a), the NdMn$_{1.7}\text{Cr}_{0.3}\text{Si}_2$ compound is single phase and exhibits the body-centred tetragonal ThCr$_2$Si$_2$-type structure (space group $I4/mmm$) over the temperature range $\sim$10-300 K. No change in crystal structure is observed over this temperature range although, as discussed below, the $a$ lattice parameter is found to increase slightly around $T_C \sim 42(2) \, \text{K}$ while the $c$ lattice parameter decreases. The patterns have been analysed using FULLPROF [30] software, and the changes in lattices
parameters $a$ and $c$ around $T_C$ (volume change $\Delta V/V \sim 0.1\%$) found to agree well with the neutron data as discussed below. The temperature dependences of the magnetization of NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ (6-295 K) and the differential scanning calorimetry curve obtained at higher temperatures (280-430 K) are shown in Figure 5.11(b). As is also evident from the analyses of the neutron diffraction data presented below, NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ exhibits three magnetic transitions over the temperature range 6-400 K. The $T_{N_{\text{intra}}} \sim 380(3)$ K and $T_{N_{\text{inter}}} \sim 320(3)$ K antiferromagnetic transition temperatures were determined from a graph of the DSC data plotted against inverse temperature with the $T_C \sim 42(2)$ K ferromagnetic transition temperature determined from the maximum of the $dM/dT$ versus $T$ curve from the zero-field cooling magnetization data. Comparison of the cooling and warming magnetisation results in Figure 5.11(b) shows that the thermal hysteresis at $T_C$ is $\Delta T < \sim 0.8$ K.

![Figure 5.11](image-url)

**Figure 5.11** (a) X-ray diffraction patterns (synchrotron radiation) of NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ over the temperature range $T=10$-300 K ($\lambda=0.8265$ Å). (b) Temperature dependence of the magnetization as measured in a field of 0.01 T (left axis: zero field cooling (ZFC) and field cooling (FC)); right axis: DSC results over the range $T=300$-420 K.)
Figure 5.12(a) shows a thermal contour plot of neutron diffraction measurements on NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ from 6 to 400 K. In addition to the set of patterns obtained in the warming ramp mode (step 1 K; counting time 1 min), patterns were obtained around the transition temperatures (5 K steps for 6-70 K; 10 K steps for 80-340 K; 5 K steps for 350-400 K; counting time 10 min). The neutron diffraction patterns in Figures 5.13(a-d) are representative of NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ in the four regions indicated by the magnetic transition in Figure 5.11(b). The different magnetic structures indicated in Figure 5.12(b) can be discerned readily from the temperature dependence of the peak intensities for selected magnetic peaks as in Figure 5.13(e). The Rietveld refinement of the pattern at 400 K (Figure 5.13(a)) confirms that NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ has the ThCr$_2$Si$_2$ structure as expected with the absence of coherent magnetic scattering above $T_N^{\text{intra}} \sim 380(3)$ K consistent with paramagnetism. Below $T_N^{\text{intra}} \sim 380(3)$ K, NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ exhibits the AFil antiferromagnetic structure with...
intralayer coupling (see e.g., the 375 K pattern of Figure 5.13(b) and Figure 5.13(e) with increased (101) peak intensities) down to $T_{N_{\text{inter}}} \sim 320(3)$ K. On cooling below $T_{N_{\text{inter}}} \sim 320(3)$ K down to $T_c$, NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ exhibits the canted AFmc structure (both interlayer and intralayer antiferromagnetic coupling; see e.g. the 100 K pattern of Figure 5.13(c) and related increases in the (101) and (111) peak intensities in Figure 5.13(e)).

Figure 5.13 Neutron diffraction patterns ($\lambda=2.4205$ Å) for NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ at: (a) 400 K; (b) 375 K; (c) 100 K; (d) 20 K (inset-3 K pattern at $\lambda=2.4395$ Å). (e) Temperature dependence of the integrated intensities of the (101), (111) and (112) reflections; (f) Lattice parameters as a function of temperature (open/closed symbols–neutron/x-ray diffraction). (g) Temperature dependence of the Mn and Nd magnetic moments (6–400 K). The full lines through the open symbols represent the Nd and Mn moments using estimation/fix Mn total moment method as discussed.

Below $T_c$, the absence of magnetic scattering from the (111) and (001) reflection at 20 K (Figure 5.13(d)), combined with the increase in intensity of the (112) and (101) peaks (Figure
5.13(e)), indicate that the interlayer spin components of the Mn moments have a parallel alignment, thus leading to a canted ferromagnetic structure ($F_{mc}$) for the Mn sublattice. The additional high resolution neutron diffraction pattern at $T=3$ K (inset to Figure 5.13(d)) confirms the absence of the purely magnetic (001) peak and any antiferromagnetic component of the Mn moment in the $ab$-plane below $T_C$.

The further increase in intensities of the (112) and (101) peaks below $T_C$ (Figure 5.13(e)) indicates an additional contribution from Nd moments coupled parallel to the Mn moments along the $c$-axis, thereby leading to the formation of the $F_{mc}(Mn)+F(Nd)$ magnetic structure. The present results agree well with the findings of Chatterji et al.[53], who demonstrated the ordering of the Nd sublattice in NdMn$_2$Si$_2$ below $T_C$ from inelastic neutron scattering. It should be noted that the $F_{mc}(Mn)+F(Nd)$ configuration in NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ differs from that of NdMn$_2$Si$_2$ [8], NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ [55] and NdMn$_{1.8}$Co$_{0.2}$Si$_2$ [29] for which the (001) peak is present. As shown in Figure 5.13(f), both the $a$ and $c$ lattice parameters exhibit monotonic decreases with temperature in the antiferromagnetic region between $T_N^{\text{intra}} \sim 380(3)$ K and $T_N^{\text{inter}} \sim 320(3)$ K, down to $T_C \sim 42(2)$ K. Below $T_C \sim 42(2)$ K, the $a$ lattice parameter expands slightly from 3.996(4) Å at 45 K ($AF_{nil}$) to 3.999(5) Å at 6 K ($F_{mc}(Mn)+F(Nd)$), whereas the $c$ lattice parameter decreases from 10.492(6) Å to 10.485(5) Å. Good agreement is found with the results of the synchrotron radiation experiments (closed symbols in Figure 5.13(f)). The anomalous changes in lattice parameter around $T_C \sim 42(2)$ K indicates the presence of strong magnetostructural coupling.

Figure 5.13(g) is a plot of the variation of the Mn magnetic moments with temperature as derived from the refinements. Within the AF$\text{Il}$ and AF$mc$ antiferromagnetic regions, the Mn total moment increases from $\mu_{\text{total}}^{\text{Mn}} = 0.82(4) \ \mu_B$ at $T_N^{\text{inter}} \sim 320$ K to $\mu_{\text{total}}^{\text{Mn}} = 2.04(5) \ \mu_B$ at
\( T_C \sim 42(2) \) K due to the fact that, with decreasing temperature, thermal disorder becomes weaker compared with magnetic interaction. The sudden rise of Mn moment around \( T_N^{\text{inter}} \) is due to the appearance of \( c \)-axis components of Mn moment. Below \( T_C \), \( \text{NdMn}_{1.7}\text{Cr}_{0.3}\text{Si}_2 \) has the magnetic structure shown in Figure 5.12(b). The contributions of the Mn and Nd moments to the ferromagnetic peaks of the neutron diffraction patterns cannot be separated as the magnetic contributions to the \((hkl)\) lines from the rare-earth and Mn sublattices overlap below \( T_C^{\text{Nd}} \) (based on the absence of the (001) peak – see Figure 5.13(d)). Using the method with extrapolated the temperature dependence of Mn moments above \( T_C^{\text{Nd}} \) to lower temperatures below \( T_C^{\text{Nd}} \) (see e.g.[56]) where both Nd and Mn order in \( \text{Fmc(Mn)}+\text{F(Nd)} \) region. This leads to the temperature dependence of the Nd moments as shown by the full line in Figure 5.13(g) leading to moment values \( \mu_{\text{total}}^{\text{Mn}} = 2.52(3) \mu_B \) and \( \mu_c^{\text{Nd}} = 2.10(4) \mu_B \) at 6 K.

\[ \text{Figure 5.14 (a) Magnetization curves for NdMn}_{1.7}\text{Cr}_{0.3}\text{Si}_2 \text{ over the temperature range 35–80 K for increasing (closed symbols) and decreasing (open symbols) and (b) the corresponding Arrott plots of } M^2 \text{ versus } B/M. \]
Comparison of the magnetization curves of NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ for both increasing and decreasing fields at 2 K intervals over the temperature region ~ 35-80 K (Figure 5.14(a)) demonstrate that there are effectively negligible magnetic hysteresis effects (< ~ 0.1 T) in this compound. This behaviour indicates that NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ has promising performance advantages when cycled over the metamagnetic transition from the antiferromagnetic to the ferromagnetic state for magnetic refrigerator applications [57]. As shown by the Arrott plots in Figure 5.14(b) and in agreement with the magnetic structures determined from the neutron data as above, NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ is ferromagnetic below 42 K (positive intercept on M$^2$ axis) and antiferromagnetic above 42 K (negative intercept on M$^2$ axis)[39]. The observed negative slope which is nature of the Arrott plots characterize a first order magnetic transition. The absence of thermal (< ~ 0.8 K; Figure 5.11(b)) and magnetic hysteresis effects (< ~ 0.1 T; Figure 5.14(a)) in NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ at T$_C$ ~ 42(2) K, compares favourably with other materials such as Gd$_5$Si$_2$Ge$_2$ (magnetic hysteresis of ~ 1 T and thermal hysteresis of ~ 2 K at T$_C$ ~ 276 K)[14] and La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{0.6}$ (magnetic hysteresis of ~ 0.08 T and thermal hysteresis of ~ 1.5 K at T$_C$ ~ 180 K)[4].

As shown by the magnetic entropy changes in Figure 5.15(a) (derived from the magnetization curves using the standard Maxwell relation [40]: (equation 5.3) , the -$\Delta S_M$ peak for $\Delta B$=0-5 T gradually broadens towards higher temperatures with increasing magnetic field, which is characteristic of a field induced transition from an antiferromagnetic to a ferromagnetic state. The entropy value at the respective Curie temperatures, -$\Delta S_M$ ~ 15.3 J kg$^{-1}$ K$^{-1}$ at T$_C$ ~ 42(2) K ($\Delta B$=0-5 T) for NdMn$_{1.7}$Cr$_{0.3}$Si$_2$, is greater than for Gd (9.5 J kg$^{-1}$ K$^{-1}$) and near that for the giant magnetocaloric effect Gd$_5$Si$_2$Ge$_2$ compound (18.8 J kg$^{-1}$ K$^{-1}$)[14]. The MCE value of NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ is comparable to those of other materials, which include: GdCoAl [43] (-$\Delta S_M$=10.4 J kg$^{-1}$ K$^{-1}$ at 100 K) and TbCoAl [43] (-$\Delta S_M$=10.5 J kg$^{-1}$ K$^{-1}$ at 70 K), all of which,
in common with NdMn$_{1.7}$Cr$_{0.3}$Si$_2$, importantly exhibit negligible field and thermal hysteresis losses.

Figure 5.15 (a) Magnetic entropy change, $\Delta S_M$, of NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ determined from heat capacity (open symbols) and magnetization (closed symbols) measurements for $\Delta B=0$-2 T and $\Delta B=0$-5 T; (b) Heat capacity of NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ for $B=0$ T, 2 T, 5 T; (c) Adiabatic temperature change, $\Delta T_{ad}$, as determined from the heat capacity measurements of Figure 5.15(b).

The magnetic entropy change, $-\Delta S_M (T, B)$, has been derived from heat calorimetric measurements of the field dependence of the heat capacity using the expression [44, 45]: $-\Delta S_M (T, B)$ (equation 5.4). The corresponding adiabatic temperature change, $\Delta T_{ad}$, be evaluated from $-\Delta S_M (T, B)$ and the zero field heat capacity data as (equation 5.5). Figure 5.15(b) shows the set of heat capacity measurements obtained for NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ ($B=0$ T, 2 T, and 5 T) with the corresponding $-\Delta S_M (T, B)$ and $\Delta T_{ad}$ values shown in Figures 5.15(a) and 5.15(c). The peak value of the adiabatic temperature change is $\Delta T_{ad}^{\text{max}} \sim 5$ K for $\Delta B=0$-5 T. As shown in Figure 5.15(a), the maximum magnetic entropy change determined from the heat capacity
measurements \(-\Delta S_M^{\text{max}} \sim 15 \text{ J kg}^{-1} \text{ K}^{-1}\) is similar to the value \(-\Delta S_M^{\text{max}} \sim 15.3 \text{ J kg}^{-1} \text{ K}^{-1}\) determined from the magnetic measurements. This good agreement confirms that the \(-\Delta S_M\) values derived for NdMn\(_{1.7}\)Cr\(_{0.3}\)Si\(_2\) from the magnetization measurements represent the MCE behaviour within experimental errors [14, 22]. The contribution to the MCE value for \(\Delta B=0\)-5 T due to the structural volume expansion is around \(-\Delta S_{\text{structural}} \sim 1.25 \text{ J kg}^{-1} \text{ K}^{-1}\) as estimated using the method described by Gschneidner et al.[54].

5.1.3.3 NdMn\(_{2-x}\)Cu\(_x\)Si\(_2\)

Confirmation that all of the NdMn\(_{2-x}\)Cu\(_x\)Si\(_2\) (\(x = 0\)-1.0) samples crystallize in the expected ThCr\(_2\)Si\(_2\) type structure with space group I4/mmm was provided by analysis of the x-ray powder diffraction patterns. The x-ray diffraction patterns at variable temperatures for \(x=0.2\) are shown in Figure 5.16(a) as a typical example. The measured data from the diffraction patterns were analysed using the Rietveld refinement temperature dependence of the magnetization of NdMn\(_{2-x}\)Cu\(_x\)Si\(_2\) (\(x = 0\)-1.0) measured in a magnetic field of \(B = 0.01\) T is shown in Figure 5.16(c) together with the differential scanning calorimetry (DSC). As using calculation in Ref [58], the Néel temperature \(T_N\) found to decreases from \(\sim 380\) K to \(\sim 320\) K with increase in Cu concentration from \(x = 0\) to \(x = 1.0\) while Curie temperature \(T_C\) increase from \(\sim 36\) K to \(\sim 100\) K. The reduction of unit cell volume due to Cu substitution as shown in Figure 5.16(b) will lead to decrease the Mn-Mn intralayer exchange interaction. Moreover, the change in electronic environment on replacing Mn (3\(d^5\)4s\(^2\)) by Cu (3\(d^{10}\)4s\(^1\)) is also expected to influence the magnetic structures and states of the NdMn\(_{2-x}\)Cu\(_x\)Si\(_2\) compounds.

The magnetization curves obtained for NdMn\(_{1.2}\)Cu\(_{0.2}\)Si\(_2\) and NdMn\(_{1.4}\)Cu\(_{0.6}\)Si\(_2\) around their ferromagnetic ordering temperatures are shown in Figures 5.17(a-b). Comparison of the
Figure 5.16 (a) XRD pattern for NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ compound at range 10-300 K ($\lambda = 0.8265(8)$ Å); (b) Variation of unit cell volume $V$, $c$ and $a$ for room temperature with Cu content and (c) Temperature dependence of magnetization, the Néel temperatures ($T_N$) and the Curie temperatures ($T_C$) of NdMn$_{2-x}$Cu$_x$Si$_2$ compound.

Magnetisation curves around the ferromagnetic ordering temperatures for NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ and NdMn$_{1.4}$Cu$_{0.6}$Si$_2$ reveal pronounced hysteresis losses keep decreasing from ~ 12 J kg$^{-1}$ to no hysteresis loss are observed for NdMn$_{1.4}$Cu$_{0.6}$Si$_2$ (indicated values for $B = 0 - 5$ T as suitable to comparison). It is demonstrated clearly that magnetic hysteresis losses decrease significantly on substitution of Cu for Mn as indicated that increasing Cu concentration contributes to a weakening of the characteristic field induced metamagnetic transition from
the antiferromagnetic to the ferromagnetic state. Figures 2(c) and (d) show the corresponding Arrott plots ($M^2$ versus $B/M$) for the $x = 0.2$ and 0.6 samples, respectively. The Arrott plots

![Graphs showing isothermal magnetization curves and Arrott plots](image)

**Figure 5.17** Isothermal magnetization curves in the vicinity of the ferromagnetic ordering temperatures for: (a) NdMn$_{1.8}$Cu$_{0.2}$Si$_2$, ($B = 0 - 8$ T) and (b) NdMn$_{1.4}$Cu$_{0.6}$Si$_2$ ($B = 0 - 5$ T) compound respectively. (c) Arrott plots of NdMn$_{2-x}$Cu$_x$Si$_2$; $x=0.2$ and (d) $x=0.6$ compounds.

are found to exhibit features characteristic of a first order transition for $x < 0.6$ to second order transition for $x \geq 0.6$ as shown in Figures 5.17(c-d). As been determined by particular the nature of the Arrott plot near $T_C$ denotes a negative order of the sign of the coefficient $c_2(T)$ in the Landau expansion of the magnetic free energy [39], thereby denoting a first order magnetic transition for $x<0.6$ and been confirmed with nature of phase transitions method [59].
The magnetic entropy change, \(-\Delta S_M\), has been determined for the set of NdMn_{2-x}Cu_xSi_2 compounds \(x = 0 - 1.0\) from their magnetization curves for decreasing field values as functions of temperature and magnetic field \(\Delta B = 0 - 5\ T\). The magnetic entropy change has been derived by applying the standard Maxwell relation as used before (equation 5.3).

**Figure 5.18** (a) The magnetic entropy change, \(-\Delta S_M\), determined from magnetization and the heat capacity measurements of Fig. 3(b) for NdMn_{1.8}Cu_{0.2}Si_2 \((\Delta B = 0 - 5\ T)\). (b) The heat capacity of NdMn_{1.8}Cu_{0.2}Si_2 as measured over the temperature range 10-90 K. (c) The adiabatic temperature change, \(\Delta T_{ad}\), for NdMn_{1.8}Cu_{0.2}Si_2.

As shown by the curves of Figure 5.18(a), the \(-\Delta S_M\) peak found consistently decrease with Cu concentration \(x = 0, 0.2, 0.4, 0.6, 0.8\ and 1.0\) as: \(-\Delta S_M \sim 27\ J\ kg^{-1}\ K^{-1}\) at \(T_C = 36\ K\); \(-\Delta S_M \sim 13\ J\ kg^{-1}\ K^{-1}\) at \(T_C = 44\ K\); \(-\Delta S_M \sim 6.5\ J\ kg^{-1}\ K^{-1}\) at \(T_C = 60\ K\); \(-\Delta S_M \sim 3.5\ J\ kg^{-1}\ K^{-1}\) at \(T_C = 70\ K\); \(-\Delta S_M \sim 1.5\ J\ kg^{-1}\ K^{-1}\) at \(T_C = 80\ K\) and \(-\Delta S_M \sim 0.5\ J\ kg^{-1}\ K^{-1}\) at \(T_C = 100\ K\). The decrease in magnetization on substitution of the non-magnetic Cu for Mn, correspondingly reduces the value of \(-\Delta S_M\). The magnetic entropy change, \(-\Delta S_M(T, B)\) has been derived from heat
calorimetric measurements using the expression (equation 5.4) for comparison with magnetization measurement.

Figure 5.19 (a), Neutron diffraction patterns for NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ at 450 K, 100 K, and 40 K respectively. (b) Expanded view of the neutron diffraction pattern for NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ at selected temperatures. (c) The lattice parameters of NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ as a function of temperature.

The corresponding adiabatic temperature change, $\Delta T_{ad}$ were been evaluated from (equation 5.5) as shown in Figure 5.18(b) the set of heat capacity measurement obtained for NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ with $B = 0, 2, \text{ and } 5$ T. The corresponding $-\Delta S_M(T, B)$ values for NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ are shown in Figure 5.18(a) with the $\Delta T_{ad}^{\text{max}} = 3.44$ K for $\Delta B = 0-5$ T values in Figure 5.18(c). The $-\Delta S_M^{\text{max}}$ for NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ as determined from the heat capacity measurement $\sim 11.5$ J kg$^{-1}$ K$^{-1}$ is comparable to the magnetic measurements using the Maxwell relation $\sim 13$ J kg$^{-1}$ K$^{-1}$ for $\Delta B = 0-5$ T as shown in Figure 5.18(a).
The diffraction patterns ($\lambda = 1.622(1) \text{ Å}$) and Rietveld refinements obtained for NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ at 450 K, 100 K and 40 K are shown in Figure 5.19(a) typify the behaviour of the three magnetic regions (paramagnetic-antiferromagnetic-ferromagnetic) as found similar to NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ [55] respectively. Rietveld refinements of the neutron diffraction pattern at 450 K (paramagnetic state) confirm that NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ has the ThCr$_2$Si$_2$ structure and below $T_N \sim 375$ K, is found to exhibit the antiferromagnetic interlayer coupling structure (AFil) down to $T_C \sim 44$ K ($T = 100$ K). The AFil structure was confirmed by the magnetic scattering observed at the (111), (113) and (201) reflections (extinction rules $h + k = 2n$ and $h + k + l = 2n+1$) indicated a collinear antiferromagnetic structure between adjacent Mn planes in a + - + - sequence along the c-axis. When cooling to below $T_C \sim 44$ K, the magnetic scattering from the (101) and (112) reflections was found to increase ($T = 40$ K), combined with the eliminate in intensity of the (111) peak as in Figure 5.19(b), confirmed that the interlayer spin components of the Mn moments align parallel, thus contribute to a canted ferromagnetic structure ($Fmc$) for the Mn sublattice. The variation in the $a$ and $c$ lattice parameters with temperature are plotted in Figure 5.19(c). Both the $a$ and $c$ values exhibit a monotonic decrease with temperature in the region of the antiferromagnetic transition between $T_N \sim 375$ K and $T_C \sim 44$ K, while below $T_C \sim 44$ K, the $a$ lattice parameter expands slightly from 4.003(5) Å to 4.005(3) Å whereas the $c$ decreases from 10.464(3) Å to 10.451(3) Å at 60 K and at 3 K. The changes in lattice parameter at $T_C \sim 44$ K according to magnetic state changes from AFil to $Fmc$+F(Nd) structure, indicates the presence of strong magnetostructural coupling contributing to the total entropy change around $T_C$. 
5.1.3.4 NdMn$_{2-x}$V$_x$Si$_2$

All of the NdMn$_{2-x}$V$_x$Si$_2$ (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) samples has been confirm crystallize in the expected ThCr$_2$Si$_2$ type structure with space group I4/mmm [31] by Rietveld refinement technique [30] analysis of the room temperature x-ray powder diffraction patterns. Substitution of V for Mn does not change the crystal structure but leads to an expansion of the unit cell. The lattice constant $a$ slightly decreases but significant increases in $c$, and correspondingly the unit cell volumes, were found with the V concentration. As shown in Table 5.4, $d_{\text{Mn-Mn}}$ decrease from 2.8312(6) Å to 2.8288(6) Å and $d_{\text{Mn-Nd}}$ increase from 3.3063(6) Å to 3.3223(6) Å for x=0 and x=0.5. However $d_{\text{Mn-Mn}}$ remains below $d_{\text{Mn-Mn}}^{\text{crit}} = 2.87$ Å for all compositions similar to other compounds from previous case study.

