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High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga

By

Mark Robert Kirkham

A Doctoral Thesis
Submitted in Partial fulfilment of the requirements for the award of
Doctor of Philosophy of Loughborough University

March 2014

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High Temperature Specific Heat Capacity Measurement of Ni_{2+\delta}Mn_{1-\delta}Ga
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High Temperature Specific Heat Capacity Measurement of Ni_{2-x}Mn_{1-x}Ga
Abstract

The investigation of Ni$_2$MnGa ferromagnetic shape memory alloys relies on accurate and complete phase diagrams for the various phase transitions these materials exhibit. However, very little work has been performed to investigate the high temperature order/disorder phase transitions. This project tries to fill some of the gap in the phase diagram through a systemic composition based investigation of Ni$_{2-x}$Mn$_{1+x}$Ga (X=-0.2, 0.0, 0.2, 0.8 and 1.0) using high temperature specific heat measurements. The work has produced a phase diagram in the composition range measured and demonstrated that the order/disorder transition temperatures and Curie temperatures follow the predicted trend as seen in similar studies of different alloy compositions. This work has also characterised the melt temperature of the five compositions measured.

As part of the investigation of the high temperature phase transitions, a ‘High Temperature Adiabatic Calorimeter’ was developed, which was commissioned using four reference samples (copper, Stainless steel, graphite and molybdenum). The developed system used a linearly drifting baseline to improve the speed, accuracy and stability of the system. This modification to the standard adiabatic calorimeter measurement scheme required extensive development of the analysis techniques and development of new approaches (e.g. heating phase analysis and finite element modelling analysis). The system was demonstrated to operate well between room temperature and 1350 K, producing accurate specific heat data that compared well with the standard data for the commissioning samples. Due to time constraints this system was not used for the Ni$_2$MnGa investigation.
High Temperature Specific Heat Capacity Measurement of Ni$_{2-x}$Mn$_{1-x}$Ga
High Temperature Specific Heat Capacity Measurement of Ni$_{2+y}$Mn$_{1-x}$Ga
1 Introduction
The ferromagnetic shape memory alloy Ni$_2$MnGa is one of the new materials that exhibits a martensitic shape memory phase transition while remaining ferromagnetic ($T_M = 202$ K, $T_C = 286$ K). This makes the material very attractive for many practical applications in medical implants and thermally/electrically/magnetically controlled actuators or sensors [1] [2]. Use in actuators is of particular interest as the magnetically controlled shape memory effect seen in Ni$_2$MnGa (and other ferromagnetic shape memory alloys) is much faster (allowing for high frequency oscillations) and with a higher power density than the current alternatives (e.g. piezoelectric). The magnetic deformation of Ni$_2$MnGa also allows for not only one-way shape memory processes (similar to thermo-elastic shape memory alloys) but also for two-way shape memory applications.

Another advantage of the Ni$_2$MnGa alloys is that small composition variations can results in significant changes in the phase transitions relevant to the ferromagnetic shape memory process. The phase transitions of interest for the ferromagnetic shape memory effect are: the martensitic phase transition (transition from cubic at high temperature to tetragonal or orthorhombic at low temperature, $T_M$) and the ferromagnetic ordering temperature (or Curie temperature, $T_C$).

The research in the literature into Ni$_2$MnGa has been not only to understand and predict the phase transitions through compositional variations and qualitative modelling, but also the research is attempting to formulate a mechanistic understanding of the ferromagnetic shape memory effect.

This research (both qualitative and mechanistic) is reliant on the experimental measurement of the phase transitions through resistivity and specific heat measurements (to identify the phase transition temperatures), as well as structural (x-ray or neutron diffraction, and ultrasound measurements) and magnetic measurement techniques (SQUID, magnetic susceptibility and polarised neutron diffraction).
High Temperature Specific Heat Capacity Measurement of \( \text{Ni}_{2\pm x}\text{Mn}_{1\pm x}\text{Ga} \)

The qualitative and mechanistic understanding of the \( \text{Ni}_{2\pm x}\text{Mn}_{1\pm x}\text{Ga} \) alloy (and non-stoichiometric compositions, (e.g. \( \text{Ni}_{2\pm x+y}\text{Mn}_{1-x}\text{Ga}_{1-y} \)), is reliant on a completed phase diagram identifying trends in the various phase transitions seen in \( \text{Ni}_{2}\text{MnGa} \) type alloys. At present the phase diagram is not complete.

To date, much of the experimental work has focused on the low temperature \( T_M \) and \( T_C \) phase transitions (and also a pre-martensitic phase transition \( T_P \), \( T_P > T_M \)) in an attempt to understand the coupling between the structural and magnetic properties (magnetoelastic effects). However, \( \text{Ni}_{2}\text{MnGa} \) has been shown to have two other phase transitions at high temperature. These transitions are order/disorder transitions between three cubic structures (upon heating to increasing transition temperatures): firstly the highly ordered L2\(_1\) structure disorders to the partially ordered B2 structure, then the B2 structure disorders further into the completely disordered A2 structure.

It is known that the order/disorder phase transitions can have an effect on the stability of the low temperature cubic structure, but very little research into the order/disorder for non-stoichiometric \( \text{Ni}_{2}\text{MnGa} \) has been performed.

This thesis has sought to address this gap in understanding by undertaking specific heat measurements and some x-ray diffraction of a range of compositions of \( \text{Ni}_{2\pm x}\text{Mn}_{1\pm x}\text{Ga} \) (\( X = -0.2, 0, 0.2, 0.8 \) and 1.0).

To allow for the measurement of large samples, and investigate the bulk properties of the polycrystalline samples, a high temperature specific heat measurement system was developed for use with samples approximately 20 g in size. This relatively large sample size resolves many of the issues effecting specific heat measurement of small samples (e.g. a small sample of a large grain structure means only a small number of grains are included, and any regions of varying composition can skew the results), and allows for investigation of bulk alloyed materials.
This thesis details the development of the high temperature specific (HTCP) measurement system for use between room temperature and 1400 K, and the commissioning work performed to verify the accuracy of the system.
High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga
2 Background
2.1 Shape Memory Alloys (SMA):

Shape memory alloys are one of a series of new materials that are termed SMART materials. SMAs have the ability to remember shapes. This is due to a martensitic/austenitic phase transition. The shape memory effect is demonstrated by the SMA’s ability to return to its original shape after deformation by undergoing the martensitic/austenitic phase transition.

The phenomenon of ‘shape memory’ was first discovered in 1938 by ‘Arne Olander’ in Au-Cd \( T_m = 303-403 \text{K} \), since this initial discovery interest waxed slightly but resumed again in 1962 with the US naval research laboratories finding the shape memory effect in Ni-Ti [4]. This interest was sparked by Ni-Ti having a near room temperature transition temperature.

The material has since been used in engineering applications, primarily medicine where its excellent biocompatibility and wear resistance making it safer than other more traditional materials. Other disciplines, such as aeronautics and space engineering, also have a number of real world applications for not only low and room temperature SMA’s but also high temperature and two-way SMA’s, for use as actuators and sensors. The discovery of magnetic shape memory alloys further increase the engineering application possibilities for SMA.

Since the discovery of Ni-Ti shape memory alloys, there are a number of newer SMA materials that have undergone vigorous experimentation, the first of which was Cu-based SMA’s such as: \( \beta \)-Brass (Cu-Zn-Al) [5] and Cu-Al-Ni [6]. Like Ni-Ti these materials exhibit temperature and strain induced martensitic phase transitions, but due to their transition temperature (Ni-Ti @310-340K [3], Cu-Zn-Al @323K [4]) and the brittle nature of the material they have limited uses.

More recently the shape memory Heusler alloys [7] (i.e.\( A_2BC \) alloys with a \( L_2 \) structure, such as Ni\(_2\)MnAl, Ni\(_2\)MnGa) have become of interest. They show
the shape memory effect (SME) at more usable temperatures. Some of these materials also demonstrate martensitic phase transition under a magnetic field. Ni$_2$MnGa shows a 6% strain induced by a 320-400 A/m field [7]. The important factor about this material is that the martensitic phase transition temperature is below its Curie temperature [8].

This sets it apart from other shape memory Heusler alloys such as Co$_2$NbSn [9] which also has a martensitic/austenitic phase transition and is ferromagnetic. However, the Curie temperature is much lower than the martensitic phase transition temperature ($T_m$). Therefore the magnetic effects on the SMA transition would be much lower in the paramagnetic temperature range where the martensitic phase transitions occur. With this said there is still some linkage between magnetism and the martensitic state in paramagnetic materials [10].

Much of the work on the ferromagnetic SMA, and in particular on Ni$_2$MnGa, is carried out investigating the magnetic effects through comparison with a similar Heusler alloy, for example the paramagnetic SMA Ni$_2$MnAl. In addition some research has been carried out to further understand the magnetic effect on the weaker and much more complex processes in Ni$_2$MnAl [10] and Mn$_2$NiGa [12].

The primary difference between these materials is that while the austenitic phase of Ni$_2$MnGa is solely a ferromagnetic Heusler L$_2$ phase, Ni$_2$MnAl can be either B$_2$ or B$_{2+L2_1}$ (anti-ferromagnetic and ferromagnetic) [11]. Both of these materials are generally considered to be one-way shape memory alloys, but there is also research into two-way shape memory effects (TWSMA) [13] [14]. These TWSMA are different to one-way SMAs in that they are constructed in such a way that the martensitic/austenitic phase transition causes the material to change between two different bulk shapes.

Most of the materials discussed so far are low or room temperature SMAs but there is a number of 'High temperature SMAs', Ni-Ti-Hf [15], Cu-Al-Ni [16], Ni-Mn [17], etc. ($T_m$ =1500K, 1113K, etc.). All of these materials exhibit shape
memory effects at higher temperatures compared to the more widely used Ni-Ti and Cu-based SMAs. The understanding of these is more complex since the SMA phenomenon is understood to be a displacive process, but at these higher temperatures there are observable diffusion processes to be considered. For example, several Ni-Mn-Ga HTSMA’s, with $T_M \approx 750$ K, show significant aging effects due to diffusion at high temperatures, with $T_M$ decreasing by 10 K in less than 20 martensitic to austenite transition cycles (@750 K) [18].

Investigation of these HTSMA’s and low temperature SMA’s is focused on making them more usable, for example, producing an SMA that can be machined easily and has a $T_m$ at the required operating temperature. ‘Tuning’ of the martensitic/austenitic phase transition can be achieved by changing the composition of the material. Slight changes in composition can greatly affect the transition temperature. For example: with the SMA Ni$_{2+x}$Mn$_{1-x}$Ga, variation of the nickel content by $X=+0.13$ causes the phase transition temperature to increase by 135 K [19]. A large amount of the research into Ni$_2$MnGa SMA’s is to understand the mechanism that produces this wide range of $T_M$ for small compositional variations. The research is performed both experimentally [20][21][22][23] and through the development of modelling techniques [24][25][26][27][28].

To understand the processes and effects present in both high and low temperature shape memory alloys, material characterisation techniques such as thermal property measurement, atomic structure determination, ‘stress-strain’ measurements and ‘SQUID’ (‘Superconducting-Quantum-Interference-Device’) magnetic measurements are used. These can not only determine the martensitic/austenitic phase transition but any other phase transition that the material undergoes, as well as producing information on material properties.

Characterisation of SMAs not only involves investigation of the SME transition but also the understanding of all the other phases and transitions of the material. These phases and transitions can be complicated and dependent
on many factors, and even interact. Taking the SMA Ni-Ti as an example, as temperature increases above 500 K precipitates of Ni$_4$Ti$_3$ begin to form. Further temperature increases to 900 K leads to a reduction in the number of precipitates; and if the temperature reaches above 1083K there is only a B2 ordered crystal lattices left [29]. These higher temperature phase changes can be seen in the thermal property characterisation (specific heat, thermal diffusivity, etc.), and can be used to determine the annealing processes necessary for producing better shape memory alloys, as well as increasing the overall knowledge about the materials and how the SME works.

Some work has been performed on the ferromagnetic Heusler alloy Ni$_2$MnGa to investigate its higher temperature phase transitions, with an order/disorder phase transition being observed (using DSC measurement) at 1083K [30]. Such work not only produces a more complete phase diagram but can be used to determine heat treatment processes (e.g., annealing conditions). This can be used to investigate what process/variables affect the SME transition temperature and in what way [31] [32] [33].

2.1.1 Martensitic and Austenitic Phases.

The martensitic transition is a displacive (diffusionless) process [34]. Atoms in the crystal structure of the material move short distances and do not break atomic bonds, retaining their relative atomic ordering (inherited ordering) and chemical composition. Rather than a diffusional transition [34] where atoms move over long atomic ranges, breaking atomic bonds and changing chemical composition (such as heating Ni-Ti above 500 K producing Ni$_4$Ti$_3$ precipitates [29]).

The ‘solid-solid’ phase transitions responsible for the shape memory effect present in SMA’s centres around two crystal structures. The high temperature phase is called the austenitic (high symmetry) phase [35], and the low temperature phase is called the martensitic (low symmetry) phase [35]. This transition is generally considered to be temperature induced with the material cooling from the austenitic to the martensitic phase. See Figure 2.1 for a simplified two-dimensional cubic example.
Starting the process in the high temperature phase (austenite, Figure 2.1a) the material begins to cool. The distances between the atoms shorten (thermal expansion) with dilation/distortion keeping the same lattice structure but overall the material will shrink (thermal expansion). As the temperature further cools, ‘shear’ distortions occur in the lattice (Figure 2.1b) so that the atoms occupy a more stable (lower symmetry) state. As the temperature further reduces more of the lattice planes adopt the lower energy configuration (Figure 2.1c) until all the material is in this new lattice structure (Figure 2.1d). The strain required to produce this new shape is known as Bain Strain [36].

Figure 2.1: Pictorial representation of a martensitic phase transformation in 2D for a simple cubic lattice.

As can be seen by the schematic representation of the process in Figure 2.1, this process alters the overall shape of the lattice significantly. However, with appropriate ‘training’, the material will not change its macroscopic form. This can be achieved in a number of ways. For steels (where the terms martensitic and austenitic originated from) this is achieved by lattice defects in the structure (Figure 2.2a). However, in shape memory alloys ‘Twinning’ takes place. The layers of the lattice undergo the same change in the unit cell (cubic to tetragonal) but in alternating directions (Figure 2.2b).
Twinning is a low energy (stable) transformation mode for which, unlike slip, no bonds have to be broken. This implies that this configuration is a highly recoverable state.

### 2.1.2 Physical Properties: Austenitic and Martensitic

Retention of the atomic ordering means no changes to chemical properties but the lattice re-orientation produces differences to the physical properties in the system [34].

This means that it is possible to determine the point of the phase transition by measuring a physical property of the crystal over a temperature range. A change in the crystal structure alters the measured response of many thermal and physical material properties (Figure 2.3).

A property that shows a marked difference in response pre- and post-transition is the stress-strain response of the material [37]. In an austenitic system (Figure 2.4a) the stress/strain characteristics arise solely from the elastic response of the bonds in the crystal (Hooke’s Law [38]). In the martensitic system (Figure 2.4b) initially the response comes solely from de-
twinning of the lattice layers, and only after this process is complete will the inter-atomic bonds begin to take the load. This gives the material a ‘rubberlike’ characteristic, the stress–strain response for which is very similar to that for ‘superelasticity’, but unlike the ‘superelastic effect’ (which is a result of a stress induced phase change) the ‘rubberlike’ effect solely occurs in the martensitic phase [39].

The double elasticity of the SMA materials means that the yield stress of a martensitic crystal is larger than that of an austenitic crystal [37].

![Figure 2.4: Diagrams representing the stress/strain characteristics of (a) austenitic and (b) martensitic systems](image)

2.1.3 The Shape Memory Cycle
The cycle for the SME is as follows (Figure 2.5):

- a Material at high temperature (Austenitic phase)
- b Material undergoes cooling to below $T_m$ (martensitic transition temperature).
- c Material in new ordering undergoes deformation (Load applied)
- d=a Material heated through $T_m$, to 100% austenitic phase, deformation removed.

![Figure 2.5: 2D representation of the SMA martensitic/austenitic cycle](image)
Non-dislocating deformations of the twinned state can be removed by heating through the transition temperature, returning it to the original austenitic state. This happens because twinned martensitic states have many degrees of freedom [40] (possible orientations of the layers) more than the austenitic state with only the one configuration. With twinned martensitic lattices it is possible to allow movement into one of the alternative orientations (new overall shape) without the unit cell being altered. In contrast above the transition temperature there is only one configuration available for the austenitic state. Therefore it must return to this original unit cell and therefore original overall shape.

Martensitic phase transitions are normally ‘thermo-elastic’ processes. This means that as the temperature drops the martensitic layers in the lattice nucleate and grow. As the temperature rises these plates disappear [34]. Being a displacive, rather than a diffusive, process martensitic/austenitic phase transitions are ‘rapid’, since they are not dependent on the diffusion rate of atoms through the lattice structure.

Since nucleation of the martensitic phase is not instantaneous at one temperature there is a need to define four transition temperatures when describing martensitic/austenitic phase changes [34]:

- \( A_f \) above this temperature 100% austenitic
- \( M_f \) below this temperature 100% martensitic
- \( A_s \) when heating the temperature at which austenite nucleation begins
- \( M_s \) when cooling the temperature at which martensite nucleation begins

To produce a device using the shape memory effect, the device is ‘shaped’ in the austenitic state. Then, while keeping the device held in the desired shape, heating to high temperatures will ensure that the material will have its minimal energy for this macroscopic form. This process is known as ‘training the material’. In the low temperature martensitic state the device can be deformed/manipulated, and then reheated above the transition temperature to return to the trained shape [41].
2.1.4 Stress Induced Martensitic Phases

The martensitic/austenitic phase transition can not only be induced by changing the material’s temperature, but also by application of a suitable shear stress while in the high temperature (austenitic) state.

The application of load also changes the martensitic/austenitic phase transition temperatures \(M_s, M_f, A_s, A_f\) [42]. As the applied load is increased, the transition temperatures increase proportional to the applied load (Figure 2.6). This means that the higher the temperature, the larger the load needed to induce the transition.

![Figure 2.6: Diagram of the temperature/load response of the phase transition](image)

The linear relationship of the ‘load/transition temperature’ is characterised by the ‘Clausius-Clapeyron’ [42] equation:

\[
\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad \text{or} \quad \frac{d\sigma}{dM_s} = \frac{\Delta H}{T \Delta \varepsilon_0}
\]  

(2.1)

Where

| \(H\) = transformation latent heat | \(\sigma\) = stress |
| \(\varepsilon_0\) = transformation strain | \(M_s\) shifted transformation temperature |

The linearity of this relationship is in effect until the temperature \(M_d\), above which the load required to cause a transition is higher than the yield stress of the material [42].

An example of this phenomenon is ‘Super-elasticity’ [39]. This occurs at a temperature between \(M_d\) and \(A_f\). A stress is applied and an unstable martensite is formed, meaning that as soon as the load is removed the martensitic state disappears, or returns it to its original shape (Figure 2.17).
This is very similar to the shape memory alloy effect without the temperature having to be changed.

![Graphical representation of the super-elasticity.](image)

*Figure 2.7: Graphical representation of the super-elasticity.*

See Figure 2.4b for a schematic representation of super-elasticity stress/strain graph.

### 2.1.5 Magnetic Shape Memory alloys

Recently there has been a great increase in research relating to the Heusler shape memory alloys; over half of presentations at SMART2000 (‘SMART’ memory conference in 2000) were concerned with the ferromagnetic shape memory alloy (FSMA) Ni$_2$MnGa [7]. With Ni$_2$MnGa being considered as the archetypal FSMA, and the increasing interest in SMA’s as a whole (see table below), the interest and research into Ni$_2$MnGa based shape memory alloys is increasing.

<table>
<thead>
<tr>
<th>Decade</th>
<th>Number of SMA related Papers published</th>
</tr>
</thead>
<tbody>
<tr>
<td>1980-1989</td>
<td>841</td>
</tr>
<tr>
<td>1990-1999</td>
<td>3244</td>
</tr>
<tr>
<td>2000-2009</td>
<td>1152</td>
</tr>
<tr>
<td>2010-2019</td>
<td>+30,000 predicted (5531 to Sept. 2013)</td>
</tr>
</tbody>
</table>

Table 2.1: Number of papers published on SMA by decade (information from “A review of shape memory alloy research, applications and opportunities (2013)” [2])

Unlike the stress and temperature shape memory effect, a magnetic shape memory alloy does not require a martensitic/austenitic phase change but it can be driven by a re-orientation of the martensitic variants under the application of a magnetic field [43].
The twinned martensitic variants (e.g. left and right variant) have preferred magnetic orientation, each variant consists of a single magnetic domain, leading to the martensite phase being described as layered alternating mechanical and magnetic domains (Figure 2.8). If an external magnetic field is applied to the twinned martensite and the energy required to change the direction of the magnetic moment of the variant is greater than is needed to re-orientated the entire variant, the variant will re-orientate. The maximum possible elastic strain that can be induced by re-orientation of martensite variants is \((1 – c/a)\) [44], [45].

The increased percentage of one martensitic variant results in a macroscopic shape change. Some FSMA’s show up to 10 % strain, and since this process is not dependent on the diffusion of heat through the material it is very rapid. As a result these magnetic shape memory alloys are finding applications as actuators and sensors [42].

![Figure 2.8: Schematic representation of an array of unit cells, with each unit cell having single magnetic domain for (a) an FSMA twinned martensitic variants showing the easy magnetisation direction with no external field and (b) the re-orientation under an external magnetic field H.](image)

The application of a magnetic field to a FSMA has been shown in increase the martensitic phase transition temperature in Ni\(_2\)MnGa (up to 2T before TM stabilises and shows very little variation with increased field [46]). The martensitic phase transition temperature \((T_M)\) in Ni\(_{2.19}\)Mn\(_{0.8}\)Ga has been
shown to increase linearly with external field from 334 K @ H=0 kOe to 335.5 K @ H=10 kOe[47]. If the increase in temperature is sufficient this can result in the thermo-elastic shape memory phase transition being caused by the application of a magnetic field [7], [48].

$\text{Ni}_2\text{MnGa}$ based alloys are of particular interest as a FSMA because of the relative high c/a ratio, which means that the material can achieve up to 10% strain[49] in single crystals through application of a magnetic field.

### 2.1.6 Band Jahn-teller effect (distortion)

In 1937 a theorem was put forward by H.A.Jahn and E.Teller to explain why some transition metal molecules did not exhibit the predicted molecular configuration [50]. The distortions observed (from predicted to observed configuration) became known as the Jahn-Teller distortion or effect. The Jahn-Teller theory concerning this process states that:

“For any non-linear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy and lower the energy.”

The Band Jahn-Teller effect is a similar process but in transition metal crystal structure rather than molecules, where the degenerate electron levels are sub-levels of the electronic band structure.

The process of distortion (phase transition) to remove degeneracy (lowering the energy of the system) in a crystal structure was first observed in A15 compounds, and at present the Band Jahn-Teller distortion (effect) is considered a driving force in the martensitic shape memory phase transitions [51].

Direct measurement of the band Jahn-teller mechanism have been made in $\text{Ni}_2\text{MnGa}$ [51] [49], showing that the martensitic phase transition results in the breaking of the electronic degeneracy near the Fermi surface. The fact the
Ni$_2$MnGa is ferromagnetic at the martensitic phase transition meant that polarised neutron diffraction could be used to assess the spin-distribution above and below the transition, and determine the changes in configuration. The measured distribution changes were compared with band calculations above and below $T_M$ assuming the Jahn-Teller effect [51].

2.1.7 Two Way Shape Memory Alloys (TWSMA)
The phenomenon used by ‘two-way’ shape memory alloys is very similar to ‘one-way’ shape memory alloys, but rather than a material being deformed in one phase and then undergoing a phase transition to return to the original configuration (Figure 2.9a), devices made using TWSMA’s have two distinctly different bulk shapes in each phase (Figure 2.9b) [34].

Figure 2.9: Diagram showing (a) one-way and (b) two-way shape memory responses.