<table>
<thead>
<tr>
<th>NdMn$_{2-x}$V$_x$Si$_2$</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$c/a$</th>
<th>$d_{\text{Mn-Mn}}$ (Å)</th>
<th>$d_{\text{Mn-Nd}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>4.0039(5)</td>
<td>10.5251(6)</td>
<td>168.73(4)</td>
<td>2.6287(3)</td>
<td>2.8312(6)</td>
<td>3.3063(6)</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>4.00302</td>
<td>10.5484</td>
<td>169.03</td>
<td>2.6351</td>
<td>2.8306</td>
<td>3.3106</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>4.00219</td>
<td>10.5633</td>
<td>169.20</td>
<td>2.6394</td>
<td>2.8299</td>
<td>3.3134</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>4.00115</td>
<td>10.5847</td>
<td>169.45</td>
<td>2.6454</td>
<td>2.8293</td>
<td>3.3173</td>
</tr>
<tr>
<td>x = 0.4</td>
<td>4.00098</td>
<td>10.5951</td>
<td>169.60</td>
<td>2.6481</td>
<td>2.8291</td>
<td>3.3193</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>4.00056</td>
<td>10.6104</td>
<td>169.81</td>
<td>2.6522</td>
<td>2.8288</td>
<td>3.3223</td>
</tr>
</tbody>
</table>

From other view with high resolution x-ray diffraction, the NdMn$_{1.7}$V$_{0.3}$Si$_2$ compound is found single phase and exhibits the body-centred tetragonal ThCr$_2$Si$_2$-type structure (space group I4/mmm) over the temperature range ~10-300 K as shown in Figure 5.20. No change in crystal structure is observed over this temperature range although, as discussed more detail
below, the $a$ lattice parameter is found to increase slightly around $T_C \sim 24$ K while the $c$ lattice parameter decreases.

![Figure 5.20](image)

**Figure 5.20** (a) X-ray diffraction patterns (synchrotron radiation) of NdMn$_{1.9}$V$_{0.1}$Si$_2$ over the temperature range $T=10$-$300$ K ($\lambda=0.8265$ Å).

The temperature dependence of the magnetization of NdMn$_{2-x}$V$_x$Si$_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and $0.5$) measured in a magnetic field of $B = 0.01$ T over the temperature range $\sim 10$-$300$ K is shown in Figure 5.21 together with the differential scanning calorimetry (DSC) curves over the temperature range $\sim 300$-$450$ K. The inset shows the values of the Néel temperature $T_N$ and the Curie temperature $T_C$, for the set of compounds as defined by $1/M$ versus temperature and the maxima of the $dM/dT$ versus temperature graphs respectively. Inspection of the insert to Figure 5.21, reveals that $T_N$ decreases from $\sim 380$ K to $\sim 345$ K with increase in V concentration from $x = 0$ to $x = 0.5$ while $T_C$ decreases from $\sim 36$ K to $\sim 16$ K. As shown in Table 5.4 $d_{\text{Mn-Mn}}$ and $d_{\text{Mn-Nd}}$ are found to increase from $d_{\text{Mn-Mn}} = 2.8312(6)$ Å, $d_{\text{Mn-Nd}} =$
3.3063(6) Å at \( x = 0 \) to \( d_{\text{Mn-Mn}} = 2.8341(6) \) Å, \( d_{\text{Mn-Nd}} = 3.3180(6) \) Å at \( x = 0.3 \) and this expansion (size effect) will lead to enhancement of the Mn-Mn intralayer exchange interaction.

**Figure 5.21** Temperature dependence of magnetization of \( \text{NdMn}_{2-x}\text{V}_{x}\text{Si}_{2} \) compounds (\( x = 0 \)) as measured in a field of 0.01 T (left axis; red open symbols for zero field cooling, ZFC, and blue open symbol for field cooling, FC); and differential scanning calorimetry measurements for the temperature range 300-450 K (right axis; solid symbols). The inset shows the Néel temperatures (\( T_N \)) and the Curie temperatures (\( T_C \)) for the set of samples.

On the other hand, increased V concentration is also expected to weaken the exchange interactions of Mn-Mn between layers and the Mn-Nd due to the magnetic dilution effect. Moreover, the change in electronic environment on replacing Mn (3\( d^54s^2 \)) by V (3\( d^34s^2 \)) is also expected to influence the magnetic structures and states of the \( \text{NdMn}_{2-x}\text{V}_{x}\text{Si}_{2} \) compounds. These results indicate in Figure 5.22 that for \( \text{NdMn}_{2-x}\text{V}_{x}\text{Si}_{2} \) compounds over the V concentration range \( x = 0.0 \) to 1.0, the electronic effects, rather than atomic size effects produce the observed decrease in magnetic transition temperature.
Figure 5.22 Experimental (squares) and calculated values (circles) of the Curie temperature $T_C$ as a function of V concentration for NdMn$_{2-x}$V$_x$Si$_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and $0.5$). The $T_C$ values were calculated using the Murnaghan equation and $dT_C/dp = -0.6$ K/kbar as described in the text. The dashed lines act as a guide to the eye with the horizontal dashed line included to emphasise the slight increase in the calculated $T_C$ values, with increasing V concentration.

The magnetization versus field curves ($B = 0$-$5$ T) for NdMn$_{2-x}$V$_x$Si$_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and $0.5$) at $10$ K are shown in Figure 5.23. The magnetization is not saturated up to $5$ T indicating large magnetic anisotropy in these samples as similar to other studies at previous compounds. The saturation magnetization, $M_S$ (at $10$ K) is found to decrease with increasing V concentration in the NdMn$_{2-x}$V$_x$Si$_2$ compounds. If we assume that the rare earth moment does not change with V content, it can be derived that the substitution of V atoms for Mn leads to a decrease of around $-2.2 \mu_B$ per V atom (from linear fitting), which is expected with a simple dilution model (in which the V atoms do not carry magnetic moment).

The magnetization curves obtained for NdMn$_{1.9}$V$_{0.1}$Si$_2$ and NdMn$_{1.9}$V$_{0.5}$Si$_2$ for fields in the range $B = 0 - 8$ T and $B = 0 - 5$ T around their ferromagnetic ordering temperatures are shown in Figures 5.24 (a) and (b), respectively. These data were obtained for increasing and
decreasing fields at 2 K intervals spanning a range around $T_C$, thus providing information about magnetic hysteresis loss effects has been eliminated which is similar to NdMn$_{2-x}$Ti$_x$Si$_2$ compounds from previous study.

![Magnetization curves (B = 0 - 5 T) for NdMn$_{2-x}$V$_x$Si$_2$ compounds (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) at T = 10 K.]

**Figure 5.23** Magnetization curves (B = 0 - 5 T) for NdMn$_{2-x}$V$_x$Si$_2$ compounds (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) at T = 10 K.

As mentioned before, significant MCE values and magnetic entropy changes are usually obtained with a first order magnetic transition due to a large rate of change of magnetisation. Figures 5.24 (c) and (d) show the corresponding Arrott plots ($M^2$ versus B/M) for the x = 0.1 and 0.5 samples, respectively. The Arrott plots are found to exhibit features characteristic of a first order transition for all of the samples. In particular the nature of the Arrott plot near $T_C$ denotes a negative order of the sign of the coefficient $c_2(T)$ in the Landau expansion of the magnetic free energy [39], thereby denoting a first order magnetic transition. The present findings demonstrate that the ferromagnetic transition at $T_C$ in NdMn$_{2-x}$V$_x$Si$_2$ remains a first order transition on substitution of V for Mn until V concentration up to x=0.5.
Figure 5.24 Isothermal magnetization curves in the vicinity of the ferromagnetic ordering temperatures for: (a) NdMn$_{1.9}$V$_{0.1}$Si$_2$ ($T_C = 24$ K with $B = 0$ - 8 T) and (b) NdMn$_{1.5}$V$_{0.5}$Si$_2$ ($T_C = 16$ K with $B = 0$ - 5 T); Arrott plots of $M^2$ versus $B/M$ for the set of NdMn$_{2-x}$V$_x$Si$_2$ compounds: (c) NdMn$_{1.9}$V$_{0.1}$Si$_2$ and (d) NdMn$_{1.5}$V$_{0.5}$Si$_2$.

The magnetic entropy change, $-\Delta S_M$, has been determined for the set of NdMn$_{2-x}$V$_x$Si$_2$ compounds ($x = 0.1$) from their magnetization curves for both increasing and decreasing field values as functions of temperature and magnetic field ($\Delta B = 0$-8 T). The magnetic entropy change has been derived by applying the standard Maxwell relation [40] using (equation 5.3): As shown by the curves of Figure 5.25 (a), the $-\Delta S_M$ peak (closed symbols for increasing field values and open symbols for decreasing field values) gradually broadens towards higher temperatures with increasing magnetic field (from $\Delta B = 0$-5 T), behaviour characteristic of a field induced transition from an antiferromagnetic to a ferromagnetic state.
The changes in magnetic entropy for the set of NdMn$_{2-x}$V$_x$Si$_2$ compounds (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) around their ferromagnetic ordering temperatures are shown in Figure 5.25 (b) as calculated from decreasing applied fields in order to satisfy the suitability of different experimental and related analytical approaches to establish the isothermal entropy change [41].

**Figure 5.25** (a) The temperature dependence of the isothermal magnetic entropy change, $-\Delta S_M$, for NdMn$_{0.9}$V$_{0.1}$Si$_2$ as determined from the magnetization isotherms (closed symbols for increasing fields and open symbols for decreasing fields). (b) The temperature dependence of the isothermal magnetic entropy change, $-\Delta S_M$, for NdMn$_{2-x}$V$_x$Si$_2$ compounds with x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5 as measured from magnetization isotherms ($\Delta B = 0-5$ T from decreasing field curves).
The entropy values at the respective Curie temperatures are \( (\Delta B = 0-5 \, \text{T}) \): \( -\Delta S_M \approx 27 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) at \( T_C = 36 \, \text{K} \); \( -\Delta S_M \approx 25.3 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) at \( T_C = 24 \, \text{K} \); \( -\Delta S_M \approx 17 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) at \( T_C = 22 \, \text{K} \); \( -\Delta S_M \approx 13.8 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) at \( T_C = 20 \, \text{K} \); \( -\Delta S_M \approx 10 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) at \( T_C = 18 \, \text{K} \) and \( -\Delta S_M \approx 8 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) at \( T_C = 16 \, \text{K} \) for \( x=0, \, 0.1, \, 0.2, \, 0.3, \, 0.4 \) and 0.5 respectively. The decrease in magnetization on substitution of the non-magnetic V for Mn, correspondingly reduces the value of \( -\Delta S_M \). Never the less it is noted that the MCE values of \( -\Delta S_M \approx 25.3 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) for \( \text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2 \) and \( -\Delta S_M \approx 17 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) for \( \text{NdMn}_{1.8}\text{V}_{0.2}\text{Si}_2 \) are comparable and higher with MCE values for other materials with small hysteresis that exhibit transitions in the temperature region below 100 K with these materials: \( \text{TbCoC}_2 \) \cite{42} \( (-\Delta S_M = 15 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) at 28 K), \( \text{GdCoAl} \) \cite{43} \( (-\Delta S_M = 10.4 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) at 100 K) and \( \text{TbCoAl} \) \cite{43} \( (-\Delta S_M = 10.5 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) at 70 K).

The magnetic entropy change, \( -\Delta S_M (T, \, B) \) derive from (equation 5.4) as heat calorimetric measurements of the field dependence of the heat capacity and the corresponding adiabatic temperature change, \( \Delta T_{ad} \) evaluated using the expression \([10, \, 44, \, 45]\). Figure 5.26 (a) shows the set of heat capacity measurement obtained for \( \text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2 \) with \( B = 0, \, 2, \, 5 \) and 8 T. The corresponding \( -\Delta S_M (T, \, B) \) values for \( \text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2 \) are shown in Figure 5.26 (b) with the \( \Delta T_{ad} \) values shown in Figure 5.26 (c). The peak value of the adiabatic temperature change is \( \Delta T_{ad}^{\text{max}} = 6.9 \, \text{K} \) for \( \Delta B = 0-8 \, \text{T} \) using the(equation 5.5). As shown in Figure 5.8(b), the maximum magnetic entropy change for \( \text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2 \) as determined from the heat capacity measurements of \( -\Delta S_M^{\text{max}} \approx 24.9 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) and 11.5 J kg\(^{-1}\) K\(^{-1}\) for \( \Delta B = 0-5 \, \text{T} \) and 0-2 T are slightly smaller to the maximum entropy change \( -\Delta S_M^{\text{max}} \approx 25.3 \, \text{J} \, \text{kg}^{-1} \, \text{K}^{-1} \) and 12.8 J kg\(^{-1}\) K\(^{-1}\) as determined from the magnetic measurements using the Maxwell relation. The good agreement between the two sets of measurements confirms that the \( -\Delta S_M \) values derived for \( \text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2 \) from the magnetization measurements represent the MCE behaviour within experimental errors \([14, \, 22, \, 46]\).
Figure 5.26 (a) The heat capacity of NdMn$_{1.9}$V$_{0.1}$Si$_2$ as measured over the temperature range 10-90 K in magnetic fields B = 0 T, 2 T, 5 T and 8 T. (b) The magnetic entropy change, $-\Delta S_M$, determined from the heat capacity measurements of Figure 5.26(a) for NdMn$_{1.9}$V$_{0.1}$Si$_2$ ($\Delta B = 0$-2 T, 0-5 T and 0-8 T). (c) The adiabatic temperature change, $\Delta T_{ad}$, for NdMn$_{1.9}$V$_{0.1}$Si$_2$ as determined from the heat capacity.

Similarly, the $\Delta T_{ad}$ values determined by combing the $-\Delta S_M$ $(T, B)$ (derived from magnetic data) and specific heat results are also drawn in Figure 5.8(c) using closed symbols to make a comparison, which are found to be consistent with the values (open symbols) derived from the specific heat only. By comparison, Nikitin et al [47] reported that the value of $\Delta T_{ad}^{max}$ in NdMn$_2$Si$_2$ compound (around $T_C \sim 32$ K) can be up to 8.2 K with a field change of $\Delta B=0$-6 T. The NdMn$_{1.9}$V$_{0.1}$Si$_2$ compound was selected for investigation by neutron diffraction measurements over the temperature range 3-450 K as representative of the magnetic behaviour of the NdMn$_{2-x}$V$_x$Si$_2$ samples (Figure 5.27). The aims were to determine the magnetic structures and to explore structural changes at the transition temperatures. It has
been confirmed that magnetic phase structure from PM to AFil following with Fmc(Mn)+F(Nd) as shown in Figure 5.27 (b).

The diffraction patterns (\( \lambda = 2.4098 \text{ Å} \)) and Rietveld refinements obtained for NdMn_{1.9}V_{0.1}Si_{2} at 450 K, 100 K and 12 K are shown in Figures 5.28 (a), 5.28 (b) and 5.28 (c), respectively. The selected temperatures typify the behaviour of NdMn_{1.9}V_{0.1}Si_{2} in the three magnetic regions (paramagnetic-antiferromagnetic-ferromagnetic) as indicated from the magnetisation and DSC measurements of Figure 5.21. Rietveld refinements of the neutron diffraction pattern at 450 K (Figure 5.28 (a)) confirm that NdMn_{1.9}V_{0.1}Si_{2} has the ThCr_{2}Si_{2} structure as expected. The absence of magnetic scattering above \( T_N \approx 375 \text{ K} \) in reflections such as (101), (111) and (112) is consistent with a paramagnetic (PM) state. Below \( T_N \approx 375 \text{ K} \), NdMn_{1.9}V_{0.1}Si_{2} is found to exhibit the antiferromagnetic interlayer coupling structure (AFil) down to \( T_C \approx 22 \text{ K} \) (see e.g. the 100 K pattern of Figure 5.28 (b)) as indicated collinear antiferromagnetic structure between adjacent Mn planes in a + - + - sequence along the \( c \)-axis from the magnetic scattering observed at the (111), (113) and (201) reflections. In order to draw out the changes in magnetic structures with temperature, the temperature dependence of the peak intensity for selected magnetic peaks is shown in Figure 5.28 (d). Furthermore, the absence of magnetic scattering from the (111), (113) and (201) reflections at 12 K in Figure 5.28 (c), combined with the increase in intensity of the (112) and (101) peaks as in Figure 5.28 (d), indicate that the interlayer spin components of the Mn moments align parallel, thus leading to a canted ferromagnetic structure (Fmc) for the Mn sublattice. The presence of the purely magnetic peak (001) below \( T_C \) indicates the existence of antiferromagnetic component of Mn moment in the ab-plane [22] as shown inset of Figure 5.28 (c) (pattern from echidna at 3 K with \( \lambda = 2.4395 \text{ Å} \)) as limitation of wombat at small angle scattering. At lower temperature (e.g. 12 K; Figure 5.28 (d)), the increase in the intensities of the (112)
Figure 5.27 (a) Neutron diffraction patterns for NdMn$_{1.9}$V$_{0.1}$Si$_2$ over the temperature range 6-450 K ($\lambda = 2.4098$ Å). (b) The magnetic structures of NdMn$_{1.9}$V$_{0.1}$Si$_2$: paramagnetism for $T > T_{N^{\text{intra}}} \sim 375$ K; AFil ordering of the Mn sublattice for $T^{\text{intra}}_N > T > T_C \sim 24$ K and combined ferromagnetic state $\text{Fmc(Mn)} + \text{F(Nd)}$ for $T < T_C$.

(contributions from both Nd- and Mn-sublattices) and (101) (contribution only from Nd-sublattice [22]) reflections further indicates an additional contribution from Nd moments coupled parallel to the Mn moments along $c$-axis thereby leading to the formation of $\text{Fmc} + \text{F(Nd)}$ magnetic structure as depicted in Figures 5.27 (b). This behavior agrees well
with the results of Welter et al [51] who demonstrated that in the RMn$_2$Ge$_2$ compounds with R= Pr and Nd rare earth moments ferromagnetically coupled with the Mn sublattice at low temperatures. This behavior, also applicable to NdMn$_2$Si$_2$ [8] and NdMn$_2$Si$_{1.6}$Ge$_{0.4}$ [22] compounds, is due to the exchange interaction between the light rare earth elements and 3$d$ transition metal as reported by references [52, 53].

Figure 5.28 (e) is a plot of the temperature dependence of the Mn magnetic moments as derived from the refinements. Within the AF$_{il}$ state region ($T_N \sim 375$ K $> T > T_C \sim 24$ K), the Mn moment increases to $\mu_{Mn} = 2.3 (1) \mu_B$ at 100 K with both Nd and Mn ordering magnetically below $T_C \sim 24$ K. The magnetic moments for Mn and Nd have been derived to be $\mu_{total}^{Mn} = 1.86 \mu_B$ (of basal plane and axial components $\mu_{ab}^{Mn} = 0.86 \mu_B$ and $\mu_c^{Mn} = 1.64 \mu_B$ respectively) and $\mu^{Nd} = 2.78 \mu_B$ at 6 K. The Nd moment and the ferromagnetic component of the Mn moment along the c-axis for NdMn$_{1.9}$V$_{0.1}$Si$_2$ are found to be 2.78 $\mu_B$ and 1.64 $\mu_B$ respectively. The resultant total moment is 4.08 $\mu_B$ per formula unit at 6 K which is higher than that obtained from DC magnetization measurement at 10 K (3.8 $\mu_B$ per formula unit). This different value of magnetic moment is related to the non-saturation behavior shown by the magnetization curve from DC measurements at 10 K even for a field applied of 5 T.

The variation in the $a$ and $c$ lattice parameters with temperature are plotted in Figure 5.28 (f). Both the $a$ and $c$ values exhibit a monotonic decrease with temperature in the region of the antiferromagnetic transition between $T_N = 375$ K and $T_C = 24$ K, while below $T_C = 24$ K, the $a$ lattice parameter expands slightly from 3.9967 Å at 30 K to 3.9988 Å at 6 K whereas the $c$ lattice parameter decreases from 10.5385 Å at 30 K to 10.5280 Å at 6 K. The variation in lattice parameters $a$ and $c$ shown in Figure 5.28 (f) for the PM, AF$_{il}$, and Fmc+F(Nd) states is comparable with the behaviour in NdMn$_2$Si$_2$ [8]. The changes in lattice parameter at $T_C \sim 24$
Figure 5.28 Neutron diffraction patterns ($\lambda=2.4098$ Å) for NdMn$_{1.9}$V$_{0.1}$Si$_2$ at: (a) 450 K; (b) 100 K; (c) 12 K (inset-3 K pattern at $\lambda=2.4395$ Å). (d) Temperature dependence of the integrated intensities of the (101), (111) and (112) reflections; (e) Temperature dependence of the Mn and Nd magnetic moments (6-450 K). (f) Lattice parameters as a function of temperature.

K when the magnetic state changes from AFil to Fmc+F(Nd) structure, indicates the presence of strong magnetostructural coupling around $T_C$. As discussed recently [7, 54], the strong magnetostructural coupling leads to a large structural entropy change around the magnetic phase transition, thereby contributing to the total entropy change around $T_C$. 

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5.1.4 Conclusion

A systematic investigation of the structural and magnetic characteristics of NdMn$_{2-x}$T$_x$Si$_2$ (T = Ti, Cr, Cu and V) compounds has been carried out. Substitution of Ti for Mn leads to decreases in the Curie temperature and the Néel temperature from $T_C \sim 36$ K and $T_N \sim 380$ K at $x=0$ to $T_C \sim 14$ K and $T_N \sim 360$ K at $x=0.3$. The variation in the value of $T_C$ with increasing Ti concentration can be understood in terms of changes in the Mn-Mn exchange interaction together with the effects of magnetic dilution and chemical pressure. A metamagnetic transition from the antiferromagnetic to the ferromagnetic state due to the application of magnetic field was observed above $T_C$ for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$. Substitution of Mn by Ti leads to a reduction of the magnetic entropy change from $-\Delta S_M \sim 27$ J kg$^{-1}$ K$^{-1}$ at $x = 0$; $-\Delta S_M \sim 15.3$ J kg$^{-1}$ K$^{-1}$ at $x = 0.1$; $-\Delta S_M \sim 13$ J kg$^{-1}$ K$^{-1}$ at $x = 0.2$ and $-\Delta S_M \sim 10$ J kg$^{-1}$ K$^{-1}$ at $x = 0.3$ respectively. However, analysis of the magnetisation data demonstrates that the first order magnetic transition of NdMn$_2$Si$_2$ around $T_C$ remains unchanged on replacement of Mn by Ti, and this substitution leads to significant reduction in magnetic hysteresis losses from 28.5 J kg$^{-1}$ for NdMn$_2$Si$_2$ to 0.8 J kg$^{-1}$ for NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ with $\Delta B = 0.5$ T and eliminates thermal hysteresis from $\Delta T = 0.3$ K at $x = 0$ to $\Delta T = 0$ K at $x = 0.1$. Neutron diffraction studies demonstrate that NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ has the AFil antiferromagnetic structure in the temperature range $T_N \sim 374$ K > $T$ > $T_C \sim 22$ K and the combined Fmc+F(Nd) ferromagnetic state below $T_C \sim 22$ K.

The magnetic structures of NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ determined from variable temperature neutron diffraction studies are: layered AFil antiferromagnetism for $T_N^{\text{inter}} \sim 320(3)$ K < $T$ < $T_N^{\text{intra}} \sim 380(3)$ K; canted AFmc antiferromagnetism for $T_C \sim 42(2)$ K < $T$ < $T_N^{\text{inter}} \sim 320(3)$ K with a combined Fmc(Mn)+F(Nd) ferromagnetic structure for $T$ < $T_C \sim 42(2)$ K. Values of the magnetic entropy,
magnetocaloric effect and adiabatic temperature change have been determined from magnetization and heat capacity measurements around the first order magnetic transition at $T_C$. The absence of thermal and magnetic hysteresis in NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ at $T_C$ combined with the magnetocaloric values: $-\Delta S_M^{\text{max}} \approx 15.3 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} \approx 5 \text{ K}$ under $\Delta B=0-5 \text{ T}$, indicate scope for NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ as an active magnetic refrigerator, especially for the helium liquefaction environment.

Substitution of Cu for Mn leads to increase in the Curie temperature and decrease the Néel temperature from $T_C \approx 36 \text{ K}$ to $100 \text{ K}$ and $T_N \approx 380 \text{ K}$ to $320 \text{ K}$ at $x=0$ and $x=1.0$. The variation in the value of $T_C$ with increasing Cu concentration can be understood in terms of changes in the Mn-Mn exchange interaction together with the effects of magnetic dilution. Analysis of the magnetisation data demonstrates that the order of magnetic phase transition around $T_C$ changes from first order at $x<0.6$ to second order transition for $x\geq0.6$ and leads to significant reduction in magnetic hysteresis losses. Substitution of Mn by Cu leads to a reduction of the magnetic entropy change from $-\Delta S_M \approx 27 \text{ J kg}^{-1} \text{ K}^{-1}$ at $x=0$ to $\approx 0.5 \text{ J kg}^{-1} \text{ K}^{-1}$ at $x=1.0$ respectively. Neutron diffraction studies demonstrate that NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ has the AF$_{il}$ antiferromagnetic structure in the temperature range $T_N \approx 375 \text{ K} > T > T_C \approx 44 \text{ K}$ and the combined Fmc+F(Nd) ferromagnetic state below $T_C \approx 44 \text{ K}$.

The replacement Mn by V in NdMn$_{2-x}$V$_x$Si$_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and $0.5$) leads to decrease in the Curie and Néel temperature from $T_C \approx 36 \text{ K}$ to $14 \text{ K}$ and $T_N \approx 380 \text{ K}$ to $345 \text{ K}$ at $x=0$ and $x=0.5$. Increment of V concentration leads to a reduction of the magnetic entropy change from $-\Delta S_M \approx 27 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T_C = 36 \text{ K}$ for $x=0$ to $-\Delta S_M \approx 8 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T_C = 16 \text{ K}$ for $x=0.5$ respectively as did not change the first order magnetic transition behaviour. The neutron diffraction study on NdMn$_{1.9}$V$_{0.1}$Si$_2$ compound indicated that magnetic structure
found from paramagnetic PM to the AFil antiferromagnetic structure in the temperature range $T_N \sim 375 \text{ K} > T > T_C \sim 24 \text{ K}$ and the combined Fmc+F(Nd) ferromagnetic state below $T_C \sim 24 \text{ K}$. 
References:

5.2 Substitution of Pr with Y in PrMn$_2$Ge$_2$ Compound

5.2.1 Introduction

The rapid change in magnetisation associated with first order magnetic transitions together with simultaneous field-induced magnetic and structural transformations lead to enhanced entropy values [1]. For example, materials based on the NiMnGa and MnCoGe systems show pronounced entropy behaviour at magnetostructural transitions around room temperature [e.g. 2, 3, and 4]. Layered rare earth compounds in the RMn$_2$X$_2$ series (R=rare-earth; X=Ge, Si) are also of interest as they enable the structural and magnetic behaviour to be controlled via substitution of R, Mn, X atoms on the 2a, 4d and 4e sites respectively [5-10]. The overall magnetic behaviour of RMn$_2$Ge$_2$ compounds is strongly influenced by two critical intralayer Mn–Mn distances $d_{\text{Mn-Mn}}^{\text{crit1}} = 2.87$ Å (related $a_{\text{crit1}} = 4.06$ Å) and $d_{\text{crit2}} = 2.84$ Å (related $a_{\text{crit2}} = 4.02$ Å) [5, 8-9]. For compounds with $d_{\text{Mn-Mn}}^{a} > d_{\text{crit1}}$, the intralayer in-plane coupling is antiferromagnetic and the interlayer coupling is ferromagnetic [5, 8-9] leading to the Fmc-type magnetic configuration.

In the case of the Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ system, given that PrMn$_2$Ge$_2$ is ferromagnetic and YMn$_2$Ge$_2$ antiferromagnetic at room temperature, the Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ system leads to an extended region of re-entrant ferromagnetism around $x \sim 0.5$ [8]. The combination of ferromagnetic ordering of the Pr-sublattice and ferromagnetic ordering of the Mn-sublattice in turn leads to enhanced magnetocaloric behaviour. Here, report extension of our studies of the structural and magnetic properties of Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ using x-ray and neutron diffraction together with magnetic measurements [8-10]. Our investigations have led to construction of the magnetic phase diagram for Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ as functions of both composition and the Mn–
Mn spacing and exploration of the nature of the magnetic transitions and entropy changes observed at the ferromagnetic. The changes in magnetic states due to Y substitution for Pr are discussed in terms of chemical pressure, external pressure and electronic effects.

5.2.2 Experimental and Procedures

The set of Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds (with x=0.0 - 1.0) were prepared using conventional argon arc melting. The starting materials contained ~3% excess Mn to compensate for the Mn loss due to evaporation during melting. The ingots were melted five times for improved homogeneity and then annealed at 900°C for one week in an evacuated quartz tube. The samples were characterized at room temperature by x-ray diffraction (CuK$_\alpha$ radiation, $\lambda = 1.5418$ Å). The temperature dependences of the DC magnetization and the AC magnetic susceptibility were measured using a superconducting quantum interference device (SQUID) and a Quantum Design Physical Properties Measurement System (PPMS) Magnetometer from 5 K to 340 K. A search for higher temperature phase transitions in the range 300 K to 570 K was carried out using differential scanning calorimetry (DSC) at a heating rate of 10 K/min. Neutron diffraction experiments were carried out on the GEM time-of-flight diffractometer at ISIS (STFC, UK) from 30-360 K [e.g. 10] and the Echidna and Wombat diffractometers at OPAL (Australia). Rietveld refinements have been carried out using the FULLPROF program package [11] which allows simultaneous refinement of the structural and magnetic parameters.
5.2.3 Result and Discussion

Analysis of the room temperature x-ray diffraction (XRD) patterns of Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ (Figure 5.29 (a)) indicates that all of the samples are single phase with the expected body-centred tetragonal ThCr$_2$Si$_2$-type structure (space group I4/mmm). The lattice parameters derived from refinement of the room temperature patterns are presented in Figure 5.29 (b) as a function of composition. The present set of lattice parameters are similar to those reported in reference [12] which are also shown in Figure 5.29 (b). Both the $a$ and $c$ lattice parameters decrease linearly with increasing Y content with rates of change: $da/dx = -0.133$ Å and $dc/dx = -0.053$ Å respectively in accord with Vegard’s Law.

With respect to PrMn$_2$Ge$_2$ as the reference, consider the influence of the reduction in unit cell volume due to Y substitution to be analogous to the effects of “chemical pressure”. The Murnaghan equation of state and the experimental unit cell volumes of Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ can be used to derive the related “chemical pressure”. It is accepted that Murnaghan equation can be described [13] as:

$$P(V) = \frac{B_o}{B_o'} \left( \frac{V_0}{V} \right)^{B_o'} - 1$$  \hspace{1cm} (1)

where $B_0$ is the isothermal bulk modulus, $B_0'$ is its pressure derivative, and $V_0$ and $V$ are the volumes at ambient pressure and pressure $p$, respectively. Using the values of $B_0 = 73.5$ GPa and $B_0' = 11.4$ from the closely related compound UGe$_2$Mn$_2$ [13], the equivalent “chemical pressure” from Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds can be derived as shown in Figure 5.29 (c). The distinct change in slope which occurs in the calculated chemical pressure around $x=0.5$-$0.6$ at room temperature (Figure 5.29 (c)), may be related to the change in magnetic state from canted ferromagnetism for $x <\sim 0.6$ to canted antiferromagnetism for $x >\sim 0.6$ as discussed
below (see Figure 5.33). This change in slope is drawn out more clearly in the insert to Figure 5.29 (c) which shows the reduced unit cell volume $V/V_0$ versus Y concentration for $Pr_{1-x}Y_xMn_2Ge_2$ compounds at room temperature ($V_0$ is the volume of the $PrMn_2Ge_2$ unit cell while $V$ is the volume).

**Figure 5.29** (a) Room temperature x-ray diffraction patterns and Rietveld refinements of the $Pr_{1-x}Y_xMn_2Ge_2$ compounds (CuK$_\alpha$ radiation); (b) composition dependence of lattice parameters (open symbols taken from reference [12]). (c) The calculated chemical pressure based on the values of $B_0=73.5$ GPa and $B_0'=11.4$ for $UMn_2Ge_2$ [13] as a function of Y content. The insert shows the composition dependence of the changes in reduced unit cell volume $V/V_0$ versus Y concentration ($V_0$ is the volume of the $PrMn_2Ge_2$ unit cell while $V$ is the volume for $Pr_{1-x}Y_xMn_2Ge_2$ compounds at room temperature). The arrow indicates the region where a change in slope is obtained between two linear regions above and below $x \sim 0.6$.

In considering the magnetic regions for the $Pr_{1-x}Y_xMn_2Ge_2$ samples ($x=0.0 - 1.0$), the transition temperatures are first identified with their predominant physical influence. In particular with decreasing temperature from the paramagnetic (PM) region: $T_N^{\text{intra}}$ defines the magnetic transition from paramagnetism to intralayer antiferromagnetic ordering within the
(001) Mn layers (AFil); $T_{C_{\text{inter}}}$ defines the transition from AFil to a canted spin structure (Fmc); $T_{c/c}$ defines the transformation temperature of the magnetic structure from Fmc to a conical configuration Fmi type, $T_{N_{\text{inter}}}$ denotes the change from Fmc to the antiferromagnetic canted structure AFmc and $T_{C_{\text{Pr}}}$ defines the transition temperature for onset of the ordering of the Pr sublattice [8, 9]. The magnetization and DSC curves for Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds were used to determine the possible magnetic phase transitions. As examples, Figure 5.30 (a) shows the composite magnetization and DSC data over the temperature range ~5-500 K for PrMn$_2$Ge$_2$ with Figure 5.30 (b) showing the DSC data for Pr$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$. In the case of the PrMn$_2$Ge$_2$ compound, four magnetic phase transitions have been observed in the range 5 K to 500 K. The transitions, as marked by arrows in Figure 5.30 (a), are indicated as $T_{C_{\text{Pr}}}$, $T_{c/c}$, $T_{C_{\text{inter}}}$ and $T_{N_{\text{intra}}}$ with increasing temperature. By comparison, only two transitions are detected in the Pr$_{0.2}$Y$_{0.8}$Mn$_2$Ge$_2$ compound with no transitions occurring below 300 K.

**Figure 5.30** (a) Composite figure showing the temperature dependent magnetization obtained on cooling PrMn$_2$Ge$_2$ in a field of $B=0.01$ T (5-350 K; left part) and the results of DSC measurements (300-500 K; right part). The transition temperatures are indicated by arrows. (b) The DSC results for the Pr$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$ compound.

A set of neutron powder diffraction patterns have been obtained for selected Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds over the temperature range 5-450 K (Figures 5.31 (a) and 5.31 (c)). As noted above, Rietveld refinements were carried out on all patterns using the FULLPROF program package which allows us to derive the structural and magnetic parameters. As explained fully in related articles [5, 8-9], the specific location of Mn atoms on the 4d site in the ThCr$_2$Si$_2$...
structure (space group \(I4/mmm\)) allows ready identification of various magnetic structures from key indicators in the neutron diffraction patterns as follows.

1. Ferromagnetic ordering of the Mn atoms – hkl reflections with \(h + k = 2n\) and \(l = 2n\); (e.g. (112) reflections);
2. Antiferromagnetic ordering of the Mn atoms within the (001) planes - reflections with \(h + k = 2n + 1\); (e.g. (101), (103) reflections);
3. Collinear antiferromagnetic structure between adjacent Mn planes - reflections with \(h + k + l = 2n + 1\); (e.g. (111), (113) reflections);

Ferromagnetic mixed incommensurate structure (\(F\bar{m}\bar{i}\)) of wave vector \((0, 0, q_z)\) - satellite reflections with \(h + k = 2n + 1\); (e.g. (101), (103)).

The refinement results for each of the four magnetic states of the PrMn\(_2\)Ge\(_2\) compound at selected temperatures (cf. transition temperatures in Figure 5.30 (a)) are shown as typical examples in Figure 5.31 (a). It is clear that the neutron diffraction pattern characteristic of each magnetic state, matches well with the intensities expected from magnetic contributions to the neutron scattering as outlined above. The refinement results for PrMn\(_2\)Ge\(_2\) at these selected temperatures are listed in Table 5.5. Figure 5.31 (c) shows the intensities of the (101), (112) and (200) magnetic peaks as a function of temperature with the transitions from the different magnetic phases identified readily from changes in the magnetic scattering. The invariant behaviour of the purely nuclear (002) peak is shown in Figure 5.31 (c) for comparison.

For Pr\(_{0.2}\)Y\(_{0.8}\)Mn\(_2\)Ge\(_2\), the lattice parameter \(a\) at room temperature is derived to be \(a = 4.020(1)\) Å with \(d_{\text{Mn-Mn}}=2.843\) Å (this \(d_{\text{Mn-Mn}}\) spacing is very close to the second critical value, \(d^{\text{rit2}}_{\text{Mn}}\).
Figure 5.31 (a) Neutron diffraction patterns and Rietveld refinements for PrMn$_2$Ge$_2$ at 450 K, 350 K, 300 K, 200 K and 10 K ($\lambda=2.4205$ Å). These temperatures were selected as characteristic of the neutron diffraction pattern for each magnetic state. (b) Representative diffraction patterns for Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ over the temperature range 5-305 K at 10 K intervals ($\lambda=2.4072$ Å). (c) The intensities of the (101), (112) and (200) magnetic peaks as a function of temperature. The temperature variation of the purely nuclear (002) peak is shown for comparison.
Mn\textsubscript{2}=2.84 Å, for occurrence of the AF\textsubscript{il} structure as mentioned above). Wang \textit{et al.} [12] reported a value of \(a=3.996\) Å (smaller than \(a_{\text{crit}}=4.02\) Å) for the lattice parameter of YMn\textsubscript{2}Ge\textsubscript{2}, Szytula and Szott [20] having earlier shown that YMn\textsubscript{2}Ge\textsubscript{2} has the AF\textsubscript{il} structure. Given the proximity of the \(a\) lattice parameter of Pr\textsubscript{0.2}Y\textsubscript{0.8}Mn\textsubscript{2}Ge\textsubscript{2} to the critical value \(a_{\text{crit}}\), considered two possible magnetic structural models (Figures 5.32 (b) and 5.32 (c)), for refinement of the 300 K neutron diffraction pattern of Pr\textsubscript{0.2}Y\textsubscript{0.8}Mn\textsubscript{2}Ge\textsubscript{2}.

The first model is the AF\textsubscript{il} structure which features a collinear antiferromagnetic structure along the \(c\)-axis. The second model is the AF\textsubscript{mc} structure in which the antiferromagnetic mixed commensurate structure is characterized by antiferromagnetic interplanar coupling of the in-plane ferromagnetic components and by the commensurate ordering of the antiferromagnetic in-plane components. Comparison of the refinements in Figures 5.32 (b) and 5.32 (c) (see inserts for details of the (101) reflection), indicates that at 300 K the AF\textsubscript{mc} structure provides a significantly improved description of the diffraction data compared with the AF\textsubscript{il} structure. This description of the AF\textsubscript{mc} structure for Pr\textsubscript{0.2}Y\textsubscript{0.8}Mn\textsubscript{2}Ge\textsubscript{2} in the temperature region below \(T_1\) (Figure 5.30 (b)) indicates that \(T_1\) can be defined as \(T_{\text{N\,inter}}\) where the AF\textsubscript{il} layered antiferromagnetic structure transforms to the canted AF\textsubscript{mc} structure. Correspondingly \(T_2\) can be assigned as \(T_{\text{N\,intra}}\) where the magnetic state changes from paramagnetism (PM) to the AF\textsubscript{il} antiferromagnetism with decreasing temperature. The refinement for the entire room temperature diffraction pattern of Pr\textsubscript{0.2}Y\textsubscript{0.8}Mn\textsubscript{2}Ge\textsubscript{2} to the AF\textsubscript{mc} structure is shown in Figure 5.32 (a) with the resultant structural and magnetic parameters shown in Figure 5.32 (d).