The two-way shape memory effect is achieved by thermo-mechanically training [52] the material in the low temperature phase and causing it to undergo the transition by heating or exposing to a magnetic field [53]. Most SMA’s can be trained to function as TWSMA’s, but the long term functionality of the TWSMA varies widely between materials, with the limit of use characterised by a trained TWSMA forgetting the trained low temperature form.

2.1.8 High Temperature Martensitic Transitions
The problem with high temperature shape memory alloys is that the martensitic/austenitic phase transition is displacive but at higher temperatures the higher mobility of atoms results in diffusion processes occurring (e.g. annealing [29], order/disorder transitions [30]). That said there are a number
of high temperature shape memory alloys (Zr-Cu-NiCo $T_m=520K$ [54], CuAlNiMn $T_m=455K$ [55], Ta-Ru $T_m=1400K$ [56]) with a recoverable strain of between 2% and 4%. These materials have similar limitations on usage as lower temperature SMAs due to less favourable mechanical properties.

Two recent candidates that fulfil the SME and practicality criteria for a high temperature SMA, are: Ti-Ni-Pt and Ti-Ni-Pd [57]. Both materials have a martensite phase transition temperature at more than 1000 K [58], [59] and do not suffer from the aging effects seen in other SMA’s [18].

### 2.2 Order/Disorder Phase Transitions

If a solid undergoes a phase transition, through heating of the material, the material passes from the low energy (cool) system to the high energy (hot) phase. In this higher energy state the atomic bonding between nearest (and next-nearest) neighbours is weaker.

In the case of order-disorder phase transitions the change from low to higher energy state (low temperature phase to high temperature phase) is characterised by the substitution or swapping of atoms between different locations in the crystal structure. This substitution can sometimes be accompanied by a small atomic displacement to accommodate the disordering.

If the problem is considered thermodynamically, and the system characterised by free energy (Equation 2.2), in a low temperature state the system is highly ordered therefore the free energy is dominated by the internal energy of the system (i.e. bond strength at a maximum). At high temperatures (i.e. disordered) the free energy is dominated by the entropy of the system and the bond strength is reduced.

$$F = E + TS$$  \hspace{1cm} (2.2)

Where: $F$=Free energy, $E$=Internal energy, $T$ = temperature, and $S$ = entropy
For a system such as a crystal structure the free energy is characterised by the Gibbs Free energy [60] which during an order/disorder phase transition remains continuous [54]. However thermodynamic properties (e.g. CTE, $C_P$ or $S$) will show a discontinuity (peak or step change) at the phase transition temperature. The order of the phase transition depends on the order of the Gibbs potential derivative to obtain the discontinuity [60].

A number of approaches have been developed for the modelling of such phenomenon from Landaus Phenomenological [61] approach to statistical mechanics approaches (e.g. Isling model [60], Monte-Carlo simulations, [62]).

A widely used method is the Bragg-William-Gorski [63] (BWG) approximation, originally known as the Bragg-William approximation (BW [64]) developed for binary alloys but extended by Gorski for applications with ternary alloys [65].

The BWG approach assumes that the probability of an atom occupying a location is the same. For the ternary, full Heusler alloys (in the form $A_2BC$), there are three atomic species $A$, $B$, and $C$, that can occupy lattice locations $\alpha_1$, $\alpha_2$, $\beta$ and $\gamma$ (Figure 2.10 below).

\textbf{Figure 2.10: Cubic Heusler Alloys structure and sub-lattice identification.}
The number of each atom in the system is defined as \([X]\) (\(X = A, B, \) and \(C\)), the number of site locations are \([I]\) (\(I = \alpha_1, \alpha_2, \beta, \) and \(\gamma\)) and the number of atom \(X\) on sub-lattice \(I\) defined as \([X_i]\) (\(X = A, B, \) and \(C\), \(I = \alpha_1, \alpha_2, \beta, \) and \(\gamma\)). The concentration of each atomic species is defined as \(x_X\).

\[
[a]_{\alpha_1} + [a]_{\alpha_2} + [\beta] + [\gamma] = N \tag{2.3}
\]

\[
[A] + [B] + [C] = N \tag{2.4}
\]

\[
x_A + x_B + x_C = 1 \tag{2.5}
\]

Where \(N = \) total number of atoms

Therefore the probability of finding atom \(X\) occupying site \(i\) is:

\[
x_i = \frac{[X_i]}{[I]} \tag{2.6}
\]

In the case of a full Heusler alloy \((A_2BC)\) the \(\alpha_1\) and \(\alpha_2\) sub-lattices can be considered as one sub-lattice, because in the ordered state atoms \(B\) and \(C\) will populate sub-lattices \(\beta\) and \(\gamma\) and the \(A\) atoms occupy the \(\alpha_1\) and \(\alpha_2\) lattices.

\[
[A_{\alpha_1}] = [A_{\alpha_1}] + [A_{\alpha_2}] \tag{2.7}
\]

The BWG approximation then selects four independent probabilities \((A_{\alpha_1}, B_{\beta}, B_{\gamma}, \) and \(A_{\alpha_2})\), from which four order parameters that describe the long range order of the system are assigned.

\[
S_1 = 2(A_{\alpha_1} - x_A), \quad S_2 = \frac{4}{d}(B_{\beta} - x_B) \tag{2.8}
\]

\[
S_2 = \frac{4}{d}(C_{\gamma} - x_C), \quad S_4 = 2(x_A - A_{\beta}) \quad a,b,c,d
\]

The BWG then uses the nearest neighbour (nn) and next-nearest neighbour (nnn) pair-wise interactions between atoms in the system and the number of pair-wise interactions of each type (i.e. \([A-A]_{nn}, [A-A]_{nnn}, [A-B]_{nn}, [A-B]_{nnn}, \) etc) to determine the potential energy for the nn and nnn interactions for the entire system \([65],[66],[67]\) Using this the free energy of the system can be calculated:\([68]\)

\[
F = E1 + E2 + \Phi \tag{2.9}
\]
Where $F =$ Total free energy of the system due to inter-atomic bonding, $E_1 =$ potential energy due to nn interactions, $E_2 =$ potential energy due to nnn interactions, and $\Phi =$ the configurationally entropy of the system.

The pair-wise interactions ($V_{AA}$, $V_{BB}$, $V_{CC}$, $V_{AB}$, $V_{AC}$, and $V_{BC}$) are replaced by the partial-order energy terms. These represent the change in energy of this system due to the exchange of atoms (varying the ordering of the system). These partial-ordering energies are defined as:

$$
W_{AV}(R) = V_{AA}(R) + V_{BB}(R) - 2V_{AB}(R) \quad (2.10)
$$
$$
W_{AC}(R) = V_{AA}(R) + V_{CC}(R) - 2V_{AC}(R) \quad a,b,c
$$
$$
W_{BC}(R) = V_{BB}(R) + V_{CC}(R) - 2V_{BC}(R)
$$

Where $V_{XY}(R)$ is the potential energy between atoms X and Y at distance R.

In the case of the Heusler alloys two order-disorder phase transitions are of interest, the $L2_1$ to B2, and B2-A2 transitions. Figure 4.2 shows the ordering present in each state. The phase transition temperatures are defined at $T_{C2}$ and $T_{C1}$ respectively.

Work performed by Y. Murakami in 1971 produced simplified equations for both $T_{C1}$ and $T_{C2}$ for ternary Heusler type alloys, and this has been used extensively since to investigate the order-disorder phase transitions in alloys such as Ni$_2$MnGa, Ni$_2$MnIn, and Co$_2$MnGa [69].

The transition temperature equations are:

$$
T_{C_{L21-B2}} = \frac{24}{k} W^{BC}(R_2)x_c(0.5 - x_c) \quad (2.11)
$$

$$
T_{C_{B2-A2}} = \frac{8}{k} \left( \left( x_a x_a W^{AB}(R_1) + x_a x_c W^{AC}(R_1) + x_b x_c W^{BC}(R_1) \right)^2 \right) \left( \right.
+ \left. \left( x_a x_b W^{AB}(R_1) + x_a x_c W^{AC}(R_1) + x_b x_c W^{BC}(R_1) \right)^2 \right)^{0.5} \quad (2.12)
$$

Where

$W_{XY}(R_2)$ is the partial order energy for the next nearest neighbour pairs.
$W_{XY}(R_1)$ is the partial order energy for nearest neighbour pairs

The determination of partial ordering energy (and pair wise potentials) can either be measured experimentally or determined through mathematical approximations such as Hartree-Fock [69] or Monte Carlo simulations [70].

The above procedure is used to determine the phase transition from calculated or measured interaction energy ($V_{XY}$) between the nearest and next nearest neighbours. However, BWG can be used in the other direction, to determine interaction or interchange energy from measured phase transition temperature (using $C_P$ [66] and electrical resistivity [72] measurement of the transition temperature), the derived interaction/interchange energy can then be used in development of models describing the system [67].
2.3 **Specific Heat Capacity**

A key part of the examination of shape memory alloys is the determination of phase transition temperatures. A measurement parameter often used is specific heat capacity ($C_P$), and this was of particular interest for this thesis. Hence some consideration is given to the background of the parameter and its measurement.

Specific heat capacity is defined as the amount of energy needed to raise a unit amount of a substance by one Kelvin. For example one kilogram of water (specific heat capacity of 418 J/kg/K at room temperature) needs 41,800 J for a temperature change of 100 K.

$$dQ = mC \, dT$$  \hspace{1cm} (2.13)

Where $\delta Q$ is the energy input into the system, and $\delta T$ is the change in temperature, $m$ is mass and $C$ is specific heat capacity.

The specific heat of a system is dependent on the nature of the system and the internal energy and free energy of the system; for example, the specific heat of an insulator is dependent solely on the internal energy of the system due to lattice vibrations (phonons) and the frequencies and modes of those vibrations.

In conductors the internal energy of the system has contributions from lattice vibrations in addition to electronic and magnetic components. Therefore the degrees of freedom in a system have a significant effect on the specific heat of that system.

An example of differing degrees of freedom can be seen with a mono-atomic gas which has only three modes of vibration (along x, y, z axis) whereas the degrees of freedom for a diatomic gas is five (x, y, z translations and two rotational) resulting in diatomic gases having a much higher specific heat capacity than mono-atomic gasses ($12.5 \text{ J.mol}^{-1}.\text{K}^{-1}$ (He) and $20.18 \text{ J.mol}^{-1}.\text{K}^{-1}$ ($\text{H}_2$)).
Classically the internal energy is defined as [73]:

\[ U = \frac{1}{2} \eta RT \]  \hspace{1cm} (2.14)

Where \( \eta \) is the number of degrees of freedom in a system, \( R \) is gas constant (8.314\,J\cdot\text{mol}^{-1}\cdot\text{K}^{-1}).

From this a simple approximation for specific heat can be determined:

\[ C_v = \frac{dU}{dT} = \frac{1}{2} \eta R \]  \hspace{1cm} (2.15a)

Taking a simple example of a diatomic ideal gas, the internal energy is:

\[ U_{\text{diatomic}} = \frac{5}{2} RT \]  \hspace{1cm} (2.16b)

with a specific heat capacity of:

\[ C_{v,\text{diatomic}} = \frac{5}{2} R \]  \hspace{1cm} (2.17c)

The same overall process occurs with solids but it is much more complex with a high degree of temperature dependence. For most solids, the temperature dependence of the specific heat capacity can be approximated with an \( n \)th order polynomial. The constant of each power is dependent on the material itself (Figure 2.11, shows specific heat for 4 materials).

![Figure 2.11: Graph of specific heat values for solids [74]](image-url)
Statistical mechanics
In thermodynamics it is usual to define two specific heat capacities, one at constant volume and the other at constant pressure. While these are generally used for gases their properties still hold true for solids.

Substituting the first law of thermodynamics \( \Delta Q = \Delta U + P \Delta V \) \[75\] into the definition of specific heat from equation 2.13:

\[
C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U + P \Delta V}{\Delta T}
\] (2.18)

where \( U \) is the internal energy, \( P \) is the pressure and \( \Delta V \) is a change in volume.

We can see that specific heat at constant volume (\( \Delta V=0 \)) can be defined as:

\[
C_V = \left( \frac{\Delta U + 0}{\Delta T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V
\] (2.19)

where as the definition of specific heat in a system at constant pressure (\( \Delta V \neq 0 \)) is:

\[
C_P = \left( \frac{\partial H}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P
\] (2.20)

From equation 2.19, it can be seen that \( C_V \) is dependent only on the changing internal energy of the system. For this reason the modelling of specific heat capacity is normally done in terms of \( C_V \). However, experimentally, \( C_P \) (equation 2.20) is measured since for solids and liquids maintaining a constant volume is very difficult. For example, how do you prevent a solid sample expanding/contracting when heated?

The conversion between \( C_P \) and \( C_V \) is defined \[76\] as:

\[
C_p = C_v + \left( P + \left( \frac{\partial E}{\partial V} \right)_T \right) dV
\] (2.21)

The dependence of specific heat on the internal energy of the system means that any changes to in the internal energy of the system (in either lattice or
electronic ordering) affects the specific heat of the system. Making it an ideal method for determining phase transitions.

2.3.1 Specific Heat Modelling

The specific heat capacity of a solid requires the consideration of modes of internal energy. For modelling purposes a conductor can be defined as a crystal lattice representing the nuclei and bound electrons, within an electron cloud (representing the valance/conduction electrons). Therefore the internal energy of a conductor is dependent on the lattice energy (phonons/lattice vibrations) and electronic structure. The electrons in an insulator are tightly bound to the atoms, meaning they are localised [77], and therefore internal energy is only dependent on the lattice energy. Therefore the specific heat of a material can be considered as a sum of the electronic and lattice specific heats.

In addition to electronic and lattice energies the internal energy of material are dependent on the ordering of the magnetic moments. The magnetic specific heat capacity is negligible except at low temperatures, for example consider the alloy Ce$_{0.84}$Gd$_{0.16}$Ru$_2$: [78], (T$_M$ –magnetic ordering temperature $= 6.3$K) where magnetic specific heat contributions reduce rapidly with increasing temperature:

- @ 10K $C_{\text{mag}} \approx 50\%$ of $C_{\text{total}}$
- @ 15K $C_{\text{mag}} \approx 18.5\%$ of $C_{\text{total}}$
- @ 18K $C_{\text{mag}} \approx 9.4\%$ of $C_{\text{total}}$
- @ 20K $C_{\text{mag}} \approx 2.5\%$ of $C_{\text{total}}$

Therefore the specific heat capacity of materials in general is defined as:

$$C_v = C_{\text{lattice}} + C_{\text{electrons}} + C_{\text{magnetic}}$$  \hspace{1cm} (2.22)

It should be noted that most modelling of specific heat is performed for $C_V$, while most measurements are produce values for $C_P$. Therefore for comparison with the modelled data, the measured data must be converted for analysis.
A number of models for lattice, electronic and magnetic specific heat capacity have been developed. The most widely accepted and known of these are the lattice specific heat models of: Dulong-Petit [79], Debye [80], and Einstein [82].

Each of these models calculate specific heat from modelled internal energy, with the Dulong-Petit model basing internal energy on ‘Maxwell Equipartition Law’, and from experimentation it was demonstrated that most solid insulators have a specific heat between 2.8R and 3.4R (where R is the gas constant)[79]. The other models, Einstein and Debye, determine internal energy by considering the material as a perfect crystal lattice of oscillating atoms that oscillate at prescribed frequencies. For the Einstein model, all atoms oscillate at the same frequency (therefore the same energy); for the Debye model the atoms/oscillators are coupled, and oscillate using a linear phonon density of states.

A phonon density of states (DOS) [81] is very similar to photon or electronic density of states in that it describes the occupancy of available/allowed energies. In the simple example of a single electron, there are prescribed energies/wavelengths that the electron can occupy, if the number of electrons is increased then the number of available energy levels increases, and in complex systems such as a solid there are even more available energy states. This would be described as a ‘high DOS’.

Phonons differ from electrons in terms of DOS in that phonons are Bosons and the exclusion principle does not apply, so each energy state can be occupied by any number of phonons. Phonons also differ from photons and electrons in that the maximum energy of the phonons is limited by the shortest wavelength (highest frequency) of oscillation, which cannot be shorter than the distance between the atoms; this limit of frequency (and energy) is known as $\omega_D$. 
“Band structure” is similar to DOS in that it describes available energies for a electrons, but the energy levels can be either discrete or split into near-continues ‘bands’ of available energy, and ranges of energy that cannot be occupied, called ‘band gaps’. The width of the bands and band gaps is dependant upon the amount of overlap between orbitals. Figure 2.12 below shows a schematic representations of the band structure for three types of material, where $E_F$ is the Fermi energy, defined as the maximum electron energy occupied at absolute zero, with occupancies of the lower energies dictated by Pauli exclusion principle [81].

![Diagram of band structure](image)

*Figure 2.12: Schematic representation of the Band structure for (a) insulators, (b) semi-conductors and (c) metals. Where $E_F = $ Fermi level and $E_g = $ energy band gap.*

It should be noted that for the electronic band structure, the electronic DOS for each band differs between material types; for metals (conductors) the DOS begins at the bottom of the valance band (lower energies assumed to be filled) and in semiconductors the electronic DOS begins at the bottom of the conduction band [81].

DOS and band structure can be useful tools in physics as if the DOS is known it is possible to model the internal energy of a system (e.g. Einstein and Debye $C_P$ models). Figure 2.13 below shows the DOS for the Einstein and Debye models.
Recent developments in computing and modelling techniques allow for a more specific modelling of both the phonon DOS or Band structure calculations for a material and by extension the internal energy and specific heat of a material [24].

This is done either through *ab-initio* calculations or analytical solutions, the first of these requires a summation of each atom’s location and interactions with every other atom in the system, the second requires solving the Hamiltonian for the system being considered. From either of these approaches internal energy can be determined and DOS derived.

These approaches are time consuming and complex to implement. A more rationalised modelling approach is the use of mean field approximations such as Density Functional Theory (DFT) which allows for the modelling of large numbers of atoms in a system by the use of probabilities of occupancies and interactions.

DFT and other numerical approximations (e.g. Monte-Carlo simulations [25], cluster variation modelling, CVM [60]), have been demonstrated to produce results very similar to the analytical solutions and measured data. See Section 4.2 for a brief description of modelling techniques.
The use of numerical modelling of the atomic system also allows for the modelling of the electronic structure of the material and the effects of electronic and magnetic internal energy. In addition computational physics allows for the modelling of phase transition, at which point the traditional models (Einstein and Debye) fail as more complex phonon and phonon-electron interactions can occur [82].

2.3.2 Measurement of Specific Heat Capacity

The measurement of specific heat capacity can be used to not only determine the specific heat of a material but also to determine the changes in internal energy of a system. The determination of these phase transition peaks is a useful aspect of specific heat measurement.

The advantage of specific heat capacity over other methods for identification of phase transition peaks and material characterisation is that unlike, resistivity for example, specific heat is a measure of the internal energy changes of a material, and for certain types of phase transition can be used to directly measured the latent heat of that transition (1\textsuperscript{st} order transitions).

Similarly since specific heat is dependent on the lattice, electronic and magnetic properties of the material, it is sensitive to phase in all three areas.
**Phase transitions**

With specific heat being dependant on the internal and free energy of a system, this means that it can be used to characterise or identify, lattice, magnetic and electronic phase transitions.

At the temperature at which a phase transition occurs a peak in the specific heat profile is observable. The nature of the phase transition (either first or second order phase transition) determines the shape of the peak.

First order phase transitions (continuous in the free energy derivative [60]) tend to be sharp well defined peaks (lambda shaped peak). Second order phase transitions (discontinuous in the free energy derivatives [60]), are much broader and less well defined. The area under the peak in first order phase transitions is the latent heat of the transition (Figure 2.14).

![Graph of Cp with a phase transition](image)

**Figure 2.14: Graph of Cp with a phase transition**

**Dislocations**

The sensitivity of specific heat capacity to the lattice structure and order of the lattice, means that it is also sensitive to defects in the lattice structure even in polycrystalline materials [26].

Essentially a defect is anything that is a flaw in the regular crystalline nature of a material. Dislocations are extended defects, while missing atoms are point defects.
Dislocations in the crystalline structure affect the phonon wave length in the material and subsequently the DOS and internal energy (therefore specific heat). The more abundant the discontinuities are the larger the effect.

This means that the presence of dislocations in a structure will have a significant effect on the heat capacity. As an example, if a cold worked copper-aluminium alloy wire was annealed (reducing the number of discontinuities in the crystal structure), the specific heat measured would vary by 10-20% between annealed and un-annealed (depending on annealing process) [26].

This means that proper annealing of a material before testing, can greatly improve the quality of the results and analysis that follows.

2.3.3 Calorimeters
There are a number of methods available for the measurement of specific heat capacity. In this section several of these methods are described, followed by a summary of the relative merits of each.

Adiabatic calorimeter (Nernst-type pulse calorimeter)
The adiabatic (Nernst-type) [27] pulse calorimeter involves the thermal isolation of the sample and then a set amount of energy is input to the sample. From the responding temperature rise the specific heat is determined, using the equation below:

$$\frac{dQ}{dt} = mC_p \frac{dT}{dt} + W_c \frac{dT}{dt}$$

(2.23)

where Q is input energy, m is mass of the sample, C_p is the specific heat of the sample and W_c is the heat capacity of the calorimeter and heater. The system is assumed to have negligible heat loss.

However, thermal isolation of the sample is very difficult to achieve resulting in heat loss from the sample in a variety of ways: conduction, convection and radiation. Therefore in the design of the apparatus a number of methods are
employed to reduce these losses through the use of radiation shields, vacuum chambers, reduced contact with the sample, etc. [27].

This method can be adapted to work for almost any material, phase and temperature range. For example the ‘Spherical Adiabatic Calorimeter’ [28] has a heater inside a fluid which is contained inside a spherical container. The engineering issue involved in compensation for heat loss are complex and vary depending on temperature and range.

The pulsed adiabatic calorimeter is very accurate (better than 5% accuracy at low temperatures [27]) but it is very slow, since the whole system is required to stabilise at each measurement temperature before the specific heat measurement can be made.

**Continuous Specific Meat Measurement Method**

The ‘Continuous’ method places an electrically conducting sample in a high vacuum and a large current is passed through it continuously. This process is similar to the adiabatic calorimeter in that the specific heat capacity is determined from the change in temperature resulting from the supplied energy (Figure 2.15). However, this technique supplies the input energy continuously instead of in discrete pulses.
Figure 2.15: Schematic representation of ‘continuous’ specific heat measurement method.

As the sample heats up (due to resistance heating), the resistance of the sample changes. The change in resistance versus time is a result of the temperature dependence of resistivity \[83\]. This temperature dependence is used in this method for the determination of the specific heat capacity (equation 2.24).

The specific heat capacity is determined \[84\] using the following equations:

\[
C_p = \frac{EI \left( \frac{dp}{dT} \right)}{m \left( \frac{dp}{dt} \right)} \quad (2.24)
\]

\[
\rho = \frac{AE}{Ll} \quad (2.25)
\]
where \( \rho \) is the resistivity of the sample (equation 2.25), \( E \) is sample potential difference, \( I \) is the current through the sample, \( m \) is the mass of the sample, \( A = \) sample cross sectional area, and \( L = \) length of sample.

This system has the advantage of being rapid. However, it is slightly less accurate than other approaches. It is only suitable for electrically conducting materials. This method has the advantage of needing slightly less thermal isolation (when compared to the adiabatic calorimeter method) due to the sample heating taking such a short amount of time.

**Differential Scanning Calorimeter (DSC)**

‘Differential Scanning Calorimeters’ are widely used in industry for specific heat measurements between 2 to 2000 Kelvin and comes in two main types: ‘Constant Power’ and ‘Constant Heat flux’.

While the engineering processes for these two techniques are very different the overall principle of the measurements are the same. To explain how the method produces specific heat data the constant heating technique will be used as an example.