Combining the present findings with the published results [12, 14-16] has enabled us to construct magnetic phase diagrams for the Pr\textsubscript{1-x}Y\textsubscript{x}Mn\textsubscript{2}Ge\textsubscript{2} system as a function of Y content.
as in Figure 5.33 (the phase diagram versus \( a \) lattice parameter and intralayer distance \( d_{\text{Mn-Mn}} \) between Mn-Mn within the ab-plane can be seen in reference [17]). Figure 5.33 demonstrates that, as expected, the magnetic states at room temperature have been modified by Y substitution due to the contraction of the unit cell. Samples with \( x > \sim 0.7 \)

\[
\begin{array}{c}
\text{Pr}_{0.2}Y_{0.8}\text{Mn}_2\text{Ge}_2 \\
\text{AFmc model}
\end{array}
\]

\begin{center}
\text{Intensity (arb. units)}
\end{center}

\begin{center}
t.o.f. (\( \mu \) sec.)
\end{center}

\begin{center}
T=300 K
\end{center}

\begin{center}
(111)
\end{center}

\begin{center}
(101)
\end{center}

\begin{center}
(a)
\end{center}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.32}
\caption{(a) Neutron diffraction pattern of Pr\(_{0.2}\)Y\(_{0.8}\)Mn\(_2\)Ge\(_2\) at 300 K and Rietveld refinement to the AFmc structure; (b) refinement for the AFil model shown over an expanded 2\( \theta \) range and (c) refinement for the AFmc model over an expanded 2\( \theta \) range; (d) temperature dependence of lattice parameters and magnetic moment values of Pr\(_{0.2}\)Y\(_{0.8}\)Mn\(_2\)Ge\(_2\) as determined from refinements to the AFmc structure.}
\end{figure}

where the lattice constant \( a \) is below \( a_{\text{crit}} = 4.06 \) Å (Figure 5.29 (b)) are antiferromagnetic at room temperature with no ferromagnetic order evident over the entire temperature range, whereas samples of Y content \( x < \sim 0.7 \) are ferromagnetic at room temperature. In RMn\(_2\)X\(_2\) compounds there are three magnetic interactions (R-R, R-Mn and Mn-Mn) below \( T_{\text{C}}^R \), the temperature at which the rare earth sublattice orders. In Pr\(_{1-x}\)Y\(_x\)Mn\(_2\)Ge\(_2\) compounds, the R-R and R-Mn magnetic interactions become weaker with increasing Y content due to the dilution effect caused by introduction of the non-magnetic Y atoms. This behaviour is evident, for
example, in the decrease of $T_{C}^{Pr}$ with increasing Y concentration from $T_{C}^{Pr} \sim 100$ K for PrMn$_2$Ge$_2$ to $T_{C}^{Pr} \sim 0$ K for Y concentration around $x \sim 0.7$ (Figure 5). As is clear from the phase diagram in Figure 5.33, Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds with Y content $x > 0.7$ show a relatively simple magnetic behaviour, transforming from paramagnetism at high temperature to AFil followed by AFmc with decreasing temperature with no evidence of ordering of the Pr-sublattice. As noted above, YMn$_2$Ge$_2$ exhibits the layered AFil structure although the boundary between the AFmc and AFil magnetic structures at high Y contents has yet to be

![Figure 5.33](image)

**Figure 5.33** Magnetic phase diagram of Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ as a function of the Y content (closed symbols - present results; open symbols - data from [12, 14-16]). As discussed in the text, $T_{NI}$ (squares) defines the transition from paramagnetism to intralayer antiferromagnetic ordering within the (001) Mn layers (AFil); $T_{CI}$ (circles) defines the transition from AFil to a canted spin structure (Fmc); $T_{C}$ (inverted triangle) defines the transformation temperature of the magnetic structure from Fmc to a conical configuration Fmi type. $T_{N}$ (triangle) denotes the transition to the antiferromagnetic canted structure AFmc and $T_{C}^{Pr}$ (stars) defines the transition temperature for onset of the ordering of the Pr sublattice. The dashed lines indicate trends in the data. As discussed in the text, the vertical dashed line located around Y concentration of $x \sim 0.86$ is used as a tentative guide to the boundary between the AFmc and AFil regions.
delineated. It is assumed that the boundary between the AFmc and AFil regions originates around the paramagnetic transition for these phases at Y concentration $x = \sim 0.86$. By comparison, Pr-rich samples ($x < \sim 0.4$) successively exhibit four magnetic states – AFil, Fmc, Fmi, Fmi+F(Pr) – on cooling from the high temperature paramagnetic phase, while re-entrant ferromagnetism has been observed for compounds with Y contents in the range $x \sim 0.4-0.6$. Figure 5.33 also indicates that the Fmi structure only occurs for Y content $x < \sim 0.4$.

This is reflected by the decrease in wave vector with Y content from $q_c = 0.272$ for PrMn$_2$Ge$_2$ at 10 K to $q_c = 0.237$ for Pr$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$ at 10 K. Similar behaviour has been detected in the PrMn$_{2-x}$Fe$_x$Ge$_2$ [5] and Pr$_{1-x}$Lu$_x$Mn$_2$Ge$_2$ [18] systems where the absence of the Fmi structure is noted for $x < 0.38$ and $y < 0.4$, respectively.

Given that the magnetic structure in RMn$_2$Ge$_2$ and related systems depends sensitively on the intraplanar Mn-Mn spacing and that both external pressure and the substitution of Y for Pr in Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ can reduce the Mn-Mn distance, it is interesting to compare the relative impact of chemical pressure and applied pressure on the magnetic order. Here consider the variation of $T_N^{\text{inter}}$ with Y content (considered here as equivalent to effects of chemical pressure) and external pressure as detected in Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ [9], where made such a comparason for $T_C^{\text{Pr}}$. As is evident from Figure 5.33, these two transitions were chosen because of their higher sensitivity to the composition change (and Mn-Mn distance [17]). With increase in Y content, $T_N^{\text{inter}}$, the transition from the canted Fmc magnetic structure to the canted AFmc magnetic structure, increases from $\sim 200$ K for $x=0.4$ to $\sim 373$ K for $x=0.8$ (Figure 5.33). The corresponding chemical pressure changes from $\sim 12.6$ kbar for $x=0.4$ to $\sim 50.7$ kbar for $x=0.8$, leading to a rate of change $dT_N^{\text{inter}}/dp = 4.5$ K/kbar compared with the rate of change in transition temperature with external pressure of $dT_N^{\text{inter}}/dp = 22.2$ K/kbar in Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ [9]. Estimation of the value of chemical pressure due to Y substitution for Pr
using the isothermal bulk modulus $B_0$ and its pressure derivative $B'_0$ of UMn$_2$Ge$_2$ \cite{13} is expected to include additional uncertainty because the magnetic states change with pressure from Fmc to AFmc (see \cite{17}) and different magnetic states are expected to have different $B_0$ and $B'_0$. Given this additional uncertainty, think the comparison for $dT_{N \text{inter}}/dp$ is consistent with change in $T_C^{Pr}$, as discussed in \cite{9} where noted the rate of change with mechanical pressure exceeds the change with chemical pressure by a factor of $\sim 2$. Comparison of the effects of chemical pressure and applied pressure demonstrates that while the Y substitution for Pr produces changes consistent with the effect of pressure, additional effects occur. These effects are associated with the differences in the electron configurations of Pr$^{3+}$ (4f$^2$) and Y$^{3+}$ (4d$^0$) ions with electronic effects likely to explain the different rates of change for both $dT_C^{Pr}/dp$ and $dT_{N \text{inter}}/dp$ for chemical pressure and external pressure.

**Table 5.5** Rietveld refinement results for PrMn$_2$Ge$_2$ at 10 K, 200 K, 300 K, 350 K and 450 K. These temperatures were selected as characteristic of the neutron diffraction pattern of each magnetic state (cf. Figure 5.31(a)). The standard errors derived from the refinements are also listed.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>10 K</th>
<th>200 K</th>
<th>300 K</th>
<th>350 K</th>
<th>450 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic state</td>
<td>$Fmi+F(Pr)$</td>
<td>$Fmi$</td>
<td>$Fmc$</td>
<td>AFil</td>
<td>PM</td>
</tr>
<tr>
<td>a (Å)</td>
<td>4.107(1)</td>
<td>4.114(1)</td>
<td>4.119(1)</td>
<td>4.121(1)</td>
<td>4.126(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.881(1)</td>
<td>10.891(1)</td>
<td>10.905(2)</td>
<td>10.919(2)</td>
<td>10.951(2)</td>
</tr>
<tr>
<td>$z_{Ge}$</td>
<td>0.3820(2)</td>
<td>0.3827(2)</td>
<td>0.3825(2)</td>
<td>0.3826(2)</td>
<td>0.3826(2)</td>
</tr>
<tr>
<td>$\mu_{\text{tot}}$ (µB)</td>
<td>2.51(4)</td>
<td>2.33(4)</td>
<td>2.08(3)</td>
<td>1.86(3)</td>
<td>-</td>
</tr>
<tr>
<td>$\mu_c$ (µB)</td>
<td>2.03(5)</td>
<td>1.95(5)</td>
<td>1.28(6)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Canting angle (°)</td>
<td>51.0(9)</td>
<td>53.6(8)</td>
<td>58.4(6)</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>$q_c$</td>
<td>3.23(7)</td>
<td>2.90(4)</td>
<td>2.44(5)</td>
<td>1.86(3)</td>
<td>-</td>
</tr>
<tr>
<td>$\mu_{\text{Pr}}$ (µB)</td>
<td>0.272(2)</td>
<td>0.214(1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The magnetocaloric effect around $T_{C \text{inter}}$ have calculated for the set of samples from magnetization data using the standard Maxwell thermodynamic relation [e.g. 19]. The magnetization results for PrMn$_2$Ge$_2$ in the region of $T_{C \text{inter}} \sim 334$ K are shown as an example in Figure 5.34 (a) with the corresponding Arrott plots of $M^2$ versus B/M presented in Figure.
The positive intercepts of the linear extrapolation of the magnetisation data with the \( M^2 \) axis below \( T_{C^{\text{inter}}} \) (determined from the temperature of zero intercept in Figure 5.34 (b)), demonstrates the ferromagnetic nature of the magnetic phase below \( T_{C^{\text{inter}}} \). The positive slopes of the Arrott plots around \( T_{C^{\text{inter}}} \) indicate that the magnetic transition at \( T_{C^{\text{inter}}} \) for \( \text{PrMn}_2\text{Ge}_2 \) is second order. Similarly, analyses of the Arrott-plots for \( \text{Pr}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2 \) and \( \text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2 \) demonstrate that the ferromagnetic transitions at \( T_{C^{\text{inter}}} \) for these compounds are also second order.

![Figure 5.34](image)

**Figure 5.34** (a) Magnetisation versus field curves \((B = 0–5 \, \text{T})\) for \( \text{PrMn}_2\text{Ge}_2 \) over the temperature region around \( T_{C^{\text{inter}}} \sim 334 \, \text{K} \); (b) the corresponding Arrott plots of \( M^2 \) versus \( B/M \) for \( \text{PrMn}_2\text{Ge}_2 \).

The isothermal magnetic entropy change, \(-\Delta S_M\), for the \( \text{PrMn}_2\text{Ge}_2 \) and \( \text{Pr}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2 \) samples are shown as a function of temperature in Figures 5.35 (a) and 5.35 (b) respectively.
Figure 5.35 Temperature dependence of the isothermal magnetic entropy change $-\Delta S_M$ for: (a) PrMn$_2$Ge$_2$ and (b) Pr$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$. (c) Dependence of $-\Delta S_M^{PK}$ (peak value of the magnetic entropy change at different B) on the parameter $B^{2/3}$ for Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds with $x$=0.0, 0.2 and 0.5. The linear fits to the data as shown by the dashed lines are discussed in the text.
The maximum entropy values $-\Delta S_M$ around the ferromagnetic transition temperature $T_C^{\text{inter}}$ for the Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds with $x=0.0$, 0.2 and 0.5 have been derived to be 3.0 J/kg K, 2.94 J/kg K and 3.47 J/kg K respectively (field change $\Delta B=0-5$ T). Compared with other rare earth intermetallic compounds which also exhibit a second order phase transition around room temperature, the present set of Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds exhibit moderate isothermal magnetic entropy. As examples, the values of $-\Delta S_M$ for Ho$_2$Fe$_{17-x}$Mnx are 3.2 J kg$^{-1}$K$^{-1}$ around $T_C=336$ K ($x=0.0$) and 2.7 J kg$^{-1}$K$^{-1}$ around $T_C=302$ K ($x=2.0$) respectively [20]. Er$_2$Fe$_{17}$ has recently been found to exhibit similar entropy value of $-\Delta S_M=3.6$ J kg$^{-1}$K$^{-1}$ around 300 K for $\Delta B = 0-5$ T [21]. The present set of entropy values are similar to those obtained for related compounds in the RMn$_2$X$_2$ series which also exhibit magnetic transitions around ~330 K. Dincer and Elerman [22A] obtained maximum entropy values in the approximate range $-\Delta S_M \sim 2-3$ J kg$^{-1}$K$^{-1}$ ($\Delta B=0-5$ T) around the paramagnetic to ferromagnetic Curie temperatures $T_C \sim 300-320$ K for re-entrant SmMn$_{2-x}$Fe$_x$Ge$_2$ ($x = 0.05$, 0.10) and SmMn$_{2-x}$Co$_x$Ge$_2$ ($x = 0.05$, 0.15) compounds. On the other hand a reduced entropy value of $-\Delta S_M \sim 1.8$ J kg$^{-1}$K$^{-1}$ was obtained for a Pr$_{0.1}$Gd$_{0.9}$Mn$_2$Ge$_2$ sample around the antiferromagnetic to ferromagnetic Curie temperature $T_C \sim 340$ K [23A].

It is well accepted that the following relationship applies for a magnetic system with a second-order phase transition [22, 23]:

$$|\Delta S_{M}^{PK}| \propto B^{2/3}$$  \hspace{1cm} (2)

where $-\Delta S_{M}^{PK}$ is the peak value of the magnetic entropy change at different magnetic fields $B$. It can be seen from Figure 5.35 (c) that this relationship is valid for the Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds with $x=0.0$, 0.2 and 0.5 around $T_C^{\text{inter}}$. This agreement of $-\Delta S_{M}^{PK}$ with relationship (2) confirms the second order nature of these transitions as demonstrated by the Arrott plot analyses and discussed above (e.g. Figure 5.34 (b) for PrMn$_2$Ge$_2$).
5.2.4 Conclusions

Replacement of Y for Pr leads to a significant reduction in the lattice parameter of Pr

\[ x \text{Y}_x \text{Mn}_2 \text{Ge}_2 \] compounds. The commensurate changes in the intralayer Mn–Mn distances correspondingly lead to a variety of magnetic structures, as also observed in related RMn2X2 systems (R – rare earth; X - Ge, Si) [e.g. 24]. The various magnetic structures of Pr

\[ x \text{Y}_x \text{Mn}_2 \text{Ge}_2 \] have determined by neutron powder diffraction over the temperature range 5 – 450 K. Together with magnetisation and differential scanning calorimetry measurements, this has enabled us to construct the magnetic phase diagram of Pr

\[ x \text{Y}_x \text{Mn}_2 \text{Ge}_2 \] compounds of Y contents x = 0.0, 0.2 and 0.5. The ferromagnetic transitions at \( T_C^{\text{inter}} \), the temperature at which the layered antiferromagnetic structure transforms to the canted Fmc structure, are found to be second order. The entropy changes around \( T_C^{\text{inter}} \) have been derived for Pr

\[ x \text{Y}_x \text{Mn}_2 \text{Ge}_2 \] compounds of Y contents x = 0.0, 0.2 and 0.5.
References

5.3 Substitution of Ge with Other Metalloid in CeMn$_2$Ge$_2$ Compound

5.3.1 Introduction

Due to the wide and interesting range of structural and magnetic phenomena - including magnetism, superconductivity, mixed valence, Kondo behavior and heavy fermion - exhibited by layered RT$_2$X$_2$ rare earth compounds, (R is a rare earth, T is transition metal and X is Si or Ge) this series has consistently attracted many researchers for further investigation [1-4]. Most of the layered RT$_2$X$_2$ crystallize in the body centred tetragonal ThCr$_2$Si$_2$-type structure with space group $I4/mmm$ in which the R, T and X atoms occupy the 2$a$, 4$d$ and 4$e$ sites respectively with the different atoms stacked along the $c$-axis in the layered sequence R–X–T–X–R [5-7]. The RMn$_2$X$_2$ series has continued to attract a great deal of attention over the past two decades due to the fact that the magnetic states of the Mn-sublattice depend sensitively on the inter-planar and intra-planar Mn–Mn distances [8, 9]. Furthermore, intensive studies of RMn$_2$X$_2$ compounds have revealed a large variety of magnetic structures and magnetic phase transitions that occur with changes in chemical composition, temperature and mechanical pressure or magnetic field applied [10-12]. As such, from this aspect, RMn$_2$X$_2$ compounds provide model systems for study of, for example, the volume dependence of magnetic ordering. They also offer scope for design of critical magnetic parameters — such as the type or order of magnetic phase transitions and ability to shift transition temperatures — by controlling the intra-planar separation distance $d_{Mn-Mn}^{a}$ with applied mechanical or chemical pressure via replacement with elements of different atomic sizes [13-15].
In this study, we report the findings of an investigation of the effects of substituting Si for Ge in CeMn₂Ge₂₋ₓSiₓ (x = 0.0-2.0) on their magnetic properties and structures using magnetic, differential scanning calorimetry (DSC), high resolution X-ray synchrotron radiation and neutron diffraction measurements. In addition to exploring the effects of the Si atoms on the metalloid Ge, it is expected that substitution of Ge (atomic radius 1.37 Å) with the smaller Si (atomic radius 1.32 Å) would modify the magnetic structure of CeMn₂Ge₂₋ₓSiₓ. This follows as \( d_{\text{Mn-Mn}}^a \sim 2.934 \) Å in CeMn₂Ge₂ while \( d_{\text{Mn-Mn}}^a \sim 2.806 \) Å in CeMn₂Si₂ [16]. These values of \( d_{\text{Mn-Mn}}^a \) are respectively greater than \( d_{\text{crit1}} \sim 2.87 \) Å (of related lattice parameter \( a_{\text{crit1}}=4.06 \) Å) and less than \( d_{\text{crit2}} \sim 2.84 \) Å (related lattice parameter \( a_{\text{crit2}}=4.02 \) Å), the first and second critical intralayer Mn–Mn distances which govern the magnetic behaviour in RMn₂Ge₂ compounds [17]. According to Welter et. al [18], the \( d_{\text{Mn-Mn}}^a \) not only affects the intralayer Mn–Mn coupling but also the interlayer exchange interaction and, as summarised below, three general categories can be delineated [19].

(i) The interlayer exchange coupling being ferromagnetic and the intralayer coupling antiferromagnetic for \( d_{\text{Mn-Mn}}^a > d_{\text{crit1}} = 2.87 \) Å leading to the canted Fmc-type ferromagnetic structure.

(ii) Both the interlayer and the intralayer coupling being antiferromagnetic (AFmc-type magnetic structure) for \( d_{\text{crit2}} = 2.84 \) Å < \( d_{\text{Mn-Mn}}^a < d_{\text{crit1}} = 2.87 \) Å.

(iii) No intralayer in-plane spin component and the interlayer coupling being antiferromagnetic, leading to the AFil-type magnetic structure \( d_{\text{Mn-Mn}}^a \) in the range \( d_{\text{Mn-Mn}}^a < d_{\text{crit2}} = 2.84 \) Å.

This interest in the behaviour of layer structure materials has been enhanced in recent years by the discovery of a giant magnetocaloric effect (MCE) near room temperature in Gd₅Si₃Ge₂.
compound [20, 21]. R₅(Si,Ge)₄ type compounds have a distinct layered structure in which the covalent Si–Si, Si–Ge and Ge–Ge bonds and interlayer distances play a vital role in determining their magnetic and magnetocaloric effect properties attention has therefore increasingly focused on understanding the fundamental properties of this type of layered material. As already noted, the CeMn₂Ge₂₋ₓSiₓ system has a sequence of atomic layers stacked along the c-axis similar to the R₅(Si,Ge)₄ system. The relatively simple body centred tetragonal ThCr₂Si₂-type structure offers scope for selection of the magnetic state via strong dependence of Mn–Mn intraplanar and interplanar exchange interactions on dₘₙ−ₘₙ, the Mn–Mn separation distance in the ab-plane for enhanced understanding of the correlation between magnetic properties and atomic distances. Our comprehensive investigation of the crystallographic, magnetic properties and critical exponent behaviour of CeMn₂Ge₂₋ₓSiₓ compounds (x=0.0-2.0 has enabled us to establish the magnetic structures across the Ge-Si concentration range and derive the magnetic phase diagram of CeMn₂Ge₂₋ₓSiₓ.

5.3.2 Experimental and Procedures

CeMn₂Ge₂₋ₓSiₓ alloys with Si concentrations x = 0.0, 0.4, 0.8, 1.0, 1.2, 1.6 and 2.0 were prepared by arc melting the high purity elements on a water-cooled Cu hearth under purified argon gas. The mass loss of Mn during melting was compensated for by adding 3% excess Mn. The ingots were melted five times to attain homogeneity and then annealed at 900 C for one week in an evacuated quartz tube. The samples were characterized by x-ray diffraction (Cu K, λ=1.5418 Å). The temperature dependence of the magnetization, M (T) was measured in a magnetic field of B applied = 0.01 T in a superconducting quantum interference device (SQUID) from 5 to 350 K. All samples were investigated by differential scanning calorimetry (DSC) to check for possible phase transitions in the higher temperature range from 300 to
450 K. Neutron diffraction patterns were collected over the temperature range 6–450 K to cover the temperature range over which long range magnetic order was observed. Further details were obtained on the Wombat (high intensity; with λ= 2.41 Å) diffractometers, OPAL, Australia.

5.3.3 Result and Discussion

5.3.3.1 CeMn$_2$Ge$_{2-x}$Si$_x$

Rietveld refinements (FULLPROF package [22]) of the room temperature X-ray diffraction patterns indicate that all of the CeMn$_2$Ge$_{2-x}$Si$_x$ samples crystallize in the ThCr$_2$Si$_2$ structure. The refined results — including lattice parameters $a$, $c$, axial ratio $c/a$ and unit cell volume $V$ — are shown in Figure 5.36. As expected, substitution of Ge by Si leads to a monotonic decrease of both $a$ and $c$ along with concomitant contraction of the unit cell volume with increasing Si content; good agreement is obtained with published results [16]. However, it is noted that the variation of the lattice constants and unit cell volume change slope with composition around $x = 1.0–1.2$, with this behaviour evident in the composition dependence of the axial ratio $c/a$.

The change in slope discerned around $x = 1.0–1.2$ is likely to be related to the change in magnetic ordering of the Mn-sublattice as in discussion of the neutron diffraction results below. At room temperature the $x = 1.2$ compound exhibits a mixture of ferromagnetic with antiferromagnetic states while compounds with $x > 1.2$ are purely antiferromagnetic. Similar tendencies in the composition dependence of the lattice constants have been detected in the related PrMn$_2$Ge$_{2-x}$Si$_x$ system [23]. As is well known and as indicated above, R(Mn$_2$X$_2$ ($X$ =
Ge or Si) compounds exhibit different magnetic behaviours around two critical values of the lattice parameter $a_{\text{crit}2} \sim 4.02 \text{ Å}$ and $a_{\text{crit}1} \sim 4.06 \text{ Å}$ [9].

![Composition dependence of lattice parameters $a$ and $c$, axial ratio $c/a$, and unit cell volume, $V$, for CeMn$_2$Ge$_{2-x}$Si$_x$ at room temperature. The arrows indicate the region where the slope changes. The dashed and full lines are guides to the eye; the $a_{\text{crit}1}$ and $a_{\text{crit}2}$ values of the upper figure are explained in the text.](image)

**Figure 5.36** Composition dependence of lattice parameters $a$ and $c$, axial ratio $c/a$, and unit cell volume, $V$, for CeMn$_2$Ge$_{2-x}$Si$_x$ at room temperature. The arrows indicate the region where the slope changes. The dashed and full lines are guides to the eye; the $a_{\text{crit}1}$ and $a_{\text{crit}2}$ values of the upper figure are explained in the text.

The bond lengths between different sites have also been calculated with the BLOKJE program [24] using the structural and positional parameters and the 12-coordinate metallic radii of 1.81 Å, 1.35 Å, 1.37 Å and 1.32 Å for Ce, Mn, Ge and Si, respectively. It was found
that the Mn-Mn intralayer exchange interaction distance decreased from $d_{\text{Mn-Mn}} = 2.9306 \text{ Å}$ at $x=0$ to $d_{\text{Mn-Mn}} = 2.8307 \text{ Å}$ at $x=2.0$. Moreover if we assume that the contraction of the unit cell volume due to Si substitution (chemical pressure) is equivalent to the influence of external pressure, the corresponding pressures can be derived to be 24.7 kbar and 68.5 kbar for the $x = 1.0$ and 2.0 samples using the Murnaghan equation as shown in Equation 5.1 In this calculation we used the modulus values $B_0 = 819 \text{ kbar}$ and $B'_0 = 4.0$ of LaMn$_2$Si$_2$ [13] as a guide for the modulus values for CeMn$_2$Ge$_2$ compound (LaMn$_2$Si$_2$ has the same crystal structure as CeMn$_2$Ge$_2$).

![Figure 5.37](image)

**Figure 5.37** Temperature dependence of magnetization of CeMn$_2$Ge$_{2-x}$Si$_x$ compounds ($x = 0.0-2.0$) as measured in a field of 0.01 T. The inset shows the region of $T_{C_{\text{inter}}}$ for the set of samples.

Figure 5.37 shows the temperature dependence of the magnetization of CeMn$_2$Ge$_{2-x}$Si$_x$ as measured in a field of 0.01 T over the temperature range of 5–340 K. DSC measurements have been used to check for possible phase transitions in the temperature region from 340 K.
up to 550 K. Figure 5.37 reveals clearly that below 340 K the magnetic phase transition temperatures change with the Si concentration as expected. The $T_{C_{\text{inter}}}^{\text{inter}}$ magnetic phase transition temperature (from interlayer antiferromagnetic AFL to canted ferromagnetic Fmc as discussed below) was found to decrease from $T_{C_{\text{inter}}}^{\text{inter}} \sim 320$ K for $x=0.4$ to $T_{C_{\text{inter}}}^{\text{inter}} \sim 305$ K for $x=1.2$ (Figure 5.37; inset). This behaviour may be related to the change in electronic environment as replacing Ge ($3d^{10}4s^{2}4p^{2}$) by Si ($3s^{2}3p^{2}$) is expected to influence the magnetic structures of the CeMn$_2$Ge$_{2-x}$Si$_x$ compounds. This is supported by Density Functional Theory calculations for RMn$_2$Ge$_2$ (R = Y or Ca) compounds [25] which indicate that to a large extent, the magnetic moment is determined mainly by the interatomic Mn-Mn distances, while the interstitial electron density contributes to the change in magnetic structures.
Figure 5.38 (a) Thermal contour plot of CeMn$_2$Ge$_2$ neutron diffraction measurements over the range of 4–450 K. The AFI and Fmi magnetic structures of CeMn$_2$Ge$_2$ are also shown; (b) Neutron diffraction patterns and Rietveld refinements for CeMn$_2$Ge$_2$ at 450 K, 350 K, 295 K, and 4 K ($\lambda=2.4179$ Å, Wombat diffractometer, OPAL).

A set of neutron powder diffraction patterns was obtained for CeMn$_2$Ge$_{2-x}$Si$_x$ compounds ($x$ =0.0-2.0) over the temperature range 6–450 K. Rietveld refinements were carried out on all patterns using the FULLPROF program package [22] which allows us to derive the structural
and magnetic parameters. As explained fully in related articles [8, 18, 23, 26], the specific location of Mn atoms on the 4d site in the ThCr$_2$Si$_2$ structure (space group $I4/mmm$) allows ready identification of various magnetic structures from key indicators in the neutron diffraction patterns as follows:

1. Ferromagnetic ordering of the Mn atoms—$hkl$ reflections with $h+k = 2n$ and $l = 2n$ (e.g. (112), (200) reflections).
2. Antiferromagnetic ordering of the Mn atoms within the (001) planes—reflections with $h+k = 2n+1$ (e.g. (101), (103) reflections).
3. Collinear antiferromagnetic structure between adjacent Mn planes—reflections with $h+k+l = 2n+1$ (e.g. (111), (113) reflections).
4. Ferromagnetic mixed incommensurate structure (Fmi) of wavevector (0; 0; $q_z$)—satellite reflections with $h+k = 2n+1$ (e.g. (101), (103)).

The neutron diffraction thermal contour plot for CeMn$_2$Ge$_2$ from 4-450 K shown in Figure 5.38(a), covers the various magnetic regions indicated by the magnetic measurements of Figure 5.37. Refinement of the 450 K neutron diffraction pattern confirms that CeMn$_2$Ge$_2$ is paramagnetic. At 350 K (i.e. below $T_N^{\text{intra}}$ ~ 417 K; Figure 3(b)) the intensity of the (101) reflection increases and, consistent with neutron diffraction condition (2) above, CeMn$_2$Ge$_2$ exhibits the AFI structure. At 295 K, below the transition temperature $T_C^{\text{inter}}$ ($T_C/C$) ~ 318 K, the appearance of the (112) peak together with the presence of satellite peaks (101)$^+$, (101)$^-$ and (103)$^+$, (103)$^-$ in the patterns and noting condition (4) above, demonstrates that CeMn$_2$Ge$_2$ has the ferromagnetic mixed incommensurate (Fmi) magnetic structure is below this temperature. The Fmi magnetic structure is found to persist with decrease in temperature.
to $T \sim 4$ K as confirmed by the absence of change in the intensities of the $(101)^+\,$ and $(101)^-\,$ reflections.

Figure 5.39 Structural and magnetic parameters for CeMn$_2$Ge$_2$ as derived from refinements of the neutron diffraction patterns: (a) Temperature dependences of the magnetic moment and propagation vector $q_z$ for CeMn$_2$Ge$_2$ (inset). $T_N^{\text{intra}}$ and $T_C^{\text{inter}}$ are denoted by arrows with the dotted lines delineating the paramagnetic (PM), antiferromagnetic (AFI-type) and ferromagnetic mixed incommensurate (Fmi) regions. (b) Temperature dependences of lattice parameters $a$ and $c$ and (c) unit cell volume and axial ratio $c/a$. 
For CeMn$_2$Ge$_2$ the values of the magnetic moments at 4 K are derived to be $M_{\text{Total}} \sim 3.16 \, \mu_B$, $M_x \sim 2.53 \, \mu_B$ and $M_z \sim 1.9 \, \mu_B$ with the magnitude of the propagation vector $q_z \sim 0.317$ as indicated in Figure 5.39(a). The values of $q_z$ for CeMn$_2$Ge$_{1.6}$Si$_{0.4}$ at 4 K are found to decrease to $q_z \sim 0.276$ and continue to reduce with increasing Si concentration. It can be concluded that the replacement of Si for Ge leads to a decrease in $q_z$; this behaviour is similar to that detected on replacement of Fe for Mn [27] and Y or Lu [9, 28] for Pr in the PrMn$_2$Ge$_2$ compound. The temperature dependences of the structural and magnetic parameters of CeMn$_2$Ge$_2$ as derived from the refinements (Figure 5.39(b)) reveal a significant change from a= 4.145 Å and c=10.934 Å for $x=0$ to a= 4.001 Å and c=10.371 Å for $x=2.0$ as reconfirmed in the temperature dependence of the $c/a$ ratio around $T_C^{\text{inter}}$ (Figure 5.39(c)). This phenomena indicates that strong coupling occurs between the magnetism and the crystal lattice in the presence of a $c$-axis component of the Mn moment which is similar to PrMn$_2$-$x$Fe$_x$Ge$_2$ system [27], where the presence of the interlayer Mn–Mn interactions rather than the intralayer Mn–Mn interactions play the major role in the anomalous thermal expansion observed at the magnetic transition in these layered systems.

Reflecting the changes in magnetisation with temperature for the CeMn$_2$Ge$_{1.0}$Si$_{1.0}$ and CeMn$_2$Ge$_{0.8}$Si$_{1.2}$ compounds (Figure 5.37), the neutron diffraction patterns of CeMn$_2$Ge$_{1.0}$Si$_{1.0}$ and CeMn$_2$Ge$_{0.8}$Si$_{1.2}$ were also found to exhibit interesting behaviour. Neutron diffraction patterns were collected for both compounds over the temperature range 6–450 K with temperature steps of around 5 K in order to obtain detailed information around the phase transitions. The set of neutron diffraction patterns for CeMn$_2$Ge$_{0.8}$Si$_{1.2}$ are shown as an example in Figure 5.40(a). Among features noted are that the intensity of the (002) nuclear reflection remains effectively unchanged over the whole temperature range and the absence of satellite peak (101)$^+$, (101)$^-$ and (103)$^+$, (103). Magnetic phase transitions at $T_N^{\text{intra}} \sim 430$
Figure 5.40 (a) Neutron diffraction patterns for CeMn$_2$Ge$_{0.8}$Si$_{1.2}$ over the temperature range 6–450 K and (b) Rietveld refinements for CeMn$_2$Ge$_{0.8}$Si$_{1.2}$ at 450 K, 350 K, 295 K, 200 K and 6 K (λ=2.4118 Å, Wombat diffractometer, OPAL).

K; T$_c$$_{\text{inter}}$ ~ 305 K; T$_{N}$$_{\text{inter}}$ ~ 270 K and completed Fmc temperature T* ~ 31 K are clearly marked by changes in the intensities of the (101), (111) and (112) reflections due to magnetic
scattering. According to neutron diffraction condition (3), the appearance of the (111) reflection peak below ~ 270 K at T ~ 200 K in Figure 5.40 (b) indicates the formation of the AFmc state while, based on neutron diffraction condition (2), the fact that the (112) reflection remains indicates that the Fmc state still exists at the same temperature as the mix magnetic state behaviour. However the mix magnetic state start to disappear when cooling to T < 31 K as absent the peak of (112) and consistently unchanged on peak (111) indicated the AFmc state behaviour as shown in Figure 5.40 (b) at T ~ 6 K. Direct evidence for the coexistence of two phases in the CeMn$_2$Ge$_{1.0}$Si$_{1.0}$ sample was obtained using high resolution synchrotron X-ray diffraction; Figure 5.41(a) indicates two distinct (101) reflections from ~ 80 K to ~ 180 K with a single (101) reflection observed above ~ 180 K. These structural features are entirely consistent with the occurrence of mixed structures of the ferromagnetic Fmc and antiferromagnetic AFmc states below ~ 180 K. This behaviour was reconfirmed by comparison on the same peak (101) with other Si concentration at 80 K; comparison with CeMn$_2$Ge$_{2-x}$Si$_x$ compounds of Si concentrations x = 0.0, x = 0.4, x = 1.0, x = 1.6 and x= 2.0 revealed that only CeMn$_2$Ge$_{1.0}$Si$_{1.0}$ present mixed peaks as depicted in Figure 5.41(b). In addition co-existence of the (111) and (112) peaks as observed in the neutron diffraction patterns of CeMn$_2$Ge$_{0.8}$Si$_{1.2}$ below $T_{N \text{ inter}}$ ~ 270 K (Figure 5.40 at T ~ 200 K), indicates co-existence of two magnetic states corresponding to the ferromagnetic Fmc and antiferromagnetic AFmc states. This behaviour is similar to the co-existence of magnetic phases first reported in La$_{0.8}$Y$_{0.2}$Mn$_2$Si$_2$ [29]. The Rietveld refinements also confirm that the unit cell for the AFmc phase is smaller than the unit cell for the Fmc phase (e.g. at T= 80 K the unit cell volume $V \sim 177.2$ Å$^3$ for Fmc while $V \sim 175.8$ Å$^3$ for AFmc). This behaviour agrees well with the other re-entrant ferromagnetism systems [19, 23, 30], with around 0.3% contraction of the unit cell observed when the magnetic state changes at $T_{N \text{ inter}}$ from Fmc to AFmc in SmMn$_2$Ge$_2$ [30].
Figure 5.41 (a) X-ray diffraction patterns over the range of 80–450 K for CeMn$_2$Ge$_{1.0}$Si$_{1.0}$ in the 2θ region around the (101) peak position, and (b) comparison of the reflections observed around the (101) peak position for CeMn$_2$Ge$_{2-x}$Si$_x$ compounds of Si concentrations $x = 0.0$, $x = 0.4$, $x = 1.0$, $x = 1.6$ and $x = 2.0$ at 80 K ($\lambda = 0.6887$ Å, Powder Diffraction, Australian Synchrotron).
Details about the phase transitions in CeMn$_2$Si$_2$ over the temperature range 6–450 K were determined from neutron diffraction patterns obtained at temperature step intervals of 2 K (Figure 5.42(a)). Rietveld refinements of the neutron diffraction pattern at 450 K confirm that CeMn$_2$Si$_2$ has the ThCr$_2$Si$_2$ structure as expected. The absence of magnetic scattering above $T_{N \text{ intra}} \sim 384$ K in reflections such as (101), (111) and (112) is consistent with a paramagnetic (PM) state (see e.g. the disordered magnetic states (PM) observed in EuMn$_2$Si$_2$ [31] and LaPrMn$_2$Si$_2$ [32]. Below $T_{N \text{ intra}} \sim 384$ K, CeMn$_2$Si$_2$ is found to exhibit the antiferromagnetic interlayer coupling structure (AFil) down to base temperature $T \sim 5$ K (Supplementary Fig. S2). The AFil structure — a collinear antiferromagnetic structure between adjacent Mn planes in a $+ - + -$ sequence along the $c$-axis — is indicated by the magnetic scattering observed at the (111), (113) and (201) reflections (extinction rules $h + k = 2n$ and $h + k + l = 2n + 1$) in agreement with those reported by Dincer et al. [32]. Figure 5.42(b) shows the temperature dependences (5-450 K) of the lattice parameters and $c/a$ axial ratio as determined from Rietveld refinements of the neutron diffraction patterns. Both the $a$ and $c$ values exhibit a monotonic decrease with temperature in the region of the paramagnetic to interlayer antiferromagnetic transition. Furthermore, Figure 5.42(b) reveals a significant change in the temperature dependence of the $c/a$ ratio around $T_{N \text{ intra}} \sim 384$ K; this behaviour indicates strong coupling between the magnetism and the crystal lattice in the presence of an $ab$-axis component of the Mn moment and further indicates the presence of strong magnetostructural coupling around $T_{N \text{ intra}} \sim 384$ K. As discussed recently [33], the strong magnetostructural coupling leads to a large structural entropy change around the magnetic phase transition, thereby contributing to the total entropy change around the magnetic phase transition.
Figure 5.42 (a) Neutron diffraction patterns for CeMn$_2$Si$_2$ over the range of 6–450 K ($\lambda=2.4118$ Å) and (b) Temperature dependences of the lattice parameters $a$ and $c$ together with the unit cell volume, $V$, and axial ratio $c/a$ for CeMn$_2$Si$_2$ as determined from Rietveld refinements of the neutron diffraction patterns.
The magnetic entropy change, $\Delta S_M$, has been determined for the set of CeMn$_2$Ge$_2$$_x$Si$_x$ compounds ($x = 0.0$-$2.0$) from their magnetization curves as functions of temperature and magnetic field ($\Delta B = 0$-$5$ T) in the region around the ferromagnetic transition $T_{C \text{ inter}}$. The set of $\Delta S_M$ values was determined by applying the standard Maxwell relation [34] as shown in equation 5.3. As shown by the curves of Figure 5.43(a), the $\Delta S_M$ peak gradually broadens towards higher temperatures with increasing magnetic field (from $\Delta B = 0$-$5$ T), behaviour characteristic of a second order magnetic transition. The changes in magnetic entropy for the set of CeMn$_2$Ge$_2$$_x$Si$_x$ compounds ($x = 0$, 0.4 and 0.8) have been derived to be 3.21 J kg$^{-1}$ K$^{-1}$, 2.86 J kg$^{-1}$ K$^{-1}$ and 2.67 J kg$^{-1}$ K$^{-1}$, respectively (field change $\Delta B = 0$-$5$ T) around $T_{C \text{ inter}}$. CeMn$_2$Ge$_2$$_x$Si$_x$ compounds exhibit moderate isothermal magnetic entropy accompanied with a second-order phase transition around room temperature comparable with other rare earth intermetallic compound in the RMn$_2$X$_2$ series. For example, Dincer and Elerman [35] obtained maximum entropy values in the approximate range $\Delta S_M \sim 2$–$3$ J kg$^{-1}$ K$^{-1}$ ($\Delta B = 0$-$5$ T) around the Curie temperatures $T_{C \text{ inter}} \sim 300$–$320$ K for re-entrant SmMn$_2$$_x$Fe$_x$Ge$_2$ ($x = 0.05$, 0.10) and SmMn$_2$$_x$Co$_x$Ge$_2$ ($x = 0.05$, 0.15) compounds. The present set of entropy values are also similar to other compound such as Ho$_2$Fe$_{15}$Mn$_2$ [36] ($\Delta S_M = 2.7$ J kg$^{-1}$ K$^{-1}$ at 302 K) and Er$_2$Fe$_{17}$ [37] ($\Delta S_M = 3.6$ J kg$^{-1}$ K$^{-1}$ at 300 K).

The magnetic entropy change, $\Delta S_M (T, B)$ has also been derived from heat calorimetric measurements of the field dependence of the heat capacity using the expression [38–40] (equation 5.4) where $C(T,B)$ and $C(T,0)$ are the values of the heat capacity measured in field $B$ and zero field, respectively. The corresponding adiabatic temperature change, $\Delta T_{ad}$ can be evaluated from $\Delta S_M (T, B)$ and the zero field heat capacity data as shown in equation 5.5. Figure 5.43(b) shows the set of heat capacity measurement obtained for CeMn$_2$Ge$_2$ with $B = 0$ T, 1 T, 2 T and 5 T. The related peak in specific heat around $T_{C \text{ inter}} \sim 318$ K was found to
Figure 5.43 (a) Temperature dependence of the isothermal magnetic entropy change $-\Delta S_M$ for CeMn$_2$Ge$_2$ in the region around the ferromagnetic transition $T_{C_{\text{inter}}}$ as determined from magnetisation measurements. (b) The heat capacity of CeMn$_2$Ge$_2$ as measured over the temperature range 10–340 K in magnetic fields $B = 0$ T, 1 T, 2 T and 5 T; (c) The adiabatic temperature change, $\Delta T_{ad}^{\text{max}}$, for the CeMn$_2$Ge$_2$ compound.

decrease with increasing magnetic field as shown by the upper inset to Figure 5.43(b). The $\Delta T_{ad}^{\text{max}}$ values derived from the specific heat data using equation (4) are shown in Figure 5.43(c). The peak value of the adiabatic temperature change is found to be $\Delta T_{ad}^{\text{max}} = 1.7$ K
for $\Delta B = 0.5$ T. Within experimental errors [21, 41, 42], the maximum magnetic entropy change for CeMn$_2$Ge$_2$ as determined from the heat capacity measurements of $-\Delta S_M^{\text{max}} \sim 2.9$ J kg$^{-1}$ K$^{-1}$ agrees well with the maximum entropy change $-\Delta S_M^{\text{max}} \sim 3.2$ J kg$^{-1}$ K$^{-1}$ determined from the magnetic measurements using the Maxwell relation.

![Figure 5.44](image)

**Figure 5.44** (a) Dependence of $-\Delta S_M$ (peak value of the magnetic entropy change at different B values) on the parameter $(B/T_C)^{2/3}$ for CeMn$_2$Ge$_2$ compound and (b) Kouvel–Fisher plots of $M_s(T)[dM_s/dT]^{-1}$ (left scale) and $\chi_0^{-1}(T)[d\chi_0^{-1}/dT]^{-1}$ (right scale) versus temperature. The lines are fits to the data around $T_C$ as discussed in the text with fits leading to the critical exponent values.
Critical exponent analysis: Mean-field theory predicts that in the vicinity of second-order phase transitions, $-\Delta S_M$ is proportional to $(\mu_0 H/T_C)^{2/3}$ [43, 44]. Figure 5.44(a) shows a graph of $-\Delta S_M$ as a function of $(B/T_C)^{2/3}$ in the region around the transformation at $T_C^{\text{inter}} \sim 318$ K. The linear fit to the data in Figure 5.43(a) clearly demonstrates that the relationship $-\Delta S_M \propto (B/T_C)^{2/3}$ is valid around the transition at $T_C^{\text{inter}}$ for CeMn$_2$Ge$_2$. According to the conventional static scaling law, the critical properties of a second-order magnetic transition can be described by critical exponents $\beta$, $\gamma$ and $\delta$ derived from magnetization measurements around the transition temperature. On applying these standard approaches, as shown by the fits to the Kouvel–Fisher plots of $M_S(T)[dM_S/dT]^{-1}$ and $\chi_0^{-1}(T)[d\chi_0^{-1}/dT]^{-1}$ versus temperature in Figure 5.44(b), the critical exponents around $T_C$ in CeMn$_2$Ge$_2$ have been determined to be $\beta = 0.33 \pm 0.03$ and $\gamma = 1.15 \pm 0.22$. Hence, on applying the relationship $\delta = 1 + \gamma/\beta$, with $\beta = 0.33$, $\gamma = 1.15$, the critical exponent $\delta = 1 + \gamma/\beta = 4.49 \pm 0.25$. The critical exponents derived from the analyses are similar to the theoretical values - $\beta = 0.365$, $\gamma = 1.386$ and $\delta = 4.80$ - based on the three-dimensional Heisenberg model corresponding to short range interactions [45]. Thus, the critical behaviour analysis in the vicinity of $T_C^{\text{inter}}$ indicates that the magnetism of the CeMn$_2$Ge$_2$ compound is governed by short range interactions.