The sample under investigation is placed within a capsule (or pan) and heated at a prescribed rate. At the same time a second capsule (empty but identical to the sample capsule) is also heated within the same chamber. It is assumed that as they are identical capsules the heat flux into both is the same (see Figure 2.16). The difference in temperature between the two capsules is recorded. This difference in the pan temperatures is only dependent on the heat capacity of the sample [85] and heating rate of the furnace.
To determine the specific heat of a sample with this system it is necessary to perform an identical run with a ‘reference sample’ which can be any material with a well known and well defined specific heat, and a third run with no sample present at all for system baseline.

Subtraction of the baseline from the reference and sample data leaves signals only dependent on the heat capacities of the two samples. The heat capacity of the sample under investigation is determined by comparing the data for the sample with the reference sample data and its heat capacity, using the equation shown below (Equation 2.26)

\[
\frac{1}{m_{\text{sample}}} \cdot c_{p,\text{sample}} \cdot (D_{\text{sample}} - D_{\text{baseline}}) = \frac{1}{m_{\text{reference}}} \cdot c_{p,\text{reference}} \cdot (D_{\text{reference}} - D_{\text{baseline}})
\]

\[
C_{\text{sample}} = \frac{(D_{\text{sample}} - D_{\text{baseline}})}{(D_{\text{reference}} - D_{\text{baseline}})} \cdot \frac{m_{\text{reference}} \cdot c_{\text{reference}}}{m_{\text{sample}}}
\]

One of the advantages of the DSC systems (either constant power or constant heat) is that they allow for a clear identification of phase transitions even without conversion from the raw data format (temperature or power difference) into specific heat capacity. The disadvantage of this method is the small sample size of the sample used, results can be very heating rate dependent and the method does not directly measure the samples specific heat but infers it from the response of the system to a comparison.
event the comparison with the reference sample is poor (due to sample shape, surface finish, etc.) the accuracy of the calculated specific heat would be more uncertain.

‘Flash’ method

This technique is primarily used for the measurement of thermal diffusivity, and by extension thermal conductivity [86]. However, it is possible to use this method for the determination of specific heat capacity [87]. There are a number of commercially available products that use this technique to measure specific heat capacity.

The process of measuring thermal diffusivity using the ‘flash’ method was originally proposed in 1961 by Parker, Jenkins, Butler and Abbot [86] as a general technique for the determination of thermal properties in thin samples. The experimental procedure is to ‘flash’ a sample on one face and measure the temperature against time (Figure 2.17a) of the ‘transmitted’ face (Figure 2.17b). The light source can be any device as long as the pulse duration is very short (typically $1/50$ of the half maximum time, $t_{0.5}$, for the sample).

Figure 2.17: Graphical representation of the ‘Flash’ pulse heating the sample (a) and a schematic representation of a thermocouple used to measure the rear (transmitted) face of a sample for the ‘flash’ method (b).
The temperature of the rear face is measured in the original experimentation using a thermocouple but any temperature sensing device can be used, such as non-contact infra-red detectors which reduces error in the measurement by removing direct heat conduction away from the rear surface. Solution of the 1D heat equation for this system produces a solution from which the following equation for diffusivity is calculated:

\[ \alpha = \frac{\omega \cdot L^2}{\pi^2 \cdot t} \]  

(2.27)

Where \( L \) = this thickness of the sample, \( t \) = the time taken for the rear face temperature to increase a percentage of the maximum change in temperature, \( \omega \) = a constant dependant on the percentage of maximum rear face temperature used.

For the determination of specific heat the both change in rear face temperature and amount of energy supplied to the sample are needed. This can be done by either direct measurement of the light supplied or by putting a reference sample with well known thermal properties into the beam, then looking at how this reference sample responds to the heat pulse and comparing this to the response of the sample being measured. This method assumes that both samples absorb the same amount of energy, from the heat pulse, and that the two samples are of identical size and have identical surfaces (emissivity, finish, etc).

The equation for determining specific heat using the laser flash technique is:

\[ \rho \cdot C_p = \frac{Q}{L \cdot T_{\text{max}}} \]  

(2.28)

where \( Q \) is the absorbed energy per unit area, \( L \) is the thickness of the sample, \( T_{\text{max}} \) is the peak temperature, \( \rho \) is the density of the sample and \( C_p \) is the specific heat capacity.

This system has the advantage that it can be used to measure the thermal properties of thin surface coatings [88], by ‘flashing’ the substrate and
measuring the temperature profile of the rear coated side. A numerical approximation method can be used to match the recorded curve to the modelled response.

The advantage of this system is that it can be used to measure both thermal conductivity and specific heat. However, the accuracy of the specific heat capacity is dependent on the assumption that the amount of heat supplied to the sample is accurately known. This is not always the case if the sample under investigation has a rough surface or a highly temperature dependent emissivity compared to the reference sample used.

**Drop Calorimeters**

The ‘drop calorimeter’ [89] system is a little different compared to the four previously discussed methods of measuring specific heat, since it does not look directly at the sample and its temperature but it indirectly looks at the heat energy within the sample.

A sample is heated to the desired test temperature and allowed to stabilise at this temperature. The sample is then dropped into water which is thermally isolated at a standard temperature.

Due to the high thermal conductivity of the cold water, energy flows from the sample altering the enthalpy of both the water and the sample. This change in enthalpy of the water is then measured.

From this change it is possible to determine the heat in the sample by use of the smoothed enthalpy data or using equation 2.29.

\[
C_p = \frac{d}{dT} \left( H_T - H_{298.15} \right)
\]  

(2.29)

The advantage of this method is that it can be used to measure the specific heat capacity of any solid material. However, it does require a large number of drops to be performed. Also the method is not suitable for materials undergoing phase transitions or chemical reactions.
3ω technique

In general the 3ω technique is used to measure the thermal conductivity of a material [90] or coating [91], but the method can also be used to measure the specific heat capacity of filaments or fine wires [92].

The technique relies upon an analytical solution of a 1D diffusion equation for a sample, with the ends assumed to be at a constant stable temperature, and the sample heated through resistance heating with an alternating current of angular frequency ω, which is applied to the sample as shown in Figure 2.18.

The solution to the 1D heat equation, with the inclusion of the variability of input energy and voltage with temperature (due to resistance dependence on temperature), produces and equation for the measured voltage across the samples which is a summation of a voltages, each voltage dependent on an increased frequency \( V = V_\omega + V_{3\omega} + V_{5\omega} + \ldots \). The equation is shown below:

\[
V_{3\omega} \approx \frac{2I_0^2R \alpha}{\pi^2 \kappa_{ap}S \sqrt{1 + (2.\omega \gamma_{ap})^2}}
\] (2.30)

\[
\kappa_{ap} = (1 + g \gamma) \kappa \quad \gamma_{ap} = \frac{\gamma}{(1 + g \gamma)} \quad g = \frac{16.\varepsilon \sigma T_0^3}{\rho C_p D}
\] (2.31)

With specific capacity determined using the equation below:

\[
C_p = \frac{\pi^2 \gamma_{ap} \kappa_{ap}}{\rho L^2}
\] (2.32)
This method seems to work well in the few papers published which present this technique. However, it is limited to fine wires and filaments, but does produce data on the frequency dependence of the thermal properties measured. Increasing the diameter of the sample would require a re-analysis of the diffusion equation for a 2D system which would be extremely difficult and unlikely to produce the suitable/required voltage fluctuation equation, (in the form of equation 2.30)

The technique can be used up to approximately 700K with a high degree of accuracy [93]. The system does require a significant stabilising period for the sample to reach steady oscillations. This long stabilising period requires that the ambient temperature of the sample and sample chamber be very stable.

This limit on sample shape prevents any material that cannot be extruded or machined to a high tolerance from being measure using this technique. However, there is a lower tolerance on sample manufacturing when only using the technique to measure thermal conductivity.

**Photo-acoustic method**

The photo-acoustic method determines the thermal properties of a material by periodically heating the sample using a monochromatic laser flashing on the surface of the sample. The sample is housed in an acoustically sealed chamber with a transfer gas. The sudden input of heat energy into the sample causes it to expand, the expansion of the sample is recorded by a microphone either directly attached to the sample or by transmission of a pressure wave through the chamber transfer gas [94]. Figure 2.19 shows a schematic of the photo-acoustic setup.
The thermal properties of the sample material are determined through the phase lag between the heat source and acoustic response, or the comparison of the sample response to a reference material with known thermal properties [93].

The relationship between the phase lag, amplitude variation and sample geometry to the thermal properties of the sample material have been well characterised and modelled [93]. As such this technique produces excellent thermal property data and, similar to the $3\omega$ technique, shows the frequency dependence of those thermal properties.

Unfortunately this technique is best suited to thin samples or coatings, and the microphone pressure transducer limits the temperature range over which this technique can be applied (nominal maximum temperature of measurement 800K) [93]. This technique is widely used for liquids and solids in medical and mineral industries as well as for the investigation of the thermal properties of coatings and layers.
### Summary of Calorimeter techniques:

<table>
<thead>
<tr>
<th>Calorimeter</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
</table>
| Adiabatic Calorimeter     | 1. Can be very Accurate  
2. Directly measured $C_p$  
3. Wide temperature range of application  
4. Large range of sample sizes.  
5. Use for any phase (solid, liquid, gas) | 1. Slow  
2. Requires complex engineering for thermal isolation of sample |
| Continuous method         | 1. Quick test  
2. Requires less thermal isolation than adiabatic calorimeter | 1. Only works with conductive materials  
2. Material must be in rod or wire form  
3. Low accuracy |
| Flash Diffusivity         | 1. Quick  
2. Measures more than just $C_p$  
3. Can be used on wide range of temperature  
4. Commercially available  
5. Works with all solids materials | 1. Dependent on accurate measure of input energy  
2. Very dependent on surface finish  
3. Low accuracy  
4. Only usable for solids |
| Drop Calorimeter          | 1. Works with all solid materials | 1. Cannot be used with materials undergoing phase transition  
2. Low accuracy  
3. Required numerous repeats  
4. Not direct measure of $C_p$ |
| DSC                       | 1. Quick  
2. Accurate  
3. widely used  
4. good for Phase transitions | 1. Very small sample sizes  
2. Require good comparison between reference and sample  
3. Susceptible to surface effects (reactions) due to volume/surface ratio  
4. Not direct measure of $C_p$ |
| 3w                        | 1. Produces Frequency dependent results  
2. Provides more than $C_p$ data | 1. New, not fully validated  
2. Only usable for filaments and wires  
3. only usable for Conductive materials |
| Photo-acoustic            | 1. Produces Frequency dependent results  
2. Provides more than $C_p$ data  
3. Can be used for thin films | 1. New, not fully validated, unproven technology  
2. Only usable for thin films  
3. Difficult to achieve at above ambient temperatures |

Table 2.2: Comparison of specific heat capacity measurement techniques
High Temperature Specific Heat Capacity Measurement of Ni$_{2+y}$Mn$_{1-x}$Ga
3 High Temperature Specific Heat Measurement System

3.1 Introduction

The measurement of specific heat capacity for solid materials is used extensively in physics and engineering to characterise the thermal properties of materials, and can be used to accurately determine any phase transition temperatures. Measuring specific heat also allows for the measurement of the latent heat of 1st order phase transitions [54].

The currently accepted methods for the measurement of specific heat are: differential scanning calorimetry (Section 2.3.3), drop-calorimetry (Section 2.3.3) and adiabatic calorimetry (Section 2.3.3). Alternative measurement techniques (e.g. flash diffusivity, 3ω) are used for specific tasks where the more traditional techniques are not applicable, but are still at the level of research only. See Table 2.1 for a summary of the advantages and disadvantages of each technique.

Considering the techniques available, adiabatic calorimetry appears to offer the most scope for development as it presents the possibility of the highest degree of accuracy, and unlike the other approaches it directly measures a material's specific heat rather than determining it from other thermal properties or a comparison with a known standard. In addition, it is possible to use adiabatic calorimetry on any size of sample, from milligrams [95] up to kilo-grams [96].

The size of sample is of significance when considering Heusler shape memory alloys (e.g. Ni$_2$MnGa), which can have alloys with a grain size as large as 3 mm [97]. The relatively large grain size means that small test samples (e.g. as used for DSC and flash diffusivity) could only contain a few grains and any alloying imperfection between grains could become dominant factors in measurements. Also, the casting of some alloys can result in materials with a range of compositions [97] in a single cast and taking a small sample may not be representative of the bulk material. Therefore, an
adiabatic calorimeter was selected to be developed for the high temperature specific heat capacity measurement system (HTCP), for the measurement of high temperature phase transitions in Heusler shape memory.

### 3.2 Developing the HTCP System

The measurement of specific heat using an adiabatic calorimeter requires that the sample be heated (or cooled) to the required measurement temperature, then a known amount of heat is put into a sample (known as a heat pulse) and the resultant change in sample temperature recorded. If the sample is perfectly thermally isolated during the measurement (adiabatic) the specific heat capacity can be determined directly using the equation below:

\[
C_p = \frac{1}{m} \frac{dQ}{dT}
\]

(3.1)

Where \(m\) = mass, \(dQ\) = supplied energy, and \(dT\) = change in sample temperature.

The new HTCP system consists of: a furnace to heat the sample to the measurement temperature; a vacuum tube, in which the measurement apparatus is located; and the measurement apparatus (i.e. thermocouples, sample heater, etc). Some of the larger components (e.g. furnace and vacuum tube) were taken from a similar project that was performed in Germany [96], which successfully produced a working HTCP system for large samples (≈ 150 g). The sizes of samples under examination using the German configuration were far larger than could be produced for the Heusler alloys (max. size 20 g) being investigated.

The German system used ‘bespoke’ components that were very fragile and prohibitively expensive, and required miniaturising for use with the much smaller size of samples possible for the Heusler alloys. It was determined that miniaturising these components to match the largest producible Heusler alloy sample would be impossible. Therefore, the decision was made to remove all measurement components/apparatus from the original German system, leaving only the structural components (e.g. supports, furnace,
vacuum system, etc.) from which the new measurement system could be developed.

3.2.1 Sample heater

The measurement of specific heat using adiabatic calorimetry requires a ‘sample heater’ to supply the heat-pulse to the sample ($dQ$ in Equation 3.1).

The sample heater used in the original German system [96] consisted of a precision machined Boron-Nitride core with a double helix channel around the outside, through which a 50 µm platinum heater wire was threaded. This heater element was then inserted into the sample and the sample was hung from wires connected to the heater (Figure 3.1).

![Figure 3.1: German sample heater configuration.](image)

This configuration meant that the sample material must be machinable enough to allow for production of fine holes through which the supporting wires could pass, and a good fit between the heater and sample is important to ensure good heat transfer. In addition, the heater elements perished during each heating cycle (between room temperature and 1300 K) and required replacement. Miniaturising of this sample heater design was impossible and the Heusler alloys could not be machined easily to the required level of precision.
The need for a new heater configuration presented two possible options:

1. Internal heater: inserting the heater into the sample (See Figure 3.2b)
2. External heating: a flat heating element on which the sample would sit during the measurement (see Figure 3.2a)

Figure 3.2: Possible sample heater configurations: (a) external contact heater and (b) internal heater

The advantages/disadvantages of each configuration are shown in Table 3.1 below:

<table>
<thead>
<tr>
<th>Heater configuration</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Heater</td>
<td>• Large surface area of contact with sample.</td>
<td>• Needs small heater element.</td>
</tr>
<tr>
<td>(Figure 3.2a)</td>
<td>• Little heat loss directly to surroundings.</td>
<td>• Requires hole/holes be machined through sample.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Difficult to support samples.</td>
</tr>
<tr>
<td>External Heater</td>
<td>• Easy to produce</td>
<td>• Large surface area not in contact with sample (potential for heat loss).</td>
</tr>
<tr>
<td>(Figure 3.2b)</td>
<td>• Flat interface between samples and heater</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Good support of sample.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Repeatable (heater used for multiple samples)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Comparison of heater configuration types

Modelling of both heater configurations (internal and external) for identical samples showed that the heat loss from the external heater at high
temperature (through radiation) would make an accurate calculation of the sample’s specific heat capacity difficult. (See Appendix A for modelling).

The use of an internal heater requires the use of a bonding agent, not only to secure the sample to the heater but also to provide good thermal contact between the sample and the heater. This was achieved with high temperature ceramic cement. The cement provided sufficient strength between the sample and heater to allow the sample to be suspended from the heater.

The sample heater was mounted using the 4-point probe (Figure 3.3) configuration. This allowed for an accurate measurement of the supplied power to the sample without having to consider the resistance of the connecting wires.

![Sample heater connection diagram](image)

*Figure 3.3: Sample heater connection.*

The heat energy supplied to the sample is assumed to be 100% of the electrical power supplied to the heater element (Power = I V).

The heater element selected for the HTCP system was a commercially available wire wound platinum resistance thermometer (PT100), which met the requirements of the sample heater: compact size; high operating temperature (melting point of Pt >2045 K); and high resistance (100 Ω).
3.2.2 Heat loss from the sample

Adiabatic calorimeters require that the sample be thermally isolated from the surrounding environment. This is not possible in reality, and as a result much of the design/development effort for adiabatic calorimeters is concerned with minimising heat loss from the sample.

Heat-loss was minimised in the HTCP system in the following ways (see Figure 3.4 for apparatus configuration):

- All specific heat measurements were made in a vacuum to prevent heat loss from the sample’s surface by convection.
- Direct contact with the sample was minimized (reducing solid/solid conduction).
- The sample was placed in the centre of the ‘hot zone’ of the furnace, meaning that the materials closest to the sample were at the same temperature (reducing thermal gradients in the chamber and therefore thermal conduction).
- The sample inserts (that supports the measurement apparatus) were made of thin-narrow walled components to reduce longitudinal heat loss out of the hot zone.
- Baffles were placed across the furnace tube above and below the sample, to reduce radiation heat loss longitudinally between the hot and cold areas of the furnace tube.
- The sample is housed in a ‘sample can’ that reduces radiation heat loss radially, with additional radiation shielding inside the can.

3.2.3 Sample can

The sample, heater and temperature sensors used in the HTCP system were housed in a ‘sample can’ suspended at the end of the furnace insert (See Figure 3.4a for the sample can location in the vacuum tube and furnace, and Figure 3.4b for the finalised ‘sample can’ configuration.). The sample can and contents can be detached from the furnace insert for the purpose of mounting of the sample.
The outer shell of the sample can is an alumina cylinder, with a wall thickness of 4 mm. The thick alumina outer can was added to the design to reduce the effect of furnace temperature oscillation caused by the furnace PID control system. The 4 mm thickness was selected to provide sufficient damping to ensure that for a ±5K oscillation of furnace temperature, the sample temperature showed negligible oscillation (<0.01K) (See Appendix A).

The floating radiation shields mounted concentrically around the sample minimized heat loss from the sample through radiation.

Since the sample can is detachable from the furnace insert, the can is required to have detachable connections to separate the electrical systems. The advantage of this is that during the heating and cooling cycles the fine wires can age and become brittle, and manipulation post-heating often results in the breaking of wires. If the internal wiring were not detachable close to the sample, the complete 1.5 m length of the wire would need to be replaced after each test.

![Figure 3.4a: HTCP system configuration.](image)
3.2.4 Furnace temperature

Traditionally, adiabatic calorimeters heat or cool the sample and measurement apparatus to the required measurement temperature, allow the system to stabilise at that temperature and then supply the heat pulse.

The configuration of the HTCP system, and location of the sample, meant that the sample was sufficiently thermally isolated from the furnace (Figure 3.4a) such that the time taken for the sample to stabilise after a 10 K change in furnace temperature was in excess of 2 hours.
Under this configuration, the long delay between heat pulse measurements (due to slow stabilising rate) would mean that a specific heat measurement between room temperature and 1300 K (measurements made every 10 K), would take more than 16 days (for both heating and cooling phases). This time does not include the time taken for the pulse measurements.

The long duration of such a test (more than five days at >1000 K) could result in: some phase transitions not being observable; modification of those phase transitions that do take place; and annealing of the material, removing any effects that may be of interest. Also, given the time taken for the system to stabilise at a temperature before a heat pulse can be made, any phase transition at or near the temperature may have already been completed prior to the pulse measurement.

In addition, the long duration of such a test would be unacceptable practically given the low resolution (10 K). Such a low resolution would miss any phase transition that produced a narrow specific heat peak. Reducing the steps between measurements to increase the resolution to permit observation of narrow $C_p$ peaks would further increase the duration of the tests.

To reduce the time taken for the testing and increase resolution it was proposed that instead of allowing the sample to stabilise at a specific temperature before making the measurement, the furnace and sample should be heated linearly and the pulse measurements made continuously (Figure 3.5).
The advantage of the linearly drifting baseline is that not only does it increase resolution (while significantly reducing the duration of the testing), but it also allows for the measurement of dynamic processes. However, the fact that the baseline is constantly drifting does mean that there are additional potential sources of error in the measurement and the system cannot be described as truly adiabatic.

Modelling of the system under both drifting and stable ambient conditions (Appendix A) showed that there is a slight difference between the two measurement conditions (Figure 3.6). This difference can be accounted for during the analysis of the pulse.

Figure 3.6: Modelled dT data for an identical sample and heat pulse with (a) a stable ambient temperature and (b) a linearly drifting baseline (dT/dt = 10 K/hour)
The modelling of the HTCP system with a drifting baseline also showed that
the selection of an appropriate baseline function, to produce a suitable
change in sample temperature data (dT), required additional consideration.
See section 3.4 for a discussion of the baseline function and the change in
sample temperature measurement.

3.2.5 Sample temperature

The measurement of the sample temperature is made with two K-type
thermocouples (see Figure 3.7) which measure the sample surface
temperature and the ambient temperature in the furnace.

Commissioning tests on the HTCP system showed that the use of a reference
junction unit resulted in unacceptable noise on the temperature signal (Figure
3.7). Since the HTCP system was housed in a temperature controlled
laboratory, at 20°C ±1°C, the removal of the reference junction, and the use of
a virtual reference junction at 20°C, had no effect on temperature signal or the
uncertainty of the measurement (uncertainty on reference unit was ±1°C).

Figure 3.7: Effects of ‘Reference junction’ noise on sample thermocouple
signal.

Further commissioning tests showed that the remaining noise on the sample
temperature thermocouple also made interpretation of the dT data difficult. To
produce a meaningful dT data for the sample, an alternative temperature measurement method had to be employed. However, the use of a Platinum Resistance Thermometer (PtRT) as the sample heater element, presents an alternative to the thermocouple.

The sample heater mounting arrangement (4-point probe) could not only be used for the measurement of the power supplied but also for the measurement of the resistance of the thermometer (or sample heater). This meant that no alterations to the testing apparatus configurations were required so that the sample heater (platinum resistance thermometer) could also be used for temperature measurement.

The standard mathematical function for the conversion from resistance to temperature for the platinum resistance thermometer does not take into account variations in the production quality of the thermometer, and the calibration of the thermometer (against a thermocouples in the furnace) cannot be performed without making the element unusable for a sample measurement. Instead, conversion of measured resistance into temperature was performed using the absolute temperature measurements made by the sample thermocouple (K-type), for each pulse measurement separately (Figure 3.8).

The fact that the temperature/resistance response of the platinum resistance thermometer is linear, over short temperature ranges, means that this approach removes the need for calibration of each thermometer element before each test, while producing a stable, low noise and accurate change in sample temperature signal.
3.3 HTCP configuration

The configuration of the HTCP system, once the design and modelling had been performed, and after a number of trials, produced the following system (Figure 3.9).

*Figure 3.9: Schematic of the entire HTCP system.*
This system has been designed to simultaneously measure the power supplied to the sample heater, the temperatures of the sample (using platinum resistance thermometer and thermocouple) and the ambient sample temperature within the furnace (thermocouple).

The temperature and power data are logged against time by the control computer for the duration of each pulse measurement. The data from each pulse is saved in a separate text file with a unique pulse ID number.

3.3.1 Measurement Apparatus;

The measurement apparatus consists of: two voltmeters (a Keithley nano-voltmeter and a Solartron 7055 multi-meter), a multiplexer/power source unit and a computer for the control of the measurement apparatus and data recording.