5.3.4 Conclusion

The total magnetic moment of CeMn$_2$Ge$_{2-x}$Si$_x$ compounds at base temperature $\sim 5$ K is found to decrease with increasing Si content. This behaviour indicates that contraction of the unit cell leads to a reduction in the Mn moment value (e.g. $M_{\text{Total}} \sim 3.16 \mu_B$ for $x = 0.0$ and $M_{\text{Total}} \sim 2.02 \mu_B$ for $x = 2.0$) and agrees well with the tendency detected for both LaMn$_2$Si$_2$ and LaMn$_2$Ge$_2$ systems where $M_{\text{Total}}$ is found to decrease with decrease in the lattice parameter $a$ [46]. First principles calculations on LaMn$_2$Si$_2$ and LaMn$_2$Ge$_2$ [46] suggest that the reduction
Figure 5.45 Magnetic phase diagram of CeMn$_2$Ge$_{2-x}$Si$_x$ as a function of Si content. As discussed in the text, $T_{N^{\text{intra}}}$ (green squares) defines the transition from paramagnetism to intralayer antiferromagnetic ordering within the (001) Mn layers (AFl) (except $x=2.0$ which exhibits AFl type antiferromagnetic order); $T_{C^{\text{inter}}}$ (red circles) defines the transition from AFl to a canted spin structure (Fmc); $T_{c/c}$ (open pink diamond) defines the transformation temperature of the magnetic structure from Fmc to a conical configuration Fmi type, $T_{N^{\text{inter}}}$ (blue triangle) denotes the transition to the mixed region with co-existence of the antiferromagnetic canted structure AFmc and the Fmc structure. The dashed lines indicate trends in the data. As discussed in the text, the vertical dashed line located around Si concentration of $x=1.85$ is used as a tentative guide to the boundary between the AFmc and AFl regions.

of Mn moments in LaMn$_2$Si$_2$ ($a = 4.11$ Å) compared with LaMn$_2$Ge$_2$ ($a = 4.19$ Å) depends primarily on the Mn–Mn distances (stronger Mn–Mn hybridization due to shorter Mn–Mn distance leads to a smaller local Mn moment [18]). However the larger hybridization strength of Si–Mn in LaMn$_2$Si$_2$ than Ge–Mn in LaMn$_2$Ge$_2$ also plays a role. In the present study, the reduction of Mn moments in the CeMn$_2$Ge$_{2-x}$Si$_x$ compound with increasing Si content can be
ascribed to these two factors: (1) decrease of the Mn–Mn spacing (at room temperature ~ 300 K, \( d_{\text{Mn-Mn}} = 2.9306 \, \text{Å} \) at CeMn\(_2\)Ge\(_2\) to \( d_{\text{Mn-Mn}} = 2.8307 \, \text{Å} \) at CeMn\(_2\)Si\(_2\)) and (2) increase of Si–Mn hybridization strengths compared with Ge–Mn hybridization [22], similar behaviour to that of PrMn\(_2\)Ge\(_{2-x}\)Si\(_x\) [23].

The temperature dependence of the CeMn\(_2\)Ge\(_{2-x}\)Si\(_x\) lattice parameters demonstrates an anomaly in thermal expansion (as shown in Figure 5.36) and is accompanied with appearance of the interlayer Mn–Mn interactions. This behaviour agrees well with others system as PrMn\(_{2-x}\)Fe\(_x\)Ge\(_x\) and PrMn\(_2\)Ge\(_{2-x}\)Si\(_x\) where it is found that the interlayer Mn–Mn interactions rather than the intralayer Mn–Mn interactions, play the major role in the anomalous thermal expansion [26]. The present findings have enabled us to construct the magnetic phase diagram for the CeMn\(_2\)Ge\(_{2-x}\)Si\(_x\) system as shown in Figure 5.45 with more detail now available compared with the previous study [16]. The shaded region in Figure 5.45 indicates the region of co-existence of the Fmc and AFmc phases. The co-existence of different magnetic states at the same temperature is considered to be related to the non-random variation of site concentrations of Si and Ge, and depends sensitively on the Mn–Mn distances in this system; this in turn leads to differences in the local environments throughout the sample [7].

As expected, the magnetic states at room temperature have been modified by Si substitution due to the contraction of the unit cell indicated in Figure 5.36. Samples with \( x \geq 1.4 \) where the lattice constant \( a \) is below \( a_{\text{crit1}} \sim 4.06 \, \text{Å} \) are antiferromagnetic at room temperature with no ferromagnetic order evident over the entire temperature range, whereas samples of Si content \( x \leq 0.4 \) are ferromagnetic at room temperature. It is interesting to note that samples with Si concentrations in the range \( x \sim 1.0–1.2 \) correspond approximately to the region of co-
existence of the AFmc and Fmc phases around room temperature as shown in Figure 5.45. A smaller unit cell in an antiferromagnetic state than in a ferromagnetic state (as indicated by the deviation from linear behaviour in the composition dependence of the lattice constants at room temperature; Figure 5.36), can be understood in terms of the difference in magnetic states at room temperature for these samples and in turn reflects the large contribution from magnetic effects to thermal expansion [26].

The compounds with rich Si concentration \( x \geq 1.85 \) have a relatively simple magnetic behaviour, transforming from paramagnetism at high temperature to AFil. By comparison, Ge-rich samples \((x = 2.0)\) successively exhibit two magnetic states as AFil and Fmi when cooling from the high temperature paramagnetic phase. The Fmi structure was eliminated when Si concentration \( x \geq 1.0 \) and co-existence of AFmc and Fmc is detected for CeMn\(_2\)Ge\(_2\)\(_x\)Si\(_x\) in the intermediate Si concentration range \(0.6 < x < 1.25\). This co-existence reflects the incompleteness of the phase transition from Fmc to AFmc with decreasing temperature and agrees well with calculations of the electronic structure of the two magnetic states (AFmc and Fmc) carried out using a spin polarized localized density approximation (LSDA) in the framework of density functional theory (DFT). These calculations show that changes to the magnetic energy of the two states are caused directly by modification of the lattice with temperature [3]. Moreover, critical properties study on the second-order ferromagnetic transition of CeMn\(_2\)Ge\(_2\) demonstrate that the magnetic interactions around \( T_C^{\text{inter}} \) can be described with the three dimensional Heisenberg model corresponding to short range interactions. Overall this investigation has demonstrated that, as expected, the Si concentration plays the dominant role in tuning the magnetic structure and properties of the CeMn\(_2\)Ge\(_2\)\(_x\)Si\(_x\) compounds.
References


Chapter 6

THE MAGNETOCALORIC EFFECT AND CRITICAL BEHAVIOUR OF MnCoGe-based ALLOYS

6.1 Substitution of Ge by other Metalloid in MnCoGe Alloy

MnCoGe, as a typical MM’X (M, M’ = transition metal, X = Si, Ge, Sn) compound, possesses magnetic and structural transitions and has been studied for decades [1]. Stoichiometric MnCoGe crystallizes in the hexagonal Ni$_2$In-type austenite (A) phase, and at about 420 K, in the paramagnetic state, it undergoes a martensitic structural transformation to another paramagnetic, orthorhombic TiNiSi-type martensite (M) [2]. The austenite and the martensite phases have Curie temperatures $T_{CA} = 273$ K and $T_{CM} = 355$ K, respectively, with both phases featuring collinear ferromagnetism [3].

6.1.1 Introduction

In the last few years, there has been a considerable increase in research on near-room-temperature magnetic cooling [4-6]. This new cooling technology, which is expected to supersede the conventional refrigeration technology based on gas compression/expansion, is of special interest because of its considerable socio-economic benefits. Compared to the refrigeration technology based on gas compression/expansion, which is widely used today, magnetic refrigeration is environmentally friendly and more efficient [7, 8]. 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 the system [9]. Material systems such as LaFeSi [10], NiMnGa [11], MnAsSb [5], and GdSiGe [12] undergo first-order magnetic transitions and have been found to possess a giant MCE. There are some major drawbacks of these material systems, however, which include large thermal and magnetic hysteresis that is detrimental to the refrigerant capacity, making them undesirable for practical applications. Hence, it is imperative to search for materials that exhibit a giant MCE as well as negligible thermal and magnetic hysteresis. One candidate is MnCoGe [13, 14], which undergoes a second-order phase transition as well as a crystallographic phase transition from the low temperature orthorhombic TiNiSi-type to the high temperature hexagonal Ni$_2$In-type structure [15]. Previously, scientists have managed to achieve a coupling of the magnetic and crystallographic transitions in the MnCoGe material system through substitution of Cr [16] and addition of boron [17] as an interstitial, thereby leading to the attainment of a giant magnetocaloric effect.

An investigation on substituting other metalloids for Ge in MnCoGe$_{1-x}$T$_x$ compounds (T = Al and Si) has been implemented in this thesis work, and it was found that an appropriate T concentration successfully shifted the structural change and magnetic phase transition into the temperature range of interest, leading to the attainment of a high contribution to the giant magnetocaloric effect (GMCE). Furthermore, the strong dependence on proper tuning for critical behaviour of the phase transition, which was due to the vacancy induced structural and magnetic transition and the field-induced martensitic transformation, acted as a guide to more interesting phenomena related to the substitution for Ge (atomic radius ≈ 1.37 Å) by Al (atomic radius ≈ 1.43 Å) or Si (atomic radius ≈ 1.32 Å) in MnCoGe$_{1-x}$T$_x$ compounds. It was recently found that MnCoGe$_{1-x}$T$_x$ provides the best example for control of the temperature window in order to investigate the effects of the structural and magnetic transition on the total
entropy change, providing an excellent vehicle for investigation of the field-induced martensitic transformation in GMCE materials. Thus, in an effort to understand the nature of the magnetic transition in MnTiGe$_{0.97}$Al$_{0.03}$, critical exponent analysis in the vicinity of the ferromagnetic (FM)–paramagnetic (PM) region [18-20] has been performed. The outcomes revealed that this material undergoes a structural transition at ~ 420 K as well as a second-order ferromagnetic–paramagnetic transition at ~ 350 K. Finally, a temperature dependent neutron diffraction experiment has been performed to clarify whether there is a coupling of the structural transition and the magnetic phase transition.

6.1.2 Experimental and Procedures

Polycrystalline MnCoGe$_{1-x}$T$_{x}$ (T = Al and Si; range $x = 0$-1.0) ingots were prepared by arc melting the appropriate amounts of Mn (99.9%), Ge (99.999%) powder, Co (99.9%), Al (99.9%), and Si (99.999%) chips in an argon atmosphere. During arc melting, a 3% excess of Mn over the stoichiometric amount was added to compensate for 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 900 °C for 120 h and then quenched in water at room temperature. The magnetization measurements were carried out using the vibrating sample magnetometer option of a Quantum Design 14 T physical properties measurement system (PPMS) and a Quantum Design magnetic properties 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 of 290–340 K with an interval of 2 K at applied fields of up to 5 T. The neutron data were collected in the temperature range of 5–340 K.
using the Wombat high intensity powder diffractometer at the Open Pool Australian Lightwater (OPAL) reactor with an incident neutron wavelength of $\lambda = 2.4205$ Å.

### 6.1.3 Results and Discussion

#### 6.1.3.1 MnCoGe$_{1-x}$Al$_x$

Figure 6.1 presents the X-ray diffraction (XRD) patterns of MnCoGe$_{1-x}$Al$_x$ ($x = 0, 0.03, 0.07, 0.10, \text{and} 0.15$) collected at room temperature. Most of the peaks could be clearly identified

![Figure 6.1](image.png)

**Figure 6.1** Powder XRD patterns of MnCoGe$_{1-x}$Al$_x$ ($x = 0.03, 0.07, 0.1$, and 0.15) measured at room temperature. The Miller indices hkl denote the typical Ni$_2$In-type hexagonal (top) and TiNiSi-type orthorhombic (bottom) structures. The refined pattern at the bottom includes the experimental and calculated results, and their difference is presented for the sample with $x = 0.15$. 

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with the TiNiSi-type structure (orthorhombic; space group $Pnma$) for $x \leq 0.03$ and the Ni$_2$In-type structure (hexagonal, space group $P6_3/mmc$) for $x > 0.03$. It can be seen that the crystal structure changes from the coexistence of TiNiSi-type and Ni$_2$In-type structures to the single Ni$_2$In-type structure with the substitution of Al for Ge atoms. This indicates that the martensitic transformation temperatures of the two series of alloys decrease from higher temperature down to lower temperature. Increasing Al substitution for Ge can effectively change the phase stability of MnCoGe compounds. From refinement analysis, as shown in Figure 6.1, the pattern for $x = 0.03$ can be indexed as a TiNiSi-type orthorhombic structure, mixed with a small amount of hexagonal phase ($4 \pm 0.2$ wt%). For the sample with $x = 0.07$, the ratio of hexagonal phase increases, and a mixed ratio of orthorhombic ($15.0 \pm 0.2$ wt%) and hexagonal ($85.0 \pm 0.11$ wt%) phase was found. The other samples ($x \geq 0.07$) are almost single hexagonal phase with Ni$_2$In-type structure ($x = 0.1; 97.4 \pm 0.03$ wt%, $x = 0.15; 99.3 \pm 0.02$ wt%), indicating that the structural transformation temperatures, $T_{str}$, of these samples are above room temperature. These results illustrate that the fraction of hexagonal austenite at room temperature increases as the Al-doping level increases. In other words, the substitution of Al for Ge tends to maintain Ni$_2$In-type austenite and lower the $T_{str}$.

In order to determine the transition temperature and the nature of the transition, temperature dependent magnetization (M–T curves) under a low field of 0.01 T and differential scanning calorimetry (DSC) measurements of MnCoGe$_{1-x}$Al$_x$ compounds were conducted in the range of 10-600 K, as shown in Figure 6.2. For the compositions with $x = 0.00$ and 0.03, there is basically no change in the magnetization below the Curie temperature, indicating that the samples’ behaviour is different from that in a previous report [21] which they shown the change of magnetization with increase the Co concentration. This difference behaviour is
probably associated with the fact that the annealing temperature for this experiment is not the same as in ref [21].

![M–T curves](image)

**Figure 6.2** (a) M–T curves measured under a magnetic field of 0.01 T for MnCoGe$_{1-x}$Al$_x$ (x = 0, 0.03, 0.07, and 1.0). (b) DSC curves collected in the range of 250-500 K. The arrows indicate the structural transition and the Curie's temperature.

The DSC measurement indicated that the structural transition temperature decreased from $T_{\text{str}} \approx 448$ K at $x = 0$ to $T_{\text{str}} \approx 420$ K at $x = 0.03$. The MnCoGe$_{0.93}$Al$_{0.07}$ compound exhibits a visible step-like behaviour in $M$-$T$ curves, indicating the mixed phase, as the temperature of the transition for austenite, $T_{C}^{A}$, is ~ 280 K and that of martensite, $T_{C}^{M}$, is ~ 320 K [22]. This phenomenon is probably attributable to the fact that the MnCoGe-based compounds undergo
a structural transition induced by the replacement of Ge by Al and “temperature change when cooling to low temperature [21]. As for further increasing the Al concentration, MnCoAl has been found in single austenite phase with $T_C^A \approx 380$ K. The DSC measurements agree well with the magnetization measurements as similar transition temperature values were determined by the maxima of the DSC signals (see Figure 6.2(b)).

The magnetization curves obtained for MnCoGe and MnCoAl for fields in the range of $B = 0$–5 T from the ferromagnetic to the paramagnetic ordering temperatures are shown in Figure 6.3(a) and (b), respectively. These data were obtained for increasing and decreasing fields at 2 K and 4 K intervals spanning a range around the Curie temperature, $T_C$, thus providing evidence for the lack of magnetic hysteresis loss effects, as is intrinsic to second order magnetic transitions [10]. Moreover, Figure 6.3(c-d) shows the corresponding Arrott plots ($M^2$ versus $B/M$) for the $x = 0$ and 1.0 samples, which are found to exhibit features characteristic of a second order transition for both of the samples. This was particularly confirmed by the absent of negative slope behaviour of the Arrott plot near $T_C$ and denotes a positive sign of the coefficient $c_2(T)$ in the Landau expansion of the magnetic free energy [23].

The magnetic entropy change, $-\Delta S_M$, has been determined for the set of MnCoGe$_{1-x}$Al$_x$ compounds ($x = 0, 0.03, 0.07, 0.1, 0.15$, and 1.0) from their magnetization curves for both increasing and decreasing field values as functions of temperature and magnetic field ($\Delta B = 0$–5 T). The magnetic entropy change has been derived by applying the standard Maxwell relation [24]:

$$-\Delta S_M(T, H) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH$$  \hspace{1cm} (6.1)
Figure 6.3 Variation in magnetization with applied field of 0-5 T for (a) MnCoGe compound and (b) MnCoAl compound; and (c, d) Arrott plots showing the second order transition type for both compounds.

Although the use of Maxwell’s relation for first order systems is still questionable, Caron et al. successfully established a method for determining the magnetic entropy change of first order systems by using decreasing field [25]. In this case study, the magnetic entropy change, $-\Delta S_M$, was also evaluated in the decreasing field mode, as is shown by the open symbol curves in Figure 6.4. A comparison of the $-\Delta S_M$ values calculated using increasing and decreasing fields, respectively, shows no difference between these values, which confirms that there is no hysteresis loss occurring in the vicinity of the magnetic transition. With increasing Al content, the temperature corresponding to the maximum $-\Delta S_M$ shifts to lower
temperature first, and then moves to higher temperature, showing the same tendency as the variation of the Curie temperature. The maximal values of the magnetic entropy change are about 4.41, 4.83, 6.23, 7.44, 8.12, and 3.73 J·kg\(^{-1}\)K\(^{-1}\) for \(x = 0.00, 0.03, 0.07, 0.1, 0.15, \) and 1.0, for a field change of 0-5 T, respectively. It is worth pointing out that the compounds

![Figure 6.4](image)

**Figure 6.4** Temperature dependence of the isothermal magnetic entropy change, \(-\Delta S_M(T, H)\), for MnCoGe\(_{1-x}\)Al\(_x\) compounds (\(x = 0, 0.07, 0.1, 0.15, \) and 1.0) calculated from magnetization isotherms with 0-5 T field change applied. Closed symbols are for increasing and open symbols for decreasing field, respectively.

with high Al content exhibit larger magnetic entropy change than those with low Al content, apart from \(x = 1.0\). The reason can be explained in terms of the effects of the structural variations and the change of the magnetization on the magnetic entropy change. As is well

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known for Mn-Co-based compounds, the saturation magnetization of the compounds decreases with increasing Al content [21] for concentrations $x > 0.15$. At low Al content, the increase in the magnetic entropy change in the Al-substituted compounds is probably associated with the structural change from TiNiSi-structure to Ni$_2$In-structure. On the other hand, for high Al content, the reduced magnetic entropy change may be attributed to the decrease in the magnetization.

In an effort to further clarify the nature of the FM – PM phase transition, an analysis of the critical behaviour near $T_C$ for MnCoGe$_{0.97}$Al$_{0.03}$ compound was performed. The isothermal magnetization versus the applied field around $T_C$ has been measured using intervals of 4 K and 2 K, as shown in Figure 6.5. A plot of $B/M$ versus $M^2$, known as the standard Arrott plot, is shown in Figure 6.6 for the temperatures in the vicinity of $T_C$.

![Figure 6.5](image.png)

**Figure 6.5** Isothermal magnetization curves for MnCoGe$_{0.97}$Al$_{0.03}$ compound in the vicinity of $T_C$. 

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According to the criterion proposed by Banerjee [26], the order of magnetic transition can be determined from the slope of the isotherm plot. If the $B/M$ 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 MnCoGe$_{0.97}$Al$_{0.03}$ compound, the always positive slope of the $B/M$, versus $M^2$ curves throughout the transition temperature range indicates that the phase transition is second order. This result is consistent with the absence of thermal and magnetic hysteresis in the vicinity of the PM – FM transition as discussed, thereby confirming the second order nature of this transition. 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 $\delta$ [27]. In this work, different methods have been used to investigate the critical behaviour of MnCoGe$_{0.97}$Al$_{0.03}$ compound, namely, modified Arrott plots (MAPs), the Kouvel-Fisher

![Figure 6.6 Arrott plots ($M^2$ vs. $B/M$) at temperatures in the vicinity of $T_C$ for MnCoGe$_{0.97}$Al$_{0.03}$ compound.](image)

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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 [27]. Quantitative fits are made to the Arrott plots using the following equations [28].

\[ M_S(T) = \lim_{H \to 0}(M) = M_0 (-\varepsilon)^\beta, \varepsilon < 0 \]  \hspace{1cm} (6.2)

\[ \chi_0^{-1}(T) = \lim_{H \to 0}(H/M) = (h_0/M_0)\varepsilon^\gamma, \varepsilon > 0 \]  \hspace{1cm} (6.3)

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, and then a plot of \( M^{1/\beta} \) versus \( (B/M)^{1/\gamma} \) is obtained. The spontaneous magnetisation, \( M_S \), 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 [29]. Next, \( M_S \) is plotted as a function of temperature. To determine the inverse initial magnetic susceptibility, \( \chi_0^{-1}(T) \), a similar procedure is used in conjunction with the \( (B/M)^{1/\gamma} \) axis. The values of \( \chi_0^{-1}(T) \) and \( M_S(T) \) are plotted as a function of temperature in Figure 6.7 and these plots are then fitted with Equations (6.2) and (6.3), 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 (6.2) and (6.3), the MAPs shown in Figure 6.7 yielded critical parameters \( \beta = 0.44 \) and \( \gamma = 0.83 \).

The Kouvel-Fisher (KF) method, which makes use of Equations (6.4) and (6.5) shown below, is a more accurate way of determining the critical exponents \( \beta \) and \( \gamma \) [29].
According to Equations (6.4) and (6.5), plotting \( \frac{dM_s(T)}{dT} \) and \( \frac{d\chi^{-1}(T)}{dT} \) versus temperature yields straight lines with slopes of \( 1/\beta \) and \( 1/\gamma \), respectively, as shown in Figure 6.7. The value of \( T_C \) is obtained from the intercepts on the x-axis. The critical exponents \( \beta \), \( \gamma \), and \( \delta \), as well as \( T_C \), obtained using the Kouvel-Fisher method are \( \beta = 0.44 \), \( \gamma = 0.83 \), \( \delta = 2.89 \), and \( T_C = 342 \) 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 (6.6) below.

\[
M_{T_C} = D H^{1/\delta} \epsilon = 0, T = T_C
\]

Figure 6.8 shows the magnetic field dependence of the magnetization at \( T_C = 275 \) K for the Mn\(_{0.94}\)Ti\(_{0.06}\)CoGe alloy. The inset shows the critical isotherm on a log – log scale. From Equation (6.6), a plot of log \( (M) \) versus log \( (H) \) is expected be a straight line with slope \( 1/\delta \). The obtained \( \delta \) value from the critical isotherm is 2.89. Another way of obtaining the critical exponent \( \delta \) is by using the Widom scaling relation shown in Equation (6.7):

\[
\delta = 1 + \frac{\gamma}{\beta}
\]
Using Equation (6.6) and the critical parameters $\beta$ and $\gamma$ obtained using the MAPs and those obtained using the Kouvel-Fisher method, the deduced $\delta$ values are 2.92 and 2.89, 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:

$$M(H, \varepsilon) = \varepsilon^\beta f_\pm (H / \varepsilon^{\beta+\gamma})$$  \hspace{1cm} (6.8)$$

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 6.9) yield two universal curves, one for
Figure 6.8 Critical isotherm analysis at $T_C$ of the MnCoGe$_{0.97}$Al$_{0.03}$ sample. The inset shows the same plot on the log–log scale (with the solid line a linear fit to Equation (6.6)).

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 exponents as well as the $T_C$ are reliable and in agreement with the scaling hypothesis.

It is well accepted that the order parameter of the phase transition around the 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 $\delta$, $\beta$, and $\gamma$ values derived for the MnCoGe$_{0.97}$Al$_{0.03}$ compound are close to the mean-field values, thus indicating that long range interactions dominate the
critical behaviour around $T_C$ in this compound. Thus, the critical behaviour analysis in the vicinity of $T_C$ demonstrates that the magnetism of the MnCoGe$_{0.97}$Al$_{0.03}$ compound is governed by long range interactions, which is in agreement with the linear fit to the data, which clearly also demonstrates that the relationship $\Delta S_M \propto (\mu_0 H/T_C)^{2/3}$ is valid around $T_C$.

![Scaling plots indicating universal curves below and above $T_C$ for the MnCoGe$_{0.97}$Al$_{0.03}$ compound.](image)

**Figure 6.9** Scaling plots indicating universal curves below and above $T_C$ for the MnCoGe$_{0.97}$Al$_{0.03}$ compound.

Figure 6.10 presents a thermal contour plot of neutron diffraction measurements on MnCoGe$_{0.97}$Al$_{0.03}$ compound from 6 to 450 K, with the orthorhombic phase (hkl) Miller indices (space group $Pnma$) being marked without * and the hexagonal phase (hkl) Miller indices (space group $P63/mmc$) marked with *. It can be seen clearly that with deceasing temperature, a structural transition takes place, starting from around 430 K and complete 350
K, which agrees well with the DSC and magnetic measurements, revealing a phase transition at approximately 420 K. Compared with the parent MnCoGe compound, which has the

structure change occurring at $T_{str} \approx 450$ K, the substitution of small amount of Al (3% wt.) for Mn leads to a slightly reduction in $T_{str}$ to ~ 420 K. In order to investigate the crystallographic behaviour of MnCoGe$_{0.97}$Al$_{0.03}$ compound, neutron diffraction patterns were collected at selected temperatures ($T = 450$ K, 400 K, 300 K, and 6 K), as shown in Figure 6.11.

Refinement of the neutron diffraction patterns in Figure 6.11 indicated that at 450 K the compound crystallizes in the hexagonal Ni$_2$In-type structure (space group $P6_3/mmc$), while at the lowest temperature of 6 K, the crystal structure changes totally to orthorhombic TiNiSi-type structure (space group $Pnma$). At the temperatures of 400 K and 300 K, there is coexistence of both phases, thus confirming our expectations from magnetic measurements.

Figure 6.10 Neutron diffraction image for MnCoGe$_{0.97}$Al$_{0.03}$ collected at 5 K steps over the temperature range of 6 - 450 K.
So, these results indicate again that the stability of hexagonal $P6_3/mmc$ phase is enhanced due to the substitution of Al for Ge.

**Figure 6.11** Measured and calculated neutron diffraction patterns for the MnCoGe$_{0.97}$Al$_{0.03}$ compound at 450 K, 400 K, 300 K, and 6 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 and the bottom solid line indicates the difference between the experimental and the calculated results.

Further analysis of the neutron diffraction data using Rietveld refinement resulted in the determination of the lattice parameters, as well as the volume phase fractions, for the orthorhombic and hexagonal phases. The peak intensities of the selected reflections (002)*
(for $P63/mmc$) and (011) (for $Pnma$) as a function of temperature are shown in Figure 6.12. The peak intensity of the (011) reflection, which decreases with increasing temperature, 

\[ T_{\text{STR}} \sim 420 \text{ K} \]

**Figure 6.12** Peak intensity as a function of temperature for the (002)* and (011) peaks of the MnCoGe$_{0.97}$Al$_{0.03}$ compound.

corresponds to the decrease of the $Pnma$ phase fraction, whilst the peak intensity of the (002)* reflection, which increases with increasing temperature, corresponds to the increase of the $P63/mmc$ phase fraction with temperature.

Figure 6.13 shows the refined structural parameters of the MnCoGe$_{0.97}$Al$_{0.03}$ compound as a function of temperature from the neutron diffraction data. The appearance of additional impurity peaks has been indicated, however, they do not affect the behaviour of this compound. The lattice parameters and unit cell volumes of these two structures can be denoted as $a = a_{\text{ortho}} = c_{\text{hex}}$, $b = b_{\text{ortho}} = a_{\text{hex}}$, $c = c_{\text{ortho}} = \sqrt{3}a_{\text{hex}}$, and $V = V_{\text{ortho}} = 2V_{\text{hex}}$ [33]. 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

![Figure 6.13 Lattice parameters and unit cell volume of MnCoGe$_{0.97}$Al$_{0.03}$ compound as a function of temperature. Open symbols with dots on the centre denote the orthorhombic phase, open symbols denote the hexagonal phase, and half-filled symbols denote the corresponding phases in the mixed phase region.](image)

the structural transition temperature, $T_{str} \approx 420$ K, it is clearly evident in Figure 6.13 that when the symmetry changes from hexagonal to orthorhombic, there is a large volume change ($\Delta V = 1/2V_{orth} - V_{hex} = 2.02 \text{ Å}^3$, so $\Delta V/V \approx 2.35\%$). For comparison, Kanomata et al. [22] estimated the difference in the unit cell volume at $T_{str}$ as $\Delta V \approx 3 \text{ Å}^3$ for MnCoGe compound.
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 difference 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 [34]. Such a difference in the volume change around $T_{\text{str}}$ for MnCoGe$_{0.97}$Al$_{0.03}$ compound will lead to a significant structural entropy change, resulting in a change in the total magnetic entropy change. So, the observed MCE around $T_{\text{str}}$ (approximately 9 J kg$^{-1}$ K$^{-1}$ for $\Delta B = 5$ T), which is larger than at $T_C$ (approximately 3 J kg$^{-1}$ K$^{-1}$ for $\Delta B = 5$ T) in the MnCoGe$_{0.97}$Al$_{0.03}$ compound can be attributed to the combined effect of an abrupt change in magnetization as well as in the unit cell volume in the vicinity of the structural transition (structural entropy change).
6.1.3.2 MnCoGe$_{1-x}$Si$_x$

In order to define the sensitivity from the substitution of another metalloid for Ge, a small amount of Si has been substituted for Ge in MnCoGe$_{1-x}$Si$_x$ compounds ($x = 0, 0.05, 0.1, 0.15,$ and 0.2). The structural properties of MnCoGe$_{1-x}$Si$_x$ were investigated by room temperature X-ray diffraction, as shown in Figure 6.14. Predominantly, the orthorhombic TiNiSi-type structure with very small hexagonal Ni$_2$In-type structure was observed with increasing the Si concentration up to $x = 0.2$.

![Refined XRD pattern of MnCoGe$_{0.80}$Si$_{0.20}$ measured at room temperature. The Miller indices hkl typically denote the Ni$_2$In-type hexagonal structure. The refinement pattern includes the experimental and calculated results, and their difference is presented. The inset shows the patterns for the indicated range of the MnCoGe$_{1-x}$Si$_x$ ($x = 0.05, 0.10, 0.15,$ and $0.20$) samples, demonstrating that the Bragg peaks shift to higher angles.](image)

From the refinement analysis, the lattice parameters and unit cell volume of all the compounds were found decrease with increasing Si concentration, as the peaks shift to higher angle positions, which is related to the smaller atomic radius of Si, $\sim 1.32$ Å, compared to Ge,
Their lattice parameters and unit cell volumes are related 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 \( V = V_{\text{ortho}} = 2V_{\text{hex}} \) [14]. Further increasing the Si concentration \((x > 0.2)\) needs to be investigated in order to define the effects of the symmetry change from orthorhombic to hexagonal, the unit cell volume change, and the variation in Curie temperature of MnCoGe\(_{1-x}\)Si\(_x\) compounds.

It is well known that the variation in the distance between the magnetic atoms will directly modify the exchange coupling and lead to a change in the transition temperature [17]. The increase and decrease of the Curie temperature closely follows the changes in the lattice parameter \(b\), indicating that exchange interaction between the Mn-Mn moments along this axis plays an important role in determining the Curie temperature. Figure 6.15(a) shows the temperature dependence of the magnetization of MnCoGe\(_{1-x}\)Si\(_x\) compounds measured in a field of 0.01 T from 10-330 K. For the compositions \(x = 0.00\) up to 0.2, the Curie temperature was found to slightly increase with enhanced Si concentration. Moreover, the transition for all compounds was found to be incomplete and did not reach zero moment, as indicated by the fact that the temperatures of the structure transition were higher than 330 K, suggesting that this behaviour is related to the smaller Si atomic radius, which is needed in order to change the symmetry of the orthorhombic TiNiSi-type structure to hexagonal Ni\(_2\)In-type structure.

Furthermore, in order to determine the thermal hysteresis, which is a characteristic of the first order transition [12, 18], the temperature dependence of the magnetization of MnCoGe\(_{1-x}\)Si\(_x\) was measured for heating and cooling. It is clear that the heating and cooling curves overlap completely, which indicates that there is no thermal hysteresis and the transition is second
Figure 6.15 (a) $M$–$T$ curves measured under a magnetic field of 0.01 T for MnCoGe$_{1-x}$Si$_x$ ($x$ = 0.05, 0.1, 0.15, and 0.2). (b) DSC curves collected in the range of 300-500 K with the arrows indicating the structural transition and Curie temperature.
order type. It is well known that the cell volume, magnetic moment, Curie temperature, and structural transition temperature $T_{str}$ all show strong dependence on the Co vacancy concentration rather than on Ge vacancy \cite{35}. It can be seen, however, that the structural transition $T_{str}$ determined from the DSC measurements decreases from 450 K for $x = 0$ to 360 K for $x = 0.2$, as shown in Figure 6.15(b). This behaviour demonstrates that replacing Ge with a small percentage of Si (20\%) leads to a decrease in the structural transition temperature and slightly increases the Curie temperature.

Figure 6.16 Variation in magnetization with applied field of 0-5 T for (a) MnCoGe compound and (b) MnCoAl compound; and Arrott plots showing the second order transition type for both compounds (c, d).
The magnetization curves obtained for MnCoGe$_{0.95}$Si$_{0.05}$ and MnCoGe$_{0.85}$Si$_{0.15}$ for fields in the range of $B = 0 - 5$ T around their Curie temperatures with 4 K interval steps are shown in Figure 6.16(a) and (b), respectively. These measurements show overlapping for increasing and decreasing fields for both compounds, thus indicating that there are no detectable magnetic hysteresis loss effects for increasing Si substitution for Ge in MnCoGe$_{1-x}$Si$_x$ compounds. Moreover, Figure 6.16(c) and (d) shows the corresponding Arrott plots ($M^2$ versus $B/M$) for the MnCoGe$_{0.95}$Si$_{0.05}$ and MnCoGe$_{0.85}$Si$_{0.15}$, which were found to exhibit features characteristic of a second order transition for all of the samples. The present findings demonstrate that the ferromagnetic transition at $T_C$ in MnCoGe$_{1-x}$Si$_x$ remains a second order transition on substitution of Si for Ge for Si concentrations up to $x = 0.2$.

The magnetic entropy change, $-\Delta S_M$, has been determined for the whole set of MnCoGe$_{1-x}$Si$_x$ compounds ($x = 0-0.2$) from their magnetization curves for both increasing and decreasing field values as functions of temperature and magnetic field ($\Delta B = 0-5$ T). The magnetic entropy change has been derived by applying the standard Maxwell relation [36] using Equation 6.1. As shown by the curves in Figure 6.17(a-c), the $-\Delta S_M$ peak gradually broadens towards higher temperatures with increasing magnetic field, behaviour characteristic of a field induced transition from the paramagnetic to a ferromagnetic state. The changes in magnetic entropy for the set of MnCoGe$_{1-x}$Si$_x$ compounds ($x = 0.05, 0.1, 0.15,$ and $2.0$) around their ferromagnetic ordering temperatures have been calculated from decreasing applied fields in order to determine the suitability of different experimental and related analytical approaches to establish the isothermal entropy change [16]. The entropy values at the respective Curie temperatures are found slightly the increase, with $\Delta B = 0-5$ T: $-\Delta S_M \sim 2.1$ J kg$^{-1}$ K$^{-1}$ at $T_C = 345$ K for MnCoGe$_{0.95}$Si$_{0.05}$; $-\Delta S_M \sim 3.5$ J kg$^{-1}$ K$^{-1}$ at $T_C = 350$ K for MnCoGe$_{0.90}$Si$_{0.10}$; and $-\Delta S_M \sim 5.1$ J kg$^{-1}$ K$^{-1}$ at $T_C = 355$ K for MnCoGe$_{0.85}$Si$_{0.15}$. The increase
in magnetization on substitution of Si for Ge, correspondingly enhances the value of $-\Delta S_M$, which is related to the exchange interaction between the Mn-Mn moments.

**Figure 6.17** Temperature dependence of the isothermal magnetic entropy change, $-\Delta S_M(T, H)$ for MnCoGe$_{1-x}$Si$_x$ compounds ($x = 0.05$, 0.10, and 0.15) calculated from magnetization isotherms with 0-5 T field change applied.
6.1.4 Conclusions

In conclusion, the substitution of Al for Ge atoms induces a structural transformation from an orthorhombic structure at \( x < 0.03 \) to a hexagonal structure at \( x > 0.03 \) at room temperature, and the concentration was employed to tune the structural transition temperature \( T_{\text{str}} \) in \( \text{MnCoGe}_{1-x}\text{Al}_x \) compounds. It was found that with increasing Al doping, \( T_{\text{str}} \) decreases and overlaps with the Curie temperature of the martensite phase \( T^M_{\text{C}} \). As a result, a transition temperature window as wide as 80 K (from 270 to 350 K) is observed, and the Curie temperature changes differently in hexagonal and orthorhombic structures with increasing Al. The origin of the reduction of \( T_{\text{str}} \) is ascribed to the strengthening of Mn–Mn covalent bonding and the lowering of the \( c/a \) ratio due to Al doping. For the optimized compositions, there was a moderate magnetic entropy change \(-\Delta S_{\text{M}}\), which was found to represent second order magnetic transition behaviour. The working temperature region from 320 to 350K is favourable for magnetic refrigeration applications in this temperature area. Further substitution of Al for Ge \( (x > 0.03) \) in \( \text{MnCoGe}_{1-x}\text{Al}_x \) compounds leads to the separation of magnetic and structural transitions.

An excellent agreement of the critical exponents of the \( \text{MnCoGe}_{0.97}\text{Al}_{0.03} \) compound was determined using the isothermal magnetization in the vicinity of \( T_C \), based on various techniques such as the Kouvel-Fisher method, modified Arrott plots, and critical isotherm analysis. Moreover, all critical exponents fulfil the Widom scaling law. The validity of the calculated critical exponents was confirmed by the scaling equation with the obtained magnetization, field, and temperature data below and above \( T_C \), showing a collapse 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.

Furthermore, the investigation of the replacement of Ge by Si in MnCoGe\textsubscript{1-x}Si\textsubscript{x} compounds demonstrated the dominant structure to be orthorhombic TiNiSi-type with very small hexagonal Ni\textsubscript{2}In-type structure for increasing Si concentration up to \( x = 0.2 \). The magnetization and DSC measurements indicated that \( T_C \) is slightly increased with increasing Si concentration, although the structural transition temperature, \( T_{str} \), is reduced. The magnetic entropy change, \(-\Delta S_M\), shows enhancement with increasing Si concentration up to \( x = 0.2 \), accompanied by the lack of any magnetic hysteresis loss, which is characteristic of second order magnetic transition behaviour and very favourable to magnetic refrigerator application. Higher Si concentrations (\( x > 0.2 \)) need to be investigated, however, in order to clarify and optimise the effects of substitution by Si in MnCoGe\textsubscript{1-x}Si\textsubscript{x} compounds.
6.2 Substitution for Mn by Ti in MnCoGe Alloy

6.2.1 Introduction

Earlier studies of the parent compound MnCoGe indicated that a martensitic structural transformation [15] from the low-temperature orthorhombic TiNiSi-type structure (space group \textit{Pnma}) to the high-temperature hexagonal Ni$_2$In-type structure (space group \textit{P63/mmc}) occurs at around $T_{\text{str}} = 650$ K. [16]. The orthorhombic TiNiSi-type structure of MnCoGe is reported to be ferromagnetic below the second-order paramagnetic to ferromagnetic transition at $T_C \approx 345$ K, while the hexagonal Ni$_2$In-type structure exhibits a ferromagnetic transition at $T_C \approx 275$ K [16,17]. Given that a large decrease in the unit cell volume of approximately 3.9% in MnCoGe compound occurs at $T_{\text{str}}$ when the crystal symmetry changes from orthorhombic to hexagonal [15], MnCoGe and related compounds are of interest because of the scope they allow to control the temperatures (by causing $T_{\text{str}}$ and $T_C$ to coincide or be close enough) at which the magnetic and structural transitions occur and thereby capitalise on both magnetic and structural entropies.

In this section, the substitution of Ti into Mn$_{1-x}$Ti$_x$CoGe compounds was investigated, and it was found that the one with the $x = 0.06$ substitution most successfully shifted the structural change and magnetic phase transition into the temperature range of interest, leading to the attainment of a giant magnetocaloric effect. Furthermore, the magnetic properties and critical behaviour of the Mn$_{0.94}$Ti$_{0.06}$CoGe and Mn$_{0.99}$Ti$_{0.01}$CoGe compounds were also investigated. Thus in an effort to understand the nature of the magnetic transition in both compounds, critical exponent analysis in the vicinity of the ferromagnetic (FM) – paramagnetic (PM) region [19–21] was performed. The results reveal that these materials undergo a structural
transition as well as a second-order ferromagnetic–paramagnetic transition, which will be discussed in more detail later.

6.2.2 Experimental and Procedures

Polycrystalline Mn$_{1-x}$Ti$_x$CoGe compound 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, 3% excess Mn over the stoichiometric amount was added to compensate for the weight loss of Mn. The polycrystalline ingots were melted many 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 h and then quenched in water at room temperature. Magnetization measurements were carried out using the vibrating sample magnetometer option of a Quantum Design 14 T physical properties measurement system (PPMS) in the temperature range of 10–600 K at applied fields of up to 5 T. Differential scanning calorimetry (DSC) measurements were carried out using a TA instrument DSC-Q100 over the range of 300-450 K to check for possible phase transitions in the higher temperature range.