The Solartron 7055 multi-meter and multiplexer unit work in tandem to measure four properties, while the Keithley nano-voltmeter was dedicated to measure one single property.

The sample temperature is measured directly by a Keithley nano-voltmeter, which is connected to the computer using an IEEE GPIB interface card, along with the Solartron. The multiplexer unit was controlled using an RS 232 series cable (see Figure 3.9).

**Multiplexer Measurements**

The multiplexer unit is responsible for the measurement of two thermocouples and the voltage/current data for the sample heater. The multiplexer is also the power source for the sample heater element. The computer controls which input channel on the multiplexer unit is output to the voltmeter. The multiplexer output is connected to the Solartron voltmeter, which in turn is connected to the computer via the IEEE GPIB interface card (see Figure 3.9).
The power supplied to the heater is determined by measuring the current and voltage across the sample heater. The heater is connected via the four point probe configuration (Figure 3.3) to the multiplexer unit, which allows for accurate measurement of current and potential. The four point probe configuration means that the resistance of the wires do not affect the measurement [98].

The current supplied to the sample heater is determined by measuring the potential difference across a reference resistor (=1 Ohm) in series with the sample heater. The potential across the sample is measured by the second pair of wires in the four point probe configuration.

As has been stated previously, the multiplexer acts as the sample heater DC power source. The sample heater DC power supply has four levels of output, which are controlled by setting four variable resistors (accessible by removal of the multiplexer cover).

**Computer Interface**

The HTCP measurement system is controlled by a specifically designed computer program written in QBASIC. Although not a widely used computer language, QBASIC was chosen for its compatibility with the IEEE cards available (interface sub-routines supplied with cards) and the speed of computer needed to interface with Keithley and Solartron voltmeters.

The computer program has three primary roles: the first is to record the temperature and power readings supplied by the voltmeters; the second is to control the switching of the multiplexer unit; and the third role is to display the data live so that an operator can observe measurements.
Computer control of multiplexer

The computer control of the multiplexer consists of sending a binary signal from the ‘COM’ port of the computer. The binary signal switches the relays in the multiplexer unit, switching the connection between the output of the multiplexer to the various inputs (see Figure 3.9).

The first two pins of the COM port are responsible for control of the measurement channels, with pins four and five controlling the sample heater power supply. Pin three is used for control of the third thermocouple channel, which is not used by the HTCP measurement system.

The multiplexer channel assignments are as follows:

<table>
<thead>
<tr>
<th>COM output, Pin No:</th>
<th>QBASIC output</th>
<th>Thermocouple Channel</th>
<th>Sample heater power</th>
</tr>
</thead>
<tbody>
<tr>
<td>L L L L L</td>
<td>0</td>
<td>Thermocouple 1</td>
<td>1mA</td>
</tr>
<tr>
<td>H L L L L</td>
<td>1</td>
<td>Thermocouple 2</td>
<td>1mA</td>
</tr>
<tr>
<td>L H L L L</td>
<td>2</td>
<td>Current</td>
<td>1mA</td>
</tr>
<tr>
<td>H H L L L</td>
<td>3</td>
<td>PD</td>
<td>1mA</td>
</tr>
<tr>
<td>L L L H L</td>
<td>8</td>
<td>Thermocouple 1</td>
<td>7mA</td>
</tr>
<tr>
<td>H L L H L</td>
<td>9</td>
<td>Thermocouple 2</td>
<td>7mA</td>
</tr>
<tr>
<td>L H L H L</td>
<td>10</td>
<td>Current</td>
<td>7mA</td>
</tr>
<tr>
<td>H H L H L</td>
<td>11</td>
<td>PD</td>
<td>7mA</td>
</tr>
<tr>
<td>L L L L H</td>
<td>16</td>
<td>Thermocouple 1</td>
<td>11mA</td>
</tr>
<tr>
<td>H L L L H</td>
<td>17</td>
<td>Thermocouple 2</td>
<td>11mA</td>
</tr>
<tr>
<td>L H L L H</td>
<td>18</td>
<td>Current</td>
<td>11mA</td>
</tr>
<tr>
<td>H H L L H</td>
<td>19</td>
<td>PD</td>
<td>11mA</td>
</tr>
<tr>
<td>L L L H H</td>
<td>24</td>
<td>Thermocouple 1</td>
<td>15mA</td>
</tr>
<tr>
<td>H L L H H</td>
<td>25</td>
<td>Thermocouple 2</td>
<td>15mA</td>
</tr>
<tr>
<td>L H L H H</td>
<td>26</td>
<td>Current</td>
<td>15mA</td>
</tr>
<tr>
<td>H H L H H</td>
<td>27</td>
<td>PD</td>
<td>15mA</td>
</tr>
</tbody>
</table>

*Table 3.2: Multiplexer control signal*
**Computer control of the system**

In addition to the control of the measurement systems and sample heater power, the computer program controls the ordering of events to ensure that a pulse measurement is performed correctly.

The program initialised the communication sub-routines and card required for the communication with the measurement devices. Once this was completed the program uses a graphical user interface for the user to select the type of measurement to be performed and enter test data.

Once the user selects the required test regime, the program proceeds to perform the measurements. Depending on the regime this consists of either single or multiple pulse measurements; under either condition a pulse measurement follows the same process. The stages of the pulse measurement are shown below with the processes is detailed in Table 3.3 below.

1. **Pre-pulse data**: Temperature and time data. The sample temperature drifting linearly and no heat supplied to the sample heater.
2. **Pulse data**: Temperature, time and electrical power data. Power being supplied to the sample heater.
3. **Post-pulse data**: Temperature and time data. No power being supplied to the sample heater with the sample temperature cooling towards the linearly drifting baseline temperature.
<table>
<thead>
<tr>
<th>Step No.</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The computer program enters the heat pulse sub-routine, and displays a temperature Vs time graph, and a power Vs time graph. A new text file is created with the pulse ID number.</td>
</tr>
<tr>
<td>2</td>
<td>The computer program logs temperature, power and time data, using the multi-plexer unit, for the duration of the pre-pulse period (defined by the user). Computer displays temperature and power data Vs time data graphically for the operator.</td>
</tr>
<tr>
<td>3</td>
<td>The pre-pulse period has elapsed, the computer continues to log temperature, power and time data using the multi-plexer. The multiplexer unit also supplies the power to the heater element. Computer displays temperature and power data Vs time data graphically for the operator.</td>
</tr>
<tr>
<td>4</td>
<td>If the change in sample temperature during the heating phase exceeds 1 K (user defined) or the heating phase has lasted more than 120 seconds (user defined), the power supplied to the heater element is switched off and the post-pulse phase begins. If not the computer continues logging data with the heater on. Computer displays temperature and power data Vs time data graphically for the operator.</td>
</tr>
<tr>
<td>5</td>
<td>The computer program moves into the post-pulse phase, the heater element power is turned off and the computer continues logging temperature, power and time data (through the multi-plexer unit). Computer displays temperature and power data Vs time data graphically for the operator.</td>
</tr>
<tr>
<td>6</td>
<td>Post pulse time has exceeded specified duration (user controlled) and the pulse measurement ends. The text file is closed, and the computer ceases displaying data graphically.</td>
</tr>
<tr>
<td>7</td>
<td>If the program is running a single heat pulse the program will return to the main menu, if a temperature scan is being performed the computer will wait a defined period of time (user controlled) before starting a new heat pulse measurement.</td>
</tr>
</tbody>
</table>

This description assumes that the user has input the required information and has setup the furnace for the desired test condition (i.e. stable temperature or temperature scan).

*Table 3.3: Computer processes for a single heat pulse measurement.*

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If multiple pulse measurements are being performed the computer will measure the sample temperature and, if this is outside the specified temperature range of the test, the program will stop and inform the user of this event.

### 3.3.2 Furnace Temperature Control.

The control of the furnace temperature is performed using a Eurotherm PID controller installed in the furnace control unit. This regulates the power supplied to the furnace heating element so that the temperature of the furnace (as measured by two R-type thermocouples external to the furnace) follows the user set heating/cooling profile. Reference [99] describes the operation of the PID controller.

Typically, the heating profile for the HTCP system consisted of: a linear heating phase ($dT/dt < 20\text{K.s}^{-1}$); a dwell period at the maximum temperature (typically <2 hours to allow the system to stabilise); and finally a cooling phase (same heating rate as the heating phase).

### 3.4 Data Analysis

Once the HTCP system has performed the measurements and the heat pulse data has been recorded, the signals require three stage of analysis:

1. Baseline
2. Supplied heat
3. Change in sample temperature

The following sections detail the analysis performed and requirements for each stage.

#### 3.4.1 Signal Analysis-baseline

The specific heat measurement using the HTCP system uses a heat pulse supplied to the sample with a constantly drifting baseline temperature. To
ensure that the change in sample temperature is measured accurately a suitable baseline needs to be subtracted from the raw temperature data.

The pre-pulse section of the heat pulse measurement was used for the determination of an appropriate baseline so that accurate dT data could be determined.

During the analysis of the commissioning data three separate approaches were trialled for the determination of baselines. These were:

- Linear baseline
- Quadratic baseline
- Measured ambient baseline (shield temperature)

These factors are discussed in more detail below.

**Linear baseline**

It may be expected that a linear baseline extrapolated from the pre-pulse data would be the optimal function, assuming that the furnace is under constant linear drift conditions.

Below are two modelled and one measured examples of a heat pulse, all at approximately 375K. One of the modelled examples is obtained for a stable ambient temperature profile, and the two other examples (one modelled, one measured) were obtained for a constant furnace drift of 10 K per hour. These are shown in Figures 3.10a, 3.11a, and 3.12a.

Subtraction of a linear baseline, as determined by using linear regression of the data in the pre-pulse sections for all three examples, produces plots of the change in sample temperature for the three systems as shown in Figures 3.10b, 3.11b, and 3.12b.
High Temperature Specific Heat Capacity Measurement of Ni$_{2+X}$Mn$_{1-X}$Ga

Figure 3.10: Modelled data for a steel sample at a stable ambient temperature of 376.9 K showing (a) the absolute temperature data and (b) temperature data with linear baseline subtracted.

Figure 3.11: Modelled data for a steel sample for a constant drift ambient temperature starting at 376.9 K and increasing at a rate of 10 K per hour, showing (a) the absolute temperature data and (b) temperature data with linear baseline subtracted.

Figure 3.12: Measured data for a steel sample in a constant drift ambient temperature condition starting at 375.1 K and increasing at a rate of 10 K per hour, showing (a) the absolute temperature data and (b) temperature data with linear baseline subtracted.
As can be seen from the two examples with drifting furnace temperatures, the $dT$ data at the end of the pulse data (post pulse) tends towards a plateau above the baseline temperature. This phenomenon was seen in a number of heat pulse measurements, becoming less apparent at high temperatures (as the radiation heat loss rate increased).

Unfortunately, the linear baseline method does not work well when there is noise in the system, either due to electrical interference or fluctuations in the ambient/sample temperature data (Figure 3.13). Specifically, linear baselines do not work well when the furnace is making the transition to linear heating/cooling. The deviation from linear behaviour may not be observable in the pre-pulse data due to its relatively short duration. However, it can have an effect over the much longer timescale of the full pulse (see Figure 3.13).

Figure 3.13: Example of the effects of non-linear furnace/sample temperature on measured $dT$ data.

Temperature fluctuations due to control issues, resulting from the PID settings in the furnace controller, invalidate the use of a linear baseline function. This issue can result in oscillations in the furnace temperature with a frequency too long for direct observation (longer than a pulse measurement) but which still affect the baseline fitting process.
• **Non-linear baseline**
The use of quadratic or higher order polynomials for baselines was investigated for two reasons. The first being to try and produce a sufficiently accurate baseline for use in non-linear but stable conditions (i.e. at the beginning of a furnace heating cycle), the second was to attempt to remove the temperature step observed at the end of some heat pulse measurements (Figure 3.11b).

The quadratic baseline method determines the baseline of a pulse measurement by a least squares fit regression of a data series consisting of the pre-pulse data and the final few recorded data points for the pulse measurement (see Figure 3.14). The final data points from the measurement pulse are needed in the baseline regression so that the calculated quadratic (n-th order polynomial) baseline conforms to the overall shape of the measurement pulse.

![Figure 3.14: Example of a pulse measurement of a graphite sample at 502K using a quadratic baseline.](image)

Figure 3.14: Example of a pulse measurement of a graphite sample at 502K using a quadratic baseline.
The quadratic approach produced more ‘idealised’ results for the dT data (see Figure 3.15) with the post pulse data tending towards the dT=0, and makes determination of the change in sample temperature due to the heat pulse easier in some cases.

![Figure 3.15: Example of a pulse measurement using linear and quadratic baselines to determine the sample change in temperature data](image)

- **Ambient temperature baseline (shield temperature)**
  
  In theory, the sample should follow the same constant drift rate as the furnace and the radiation shield surrounding the sample, with a slight difference in absolute temperature (modelled example in Figure 3.16). Therefore, subtraction of the shield temperature from the sample temperature should leave only the change in sample temperature resulting from the sample heater input.
The use of the shield temperature data as the baseline should also work when in unstable conditions that cannot be addressed using linear or quadratic baselines.

Unfortunately, the two temperatures (shield and sample) are measured using two different measurement techniques (thermocouple and platinum resistance thermometer) and the incompatibility of the two temperature measurements prevents direct subtraction (due to noise on the thermocouple signal).

However, trials were undertaken to use a variation of the approach that entailed the fitting of a regression line (linear or quadratic) to the shield temperature, and offsetting the regression line so that it coincided with the pre-pulse data for the sample temperature. It was found that this approach was only applicable for long duration furnace fluctuation, and was very poor when used for ‘linearly stable’ conditions.

Figure 3.16: Example of the temperature difference between the sample and shield temperature. “Skin” and “Heater” are the sample temperatures on the inside and outer-surface of the sample, and “Shield” is the furnace temperature.
3.4.2 Signal Analysis-supplied heat:
The heating of the sample (heat pulse) occurs during the heating phase of the data. The energy input during this phase of the pulse is determined from the measured electrical power and time between measurements:

\[ dE = \sum_{i=1}^{N} P_i \times dt_i \]  

(3.2)

where \( P_i \) is the power supplied for the \( i^{th} \) data set, and \( dt_i \) is the duration of that point of the data set.

Since the heater element is also being used as a platinum resistance thermometer there was a small excitation current being supplied during the non-heating phases of a pulse measurement. This current was much smaller than supplied during heating and is considered negligible as a heat input.

3.4.3 Signal Analysis-change in sample temperature
The HTCP system is not a perfectly adiabatic system, meaning that heat loss from the sample begins as soon as there is a temperature differential between the sample and ambient conditions (Figure 3.17).

![Figure 3.17: Post pulse curve fitting of example data.](image)

Therefore, the maximum change in sample temperature recorded during a pulse measurement is not the change in sample temperature due to the
supplied heat to the sample, but a systemic maximum reached by the heater element.

The determination of the change in sample temperature, due to the heat pulse (and the heat capacity of the sample), is the main focus of the analysis of the data produced from the HTCP system, and three techniques have been used, these are:

1. Post-pulse regression.
2. Heating pulse analysis.
3. FEM modelling.

The following sections discuss these approaches:

- **Post-pulse regression**
  As can be seen in Figure 3.17, the post-pulse temperature of a non-adiabatic system such as the HTCP system (minus a suitable baseline), can be interpolated to determine the change in sample temperature due to a heat pulse. To do this, two things must be considered:
    1. A regression curve fit to the post pulse data.
    2. The theoretical dT time, to which the regression line should be interpolated to (for example extrapolation of the post pulse regression line to the beginning of the heat pulse would produce a different dT value compared to that for extrapolation of the line to the end of the pulse).

- **Curve fitting**
  The complicated nature of the platinum resistance thermometer data, with the large spike due to the heater element heating rapidly before slowly transferring the input heat to the heater body and sample, makes the analysis of the post pulse data too difficult for automated analysis (RST in Figure 3.18).
The sample thermocouple data is much simpler but susceptible to the effects of heat loss and noise, especially at high temperatures. This makes it useless for the purpose of ideal dT determination.

![Image](image.png)

*Figure 3.18: dT pulse data for a stainless steel sample with a stable furnace temperature at 292 K.*

The other factor causing the sample thermocouple to be of little use is that one of the mechanisms for heat loss from the sample is conduction through the heater connector wires. Heat loss by this mechanism during the heating phase of the sample will not be taken into account as part of the post pulse analysis of the sample thermocouple, as this heat never interacts with the sample but is recorded as input energy.

Fitting of polynomials directly to the dT data (from the PtRT) produces poor dT results. Figure 3.19 shows the results of fitting 2nd and 4th order polynomials to the post pulse regression data for a graphite sample at 477 K (constant drift = 10K/hr). The specific heat capacities calculated using these polynomials are:

\[
C_p (2^{\text{nd}} \text{ order polynomial}): 1,682 \text{ J.kg}^{-1}.\text{K}^{-1}
\]
\[
C_p (4^{\text{th}} \text{ order polynomial}): 1,586 \text{ J.kg}^{-1}.\text{K}^{-1}
\]

The standard value for graphite at this temperature is 1,183 J.kg^{-1}.K^{-1}.
High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga

Analysis of modelled and real data showed that the post pulse temperature should decay exponentially under both stable and constant furnace drift conditions (Figure 3.20).

**Figure 3.19:** Post pulse regression with 2$^{nd}$ and 4$^{th}$ order polynomial fit to the post pulse regression data.

**Figure 3.20:** Example of a pulse on a logarithmic plot. The data tends to a linear trend line for the post pulse section.
High Temperature Specific Heat Capacity Measurement of \( \text{Ni}_{2+\delta}\text{Mn}_{1-x}\text{Ga} \)

The modelled data for stable furnace pulse measurements suggests the use of linear regression for the \( \ln(dT) \) data, while data produced during constant drift conditions required \( n^{\text{th}} \) order polynomials.

Therefore, two questions that need to be considered when performing the analysis of post pulse data using this technique are:

- What order polynomial is to be fitted to the \( \ln(dT) \) data?
- What data is to be included in the post pulse analysis?

This technique is best used when the largest amount of post pulse data can be included in the regression analysis. However, the determination of the regression range is dictated by the operator and thus open to interpretation. Therefore, it can be susceptible to user errors.

As a guide for the analysis, the start time for the post pulse analysis data is nominally identified by a sudden increase in the noise on the sample temperature data or a sudden change in the rate of change of the sample temperature (Figures 3.21 and 3.22). Both events are indicative of the heat from the heater element having transferred to the sample, and the data from this point on is dominated by the effects of the sample rather than the thermal properties of the heater element and heat transfer between the element and sample.

The choice of the range over which the regression analysis is to be performed is dictated by the maximum number of data points that can be used in the data analysis that still maintain the curve fit at the beginning of the data analysis. The analysis can then be fine-tuned to better match the real data by tuning the range over which the post pulse analysis is performed.
Testing has shown that as the temperature increases the order of the exponent polynomial reduces, until the exponential of a linear function best fits the sample post pulse data. This is likely to be a result of the increased heat transfer between the sample and the shield at elevated temperature (thermal radiation proportional to $T^4$).
The trend of reducing the order of the exponential polynomial as the temperature increases is not only observed in real data but modelled data too. Figure 3.23 below shows the sample temperature change data for a stainless steel sample under constant drift condition.

![Figure 3.23: Example of the post pulse curve differences for an identical sample at three temperatures.](image)

The modelled data in Figure 3.23 is based on the furnace temperature maintaining a constant drift of 10 K per hour, with identical sample data (sample heat input, mass, $C_p$, thermal conductivity and sample dimensions) and heat loss factors (sample emissivity and heater connector wire thermal information) at all three temperatures.

To demonstrate the different optimum polynomial orders for the curve fitting of the post pulse data at different temperatures, Figure 3.24 shows the ln(dT) data for the three example pulses from Figure 3.23. Each of ln(dT) for the three pulses has the lowest order polynomial that produces an $R^2$ (regression coefficient) value of 1 (to four decimal places).
These examples clearly show that the post pulse data for modelled heat pulses are best fitted with exponential curves with polynomial exponents, where the polynomial order decreases as the temperature rises. The exact polynomial order is sample and test specific.

In some cases additional data manipulation is required. For example, Figure 3.25 below shows a sample with a temperature that falls below the calculated baseline (linear). In the pure dT form this data clearly decays with a constant rate. However, due to the post pulse data dropping below zero, the post pulse regression technique of curve fitting to the ln(dT) data can only be performed on a small portion of the available dT data.
High Temperature Specific Heat Capacity Measurement of Ni$_{2-x}$Mn$_{1-x}$Ga

(a)  
(b)

Figure 3.25: Example of a pulse measurement with the sample temperature dropping below the baseline (a) and the effect this has on the logarithmic data analysis (b).

If the dT data is offset by a small amount such that the post pulse data did not become negative at any point, the post pulse regression of the ln(dT) could take advantage of all of a much larger sample of the post pulse data (see Figure 3.26).

(a)  
(b)

Figure 3.26: Example of a pulse measurement with the sample temperature dropping below the baseline offset to the minimum post pulse value (a), and the effect this has on the logarithmic data analysis (b).

The analysis of the post-pulse section of both data sets, offset and raw, produced specific heat capacity values for the sample of 629 and 414 J.kg$^{-1}$.K$^{-1}$, respectively. The actual standard value for the material at that temperature is 603 J.kg$^{-1}$.K$^{-1}$[100], which is close to that produced when analysing the offset data.
**Heating Pulse Analysis**

The analysis of some of the pulse measurement data revealed that during the heating phase of the measurement pulse the data follows the following pattern (Figure 3.27):

1. Rapid heating of the heater.
2. Heating rate slows as heat begins to transfer to the sample from the heater element.
3. Heating rate tends to linear heating rate proportional to the energy supplied to the heater.

![Figure 3.27: The heating phase of a molybdenum sample heat pulse measurement demonstrating the trend towards a linear heating rate.](image)

The theoretical data shown in Figure 3.27 (blue line), is calculated by determining the change in sample temperature between each of the measured data points, using the measured power input to the sample heater.

\[
\frac{dT(t_n)}{dt} = \frac{\sum_{i=1}^{N} V_i I_i (t_i - t_{i-1})}{m C_p}
\]

where

\[V_i = \text{measured voltage in the } i^{\text{th}} \text{ data set} \quad I_i = \text{measured current in the } i^{\text{th}} \text{ data set}\]
\[ m = \text{mass of the sample} \quad C_p = \text{specific heat of the sample} \]
\[ t_i = \text{time stamp of the } i^{\text{th}} \text{ data set} \quad t_N = \text{time stamp of the } N^{\text{th}} \text{ data set} \]

The linear portion of the measured heating data (between 220 and 250 seconds) has a similar rate of change as the theoretical data. Figure 3.28 below shows the change in temperature (\(dT\) between data points for the theoretical data and measured data).

![Figure 3.28: Change in dT for the heating phase of a measurement pulse of a molybdenum sample at room temperature.](image)

The data shown in Figure 3.28 clearly demonstrates that the linearly stable portion (approximately 220 to 250 seconds) of the heating phase of the measurement pulse compares well with the theoretical \(dT\) data determined using the sample heat capacity and energy input.

Two methods have been developed for utilising the above effects. These are:

- **Numerical Method**

  An iterative method was developed to take advantage of this phenomenon. The method involved varying specific heat values and calculating the
theoretical dT against time and comparing this with the measured data (as shown in Figure 3.29).

![Figure 3.29: Example of the use of the numerical method for manual analysis of the heating phase.](image)

The example in Figure 3.29 indicates that the measured dT data is approaching a stable plateau between the theoretical dT lines for the $C_P = 150$ and 250 J.kg$^{-1}$.K$^{-1}$. Further analysis with specific heat values between 200 and 250 J.kg$^{-1}$.K$^{-1}$ allowed for a more accurate measure of the specific heat of the sample. The more accurately measured specific heat for the molybdenum sample, based upon the data shown in Figure 3.29 is $220 \pm 20$ J.kg$^{-1}$.K$^{-1}$. The standard value for the specific heat of molybdenum at the test temperature is 247 J.kg$^{-1}$.K$^{-1}$[101].