6.2.3 Results and Discussion

6.2.3.1 Mn$_{1-x}$Ti$_x$CoGe

The temperature dependence (100–340 K) of the magnetization of the Mn$_{1-x}$Ti$_x$CoGe (x = 0.1 and 0.06) compounds was measured in various magnetic fields, as shown in Figure 6.18. A decoupling of the structural and magnetic transitions is clearly observed in the $M$–$T$ curves as
a two-step transition, which can be discerned at $T_C \approx 270$ K and $T_{str} \approx 235$ K for $x = 0.06$, and $T_C \sim 178$ K and $T_{str} \sim 280$ K for $x = 0.1$, respectively. Based on the analogous magnetic behaviour between Mn$_{0.9}$Ti$_{0.1}$CoGe [37] and Mn$_{0.94}$Ti$_{0.06}$CoGe [38], these transitions can be described as representing the change from orthorhombic to hexagonal structure at $T_{str}$, with $T_C$ indicating the paramagnetic to ferromagnetic transition in the hexagonal phase. The inset in Figure 6.18(b) shows a plot of $M^2$ versus $T$, 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 $T_{str} \sim 235$ K. The absence of thermal hysteresis in the vicinity of the magnetic PM to FM transition is clear evidence of the second-order nature of this transition.

A notable thermal hysteresis is observed, however, in the vicinity of the magnetostructural transition from the antiferromagnetic TiNiSi-type to the ferromagnetic Ni$_2$In-type structure.

Figure 6.18 Temperature dependence of the magnetization (a) for $x = 0.06$ and (b) for $x = 0.1$. The insets show $dM/dT$ versus $T$, used for the determination of $T_{str}$, as well as $M^2$ versus $T$, used for the determination of $T_C$. 
confirming its first-order nature. It has been previously established that the presence of a small hysteresis at $T_{\text{str}}$ is indicative of a magnetoelastic character of the FM to antiferromagnetic (AFM) transition [17].

The magnetic entropy changes, $\Delta S_M$, of the materials have been calculated using the Maxwell relation in Equation 6.1 [23] and are shown in Figure 6.19 as a function of temperature and field. The magnetic entropy change, $\Delta S_M$, was also evaluated in the decreasing field mode, which is shown by the dotted and open symbol curves in Figure 6.19(a). A comparison of the $\Delta S_M$ values calculated using increasing and decreasing fields for both compounds 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 increasing applied magnetic field. The temperature dependence of the magnetic entropy changes in the vicinity of $T_{\text{str}}$ and $T_C$ for Mn$_{0.9}$Ti$_{0.1}$CoGe and Mn$_{0.94}$Ti$_{0.06}$CoGe is shown in Figure 6.19.

Figure 6.19(a) reveals that the entropy change is significantly higher at $T_{\text{str}}$ with a maximum value of $\Delta S_M$ of $\sim 6.6$ J/kg K, compared with the value at $T_C$ of $\Delta S_M \approx 4.2$ J/ kg K for a field change of $\Delta B = 8$ T for Mn$_{0.9}$Ti$_{0.1}$CoGe. The inset in Figure 6.19(b) showing the variation of the magnetic entropy with temperature at 1 T clearly displays two maxima for Mn$_{0.94}$Ti$_{0.06}$CoGe, 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 $T_{\text{str}}$ and is $\Delta S_M \approx 11.3$ J kg$^{-1}$ K$^{-1}$ for a magnetic field change $\Delta B$ of 5 T, which is about one order of magnitude higher than that found for the undoped MnCoGe ($\sim 4.8$ J kg$^{-1}$ K$^{-1}$ for a
change from 0-5 T) [17]. Around the FM to PM transition temperature $T_C$, $\Delta S_M$ is found to be $\sim 3 \text{ J kg}^{-1} \text{ K}^{-1}$ for a magnetic field change $\Delta B$ of 0-5 T. The difference in the $\Delta S_M$ values at $T_{str}$ and $T_C$ can be understood in terms of the difference in order of the phase transitions. Compared with findings for some alloys with a second-order magnetic transition, the $\Delta S_M$ peak of Mn$_{0.94}$Ti$_{0.06}$CoGe is comparable to that of Gd [25] ($\sim 10.2 \text{ J kg}^{-1} \text{ K}^{-1}$ for a change of

![Figure 6.19](image)

**Figure 6.19** Temperature dependence of the isothermal magnetic entropy change $\Delta S_M$ for (a) Mn$_{0.9}$Ti$_{0.1}$CoGe and (b) Mn$_{0.94}$Ti$_{0.06}$CoGe calculated from magnetization isotherms, with the inset showing the variation of magnetic entropy at 1 T; (c) dependence of the maximum magnetic entropy change on $B(T)$ for Mn$_{0.9}$Ti$_{0.1}$CoGe and (d) on the parameter $(\mu_0 H/T_C)^{2/3}$ for Mn$_{0.94}$Ti$_{0.06}$CoGe. The solid line represents a linear fit to the data.

0-5 T). Figure 6.19(c) shows that for the region around the structural transformation at $T_{str} \approx 178$ K, the maximum values of the entropy change $\Delta S_M$ vary linearly with magnetic field, indicating the existence of the proportional relationship $\Delta S_M \propto B$ at this transition for
Mn$_{0.9}$Ti$_{0.1}$CoGe. On the other hand, it was found that the dependence of the magnetic entropy change on the parameter $(\mu_0 H/T_C)^{2/3}$ for Mn$_{0.94}$Ti$_{0.06}$CoGe in Figure 6.19(d) was linear. The mean-field theory predicts that in the vicinity of second-order phase transitions, $-\Delta S_M$ is proportional to $(\mu_0 H/T_C)^{2/3}$ [26, 27]. The linear fit to the data in Figure 6.2(d) clearly demonstrates that the relationship $-\Delta S_M \propto (\mu_0 H/T_C)^{2/3}$ is valid around $T_C$.

Figure 6.20 Kouvel–Fisher plots for the spontaneous magnetization of $M_s(T)[dM_s/dT]^{-1}$ (left scale) and $\chi_0^{-1}(T)[d\chi_0^{-1}/dT]^{-1}$ (right scale) versus temperature for (a) Mn$_{0.94}$Ti$_{0.06}$CoGe and (b) Mn$_{0.9}$Ti$_{0.1}$CoGe compounds. The lines are fits to the data around $T_C$, as discussed in the text, with the fits leading to the critical exponent values.
According to the conventional static scaling law, the critical properties of a second-order magnetic transition can be described by the critical exponents $\beta$, $\gamma$, and $\delta$ derived from magnetization measurements around the transition temperature, as in the previous section. On applying these standard approaches, as shown by the fits to the Kouvel–Fisher plots of $M_S(T)[dM_S/dT]^{-1}$ and $\chi_0^{-1}(T)[d\chi_0^{-1}/dT]^{-1}$ versus temperature in Figure 6.20, the critical exponents around $T_C$ in $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ have been determined to be $\beta = 0.61$ and $\gamma = 0.91$. Hence, on applying the relationship $\delta = 1 + \gamma / \beta$, with $\beta = 0.61$, $\gamma = 0.91$, the critical exponent $\delta = 1 + \gamma / \beta = 2.49$. For the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ compound, the critical exponents have been found to be $\beta = 0.45$, $\gamma = 0.83$, and $\delta = 2.84$, respectively. The critical exponents determined for both compounds are similar to the theoretical values from the mean-field model, for which $\beta = 0.5$, $\gamma = 1.0$, and $\delta = 3.0$, consistent with the existence of long-range ferromagnetic interactions [27]. Thus, the critical behaviour analysis in the vicinity of $T_C$ demonstrates that the magnetism of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ and $\text{Mn}_{0.9}\text{Ti}_{0.1}\text{CoGe}$ compounds is governed by long range interactions. This is in agreement with the linear fit to the data in Figure 6.19(d), which clearly demonstrates that the relationship $-\Delta S_M \propto (\mu_0 H/T_C)^{2/3}$ is valid around $T_C$.

### 6.2.4 Conclusion

The structural and magnetic properties of $\text{Mn}_{1-x}\text{Ti}_x\text{CoGe}$ compounds have been investigated by magnetic measurements and critical exponent analysis. Substitution of Ti for Mn in the parent MnCoGe compound leads to a significant reduction in both $T_{str}$ (from ~ 645 K for MnCoGe to ~ 235 K for $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ and ~ 178 K for $\text{Mn}_{0.9}\text{Ti}_{0.1}\text{CoGe}$) and $T_C$ (from ~ 345 K for MnCoGe to ~ 270 K for $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ and ~ 280 K for $\text{Mn}_{0.9}\text{Ti}_{0.1}\text{CoGe}$). Moreover, all the critical exponents for $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ and $\text{Mn}_{0.9}\text{Ti}_{0.1}\text{CoGe}$ fulfil the Widom scaling law. The validity of the calculated critical exponents was confirmed by the
scaling equation, with the magnetization, field, and temperature data obtained below and above $T_C$ collapsing onto two different curves. Thus, the scaling of the magnetization data above and below $T_C$ was obtained using the respective critical exponents, and the consistency of the values of the critical exponents determined by different methods confirm that the calculated exponents are unambiguous and intrinsic. The critical exponents determined are close to those predicted by the mean-field theory for long range interactions.

References

CHAPTER 7

CONCLUSIONS AND OUTLOOK

In the summary, structural, magnetic and magnetocaloric properties of some selected magnetic materials with different crystal structures such as cubic NaZn$_{13}$-type structure, body centred tetragonal ThCr$_2$Si$_2$-type structure; hexagonal Ni$_2$In-type structure and orthorhombic TiNiSi-type structure have been systematically investigated. The aim of this study 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 magnetic properties. This work has important contributions towards an understanding of the role of atomic substitution as chemical pressure effect in tuning the magnetocaloric properties, magnetic phase transition and magnetic structure. The main outcomes of the thesis are summarized as follows:

- A systematic investigation of the structural and magnetic characterization of La$_{0.7}$Pr$_{0.3}$Fe$_{11.4-x}$Cu$_x$Si$_{1.6}$ ($x = 0, 0.06, 0.12, 0.23, 0.34$) for high temperature annealing (HTA) and low temperature annealing (LTA) samples has been carried out. The results show that the HTA process resolves the problem of non-equilibrium solidification behaviour due to the incomplete peritectic reaction $\gamma$-Fe+L $\rightarrow$ La(Fe$_x$Si)$_{13}(\tau_{1a})$ that occurs in the LTA process. The HTA sample with $x = 0$ shows promising values of $-\Delta S_M$ and RCP with very small hysteresis loss. This indicates the
elevated temperature in HTA plays an important role to form the NaZn_{13} type structure in the La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6} compound.

- Substitution of Cu for Fe leads to a decrease in the magnetic entropy change and eliminates hysteresis loss. Increasing the Cu concentration (starting from x = 0.06) also results in a change in the magnetic phase transition type from first to second order and reduces the characteristics of the IEM transition. The Curie temperature, T\text{C}, increases with increasing Cu content, which can be ascribed to the increase in the lattice parameter and the modification of the composition. The compound with a small amount of Cu substitution shows a promising magnetic performance for magnetic refrigerator application, with no hysteresis loss and reasonable RCP.

- Replacement of Fe by Cr in La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_{x}Si_{1.6} compounds leads to decreases in lattice parameter but variation behaviour on temperature transition, T\text{C}. The variation in the value of T\text{C} with increasing Cr concentration can be understood in terms of sensitive changes of Fe1-Fe2 and Fe2-Fe2 distances. Analysis of the magnetisation data demonstrates that the order of magnetic phase transition around T\text{C} is consistent on first order type even x=0.34 for La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_{x}Si_{1.6} compounds. Replacement of Fe by Cr leads to a reduction of the magnetic entropy change from beginning at x=0; (-\Delta S\text{M} = 17 \text{ J kg}^{-1} \text{ K}^{-1}) to x=0.06; (-\Delta S\text{M} = 12 \text{ J kg}^{-1} \text{ K}^{-1}), however starts to enhance again when keep increasing Cr concentration until x=0.34; (-\Delta S\text{M} = 17.5 \text{ J kg}^{-1} \text{ K}^{-1}).

- High intensity neutron and X-ray diffraction studies demonstrate that La_{0.7}Pr_{0.3}Fe_{11.06}Cr_{0.34}Si_{1.6} compound has contraction in unit cell from ferromagnetic to
A systematic investigation of the structural and magnetic characteristics of NdMn$_{2-x}$Ti$_x$Si$_2$ (T = Ti, Cr, Cu and V) compounds has been carried out. Substitution of Mn by Ti leads to a reduction of the magnetic entropy change. However, analysis of the magnetisation data demonstrates that the first order magnetic transition of NdMn$_2$Si$_2$ around $T_C$ remains unchanged on replacement of Mn by Ti, and this substitution leads to significant reduction in magnetic hysteresis losses and eliminates thermal hysteresis. Neutron diffraction studies demonstrate that NdMn$_{1.9}$Ti$_{0.1}$Si$_2$ has the AF$_{il}$ antiferromagnetic structure in the temperature range $T_N \sim 374$ K $> T > T_C \sim 22$ K and the combined Fmc+F(Nd) ferromagnetic state below $T_C \sim 22$ K.

The magnetic structures of NdMn$_{1.7}$Cr$_{0.3}$Si$_2$ determined from variable temperature neutron diffraction studies are: layered AF$_{il}$ antiferromagnetism for $T_N^{\text{inter}} \sim 320(3)$ K $< T < T_N^{\text{intra}} \sim 380(3)$ K; canted AF$mc$ antiferromagnetism for $T_C \sim 42(2)$ K $< T < T_N^{\text{inter}} \sim 320(3)$ K with a combined Fmc(Mn)+F(Nd) ferromagnetic structure for $T < T_C \sim 42(2)$ K. Values of the magnetic entropy, magnetocaloric effect and adiabatic temperature change have been determined from magnetization and heat capacity measurements around the first order magnetic transition at $T_C$.

Substitution of Cu for Mn leads to increase in the Curie temperature and decrease the Néel temperature. The variation in the value of $T_C$ with increasing Cu concentration...
can be understood in terms of changes in the Mn-Mn exchange interaction together with the effects of magnetic dilution. Analysis of the magnetisation data demonstrates that the order of magnetic phase transition around $T_C$ changes from first order at $x<0.6$ to second order transition for $x\geq0.6$ and leads to significant reduction in magnetic hysteresis losses. Substitution of Mn by Cu leads to a reduction of the magnetic entropy change and neutron diffraction studies demonstrate that NdMn$_{1.8}$Cu$_{0.2}$Si$_2$ has the AF$_{il}$ antiferromagnetic structure in the temperature range $T_N \sim 375$ K $> T > T_C \sim 44$ K and the combined Fmc+F(Nd) ferromagnetic state below $T_C \sim 44$ K.

- The replacement Mn by V in leads to decrease in the Curie and Néel temperature from. Increment of V concentration leads to a reduction of the magnetic entropy change respectively as did not change the first order magnetic transition behaviour. The neutron diffraction study on NdMn$_{1.9}$V$_{0.1}$Si$_2$ compound indicated that magnetic structure found from paramagnetic PM to the AF$_{il}$ antiferromagnetic structure in the temperature range $T_N \sim 375$ K $> T > T_C \sim 24$ K and the combined Fmc+F(Nd) ferromagnetic state below $T_C \sim 24$ K.

- Replacement of Y for Pr leads to a significant reduction in the lattice parameters of Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds. The commensurate changes in the intralayer Mn–Mn distances correspondingly lead to a variety of magnetic structures, as also observed in related RMn$_2$X$_2$ systems (R – rare earth; X - Ge, Si) [e.g. 24]. The various magnetic structures of Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ have determined by neutron powder diffraction over the temperature range 5 – 450 K. Together with magnetisation and differential scanning calorimetry measurements, this has enabled us to construct the magnetic phase
diagram of Pr\(_{1-x}\)Y\(_x\)Mn\(_2\)Ge\(_2\). The ferromagnetic transitions at \(T_{C}^{\text{inter}}\), the temperature at which the layered antiferromagnetic structure transforms to the canted \(Fmc\) structure, are found to be second order. The entropy changes around \(T_{C}^{\text{inter}}\) have been derived for Pr\(_{1-x}\)Y\(_x\)Mn\(_2\)Ge\(_2\) compounds of Y contents \(x = 0.0, 0.2\) and 0.5.

The temperature dependence of lattice parameters for CeMn\(_2\)Ge\(_{2-x}\)Si\(_x\) demonstrates an anomaly in thermal expansion which is accompanied with appearance of the interlayer Mn–Mn interactions. The co-existence of different magnetic states at the same temperature is considered to be related to the non-random variation of site concentrations of Si and Ge, and depends sensitively on the Mn–Mn distances in this system. Moreover, critical properties study on the second-order ferromagnetic transition of CeMn\(_2\)Ge\(_2\) demonstrate that the magnetic interactions around \(T_{C}^{\text{inter}}\) can be described with the three dimensional Heisenberg model corresponding to short range interactions. Overall this investigation has demonstrated that, as expected, the Si concentration plays the dominant role in tuning the magnetic structure and properties of the CeMn\(_2\)Ge\(_{2-x}\)Si\(_x\) compounds.

The substitution of Al for Ge atoms in MnCoGe induces a structural transformation from an orthorhombic structure at \(x < 0.03\) to a hexagonal structure at \(x > 0.03\), and the variation in concentration was employed to tune the structural transition temperature \(T_{str}\) in MnCoGe\(_{1-x}\)Al\(_x\) compounds. The origin of the reduction of \(T_{str}\) is ascribed to the strengthening of Mn–Mn covalent bonding and the lowering of the \(c/a\) ratio due to Al doping. Further substitution of Al for Ge (\(x > 0.03\)) in MnCoGe\(_{1-x}\)Al\(_x\) compounds leads to the separation of magnetic and structural transitions.
Furthermore, the investigation of the replacement of Ge by Si in MnCoGe\(_{1-x}\)Si\(_x\) compounds indicated that the dominant structure is orthorhombic TiNiSi-type with very small hexagonal Ni\(_2\)In-type structure being present for increasing Si concentration up to \(x = 0.2\). The magnetization and DSC measurements indicated that \(T_C\) is slightly increased with increasing Si concentration, although the structural transition temperature, \(T_{str}\), is reduced. The samples with higher Si concentrations (\(x > 0.2\)) are needed to be further investigated in order to clarify and optimise the effects of substitution by Si in MnCoGe\(_{1-x}\)Si\(_x\) compounds.

Finally, the structural and magnetic properties of Mn\(_{1-x}\)Ti\(_x\)CoGe compounds have been investigated by magnetic measurements and critical exponent analysis. Substitution of Ti for Mn in the parent MnCoGe compound leads to a significant reduction in both \(T_{str}\) and \(T_C\). Moreover, all the critical exponents for Mn\(_{0.94}\)Ti\(_{0.06}\)CoGe and Mn\(_{0.9}\)Ti\(_{0.1}\)CoGe fulfil the Widom scaling law. The validity of the calculated critical exponents was confirmed by the scaling equation, with the magnetization, field, and temperature data obtained below and above \(T_C\) collapsing onto two different curves. Thus, the scaling of the magnetization data above and below \(T_C\) was obtained using the respective critical exponents, and the consistency of the values of the critical exponents determined by different methods confirm that the calculated exponents are unambiguous and intrinsic. The critical exponents determined are close to those predicted by the mean-field theory for long range interactions.

The overall of this intensive study has provided an insight on the effect of atomic substitutions in term of chemical pressure for tuning the magnetic structure and magnetocaloric effect properties as well as the magnetic phase transitions. It is ambition
that this work may act as a foundation for further research in order to development of new materials that can fulfil specific requirements of cooling devices. Future work may include:

- It would be very favourable to tune the La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ compound with substitution Fe with other transition metal in order to produce room temperature transition belonging with higher magnetic entropy change.

- There is a need to perform pressure dependent magnetisation measurements of the layered RT$_2$X$_2$ rare earth compounds, (R is a rare earth, T is transition metal and X is Si or Ge) in the diamond anvil cell up to a pressure of 10 GPa. Such an experiment will help to explain if at all, it’s 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 and change magnetic properties.

- Further study on critical concentration by doping or substitution need to be done in order to combine 2 different structure temperature transition on MnCoGe, as a typical MM’X (M, M’ = transition metal, X = Si, Ge, Sn). This compound shown the strong dependence on proper tuning for critical behaviour of the phase transition, which was due to the vacancy induced structural and magnetic transition and the field-induced martensitic transformation, acted as a guide to more interesting phenomena related to the substitution for Ge.
List of Publications


2. **M. F. Md Din**, J. L. Wang, A. J. Studer, Q. F. Gu, R. Zeng, J. C Debnath, P. Shamba, S. J. Kennedy, and S. X. Dou “Effects of Cr substitution on structural and magnetic properties in La$_{0.7}$Pr$_{0.3}$Fe$_{11.4}$Si$_{1.6}$ compound” (*Journal of Applied Physics*) **115**, 17A942 (2014)


5. Jiantie Xu, Shu-Lei Chou, Qin-Fen Gu, **Md-Din Muhamad**, Hua-Kun Liu and Shi-Xue Dou “Study on Vanadium Substitution to Iron in Li$_2$FeP$_2$O$_7$ as Cathode Material for Lithium-ion Batteries”, (*Electrochimica Acta*) **141**, 195-202 (2014)


12. M.F. Md Din, J.L. Wang, R. Zeng, P. Shamba, J.C. Debnath and S.X. Dou “Effects of Cu substitution on structural and magnetic properties of La₀.₃Pr₀.₃Fe₁₁.₄Si₁.₆ compounds” (*Intermetallics*) 36, 1-7 (2013)


19. J.L. Wang, **M.F. Md Din**, S.J. Campbell, S.J. Kennedy, F.M. Yang, G.H. Wu and S.X. Dou “$^{57}$Fe Mössbauer and Magnetic studies of Nd$_3$Fe$_{24.5}$Cr$_{4.5}$”. *(Hyperfine Interactions)*


22. **M. F. Md Din**, J. L. Wang, S. X. Dou, S. J. Kennedy and S. J. Campbell “Magnetic Properties and Magnetocaloric Effect of NdMn$_{2-x}$V$_x$Si$_2$ Compounds” (*In preparation*)