This method for the determination of the specific heat of a sample only works for long duration heat pulses. Otherwise stable heat transfer conditions are not reached and the sample heater temperature does not increase linearly.

In an effort to improve the accuracy of this method an attempt was made to develop an analytical procedure. The noise on the signal and shape of the heating phase meant that the fitting of polynomial and exponential functions was impossible (see Figure 3.30).
Figure 3.30: Polynomial fit to dT data for a molybdenum measurement pulse.

- **Graphical method**
  
The numerical method for analysing the heating phase data is affected significantly by the noise of the signal. Thus a second method of analysis was developed with the intention of overcoming these issues. The method developed was a graphical technique. This method relies upon production of an ‘ideal’ or ‘standard’ curve representing the heating phase (Figure 3.31). This curve is then rescaled (by constant scaling factors in both the x and y directions) to fit the data for the pulse being analysed (Figure 3.32). The linear portion of the rescaled ‘standard curve’ is then used as the basis for the determination of the specific heat of the sample.
Figure 3.31: The ‘standard’ heating phase curve, taken from a molybdenum pulse measurement.

Figure 3.32: Example demonstrating the re-scaling of the ‘standard’ heat pulse curve to fit a measurement pulse. The raw data is taken from a measurement pulse of a Mo sample at 678K with a constant drift of 10 K per hour.

The ‘standardised curve’ fit to the measurement pulse data produces a specific heat capacity value for the sample of approximately 292.8 J.kg\(^{-1}\).K\(^{-1}\). This measured value for the specific heat capacity of molybdenum at 678 K compares well with the standard of 278 J.kg\(^{-1}\).K\(^{-1}\).[101]
This graphical method has the advantage of not requiring the heating phase data to have a ‘linear portion’ (Figure 3.33).

![Graphical heating phase example fit to a partial heating pulse.](image)

Figure 3.33: Graphical heating phase example fit to a partial heating pulse.

The linear portion of the standardised heating curve, when fitted to the stainless steel sample above, produced dT data that resulted in a measured $C_p$ value of 487 J.Kg$^{-1}$K$^{-1}$ (the standard value for this material is 493 J.kg$^{-1}$.K$^{-1}$). [101]

This method is very susceptible to misinterpretation when fitting of the standard curve is difficult for pulses where the measurement does not have a clearly established ‘linear zone’.

To demonstrate the problem of interpretation we consider the data shown in Figure 3.32 and try to fit the standardised curve using two methods: With one of the fits the focus was on getting the best curve fit at the beginning of the data, while the second fit aimed for a good fit during the latter portion of the heating phase (Figure 3.34).
Figure 3.34: Curve fitting of the standard curve to the early (red) and latter (blue) stages of the heating phase data.

The two example standard curves fitted to the data in Figure 3.32, produce specific heat values of 222.0 J.kg\(^{-1}\).K\(^{-1}\) for the ‘early-fit’ and 333.9 J.kg\(^{-1}\).K\(^{-1}\) for ‘later-fit’ data. Therefore, it is advisable to fit the standard curve to the raw data for both the early and later stages of the heat pulse and then average the results. For the example above (Figure 3.34) the averaging of the two curves produces a specific heat value for the Mo at 678 K, of 277.95 J.kg\(^{-1}\).K\(^{-1}\) (standard data \(C_P = 278\) J.kg\(^{-1}\).K\(^{-1}\)[101]).

- **Finite Element Modelling**
  Fitting of numerically modelled data to measured data can be a challenge due to the complex nature of the data recorded during a measurement pulse and the noise in the data, as well as temperature fluctuations which are present in the system. These problems, and the none ideal nature of the system, prevent analytical solutions being readily used for analysis.
The fitting of two models to the real data is discussed in this section of this thesis. These two methods are numerical and employ a simplified Finite Element Modelling (FEM) method (see section 3.4) to produce an ideal curve which is then fit to the measured data. The two models can be described as follows:

1. Single body model
2. Multiple bodies (2 segments)

A brief description of each is provided below for the modelling techniques, followed by a discussion of the merits, and any conclusions that can be made concerning the techniques.

- **Single body model**
This model is the simplest of the possible numerical models. The model consists of a body of homogeneous material, with a surface area defined by the 'real' sample. The modelled single body sample loses energy, via radiation and conduction, and energy is input into the body in accordance with power data for the real pulse being analysed.

The aim of the analysis is to tune the thermal properties of the sample (heat loss, specific heat, etc.) so that the modelled data fits the measured data (Figure 3.35).

![Figure 3.35: Example of pulse data analysis using the single body model.](image-url)
The simplified nature of the model means that the modelled data cannot be
tuned to match the heating phase of the pulse data, the shape of which is an
effect of the interface between the platinum heater element, the ceramic
housing, and the sample. However, it is possible to produce an
approximation of the post pulse data.

The difficulty in fitting the modelled data to the real measured pulse data with
this simplified model makes this analysis method only usable as a guide or
approximation for the determination of range for which another analytical
technique can be applied to produce more accurate results.

- **Multiple body model**
  
The use of a multiple body model for the analysis of measured data has the
advantage over the single body method of being able to incorporate the
effects of the interfaces in the sample/heater system (e.g. between sample
and heater, between Pt element and housing).

  The fitting of the two body model splits the sample/heater configuration into
two entities: the heater and the sample, with a heat transfer coefficient
between the two bodies. The model is tuned to the measured pulse data by
manipulation of this transfer coefficient, the sample radiation heat loss
coefficients, the heater conductive heat loss coefficients and finally the
specific heat of the sample (the property being measured).

  The use of the two body model allows the model to be fitted to not only the
post pulse data, but also to the heating phase data. This allows for a better fit
in high heat loss situations and un-stabile scenarios.

  The multiple body method also allows for the calculation of the surface
temperature of the sample, which allows for a comparison of both the
platinum resistance thermometer and sample thermocouple data. Figure 3.36
below shows the fitting of the two body model to a real pulse measurement of
a graphite sample at approximately 400K with a constant furnace drift of
10K/hr.
Figure 3.36: Example of an analysis of a measured heat pulse for a graphite sample using the two body model.

In the Figure above the measured dT data was determined by subtracting a linear baseline from the measure sample temperature. The modelled data is determined by performing the modelling twice: once with no supplied heat pulse (for a baseline), and again with the heat pulse (for the dT data).

Similar to the single body example, this technique is open to misinterpretation, by inputting impractical heat transfer coefficients. However, the fact that the two-body model is optimized for more of the measured data suggests that it is a more robust analysis technique.

The splitting of the sample into more bodies (more than two) would improve the fit of the model but would introduce another unknown variable (thermal conductivity of the sample) that would have a significant effect on the tuning of the model, since it would be possible to produce identical heat pulse data with different specific heats using different thermal conductivity and heat transfer coefficients.
FEM Summary.
The FEM modelling approach is very promising and seems to produce very good data (see commissioning test results section 3.5). The limitations of the single body model make it only usable as a way of determining a starting point for more accurate analysis techniques (e.g. post-pulse regression or multi-body FEM).

The two-body FEM analysis technique is much stronger and can be used as a stand alone analysis technique, but care must be taken to use appropriate heat transfer coefficients in the modelling or the specific heat value produced could be inaccurate.

3.5 Commissioning

After the initial testing was performed to investigate the methodology and the development of the analysis approach finalised, four samples were selected to test the system. The variety of the samples also served to investigate the scope of application for the HTCP system.

The samples tested were in two forms: three of the four test samples were cylindrical and the fourth was rectangular. Tables 3.4a and 3.4b below detail the test sample information:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Material</th>
<th>Sample information</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Diameter (mm)</td>
</tr>
<tr>
<td>1</td>
<td>Copper</td>
<td>8.536</td>
</tr>
<tr>
<td>2a*</td>
<td>Stainless Steel (Type 304)</td>
<td>7.905</td>
</tr>
<tr>
<td>2b*</td>
<td>Stainless Steel (Type 304)</td>
<td>7.905</td>
</tr>
<tr>
<td>3</td>
<td>Molybdenum</td>
<td>16.015</td>
</tr>
</tbody>
</table>

* sample 2a and 2b are the same piece of material with testing performed on the larger 6.235g sample (2a) then the sample reduced in size to produce the smaller 5.7859g sample (2b)

Table 3.4a: Cylindrical sample information
Table 3.5b: Rectangular sample information.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Material</th>
<th>Width (mm)</th>
<th>Depth (mm)</th>
<th>Length (mm)</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Graphite</td>
<td>5.935</td>
<td>5.802</td>
<td>15.325</td>
<td>0.983</td>
</tr>
</tbody>
</table>

The following sections describe the testing performed on these samples and the results.

### 3.5.1 Copper

Testing on this sample was performed at room temperature only. The testing was designed to investigate the suitability of the suggested sample heater and thermocouple configuration in ambient and low pressure environments. This testing was not repeated above room temperature. This restriction was imposed due to the sample heater becoming damaged during trials of this sample configuration. The data produced shows that the test procedure for stable temperature testing at room temperature, with the sample dT data determined using the Pt100 resistance thermometer (sample heater, see section 3.2.1), was satisfactory. Figure 3.37 below shows a typical pulse for the copper sample.
Post-pulse regression

Analysis of these pulses was performed using the post-pulse regression technique described in section 3.4. (Figures 3.38 and 3.39). Other analysis techniques were unnecessary for most of these pulses. However, to investigate the effectiveness of the FEM modelling analysis technique (section 3.4) the copper data analysis was repeated using this alternative analysis technique. Unfortunately the same process could not be undertaken for the ‘Heating phase analysis’ technique as the pulse duration for the copper sample was far too short (Figure 3.74). The copper sample was measured in both air and a vacuum to investigate the impact of the test environment on the stable ambient temperature heat pulse measurements.

Figure 3.37: Typical Heat pulse measurement for the copper sample at room temperature.
Figure 3.38: $dT$ data for a copper pulse measurement with a linear baseline subtracted.

Figure 3.39: The $dT$ data for a copper pulse measurement pulse with a linear baseline subtracted plotted on a logarithmic scale.

It should be noted that the data recorded after 1300 seconds was removed from the post pulse analysis as there is a temperature drop that could affect the regression. The anomaly in the $dT$ data is observed in all three temperature profiles (sample TC, sample PtRT and shield TC) suggesting that this was an ambient temperature effect.
The results of the regression on the pulse presented in Figures 3.37, 3.38, and 3.39 are:

Calculated $C_p$ – from Sample thermocouple: $471.2 \text{ J.kg}^{-1}.\text{K}^{-1}$
Calculated $C_p$ – from Sample resistance thermometer: $389.8 \text{ J.kg}^{-1}.\text{K}^{-1}$

The standard specific heat capacity of copper at 293 K is $385 \text{ J.kg}^{-1}.\text{K}^{-1}$ [102].

The two specific heat capacities measured using the HTCP system for the sample thermocouple and resistance heater differ from the reference data by 22% and 1.2%, respectively.

The graph below shows the results for the remaining pulse measurements performed (a total of 80 heat pulses) on the copper sample using the same analysis technique (Figure 3.40).

![Figure 3.40: Measured specific heat capacity determined using post pulse regression on both the sample thermocouple (blue) and the platinum resistance thermometer (red), with the standard value for specific heat capacity.](image)

The results in Figure 3.40 above show that there is very little difference in the results when performed in vacuum or air. The vacuum system used reduces the pressure in the furnace chamber to less than $2.2 \times 10^{-2}$ mbar. The results presented in Figure 3.40 confirm that the measurement of temperature using the thermocouple mounted on the exterior of the sample is insufficient for the
accurate measurement of the sample change in temperature and as a result produces poor specific heat capacity data for the sample.

The measurement of the specific heat capacity of the copper sample using the resistance thermometer produced results very similar to the standard value for the material. Figure 3.41 below shows the difference between the measured value and the standard value.

![Figure 3.41: The percentage deviation of the measured specific heat of the copper sample from the standard value.](image)

The calculated uncertainty of measurement for the post pulse regression technique for the copper sample ranges between ±1% and ±2.5. See Appendix B for the calculation of the uncertainty of measurement.

- **FEM modelling**

The results of the analysis of the same pulse data using the FEM modelling technique has similarly produced specific heat data in agreement with the standard data (Figure 3.42). The error on the technique was assumed to be 5%.
Figure 3.42: Measured specific heat of copper at room temperature, produced using the two-body FEM analysis.

The results of the FEM modelling analysis compare very well with those measured using the post pulse regression technique, and the standard data.

**Conclusion**
The HTCP system has produced good specific heat capacity data for copper at room temperature. The testing of the copper sample has shown that under stable conditions at room temperature the effects of performing the testing in atmosphere is minimal when compared to tests performed in a vacuum.

Both FEM and post pulse regression analysis techniques have produced specific heat data that compares well with the standard value for copper at room temperature. The fact that this testing could not be completed above ambient temperature is unfortunate as this data is very promising. At room temperature, due to the ease of application, the post-pulse regression technique could be described as the best approach.
3.5.2 Stainless Steel
The steel sample was selected due to its availability and the stability of the material. The stainless steel sample was the most investigated sample. It was used for testing of various test configurations and test programs. The low oxidation of stainless steels [100] allowed for numerous heating and cooling cycles with the sample suffering no detrimental effects.

As shown in Table 3.4 the stainless steel material was measured in two forms (6.235 grams and 5.785 grams). This was due to the need to remove a broken sample heater from the sample. In addition to the sample mass being different the two stainless steel samples were measured using two different sample mounting techniques. The second sample (5.785 grams) was mounted suspended from wires welded to the side of the sample, and the first was suspended from the heater element.

The measurement of the same material using two different samples, with different mounting techniques, allows for the comparison of the mounting techniques. The difference in sample masses should not be relevant since specific heat is a bulk property and the normalisation to unit mass. The variation in to sample mass between the two samples is less than 7%.

3.5.3 Stainless Steel Sample 1 (6.235 grams)
The measurement of the specific heat capacity of this sample was used to fine tune many of the test parameters such as the pre- and post-pulse duration, heat pulse duration and input energy. Due to this, there is a large amount of data for this sample at room temperature under stable conditions. The majority of tuning of the technique was performed at room temperature so as not to introduce variations in the signal due to the furnace drifting while attempting to optimize the setup.

The large number of repeat pulses also serves to show what to look out for when things have gone wrong. For example, Figure 3.43 shows the dT data for pulses “PULD2426” to “PULD2449” both measurement are at room
temperature using identical test parameters, with the measurement performed less than 2 hours apart.

![Figure 3.43](image.png)

**Figure 3.43:** The temperature change data for two stable room temperature pulse measurements performed on a stainless steel sample (mass: 6.235 g).

Notionally these pulse measurements should be identical, however the second pulse (PULD2449) shows a higher peak temperature and a much broader pulse than the first measurement (PULD2326). The ‘slowing’ of the pulse suggesting that the rate of heat transfer of away from the heater is less, suggesting a reduction in the conduction of heat into the sample. Assuming all other factors are identical this would imply that the sample had become detached from the heater. Upon inspection of the sample this was proved to be the case.

Other than room temperature testing, the first stainless steel sample was tested in the HTCP furnace between room temperature and 650 K at 10 K/hour (heating and cooling) and between room temperature and 750K at 6 K/hour. The 6 K/hour test cycle had to be stopped at 750 K due to a leg on the heater becoming detached, prevent measurement of cooling data at 6 K/hour.
• **Post pulse regression**

The results of the analysis of the pulse measurement data (Figure 3.44) for the first stainless steel sample showed that they compare well with the standard data for type 304 stainless steel [100]. (Figure 3.45), under both heating and cooling conditions at 10 K/hours and during heating at 6 K/hour.

![Figure 3.44: Measured specific of stainless steel (sample 2a, mass: 6.235 grams) between room temperature and 650K with a constant heating/cooling rate of 10K/hour.](image1)

![Figure 3.45: Measured specific of stainless steel (sample 2a, mass: 6.235 grams) between room temperature and 750K with a constant heating rate of 6K/hour.](image2)
**FEM modelling analysis**
The FEM analysis technique was applied to 10% of the pulse data for the first heating cycle, the large amount of data and strong agreement with the post-pulse regression results meant further analysis would be redundant. The analysis showed good agreement with the standard data at high temperatures (above 500K) with some scatter at lower temperatures (Figure 3.46).

![Figure 3.46: Measured specific heat capacity of Type 304 stainless steel analysed using the FEM modelling technique.](image)

### 3.5.4 Stainless Steel Sample 2 (5.785 grams)

This sample was produced from the first stainless steel sample (Section 3.5.3), after the first sample heater element broke. The slight difference in mass is due to the drilling out of the original heater element.

This sample was mounted in the HTCP system with the thermocouples spot welded to the surface. The sample was supported by the thermocouple wires. The thermocouple data for these heat pulses was unusable (Figure 3.47) for any type of analysis.
This stainless steel sample was measured under stable room temperature conditions and in the furnace with a constant drift of 6K/hr between room temperature and 1150K. All measurement were made under vacuum <10^{-3} Bar. The data from this sample has been analysed using both the post-pulse regression technique and the heat phase analysis technique (section 3.4). The results for these analyses are presented below.

- **Post pulse regression**

The data produced for this sample has been analysed using the post pulse regression technique. Figure 3.48 below shows the results of the analysis. As can be seen in Figure 3.48 the data above 900K is more scattered than the data recorded below this temperature. Figure 3.49 shows the specific heat data measured between room temperature and 900K.
Figure 3.48: Measured specific heat of stainless steel (mass: 5.785 grams) between room temperature and 900K with a constant heating rate of 6K/hour as determined by using post-pulse regression on the PtRT temperature data between room temperature and 1150K.

Figure 3.49: Measured specific heat of stainless steel (mass: 5.785 grams) between room temperature and 900K with a constant heating rate of 6K/hour as determined using post-pulse regression on the PtRT temperature data between room temperature and 900K.

The scatter in the data above 900 K (Figure 3.48) may be indicative of a phase transition in either the sample or the measurement equipment or a fault with the HTCP system. The possibility of a phase transition in any of the materials in the system is unlikely, as none of the materials connected with the sample (stainless steel, platinum, alumina) have shown phase transitions.
at this temperature in any other testing [101], [103], [104]. Suggesting some form of fault with HTCP measurement system, given the failure of the heater leg at 1150 K it would be suitable to assume that the heater leg is weakened or beginning to fail above 900 K.

- **Heat Pulse Analysis**

  The heat pulse analysis technique has been applied to the pulse data of the second stainless steel sample (5.78 grams) using both the numerical and graphical approaches. The results are presented in Figure 3.50 below.

![Figure 3.50: Measured specific heat capacity of a stainless steel sample (5.78 grams) determined using the ‘heating phase’ analysis technique between room temperature and 1000K.](image)

It should be noted that the pulse duration for temperatures below 600K was 100-120 seconds and above 600K the duration was reduced to between 50 and 70 seconds. The reduced pulse duration prevented the sample and heater reaching a stable heating rate, and therefore increased the reliance of the technique on operator interpretation. The reduced heating time also meant that the numerical approach could not be used as the change in rate of change of the sample temperature could not reach stable condition (Figure 3.51).
The numerical method produced specific heat data in good agreement with the standard data up to approximately 500 K, but at temperatures above this point the results begin to drift.

The graphical method worked very well with the long duration stable room temperature heat pulse, the apparent accuracy of this technique at room temperature is only to be expected as standard graphical data set was produced from a room temperature stainless steel sample. Above room temperature the results are less accurate, but still show the overall trend of increasing CP with temperature.

**Conclusion**

The standard of the pulse measurement data for the stainless steel samples has produced good data that agrees with the standard specific heat data for type 304 stainless steel (Figure 3.52).
Figure 3.52: Measured specific heat capacity of type 304 stainless steel measured at a drift rate of 10 and 6 Kelvin per hour for samples with a mass of 6.235 grams and 5.785 grams.

The measured data for the two stainless steel samples shows good agreement with the measured data, but shows more scatter at high temperature (6 K/hour sample one, and sample two). It should be noted that both data sets showing large amounts of scatter experienced a failure in the heater wire with just above temperature at which increased scatter occurs.

The uncertainty, for the results of the specific heat measurements made using the post pulse regression technique varied widely from room temperature to 900K (above this temperature the UOM >20%). Since the calculated uncertainty of measurements for this technique shows no temperature dependence, a reasonable approximation for the uncertainty of measurement for the stainless steel would be ±5% irrespective of temperature with any pulse measurements with an extreme UOM (>>5%) being considered invalid for the post pulse regression technique and the pulse being omitted from the analysis.

The FEM modelling of the first stainless steel data produced very good specific heat data in agreement with the standard values. However, this was susceptible to some scatter below 500K (Figure 3.46).
The heating phase analysis of the second sample produced reasonably good results which agreed with the standard data at room temperature under stable conditions, but it became less accurate above room temperature with the furnace under constant drift conditions. The shorter heat pulse duration of the pulse measurements made above 600K meant that only the graphical approach for this technique could be used. This method produced results that compared poorly with the absolute values for specific heat but did show a similar trend to the standard $C_p$ data for this material.

Even with the large amount of scatter in the specific heat data derived using the HTCP system the overall trend of the data is very similar to that seen in the standard data, and the technique appears sound and should be accurate enough to measure the specific heat capacity of a material with a sufficient resolution to discern phase transitions.

### 3.5.5 Graphite

The third sample used in testing of the HTCP system was a graphite sample. The sample consisted of a rectangular section of PGA graphite with a hole machined into the centre for the sample heater/temperature sensor.

As with the other samples the heater was cemented in place with an alumina based high temperature cement. However, unlike the metal samples the graphite sample could not be suspended from thermocouples spot welded to the surface. Instead it was hung from the heater wires (see Figure 3.53).
Figure 3.53: Schematic of the graphite sample mounting configuration.

The fact that the sample thermocouple wires could not be welded to the sample required that an alternative method of fixing the sample thermocouple to the sample needed to be used. The method finally selected (after some trials) was to machine a small hole into the surface of the sample (diameter 0.5mm) in which the thermocouple bead is inserted. The thermocouple is held in place with a small amount of the high temperature cement (Figure 3.54).
The additional mass of the cement used in attaching the thermocouple cannot be measured due to the presence of the thermocouple. However, an approximation of the mass of the cement can be obtained assuming a conservative size estimate of 1mm x 1mm x 1mm and assuming that the cement has the density of alumina [104]. This procedure yielded a calculated mass of 0.00397 grams. This is approximately 0.4% of the sample mass.

Due to the fact that the exact mass of the thermocouple mounting cement is unknown and the relatively small size (even with the over-estimation) the additional mass of the sample due to the thermocouple mounting cement will be ignored as part of the specific heat calculations but included in the uncertainties on the measurements.
The graphite sample metrology is listed in Table 3.5 below.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width</td>
<td>5.935</td>
<td>mm</td>
</tr>
<tr>
<td>Depth</td>
<td>5.802</td>
<td>mm</td>
</tr>
<tr>
<td>Length</td>
<td>15.325</td>
<td>mm</td>
</tr>
<tr>
<td>Sample mass</td>
<td>0.983</td>
<td>g</td>
</tr>
<tr>
<td>Sample and heater (including cured cement)</td>
<td>1.168</td>
<td>g</td>
</tr>
</tbody>
</table>

Table 3.6: Graphite sample metrology data.

The measured density of the graphite sample is 1785.4 kg.m\(^{-3}\). This compares well with the standard density of PGA graphite which is 1743 kg.m\(^{-3}\) [105].

The test program used for the graphite sample was a furnace heating rate of 10 K/hr between room temperature and 1200 K. Unfortunately the testing had to be interrupted with the furnace temperature at approximately 600K due to the loss of signal on the sample heater element. This is suggestive of a broken connection to the heater element in the furnace vacuum chamber.

Upon opening of the vacuum chamber and inspection of the measurement head it was discovered that some components had become coated in a dark grey/black deposit which had created a short across the heater element connection wires.

Inspection of the sample showed weight loss of approximately 27% (post testing mass of sample including alumina: 0.764 grams). This significant weight loss is indicative of oxidation/burning of the sample, possibly due to residual oxygen present in the system (i.e. in the ceramic components) or a leak in the vacuum system.

With the evidence of oxidation/burning of the sample the dark-grey/black deposit was assumed to be ash from the damaged sample condensing on
cooler portion of the HTCP measurement insert. Before any further testing could be performed the internals of the furnace vacuum chamber had to be cleaned and any graphite deposit removed to prevent any contamination of subsequent testing.

The rectangular nature of the graphite sample was intended to prove that the measurement system could be used with a variety of sample configurations. This was to be achieved by comparison of the measured data with a second sample of graphite with a circular cross section. However, due to the difficulties encountered during the measurement of the rectangular graphite sample it was decided not to proceed with the testing of the round graphite sample.

- **Post pulse regression**
Analysis of the pulse data using the post pulse regression technique (section 3.4) showed that the measured specific heat data for the graphite sample compares well with standard data [105]. It begins to deviate as the temperature increases above 480K (Figure 3.55).

This deviation is likely due to the weight loss from the sample. If the data recorded above 480K is corrected for weight loss (assuming continuous weight loss from the sample at a constant rate) the corrected data agrees better with the standard data than the uncorrected data. However, such a procedure is not perfect (Figure 3.55).
Figure 3.55: Measured specific heat capacity of graphite as analysed using the post pulse regression technique. Also shown is standard data for graphite with 5% error bars.

- **FEM modelling**

The analysis of the graphite measurement pulse data was performed using the “2 medium modelling” technique (see section 3.4). The results of the analysis are shown in Figure 3.56. The majority of the data compares well with the standard specific heat data for this material [105]

Figure 3.56: Measured specific heat of graphite using the “2-medium modelling” technique.
An anomaly in the specific heat data between 480K and 520K (as noted previously) indicates that an unknown process is taking place. The data recorded above 480K shows more scatter and is less suited to analysis with this technique, due to the heat energy being released by the oxidation of the sample.

If we consider one of the higher temperature measurement pulses (Figure 3.57) and compare it with a lower temperature pulse (Figure 3.58) it is obvious that the higher temperature pulse does not conform to the predicted heating and cooling models. The later stages of the post pulse data increase rather than decrease (suggesting energy being input from another source i.e. oxidation).

![Graph showing high temperature pulse data](image)

*Figure 3.57: High temperature (T= 504K) dT pulse data for the graphite sample with linear baseline subtracted.*
Figure 3.58: Low temperature (T= 287K) dT pulse data for the graphite sample, with linear baseline subtracted.

This increase in the post pulse temperature away from the baseline might be the result of the oxidation/burning of the sample and the heat released from the reaction (oxidation is an endothermic reaction, H=30,000 J.kg\(^{-1}\)). The ‘non-standard’ shape of the measurement pulse data implies that for temperatures above 480K the “2 medium modelling” analysis technique does not work properly, as the model does not consider the input of energy from an alternative source. Therefore the results in this region should be discarded.

- **Heat pulse analysis**
  The relatively short heat pulse duration of <50 seconds prevents the use of the heating phase analysis technique (section 3.4). There is insufficient data to which the standard curve can be fitted.

- **Conclusions**
  The specific heat data for the graphite sample, produced using the FEM modelling and post-pulse regression techniques, compare well with standard data [105] between room temperature and 480 K (before oxidation begins)
Above 480 K the measured data compares less well with the measured data, this deviation is assumed to be due to oxidation of the sample. The input of energy due to the exothermic oxidation of graphite invalidating the adiabatic nature of the analysis. Correction of the specific heat data 480 K, for weight loss due to oxidation produces a better fit with standard data; supporting the hypothesis that oxidation is taking place.

See Figure 3.59 for the final results using the post pulse regression technique with the calculated uncertainty of measurement data.

![Figure 3.59: Measured specific heat capacity of graphite including calculated UOM data.](image)

It should be noted that the much smaller sample size of the graphite sample and higher thermal diffusivity ($\alpha = 1220 \times 10^{-6} \text{ m}^2 \text{s}^{-1}$[105]), compared to the other HTCP sample materials, means that the sample temperature data recorded by the sample thermocouple and platinum resistance thermometer compare better than observed in other tests. The strong agreement between the two temperature sensors allows for better accuracy analysing the measurement pulse data.
The measurements performed on the graphite sample suggest that smaller samples produce better results and that testing of highly oxidising material (e.g. graphite, Zirconium, Hafnium, etc) must be performed in a higher vacuum environment or in the presence of an inert gas such as argon. Trials of these test conditions would be advisable to confirm the suggested improvement to the test procedure.

### 3.5.6 Molybdenum

The molybdenum sample was by far the largest of the five samples measured. It was almost seven times the mass of the next largest sample. The aim of using such a large sample was to demonstrate that the HTCP system could operate with much larger samples than had previously been measured. In addition, molybdenum is considered the standard specific heat calibration material [101].

It was noted in all recorded test pulses that the sample thermocouple did not record a significant change in sample temperature due to the heater input energy. Modelling performed of high temperature pulse measurements suggested that large samples would show only a small change in surface temperature while the PtRT data would still produce of a dT signal of sufficient strength to allow suitable analysis.

Unfortunately due to the large size of the sample and poor spot welding of the thermocouple wires (due to the high melting point of molybdenum), the sample support wires became detached and the sample dropped within the ‘sample can’ causing the platinum resistance thermometer connecting wires to short producing spurious data. Therefore the HTCP system could only record data for the molybdenum sample up to approximately 1100K, with no cooling data available.
- **Post pulse regression**

The use of the post pulse regression technique when applied to the PtRT data for the molybdenum sample, proved very satisfactory (Figure 3.60). A clear delineation was visible between the heater transferring heat to the sample and the actual changes in sample temperature as the sample cooled (post pulse). This made it easy to define the post pulse regression data range over which the regression should be performed.

![Figure 3.60: Example of molybdenum dT data with linear baseline subtracted (at 376K).](image)

As the sample temperature increases above 600K and the radiation heat loss increases, the delineation indentifying the post pulse regression range became more difficult to define (Figure 3.61). However, up to 900K defining the regression range was still possible with a reasonable degree of ease (Figure 3.62).
Figure 3.61: Example of HTCP pulse measurement of molybdenum sample and approximately 600K.

Figure 3.62: Example of HTCP pulse measurement of molybdenum sample and approximately 900K.

Above 900K the identification of the post pulse regression range became increasingly difficult due to the smooth graduation of the dT data immediately post pulse into the long term cooling of the sample (Figure 3.63). The increased difficulty in defining the post pulse regression range results in the measurement of the specific heat capacity of the sample to vary over an increasing range (Figure 3.64).
High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga

![Graph showing temperature vs. time](image)

**Figure 3.63:** Example of HTCP pulse measurement of a molybdenum sample at approximately 1100K.

![Graph showing specific heat vs. temperature](image)

**Figure 3.64:** Measured specific heat capacity data for a molybdenum sample measured using the HTCP system and the post pulse regression analysis technique.

The overall specific heat capacity measurements performed by the HTCP system on the Molybdenum sample were good, approximately 90% of
measure specific heat capacities within ±5% of the standard value [101] with increasing scatter at high temperatures.

- **FEM modelling**
  Analysis of the pulse data for the molybdenum sample using the two body FEM modelling analysis technique (Section 3.4) was performed on only one in ten of the pulse data files. The decision to only analyse 10% of the molybdenum pulse data using this technique was made due to the excellent results produced by the post-pulse regression technique. A full analysis using this technique seemed redundant and time consuming. Instead, a nominal 10% of the data was analysed to demonstrate the effectiveness of the technique.

The results of the analysis performed using the FEM modelling technique produced specific heat data that compares well with the standard specific heat data for molybdenum, with more than 95% of the results within 10% of the standard $C_p$ value (Figure 3.65). Showing a good agreement with data measured using post-pulse regression.

![Figure 3.65: Measured specific heat of molybdenum using the “2-medium modelling” technique.](image-url)
• **Heat pulse analysis**
Similar to the graphite sample the heat pulse duration for the molybdenum sample was far too short for the use of the heat pulse analysis technique. Therefore no analysis using this technique will be presented.

• **Conclusion**
The results of the molybdenum measurements, using both the post pulse and FEM modelling techniques, show a good agreement the standard values [101]. The much larger sample size did not affect the accuracy of the system using the PtRT temperature sensor, but the data from the thermocouple was unusable.

The high melting point of the Mo sample made attaching the sample support wires to the sample using spot welding and this coupled with the large mass of the sample resulted in the sample becoming detached during measurement, resulting in the in failure of testing at high temperature. When using

The post pulse regression technique produced good $C_P$ results for the molybdenum sample up to 900K. Above this temperature (approximately 1100K) the data become very noise. A reason may have been that below this temperature the support wires became detached and caused the heater element to ‘short-out’.

The calculated uncertainty of the post pulse regression for the molybdenum sample ranged between 0.5% at room temperature up to 5% at 900K (See Appendix B). The measured specific heat for the molybdenum sample is shown in Figure 3.66 including the calculated uncertainty.
3.5.7 Conclusion

For those pulse measurements that could be analysed the specific heat data produced by the HTCP system for the four materials was in good agreement with the standard data.

The dominant factors affecting the accuracy of the technique were:

- the size of the sample
- the stability of the wiring in the heater.

With the smaller sample (graphite) producing the most accurate data (until oxidation of the sample invalidated the measurement). The stability of the heater wiring was also important in the measurement as not only did it limit some testing but results in increased scatter on the data prior to failure.

Of the three analysis techniques applied to the measured pulse data, only two of these should be considered successful (‘post-pulse regression’ and ‘FEM modelling’). The third technique proved un-usable on much of the data produced by the HTCP system, however changing the test parameters to a
system more suited to the heat-pulse technique (longer duration heat pulse) may improve the accuracy and usability of the approach.

The thermocouple measurements of the sample and shield temperatures have been susceptible to noise in the system. They are for the most part unusable. The pulse data with usable sample thermocouple data (i.e. graphite) produced some of the best specific heat results, as the thermocouple allowed for better interpretation of the post-pulse region. (for curve fitting).

An area of additional work would be to produce a better thermocouple signal, possibly by the use of manufactured thermocouples attached to the surface of the sample with additional wires for sample support. Also it might be worth investigating the effects of the furnace environment by obtaining a better vacuum or the injection of a transfer gas.

To date the HTCP system has produced good specific heat data for four materials from room temperature up to approximately 1000K which compare well with standard specific heat data for that material.

The advantages of the system are the size of the sample that can be measured (between 1 g and 50 g) and the potential for a high level of accuracy, even in non-ideal situations. The system has also been shown to operate with a variety of sample geometries (unlike other C_P measurement systems, e.g. DSC) and produce very good data.
High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga
4 Order-Disorder Phase Transitions in Ni$_{2-x}$Mn$_{1+x}$Ga

4.1 Introduction

The Heusler alloy Ni$_2$MnGa is the prototype ferromagnetic shape memory alloy and extensive research has been undertaken to investigate the practical application of the ferromagnetic shape memory phenomenon [3] and to understand the mechanism causing it [106].

The possible practical application of Ferromagnetic Shape Memory Effect (FSME) make it very attractive as an actuator, as unlike alternative actuator drivers (e.g. piezoelectric), the FSME effect is very fast and can achieve strains of approximately 10% [107].

As part of the experimental research, much effort has endeavoured to understand the full phase diagram of the material and the composition dependence of the phase transformations both from a phenomenological and mechanistic standpoint [108][109][110].

To date the experimental research has predominantly focused on increasing the Ni-concentration. This focus has been due to the fact that increasing the Ni content in Ni$_2$MnGa, increases $T_M$ to around room temperature, whilst the material remains ferromagnetic. This makes for a material that is more usable for practical applications.

The experimentally determined martensitic and ferromagnetic (Curie point) phase transitions, have produced phase diagrams for a variety of non-stoichiometric compositions (Ni$_{2-x-y}$Mn$_{1-x}$Ga$_{1-y}$). From the phase diagrams, relationships between composition (or the number of valence electron per atom, e/a) and the phase transitions ($T_M$ and $T_C$) have been produced. Figure 4.4 shows a phase diagram for the martensitic transition temperature and Curie Temperature for Ni$_{2-x}$Mn$_{1-x}$Ga.

In addition to Ni$_2$MnGa, recent research of Mn$_2$NiGa has shown it to be of interest, as it is a low temperature FSMA with a much larger magnetic induced
displacement (up to 20% Strain [12], Ni$_2$MnGa = 10% [107]). This material has been shown through neutron diffraction measurement to have a modified ‘L2$_1$B’ structure [12].

High temperature investigation of Ni$_2$MnGa alloys has shown that the material undergoes two order/disorder phase transitions: L2$_1$ to B2 and B2 to A2 [110], but very little work has been performed to investigate these transitions in non-stoichiometric compositions. This lack of research in this area has left a large gap in the phase diagram for Ni$_2$MnGa alloys. A similar gap in knowledge is present for the recently investigated NiMn$_2$Ga and nickel depleted Ni$_2$MnGa (i.e. Ni$_{2-x}$Mn$_{1+x}$Ga X= 0 to 1),

Therefore the aim of this research is to fill this gap in knowledge and to confirm the continuation of the proposed trends in order/disorder phase transitions and Curie temperature (with respect to e/a), and to investigate if any other new phase transitions are present in this region.

The research will be performed through specific heat measurements of Ni$_{2-x}$Mn$_{1+x}$Ga, with X =-0.2, 0…1, between room temperature and 1400 K. This temperature range should allow for observation of:

1. Curie Temperature
2. Martensitic phase transition (for x ≤ 0.2)
3. L2$_1$-B2 order-disorder phase transition ($T_{C2}$)
4. B2-A2 order-disorder phase transition ($T_{C1}$)
5. Melt temperature
6. and any unknown phase transitions

The HTCP system (described in Section 3) was developed to perform the measurement of high temperature phase transitions observed in Ni$_{2-x}$Mn$_{1+x}$Ga, however, the time required to make the system operational meant that an alternative measurement system had to be used.

As an alternative to the HTCP system, Differential Scanning Calorimeters (DSC’s) were used to perform the high temperature specific heat
measurement. See section 2.4.3 for discussion of the advantages and disadvantages of the DSC technique).

The temperature range of phase transitions being investigated required the use of two DSC systems. The first to perform measurements between room temperature (293K) and 900 K, the second between 500 K and 1400 K.

Once the measurements were completed (Section 4.4) a statistico-thermodynamic analysis of the phase transitions was performed using a Bragg-William-Gorski approximation (Section 4.5).

In addition these results contain three XRD measurements performed on unannealed samples (Ni$_{1.8}$Mn$_{1.2}$Ga, Ni$_2$MnGa, and Ni$_{2.2}$Mn$_{0.8}$Ga) to confirm that the samples in their ‘as cast’ form conform to the predicted crystal structure before DSC measurements (Section 4.3).

4.2 Current understanding of Ni$_2$MnGa alloys

Ni$_2$MnGa literature review

The discovery of the addition of Al, Sn, Sb, Bi, or In to Cu-Mn binary alloys making the material ferromagnetic despite the constituent elements being paramagnetic, diamagnetic or anti-ferromagnetic, was made by Friederich Heusler in 1903 [112], and recently these alloys showing, the Heusler structure Figure 4.1) have received attention for their unique properties. Of particular interest are the magnetocaloric [111] and ferromagnetic shape memory effects (FSME) [107], because of their novel properties and potential for practical applications (e.g. FSME for fast actuators, and medical implants).

Considered by many the prototype Heusler ferromagnetic shape memory alloy (FSMA), Ni$_2$MnGa has received a large amount of attention in an attempt to not only produce a practical/usable material but also to understand the mechanisms present in the FSME phenomenon. The alloy Ni$_2$MnGa is one of the Heusler alloys of particular interest, as not only is it a thermo-elastic shape memory alloy, the presence of the martensitic phase in the ferromagnetic
High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga

phase ($T_M=202$ K and $T_C = 276$ k)[21] makes the alloys a FSMA. In fact Ni$_2$MnGa is considered one of the first FSMAs, being a material of interest since 1984 [113].

The full Heusler alloys of the form A$_2$BC, have a cubic structure of a L2$_1$ form (Figure 4.1), with the A atoms occupying the $\alpha_1$ and $\alpha_2$ sub-lattices and the B and C atoms on the $\beta$ and $\gamma$ lattices respectively.

![Figure 4.1: Cubic L2$_1$ Structure of Ni$_2$MnGa Heusler alloy](image)

Upon cooling the A$_2$BC Heusler alloy undergoes a martensitic phase transition to a tetragonal [114] or orthorhombic [114] structure.

The Heusler structure is observed for a variety of elementary combinations with atom “A” a transition metal such as Co, Cu, Ni, or Fe; atom “B” typically Mn or C; and atom “C” Ge, Si, Ga, Sn, Sb, Al, or In [121].

If atoms A and C are non-magnetic then the magnetism for the alloys will be localised on the B sites [121], but if the A atoms are magnetic (Ni or Co) then there is an additional magnetic moment on the A site (much smaller in magnitude than on the B site) [121].

In the following section a more detailed review of the Ni$_2$MnGa alloys is presented, especially in terms of crystallography and phase transitions.
Stoichiometric Ni$_2$MnGa.

The parent phase of stoichiometric Ni$_2$MnGa has been measured using neutron diffraction [113] and shown to have the full Heusler L$_2$\textsubscript{1} phase structure (with sub-lattices $\alpha_1$, $\alpha_2$, $\beta$ and $\gamma$) [113]. The lattice occupancies measured were: Ni on the (0,0,0), ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) sub-lattice and Mn and Ga on the ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), and ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$), sub-lattices respectively (Figure 4.2a).

At high temperatures the ordered system undergoes two order/disorder phase transitions at temperature: $T_{C_1}$ and $T_{C_2}$. $T_{C_1}$ is the transition from L$_2$\textsubscript{1} ordered to partially ordered B$_2$, and $T_{C_2}$ is the transition from B$_2$ partially ordered to A$_2$ completely disordered. Figure 4.2 shows the L$_2$\textsubscript{1}, B$_2$ and A$_2$ structures.

![Figure 4.2](image_url)

*Figure 4.2: Crystal structure of Ni$_2$MnGa in (a) L$_2$\textsubscript{1}, (b) B$_2$, and (c)A$_2$ phases.*
During cooling, stoichiometric Ni$_2$MnGa undergoes a martensitic phase transition (first order transition) from the austenitic cubic parent phase to a modulated tetragonal [114] or orthorhombic [114] structure. This structural change is due to a compression along the C [100] axis and elongation in the other direction, with the relative atomic position staying the same. X-ray diffraction of this structure shows a tetragonal structure with $c/a = 0.94$ [114]. The martensitic phase transition being displacive (diffusionless) means that the low temperature tetragonal/orthorhombic phase, retains the chemical ordering of the parent cubic phase [114].

In addition to the main peaks observed for the above structure in x-ray [122] and neutron diffraction [123]. A number of much smaller peaks (intensity 3% of main peak), between the main peaks have been observed. Research into these smaller peaks, has shown that they are due to the modulation in the atoms in the [22] direction. This modulation has been shown to have a periodicity of 5 lattice spacing of the tetragonal structure [123], and are known as 5M [115]. In addition, alternative compositions have been found to exhibit modulations of 7M [115], 10M [116] and 14M [117].

Neutron diffraction of the Ni$_2$MnGa alloys in the ferromagnetic phase has shown that the majority of the magnetic moment is localised on the Mn atoms (3.8 to 4.2 $\mu_B$), with some on the Ni atoms (0.2 to 0.4 $\mu_B$) [113]. Since the original work by Webster in 1984 [113], experimental [118] and modelling [119][117] work have been performed confirming the atomic distribution of the magnetic moments.

During the martensitic phase transition this magnetisation changes, and this has lead to the theory that the martensitic phase transition in Ni$_2$MnGa is driven by the Band Jahn-Teller effect, of redistribution of electrons in the different 3d sub-orbits [114] between the two crystallographic symmetries (cubic and tetragonal). This theory was supported by polarised neutron diffraction of the alloy in both parent and tetragonal phases showing a shift of magnetic moment between Mn and Ni, and the Band Jahn-Teller effect is now accepted by most as the driving process in the Ni$_2$MnGa martensitic phase.
transition. Electronic and X-ray measurements in other forms of Ni$_2$MnGa (e.g. thin films) have confirmed these initial measurement, with transitions seen in x-ray absorption at $T_M$ associated with the lifting of the Ni 3d degeneracies [49]. This work has also shown that structural changes at or near $T_M$ results in the moment on Ni reaching a maximum [49]. The magnetic change on Ni atoms at phase transitions has been observed at both $T_M$ and the pre-martensitic phase transition ($T_{PM}$) [120].

Ni$_2$MnGa undergoes a pre-martensitic (PM) phase transition (at $T_{PM}$), at a temperature above $T_M$, which can be seen using x-ray [124], electron [125] and neutron scattering [128] and ultrasound measurements [131]. For inelastic scattering the transition is observed as a softening (anomaly) in the TA2 phonons Figure 4.3 [135]. The PM transition can also be observed in magnetisation experiments [131] as a peak in the magnetisation well above the martensitic transition. The exact value of $T_{PM}$ was dependent on the applied magnetic field [131].

In the temperature range between $T_{PM}$ and $T_M$ the crystal structure is essentially a FCC L$_2_1$ type, but with modulation along the 1/3<110> vector. Therefore the structural transition from austenitic to martensitic is a two stage transition, starting as an austenite structure, going to the pre-martensite

![Figure 4.3: Experimental acoustic-phonon curve for L2$_1$ phase of Ni$_2$MnGa from inelastic neutron scattering. (This Figure was taken from work of A.Zheludev [135]. The black arrow denotes the softening of the phonon DOS on the TA$_2$.](image-url)
phase (modulated cubic, or pseudo-orthorhombic) and completing the transition as martensite (tetragonal) [126]. Similar pre-martensitic phase transitions are observed in other SMA such as Ni-Ti-Cu [127].

Application of an external field has shown that $T_{PM}$ decreases with magnetisation and $T_M$ increase, up to a field of 2 T. A field of more than 2 T does not cause any further changes to either $T_M$ or $T_{PM}$ in stoichiometric Ni$_2$MnGa [126].

Another area of interest regarding Ni$_2$MnGa is the magnetically induced re-orientation of twinned variants in the martensitic phase (see section 2.3), this switching of variant under an applied magnetic field (see section 2.3) was first seen in a Ni-Mn-AL single crystal with recoverable strain of 0.2% [137]. Later research into tuning $T_M$ to produce a usable room temperature magnetic actuator/sensor has been performed, with Ni$_2$MnGa single crystal material producing a recoverable strain of up to 10%.

**Non-Stoichiometric Ni$_2$MnGa**

It has been shown in a number of experimental studies [20][21][22][23], that the composition of the Ni-Mn-Ga Heusler alloys has a significant effect on phase transition temperature (e.g. N$_2$MnGa $T_M$ = 202 K [21], Ni$_{2.1}$Mn$_{0.9}$Ga $T_M$ = 250 K [20]). This has been the focus of a lot of research to not only understand the mechanisms present in the FSME but also for more phenomenological studies trying to produce usable FSMAs.

The tuning of $T_M$ and $T_C$ can be controlled through composition variations (Ni$_{2+X,Y}$Mn$_{1-X}$Ga$_{1-Y}$) [22], however, this can alter the maximum recoverable strain and other mechanical properties of the alloys. This work has shown that increasing the valence electron per atoms (e/a) for the alloy increases $T_M$. The phase diagram for Ni$_{2+X}$Mn$_{1-X}$Ga below clearly shows this relationship (Figure 4.4). With e/a for each composition calculated using:

$$e/a = \frac{\left(10 \times x_{Ni} + 7 \times x_{Mn} + 3 \times x_{Ga}\right)}{4}$$

(4.1)

Where $x_i$ is the bulk atomic concentration of the element $i$. 
The numbers: 10, 7 and 3 are the valence electron numbers for Ni, Mn and Ga respectively (Ni[3d⁸4s²], Mn[3d⁵s²], and Ga[4s²4p¹])

Figure 4.4: Phase diagram for Ni₂₋ₓMnₓ₋₁Ga for varying concentration of Ni and e/a (Data from [20][21][22][23] (Stoichiometric at e/a = 7.5). TM = Martensitic transition and TC = Curie Temperature

Similar systematic studies of other off-stoichiometric compositions in the form of Ni₂₋ₓMn₁₊ₓGa [129] and Ni₂₋ₓMnₓGa₁₋ₓ [130]. have been performed but for limited variation in compositions.

The above relationship between e/a and T_C is consistent across the measured data excluding the region between X = 0.19 and 0.22 (e/a = 7.6425 to 7.665) when T_M and T_C occur at the same temperature.

The decrease in T_C with respect to e/a is explained by the increase in displacement between the Mn atoms in the Ni₂₋ₓMn₁₊ₓGa alloys [21][20] [22][23], with the majority of the magnetic moment localized on the Mn atoms. Increasing the distance between them reduces the magnetic interaction energy, therefore reducing the energy required to disorder.
This variability between differing atomic ratios makes it difficult to produce a simple relationship between e/a and $T_C$ or $T_M$ for $\text{Ni}_{2+X,Y}\text{Mn}_{1-X}\text{Ga}_{1-Y}$. Reducing the Ni content from the stoichiometric composition of $\text{Ni}_{2+X}\text{Mn}_{1-X}\text{Ga}$ has been shown to lead to $T_C$ continuing the previously observed relationship with e/a (e/a decrease, $T_C$ increase). In contrast, $T_M$ decreased initially at low Ni-depletion, but shows a minimum at $X = -0.5$, before increasing again ($T_M$ at $\text{NiMn}_2\text{Ga} = 286$ K) [138].

The example of $\text{Mn}_2\text{NiGa}$ as an alternative composition to $\text{Ni}_2\text{MnGa}$ has also received a lot of interest since it was first postulated as an SMA. Like $\text{Ni}_2\text{MnGa}$, $\text{Mn}_2\text{NiGa}$ is a FSMA, but with a $T_M$ below room temperature ($T_M = 270$ K, $T_C = 588$ K). At present there is some debate about the crystalline structure of $\text{Mn}_2\text{NiGa}$, with some claiming Fm-3m with $L_{21}$B ordering [12][132] and other work suggesting it has a F-43m structure [133].

$\text{Mn}_2\text{NiGa}$ is also interesting because early studies of $\text{Ni}_{2-x}\text{Mn}_{1+x}\text{Ga}$ with excess Mn, showed that the moment on Mn atoms in Ni locations aligned anti-ferromagnetically with those on Mn sites [134]. However, in $\text{Mn}_2\text{NiGa}$ this is not the case with the moments on the Mn atoms aligning ferro-magnetically.

The experimentation in varying composition such as $\text{Mn}_2\text{NiGa}$, and off-stoichiometric $\text{Ni}_2\text{MnGa}$, is an attempt to produce a more practical FSMA, but another method of tuning the properties involves the addition of further alloying elements ($\text{Ni}_{2-X}\text{Mn}_{1-Y}\text{Ga}_{1-Z}\text{A}_{X+Y+Z}$, $\text{A} = \text{Fe}$[139], Co[139]) with varying success. Recent work performed by K.Neumann [136], focusing on the isoelectronic alloy $\text{Ni}_2\text{Mn}_x(\text{CrFe})_{1-x/2}\text{Ga}$, which has the same average valance electron number for any value of $X$, and comparing the change in physical properties (e.g. $T_m$ and $T_C$) with $\text{Ni}_2\text{MnGa}$, suggests that local lattice distortions have a more significant effect than band filling with valance electrons (e/a).
A final approach for the tuning of the Ni$_2$MnGa properties has been to use different annealing techniques [26][97]. In terms of making practical FSMA components, a lot of work is being focused on thin films [97][141][143] through microstructural analysis and deposition techniques, with a study in 2006 showing that ordering in the crystal structure is very important and can result in the loss of ferromagnetism in disordered Ni$_2$MnGa films [140].

In addition to the work focused on tuning and understanding $T_M$ and $T_C$, investigation of the pre-martensite phase transition in Ni$_2$MnGa alloys has been performed. This has shown that unlike the $T_C$ and $T_M$ transitions, the pre-martensitic phase transition ($T_{PM}$) shows very little change due to composition across the concentration in Ni$_{2+X}$Mn$_{1-X}$Ga for $X = 0$ to 0.1 [109]. Above this concentration the pre-martensitic transition disappears/merges with the martensitic transition [109].

The structure of the non-stoichiometric Ni$_2$MnGa alloys have been shown to have an effect on the c/a crystal structure ratio in the tetragonal martensitic phase [106], and an abrupt change between $c/a<1$ to $c/a > 1$ occurs at $e/a=7.7$ [106], above which $T_M>T_C$.

The high temperature order-disorder phenomenon has received very little investigation, in spite of the effect of the ordering on the stability of the cubic structure at low temperatures [110].

However, one study investigates the L2$_1$-B2 and B2-A2 transitions in Ni$_2$Mn$_{1+X}$Ga$_{1-X}$ between $X=0$ and 1 [69]. This study produced an approximation of the interaction energy between nearest and next-nearest neighbour using a Hartree-Fock approach and used a Bragg-Williams-Gorski approximation to investigate the transition temperature (summary of the BWG given in section 2.3). This theoretical and experimental study showed that the order/disorder transition temperatures followed the predicted trends. However, the models produced (interaction energy and BWG) did not fit the measured data perfectly. A second study of the high temperature order/disorder phase transition [142] in Ni$_{55}$Mn$_{20-X}$Ga$_{25+X}$ ($x=0$ to 2),
demonstrates a similar e/a relationship to ordering temperatures (see figure below), but offset slightly.

Figure 4.5: Order-disorder relationships to e/a for $\text{Ni}_{2-x}\text{Mn}_{1+x}\text{Ga}$ and $\text{Ni}_{55-x}\text{Mn}_{20}\text{Ga}_{25+x}$.

The potential direct effect on lower temperature physical properties of the higher temperature phase transition [144] [140] and the relationship of local distortions with the lower temperature physical characteristics of a FSMA such as $\text{Ni}_2\text{MnGa}$ [136] would suggest this area is one that requires further clarification to complete the structure/crystallographic understanding of this type of material.

One of the key areas and reasons for tuning $T_M$ is to produce a martensitic ferromagnetic material at or near room temperature which would allow for practical application of the magnetically induced deformation that make FSMAs so interesting. Composition has a significant effect on not only the maximum possible induced strain but also the field strength required.

The following papers discuss the field strength to induced strain for various compositions: [145], [146], [147], [149] [148], [132]. Recoverable strains of up
to 10% have been observed in near stoichiometric Ni$_2$MnGa and since this deformation is not diffusion based, the transition is very quick with the application of a magnetic field (H) [150]. To date, no phase diagram for induced strain as a function of magnetic field for variations in composition has been produced.

In addition to the work looking at the magnetic induced deformation of variant re-orientation, research has been performed to use the effect of a magnetic field on the martensitic phase transition temperature (in a magnetic field $T_M$ increases [151],[126]), and the tuning of the alloy composition so the application of the magnetically induced martensitic phase transition occurs near room temperature. An excellent candidate for this process is Mn$_2$NiGa, where the recoverable strain during the structural transition is approximately 20%, with $T_M$ = 270 K [35].

The wide temperature range over which the composition of Ni-Mn-Ga alloys can be tuned to produce the SME means that several compositions have been used as ‘High Temperature Shape Memory Alloys’ (HTSMA) [18]. The high operating temperature of systems/applications using the HTSMA Ni-Mn-Ga alloys ($T_M = 750$ K) means that they age rapidly, due to an increased rate of diffusion of the alloy elements [18]. A systematic study of Ni-Mn-Ga HTSMA’s showed that the aging effect could reduce $T_M$ by 10 to 20 K in less than 20 cycles (Martensite to Austenite) [18][153][14].

The aging effect of lower temperature Ni-Mn-Ga SMA’s has also been studied, showing that these are also susceptible to aging effects. A study looking at aging of Mn$_{52}$Ni$_{25}$Ga$_{22}$, shows that $T_M$ can be affected by aging at elevated temperature within 10 minutes at 773 K [153]. The study showed that for 60 minutes aging at 773 K, the martensitic phase transition fell by 40 K [153]. Further research into the aging effect on the martensitic phase transition temperatures, and the amount of recoverable strain, is being performed considering heating rate, temperature, duration, number of transition cycles, etc [14]. There has also been some work performed looking at room temperature aging of Ni$_2$MnGa alloys to investigate the thermal
stability of the material, and alternative manufacturing techniques [156] that may help extend life.

In addition to being an SMA several Ni-Mn-Ga alloys are ‘Two-Way Shape Memory Alloys’ (TWSMA’s). The advantage of TWSMA controlled using the magnetically induced martensitic phase transition (over magnetic-deformation) is that the volume change accompanying the martensitic transition can be up to 20% [145], and the loads required to retard such a transition are much higher than for other types of actuators [150]. Also initiating the phase transition through a magnetic field is easier to achieve in most applications than heating or cooling.

**Theoretical Studies**

Theoretical studies of Ni$_2$MnGa Heusler alloys are either working with the measured data to produce a phenomenological models [152],[158] [160] to describe the FSME process or first principle modelling [154], [82], [162] of the system to produce phase diagrams and phase stability information.

It has been shown that the structural and magnetic properties of Ni$_2$MnGa can be determined accurately with the use band structure calculation and *ab initio* calculations [25] [164] base on modelling of the electron DOS.

Studies performed to understand the phase transitions (T$_M$, T$_C$ and T$_P$) have been undertaken using numerical methods such as Density Function theory [26] [166] [168] [169], Cluster Variation methods [125], Monte-Carlo simulations [28] [162] and muffin-tin approximations such as Korringa-Kohn-Rostocker (KKR) [24].

Density functional theory (DFT)[170], and Hartree-fock [171], are two of the many types of *ab initio* modelling techniques to help model physical and chemical processes, such as internal energy and specific heat. In this context *ab initio* is generally accepted to mean ‘from first principles of quantum mechanics’, and is mainly focussed on determination of the electron interactions and electronic structure in condensed matter.
DFT is widely considered as the backbone of atomic-scale computational physics and is based on the determination of ground state electron charge density [170]. DFT has been successfully used in the modelling of the physical properties of a number of many-electron systems such as molecules and solids [170]. DFT works by the determination of the electron density function to solve the Schrodinger equation and unlike other techniques, such as Hartree-Fock that directly solve the wave function, the use of electron density functional drastically reduces the solution time since electron density is only a function of x,y,z co-ordinates [170].

Hartree-fock [171] is concerned with the determination of the wave-function and energy of quantum-mechanical systems, and is typically used to solve the time-independent Schrodinger equation for atoms, molecules and solids. The method works by considering each electron in the system as a stand-alone orbital; each electron interacts indirectly through the presence of an effective potential field permeating the system. The determination of a variation wave function based on the single-electron wave-function of the orbitals is the Hartree approximation[172] the solving of these wave function equations is normally performed iteratively.

Other widely used modelling techniques are the cluster variation method (CVM) [157], the muffin tin approximation [24] and Monte Carlo simulation [25][162]. CVM [173] determines internal energy and entropy of a system by approximation using long and short order parameters, and determining the equilibrium state by minimizing the free energy of a system in relation to these factors. The CVM method is especially useful for the determination of regions of instability and phase separation, and for the calculation of phase transition temperatures [173].

The muffin tin approximation [174] is used to simplify the potential in a complex atomic system (e.g. lattice structure). It simplifies the complex system so that is can be described as a number of non-overlapping spheres surrounding atomic locations. Inside the spheres the potential is screened.
and spherically symmetric about the nucleus. Between the spheres the potential is essentially uniform [174]. Many techniques have been used to solve electronic wave equations in this space, such as KKR [24] which calculates the electronic band structure of the min-tin approximation field using a green-function method [24]. The KKR wave-functions/potentials consist of two parts to treat with the different potentials in the potential field (i.e. atom location, interstitial space).

Monte Carlo simulations are a class of computational modelling methods that uses randomisation of parameters in a model to fit the model to observed data. Typically, a simulation can be run many times to tune the parameters to the required data. Monte Carlo simulation can also be used to solve complex mathematical models for which an empirical solution can be found, such as the Schrödinger equation, and as with other techniques once this is determined then the internal energy and entropy can be found.

These various theoretical modelling techniques all rely on the modelling of the internal energy of the system under varying temperature and structural compositions, and what the interaction between structural and magnetic coupling are being considered.

Modelling has been shown to predict the phase transitions and phases diagram for stoichiometric Ni$_{2}$MnGa [24] [25] [155] [157]. Modelling concerning non-stoichiometric compositions has been carried out that predicts electronic and phonon properties [175], and simple models have some success in describing large scale magnetic effects [175]. However, work is still underway on to understand the full range of interaction in the multifunctional SMA alloys (e.g. magnetoelastic coupling [159]) including how magnetic superelasticity, magnetic shape memory, and magnetocaloric effects all interact and how the phonon-magnetic interaction drives each [148] [176] [169]. The verification of these models requires the complete phase diagram of the material and at present some areas are lacking in data.
To date the development of non-stoichiometric modelling has produced some success in confirming the relationship between average valance electrons per unit cell (e/a) and physical characteristics (e.g. martensitic transition temperature, the stability of the cubic structure and the vibrational spectra) though the use of DFT [166] [168] [169].

DFT modelling has also been used to consider non-stoichiometric Ni$_2$MnGa$_{1+x}$. This work postulated that Ga$_2$NiMn would be a ferromagnetic SMA. Experimental work performed as part of the same project confirmed that Ga$_2$NiMn was a FSMA, with T$_M$ = 780 K and T$_C$ = 330 K [177], but a full phase diagram (including order/disorder, T$_C$, T$_M$ and melt) has yet to be produced for the compositions Ni$_{2-x}$MnGa$_{1+x}$, x = 0 – 1.

Modelling continues to be an important part of the understanding of the process and interactions taking place in Ni$_2$MnGa alloys. The success of these models, when compared to real data is improving with better understanding of the fundamental processes involved with the properties of the material, and the interaction between these properties.

**Magnetocaloric Effect (MCE)**

Ni$_2$MnGa and non-Stoichiometric alloys have been shown to have magnetocaloric properties [161], which has application in refrigerators by replacing the current vapour-pressure compressor configuration with a permanent magnet and a refrigerant material [163].

The effect of cooling a metal with application of a field (magnetic refrigeration) was demonstrated in 1881 in iron, and later in some FSMAs. This process involved is very similar to the Carnot Cycle for compressible gases [163], but using the magnetocaloric material [164]. In addition, the MCE in Ni$_2$MnGa alloys is reversible unlike other MCE materials [165].

The advantage of the FSMAs in cooling devices is that the magnetocaloric MCE is increased if, during the transition from ordered to disordered magnetic
moments the material also undergoes a solid/solid phase transition [161][165]. Ni$_{2.2}$Mn$_{0.8}$Ga is of interest as $T_M$ and $T_C$ occur at the sample temperature.

Modelling of the magnetocaloric effect in Ni$_2$MnGa suggests that it should have a magnetic entropy change of a similar order of magnitude to those measured in the best non-SMA MCE materials (known as Great Magnetocaloric Effect materials, or GMCE), such as gadolinium alloys [165]. However, experimental studies suggest this is not the case with stoichiometric Ni$_2$MnGa [178], but compositions with depleted Mn (substituted with Ni) show improved magnetocaloric responses for composition with $T_M$< $T_C$ [148].

The research into the MCE in Ni$_2$MnGa is focused upon investigating the production and alloying effects [148], and first principle calculation to predict the process [179].

### 4.3 Experimental methodology
The determination of high temperature phase transitions for Ni$_{2-x}$Mn$_{1+x}$Ga was undertaken using specific heat ($C_P$) measurement. The use of $C_P$ measurement allows for visualisation of the predicted order-disorder phase transitions as well as characterising the thermal properties of the material (not previously measured).

The range of alloy compositions comprising the investigation were: Ni$_{2.2}$Mn$_{0.8}$Ga, Ni$_2$MnGa, Ni$_{1.8}$Mn$_{1.2}$Ga, Ni$_{1.2}$Mn$_{1.8}$Ga, and NiMn$_2$Ga. These compositions represent the extremes of nickel depleted Ni$_2$MnGa compositions. Interpolation between the two groups (just off-stoichiometric Ni$_2$MnGa and just off-stoichiometric NiMn$_2$Ga) should provide a good approximation of the phase diagram between these points.
4.3.1 Sample preparation

The sample alloys were produced, in house at Loughborough University, using an argon arc furnace to melt the constituent alloying elements, in a water cooled crucible. To maximise homogeneity of the melt, the alloy ingot was rotated at least three times during melting. The constituent alloying elements used were supplied with certification stating a purity of at least 99.999%.

The alloyed ingots (approximately 20 g) were then annealed in argon filled quartz tubes at 1000°C (1273 K) for at least three days before being allowed to cool naturally. This annealing process was undertaken to further improve the homogeneity of the sample ingots. From the annealed ingots small square DSC samples (3 mm x 3 mm x 1.5 mm) were cut using spark erosion.

In addition to the annealed sample three ingots (nominal composition Ni$_{2.2}$Mn$_{0.8}$Ga, Ni$_2$MnGa and Ni$_{1.8}$Mn$_{1.2}$Ga) were produced that were not annealed. These were used during the initial measurements on the DSC to determine the best test profile and also to investigate an anomaly, described in a paper published in 2002, at or near the L2$_1$-B2 phase transition for Ni$_2$MnGa [167].

The sample ingots produced using the argon arc melting furnace showed a weigh loss of less than 1% during melting.
4.3.2 Apparatus

The DSC measurements of the Ni$_{2-x}$Mn$_{1+x}$Ga samples were performed on two DSC systems one a power compensation DSC and the other a heat flux DSC. While both use the same principle (See section 2.3.3) the measurements performed are different. The heat flux DSC contains an empty reference pan and sample pan, both in a single argon purged furnace which heats and cools at a set rate. Since both pans are assumed to be identical and located in similar (symmetric) locations in the furnace they should receive the same ‘heat’ energy from the furnace. The difference in heat capacity between the pans (due to the sample material) results in a temperature differential between the pans, this is used to determine specific heat. This difference in thermal mass between pans also allows for visualisation of the phase transition in heat flux data.

The power compensation DSC uses two identical but separate argon purged furnace chambers, one for the sample pan and one for the reference pan. The control system heats and cools both chambers over identical temperature profiles, but the difference in heat capacities of the pans, means each chamber requires a different power for the same heating rate. This difference in supplied heat is then used to determine specific heat (or characterise phase transition temperatures).

The measurement of specific heat capacity using a DSC requires three separate measurements all of which must follow identical heating/cooling profiles. The first run is with both pans empty to give a baseline for the system; the second is with a reference material (with a known specific heat) in the sample pan, to produce a sensitivity curve for the system; and the final run is with a sample in the sample pan. Ideally the reference material and sample should be physically the same and with similar specific heat or this can result in a poor conversion from heat flux (temperature differential) data into specific heat.
4.4 Results

4.4.1 X-ray diffraction

The X-ray diffraction (XRD) of the three un-annealed samples was performed using a diffractometer using a non-monochromatic copper source on samples taken from off-cuts of the DSC samples. Typically the XRD samples were 1 x 1 x 3 mm in size. The XRD measurements were performed to confirm that the argon arc alloying process had produced a single phase alloy of the predicted composition.

This confirmation was needed to ensure the validity of the stated compositions for each sample prior to the DSC measurement performed to characterise phase transitions (Section 4.4.2) with respect to composition. The annealed samples did not undergo XRD analysis as the annealing process has been shown in the past to produce reliable homogeneous samples for Ni$_2$MnGa and non-stoichiometric compositions.

The XRD patterns measured for the three samples can be used to determine information about the structure of each sample/composition. The XRD data provides structural information in four key ways through:

1. **Peak position** – provides general crystallographic information (lattice parameters, Space group, symmetry, centring, etc.)
2. **Peak intensities** – used with a model provides information on atoms present and relative locations.
3. **Peak width** – microstructure, and atomic displacement information
4. **Background oscillations** – can provide information on short range ordering.

The analysis of the XRD data to produce the above information is achieved by fitting of a mathematical model to the measured data. The modelling parameters (e.g. lattice parameters, space group, unit cell, atomic occupancies, etc.) are refined to improve the fit between observed data and the model.
Two widely used analytical techniques for the fitting process are; Pawley [181] or Rietveld [181]. Both the techniques are iterative methods that fit modelled XRD data to the measured data by incrementally varying user specified parameters.

The Pawley technique [181] is a whole powder pattern refinement that can be used to optimise structural parameters such as lattice spacing, with only the space group and unit cell being known. The method works by fitting Bragg reflections with arbitrary peak intensities to the measured data, and varying the lattice parameters (d in Bragg equation, below [182]) to align the modelled and measured data.

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

(4.2)

Where, n is an integer, \( \lambda \) is the wavelength of the incident ray, d is the spacing between the planes in the atomic lattice, and \( \theta \) is the angle between the incident ray and the scattering plane.

Unlike Pawley, Rietveld refinement uses a structural model for comparison with measured data [180]. The model includes a wide range of physical parameters from crystal structure information (space group, lattice parameters, atomic location and occupancies, etc.) to sample and measurement specific factors (temperature effects, internal strain, absorption coefficients, sample geometry, background, etc).

Like Pawley refinement the Rietveld technique uses a non-linear least square regression to optimize the parameters of the model. Non-linear least square regression is an iterative process that refines the parameter to minimise the sum of the square of the difference between the model and measured data (minimize \( \chi^2 \)).

The fact that the Rietveld refinement is based on the structural model of the material means that it can provide information on a wide range of parameters, including structural parameters, atomic locations and relative occupancies, profile parameters (from instrument and sample effects), and background
effects, where as Pawley only provides structural parameter information [181]. The selection of which process to use is dependent on the nature and quality of the XRD pattern.

**Analysis**

The measured materials, Ni$_2$MnGa, Ni$_{1.8}$Mn$_{1.2}$Ga and Ni$_{2.2}$Mn$_{0.8}$Ga should at room temperature have the following structures:

1. Cubic space group:Fm-3m with L2$_1$ ordering, for Ni$_2$MnGa and Ni$_{1.8}$Mn$_{1.2}$Ga, $T_m$(Ni$_2$) = 202 K and $T_m$(Ni$_{1.8}$) = 186K, see Section 4.2
2. Tetragonal – Ni$_{2.2}$Mn$_{0.8}$Ga, $T_m$(Ni$_{2.2}$) = 338K [43], see Section 4.2

The above crystal structure for the Ni$_2$MnGa compositions are as observed in solution annealed samples, but the measured XRD data for the Ni$_2$MnGa, Ni$_{1.8}$Mn$_{1.2}$Ga, and Ni$_{2.2}$Mn$_{0.8}$Ga samples have not been annealed. Therefore, the material could be in any of the phases predicted for Ni$_2$MnGa materials. Assuming that the alloying process has produced a single phase alloys with the predicted composition, four possible phase for Ni$_2$MnGa, which are

1. Cubic Fm-3m – Highly ordered - L2$_1$
2. Cubic Fm-3m – Partially Ordered – B2
3. Cubic Fm-3m – Totally Disordered – A2
4. Tetragonal/Orthorhombic  with a 3, 5, 7 and 14 layer modulation (see section 4.2)

The different phases of Ni$_2$MnGa listed above have distinctive XRD patterns, Figure 4.6 below shows modelled XRD profiles for the cubic phases listed above and an example tetragonal structure as suggested in reference [43]. These models were created using FullProf Suite crystal calculator [184], using the structures described in Section 4.2.
High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga

Figure 4.6: Modelled XRD data for Ni$_2$Mn$_x$Ga in (a) A2 disordered state cubic phase, (b) B2 partially ordered cubic phase, (c) L21 ordered Cubic phase and (d) low temperature Tetragonal phase (Martensite)
The three un-annealed samples underwent XRD analysis between 2θ = 5° and 85°. (Figure 4.7, Figure 4.8, and Figure 4.9). Figure 4.10 shows all three diffraction patterns together. A qualitative assessment of the profiles showed that the Ni$_2$MnGa and Ni$_{1.8}$Mn$_{1.2}$Ga samples produced XRD data in accordance with expected cubic structure (Fm-3m) [19], but the limited number of observable peak, and the relatively low intensity of those visible, make it difficult to determine if the structure is ordered (L2$_1$) or disordered (B2 or A2).

The third sample Ni$_{2.2}$Mn$_{0.8}$Ga was predicted to have a tetragonal structure at room temperature, but has the same cubic structure as the other two alloys. At least two possible explanations for this apparent anomaly are available, either the alloying process did not produce the desired Heusler alloy or the fact that the sample was measured in an as cast form with no annealing may have resulted in the material remaining in the high temperature phase (Ni$_{2.2}$Mn$_{0.8}$Ga, T$_M$ = 338K [43], i.e. it may be in a metastable state). This latter effect could be due to the rapid cooling of the sample caused by the cooling water flowing around the argon arc crucible.

![Ni$_2$MnGa XRD results, and reference data](image)

*Figure 4.7: Ni$_2$MnGa XRD results, and reference data*
High Temperature Specific Heat Capacity Measurement of Ni$_{2+X}$Mn$_{1-X}$Ga

Figure 4.8: Ni$_{2.2}$Mn$_{0.8}$Ga XRD result, and reference data

Figure 4.9: Ni$_{1.8}$Mn$_{1.2}$Ga XRD result and reference data
A set of guidelines presented by the ‘International Union of Crystallography Commission on Powder Diffraction’ (1999) [183] describes the Rietveld process and outlines when XRD pattern data is appropriate for Rietveld refinement. These guidelines dictate that of the three samples measured, the Ni$_2$MnGa data provided the best candidate for Rietveld analysis, due to the high relative intensity of the measured peaks and the overall clarity of each peak (Figure 4.7). The broader and less well defined peaks in the Ni$_{2.2}$Mn$_{0.8}$Ga and Ni$_{1.8}$Mn$_{1.2}$Ga XRD data, coupled with the limited range of data, make Rietveld a poor analysis tool for these two materials.

Therefore, Pawley analysis has been used to analyse the XRD data from all three patterns to allow direct comparison between the measured values, without any interference from using different analysis techniques. An additional Rietveld refinement was performed for the Ni$_2$MnGa data to determine if additional information (not observable using Pawley analysis) can be provided by the XRD data.

**Pawley Analysis of Ni$_2$MnGa, Ni$_{1.8}$Mn$_{1.2}$Ga and Ni$_{2.2}$Mn$_{0.8}$Ga**

The Pawley analysis of the three Ni$_{2-x}$Mn$_{1+x}$Ga compounds was performed using FullProf [184] using the ‘pattern/profile’ matching feature. The process is identical to the Rietveld analysis performed by the program, but with the
atomic composition, relative atomic position and occupancy parameters removed from the analysis.

Using the Pawley technique resulted in the following lattice parameters for the three compositions:

<table>
<thead>
<tr>
<th>Composition</th>
<th>e/a</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{1.8}$Mn$</em>{1.2}$Ga</td>
<td>7.35</td>
<td>5.8589 ± 0.0026</td>
</tr>
<tr>
<td>Ni$<em>2$Mn$</em>{0.8}$Ga</td>
<td>7.65</td>
<td>5.8364 ± 0.0032</td>
</tr>
</tbody>
</table>

Table 4.1: Measured lattice parameters determined using Pawley analysis of XRD profiles for Ni$_2$Mn$_{0.8}$Ga, Ni$_{1.8}$Mn$_{1.2}$Ga and Ni$_{2.2}$Mn$_{0.8}$Ga.

The measured lattice parameter for Ni$_2$Mn$_{0.8}$Ga is slightly higher than has been observed in other studies, with the accepted value being 5.8285 Å [1]. The difference between measured and accepted value is less than 0.04%, but given the scatter in published data (Figure 4.12) and the fact that this sample is un-annealed this size of error is to be expected.

The Pawley analysis also shows that the material measured consisted of a single phase with a cubic structure, with an Fm-3m space group. The presence of only a single structural phase confirms that the argon arc melting technique produced homogenous cast material but with the structure of the Ni$_{2.2}$Mn$_{0.8}$Ga sample pinned in the high temperature cubic phase, due to quenching. All samples may be in a high temperature phase, e.g. B2 partially-ordered or A2 disordered, but from the current data presented here the Pawley refinements are not able to determine this.
Rietveld Analysis of Ni$_2$MnGa

The Rietveld refinement of the XRD pattern for the Ni$_2$MnGa sample produced a fit with a Chi-squared of 16.4 (Figure 4.11).

![Rietveld Analysis of Un-annealed Ni$_2$MnGa XRD data](Image)

The above fit assumes that the sample has B2 partially-disordered, Fm-3m structure. The Rietveld refinement producing a lattice parameter of 5.831437 ± 0.00028 Å, and determined the measured composition of the single phase as: Ni$_{200}$Mn$_{99}$Ga$_{100}$, with uncertainty on those atomic occupancies of between 1% and 3%. The analysis also provided thermal displacement factors (B) for the three lattice location in the Fm-3m Heusler structure (Table below)

<table>
<thead>
<tr>
<th>Location</th>
<th>Occupancy</th>
<th>Thermal (B) Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0,0)</td>
<td>50% Mn, 50% Ga</td>
<td>1.40 ± 0.48</td>
</tr>
<tr>
<td>(¼,¼,¼)</td>
<td>100% Ni</td>
<td>0.80 ± 0.29</td>
</tr>
<tr>
<td>(½,½,½)</td>
<td>50% Mn, 50% Ga</td>
<td>1.45 ± 0.52</td>
</tr>
</tbody>
</table>

*Table 4.2: Rietveld refinement results for Ni$_2$MnGa sample*
Further refinement to improve the fit is limited by the quality (2θ range, clarity of peaks, resolution, etc.) of the data, and it is suggested that better quality raw data be produced using either neutron diffraction or XRD using synchrotron source or a lab type system, paying close attention to sample preparation (increased sample size, polish surface, focus beam, etc.) and improving data capture (higher resolution data) [183].

Overall the refinement clearly supports the Pawley analysis that the sample consisted of a single phase of a cubic structure in the form of Fm-3m. The lattice parameter for the Rietveld refinement was $a = 5.8314 \, \text{Å}$, with the Pawley analysis giving a value of $a = 5.8308 \, \text{Å}$. The Rietveld refinement suggests that the composition of the ‘Ni$_2$MnGa’ material is slightly off, but given the deviation from stoichiometric indicated by the analysis (≈0.25%) and the larger error on the refinement ($\chi^2 = 16.4$) the material should continue to be treated as stoichiometric.

**Summary**

The Pawley analysis of the three XRD profiles showed that all three materials were in a single cubic phase (space group Fm-3m) during XRD measurement, but the resolution of the peaks make it difficult to determine how the system was ordered. Using a qualitative analysis of the XRD profile, comparing the modelled data in Figure 4.6 and measured data in Figure 4.10, the three systems were most likely in L2$_1$ or B2 order, since they have no discernable [222] or [400] peaks. The higher relative peak intensity expected for peaks [222] and [420] in the A2 phase make this phase least likely. The Rietveld refinement supports the B2 partially–ordered phase, but the large $\chi^2$ and similarities between L2$_1$ and B2 XRD patterns make it difficult to guarantee the B2 structure used in the refinement.

The analysis of the three profiles shows that the lattice parameter in the cubic phase for all three compositions was between 5.830 and 5.865Å. These
measured results compare well with other studies performed on Ni$_2$MnGa and off-stoichiometric compositions (See Figure 4.12 below)

![Figure 4.12: Lattice parameter for cubic Ni$_{2-x-y}$Mn$_{1+x}$Ga$_{1+y}$ compositions.](image)

Of the three XRD profiles only the Ni$_2$MnGa material was appropriate for Rietveld analysis, as the other two materials showed too much peak broadening and low intensity relative to the background. The Rietveld refinement confirms the results of the Pawley analysis, e.g. Fm-3m single phase composition of all three samples.

The broadening and lower relative intensity of the peaks for the nickel rich/depleted samples, which make them invalid for Rietveld refinement, could be a result of residual stress in the lattice arising from the rapid cooling after the melting process or a fine grain structure in the samples.

The XRD analysis for the Ni$_{2.2}$Mn$_{0.8}$Ga sample, which at room temperature should have the martensitic (tetragonal) structure rather than the cubic structure (Fm-3m) observed has the least well defined peaks of the three samples. The broader and lower peaks evident in the XRD analysis for this sample supports the notion that the sample was quenched by the cooling system in the argon arc furnace and therefore retains the high temperature
cubic structure (with the peak broadening due to the residual stress in the lattice structure or generation of small crystalline size).

The notion of quenching the $\text{Ni}_{2.2}\text{Mn}_{0.8}\text{Ga}$ causing the retention of the high temperature cubic phase is further supported by the DSC testing. The DSC measurements showed after multiple heating and cooling cycles (more than 3) in the lower temperature DSC (between room temperature and 800K) a phase transition at approximately 338 K (see Section 4.4.2). This transition temperature compares well with the martensitic phase transition temperatures observed in other measurements (Figure 4.4).

### 4.4.2 Differential scanning calorimeter measurements

The measurement of the specific heat of the sample from room temperature to 1400 K required the use of two DSC systems. The Perkin-Elmer DSC 7 for the low temperature range (room temperature to 900 K) and the Netzsch DSC 404 for the high temperature measurements (500 K to 1400 K).

The low temperature range testing allowed for measurement of the Curie temperature and martensitic phase transitions, whilst the high temperature measurements were used to investigate the higher temperature order/disorder phase transition.

The following two sections present the results of the low and high temperature measurements.

The problems inherent with using small samples for a DSC measurement and the nature of the materials meant that measurement of the specific heat capacity of the $\text{Ni}_{2-x}\text{Mn}_{1+x}\text{Ga}$ alloys was difficult and only a small number of successful measurements of specific heat were achieved. However, for the data that could not be converted to specific heat successfully the phase transition peaks are clearly identifiable from the DSC signal and as such can be used for phase transition temperature characterisation.
It was found early, on that many of the samples required multiple heating and cooling cycles before the phase transition peaks became visible, and as such this increased the required testing time for each material.

**Low temperature (293 K to 900 K)**
The ‘low temperature’ results between room temperature (293 K) and 900 K, were performed using a Perkin-Elmer DSC 7 power compensation DSC.

The DSC heated and cooled the samples at a rate of between 5 K/min and 20 K per minute. After the first three samples were measured, it was decided that a heating rate of 10 K/min produced the best signal to noise ratio. All subsequent measurements were made using this heating rate. To allow an accurate comparison between samples the data discussed below only concerns samples measured using a 10 K/minute heating/cooling rate.

The first three samples measured were the un-annealed Ni$_{1.8}$Mn$_{1.2}$Ga, Ni$_2$MnGa and Ni$_{2.2}$Mn$_{0.8}$Ga alloys. The specific heat data for the three samples is shown below (Figure 4.13).

*Figure 4.13: Measured Specific heat for Ni$_{1.8}$Mn$_{1.2}$Ga, Ni$_2$MnGa, and Ni$_{2.2}$Mn$_{0.8}$Ga between room temperature (293 K) and 900 K.*
The poor conversion of the DSC signal to specific heat was due to the dissimilarities between the reference sample and alloy sample (reference sample round and smooth, alloy sample smaller, rectangular and rough), and the fact the outer surface of the sample appeared to react during heating. This reaction was evident when removing the samples from the test equipment, as all three samples had discoloured during heating (turning green), even though the testing was performing in argon purged chambers.

The relatively small size and surface area to volume ratio of such small samples is an issue inherent with DSC measurements. This issue can make surface effects dominant during DSC measurements and affect the accuracy of specific heat results.

Of the other four annealed samples only Ni$_{1.0}$Mn$_{2.0}$Ga produced ‘good’ specific heat data (Figure 4.14 below). The signal noise on the other alloys was unacceptable and could not be used to produce specific heat data. This successful Ni$_{1.0}$Mn$_{2.0}$Ga specific data measured during cooling was identical to all of the other measurements but unlike the others has produced usable data (the reason for the difference is unknown).
High Temperature Specific Heat Capacity Measurement of Ni$_{2-x}$Mn$_{1-x}$Ga

Figure 4.14: Measured Specific heat of Ni$_{1.0}$Mn$_{2.0}$Ga between 400 K and 800 K.

The poor conversion to specific heat does not affect the accuracy of phase transition temperature determination using the heat flux data. Figure 4.15 to Figure 4.19 below show the phase transition peaks in the heat flux data for annealed ingots of Ni$_{1}$Mn$_{2}$Ga, Ni$_{1.2}$Mn$_{1.8}$Ga, Ni$_{1.8}$Mn$_{1.2}$Ga and Ni$_{2}$MnGa.

Figure 4.15: DSC measurement of Ni$_{1.0}$Mn$_{2.0}$Ga, showing the Curie temperature phase transition peak.
Figure 4.16: DSC measurement of $\text{Ni}_{1.2}\text{Mn}_{1.8}\text{Ga}$, showing the Curie temperature phase transition peak.

Figure 4.17: DSC measurement of $\text{Ni}_{1.8}\text{Mn}_{1.2}\text{Ga}$, showing the Curie temperature phase transition peak.
The Curie temperature in all five alloys measured (Figure 4.15 to Figure 4.19) has a reasonably well defined peak, but because the onset temperature is near the minimum temperature measured it can be susceptible to instrument
effects. However, the peak value of the transition peaks were clearly identifiable.

The peak widths for the majority of the observed transitions was approximately 20 K to 100 K. The peak width of all four measurements (two heating, two cooling) for Ni\textsubscript{1.2}Mn\textsubscript{1.8}Ga was much wider at between 300 K and 500 K. Widening of the peak in this fashion suggests the presence of regions of varying composition, with in the sample [167].

The measured Curie temperature for the five alloy compositions are shown in the Table below (Table 4.3). The transition temperatures are presented graphically in a phase diagram (Figure 4.35) in section 4.6.5

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Run No.</th>
<th>Measured Curie Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsubscript{1.0}Mn\textsubscript{2.0}Ga\textsubscript{1.0}</td>
<td>1</td>
<td>586</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>602</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>601</td>
</tr>
<tr>
<td></td>
<td></td>
<td>592</td>
</tr>
<tr>
<td></td>
<td></td>
<td>594</td>
</tr>
<tr>
<td>Ni\textsubscript{1.2}Mn\textsubscript{1.8}Ga\textsubscript{1.0}</td>
<td>1</td>
<td>487</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>560</td>
</tr>
<tr>
<td>Ni\textsubscript{1.8}Mn\textsubscript{1.2}Ga\textsubscript{1.0}</td>
<td>1</td>
<td>392</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>386</td>
</tr>
<tr>
<td>Ni\textsubscript{2.0}Mn\textsubscript{1.0}Ga\textsubscript{1.0}</td>
<td>1</td>
<td>378</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>374</td>
</tr>
<tr>
<td>Ni\textsubscript{2.2}Mn\textsubscript{0.8}Ga\textsubscript{1.0}</td>
<td>1</td>
<td>338</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>365</td>
</tr>
</tbody>
</table>

Table 4.3: Measured Curie temperature for Ni\textsubscript{2-x}Mn\textsubscript{1+x}Ga (X = -0.2, 0, 0.2, 0.8, and 1.0)

**High temperature (500 K to 1400 K)**

The ‘high temperature’ DSC measurements were made between 500 K and 1400 K, and performed using a Netzsch DSC 404 heat flux differential scanning calorimeter.
The alloys are predicted to undergo three structural phase transitions in this temperature range: 1. L2\textsubscript{1} to B2 order-disorder phase transition 2. B2 to A2 order-disorder phase transition 3. Melting of the alloy.

In addition, the NiMn\textsubscript{2}Ga alloys (and near compositions) may show the Curie phase transition.

To allow for clear identification of the phase transitions this section of the thesis will present only the temperature ranges of the DSC signal containing the phase transitions under discussion.

**L2\textsubscript{1}-B2 phase transition**

The L2\textsubscript{1}-B2 phase transition was clearly visible in all five alloy compositions measured (See Figure 4.20 to Figure 4.23.). Given the lack of structural measurements these peaks have been assumed to be the proposed transitions as they occur at temperatures that continue the trends observed in other measurements.

![DSC signal for Ni\textsubscript{2}MnGa, showing L2\textsubscript{1} to B2 order/disorder phase transition during heating and cooling.](image)

*Figure 4.20: DSC signal for Ni\textsubscript{2}MnGa, showing L2\textsubscript{1} to B2 order/disorder phase transition during heating and cooling.*
High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga

Figure 4.21: DSC signal for Ni$_{1.2}$Mn$_{1.8}$Ga, showing $L2_1$ to $B2$ order/disorder phase transition during heating and cooling.

Figure 4.22: DSC signal for Ni$_{1.8}$Mn$_{1.2}$Ga, showing $L2_1$ to $B2$ order/disorder phase transition during heating and cooling.
Figure 4.23: DSC signal for Ni$_2$MnGa, showing L2$_1$ to B2 order/disorder phase transition during heating and cooling.

See Figure 4.26b for the L2$_1$-B2 phase transition for Ni$_{2.2}$Mn$_{0.8}$Ga

The peaks showing the L2$_1$-B2 phase transition are well defined in all of the measured alloy compositions. Each sample showing a hysteresis of approximately 20 K to 50 K, between heating and cooling. The Table below (Table 4.4) shows the measured L2$_1$-B2 phase transition temperatures.
### Measured L2₁-B2 Phase transition Temperatures for Ni₂₋ₓMn₁₊ₓGa

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Run No.</th>
<th>Measured L2₁-B2 Phase transition Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₁.₀Mn₂.₀Ga₁.₀</td>
<td>1</td>
<td>1038 1006</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1033 1006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1036 996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1031 1012</td>
</tr>
<tr>
<td>Ni₁.₂Mn₁.₈Ga₁.₀</td>
<td>1</td>
<td>1049 1034</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1051 1029</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1056 1041</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1061 1038</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1049 1003</td>
</tr>
<tr>
<td>Ni₁.₈Mn₁.₂Ga₁.₀</td>
<td>1</td>
<td>1074 1073</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1075 1063</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1077 1059</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1077 1064</td>
</tr>
<tr>
<td>Ni₂.₀Mn₁.₀Ga₁.₀</td>
<td>1</td>
<td>1084 1052</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1082 1044</td>
</tr>
<tr>
<td>Ni₂.₂Mn₀.₈Ga₁.₀</td>
<td>1</td>
<td>1046 1046</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1046 1046</td>
</tr>
</tbody>
</table>

Table 4.4: Measured L2₁-B2 phase transition temperatures for Ni₂₋ₓMn₁₊ₓGa

(X = -0.2, 0, 0.2, 0.8, and 1.0)

### Unknown Phase transition

An unknown peak, possibly associated with some unidentified phase transition is observed in the DSC data for Ni₁.₀Mn₂.₀Ga, Ni₁.₂Mn₁.₈Ga, Ni₁.₈Mn₁.₂Ga and Ni₂.₂Mn₀.₈Ga. This peak may be due to:

- residual stress in the crystal structure due to potential chemical inhomogeneity or from rapid cooling during the annealing process
- since the anomaly is not seen in the stoichiometric Ni₂MnGa it may be an ordering between the Ni and Mn on the α₁ and α₂ lattice (for Ni depleted alloys) or on the β and γ (in Ni enriched alloys).

A further discussion of the process is considered in section 4.3 analysis.
B2 to A2 and melting

The B2 to A2 phase transitions peaks are more difficult to determine from the DSC data, due to the phase transition temperature being close to the melting temperature for the material in most cases. This may result in the merging of the two phase transition peaks, a suggested scenario for the merging of the phase transition and melting temperature is shown in Figure 4.24 below.

![Figure 4.24: DSC heat flux signal for Ni$_2$MnGa showing B2-A2 phase transition and melt temperature during heating.](image)

For the Ni$_2$MnGa measurement shown above (Figure 4.24), it is assumed that the heat flux peaks representing each event (melting and B2-A2 transition) have merged and the small bulge at 1375 K is due to the B2-A2 phase transition and the much larger peak at 1440 K is the sample melting. The other alloys show similar merging of transition and melting peaks (Figure 4.25 below).
Figure 4.25: Peak in the heat flux data for Ni$_{1.8}$Mn$_{1.2}$Ga with background data subtracted.

The ‘bulge’ in the heating cycle 1 data in Figure 4.25 above, is assumed to be a residual stress feature (see section 4.3.3) observed in other studies [16], since after the first heating the anomaly is gone.

The B2-A2 phase transition temperatures for the other four alloys are in Figure 4.26 to Figure 4.29 and Table 4.5.
High Temperature Specific Heat Capacity Measurement of Ni$_{2-x}$Mn$_{1-x}$Ga

Figure 4.26: DSC signal for Ni$_{1.0}$Mn$_{2.0}$Ga showing the A2-B2 and melting temperature phase transitions

Figure 4.27: DSC signal for Ni$_{1.2}$Mn$_{1.8}$Ga showing the A2-B2 and melting temperature phase transitions
High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga

**Figure 4.28:** DSC signal for Ni$_{1.8}$Mn$_{1.2}$Ga showing the A2-B2 and melting temperature phase transitions

**Figure 4.29:** DSC signal for Ni$_{2.2}$Mn$_{0.8}$Ga showing the A2-B2 and melting temperature phase transitions
## Table 4.5: Measured B2-A2 phase transition temperatures for Ni$_{2-x}$Mn$_{1+x}$Ga

$(X = -0.2, 0, 0.2, 0.8, \text{ and } 1.0)$

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Run No.</th>
<th>Measured B2-A2 Phase transition Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{1.0}$Mn$</em>{2.0}$Ga$_{1.0}$</td>
<td>1</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1161</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1160</td>
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<tr>
<td></td>
<td></td>
<td>1157</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1154</td>
</tr>
<tr>
<td>Ni$<em>{1.2}$Mn$</em>{1.8}$Ga$_{1.0}$</td>
<td>1</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1174</td>
</tr>
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<td></td>
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<td>1174</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1184</td>
</tr>
<tr>
<td>Ni$<em>{1.8}$Mn$</em>{1.2}$Ga$_{1.0}$</td>
<td>1</td>
<td>1299</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1256</td>
</tr>
<tr>
<td></td>
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<td>1340</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1354</td>
</tr>
<tr>
<td>Ni$<em>{2.0}$Mn$</em>{1.0}$Ga$_{1.0}$</td>
<td>1</td>
<td>*</td>
</tr>
<tr>
<td>Ni$<em>{2.2}$Mn$</em>{0.8}$Ga$_{1.0}$</td>
<td>1</td>
<td>1303</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1339</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1394</td>
</tr>
</tbody>
</table>

* Data not available due to inability to discern phase transition peak
The melt temperature results for shown in Table 4.6 below:

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Run No.</th>
<th>Measured Melting Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Heating</td>
</tr>
<tr>
<td>Ni$<em>{1.0}$Mn$</em>{2.0}$Ga$_{1.0}$</td>
<td>1</td>
<td>1180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1185</td>
</tr>
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<td></td>
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<td></td>
<td>1179</td>
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<td>1187</td>
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<td>1197</td>
</tr>
<tr>
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<tr>
<td></td>
<td></td>
<td>1202</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1202</td>
</tr>
<tr>
<td>Ni$<em>{1.8}$Mn$</em>{1.2}$Ga$_{1.0}$</td>
<td>1</td>
<td>1363</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1378</td>
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<tr>
<td></td>
<td></td>
<td>1382</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1392</td>
</tr>
<tr>
<td>Ni$<em>{2.0}$Mn$</em>{1.0}$Ga$_{1.0}$</td>
<td>1</td>
<td>1412</td>
</tr>
<tr>
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<td></td>
<td>1413</td>
</tr>
<tr>
<td>Ni$<em>{2.2}$Mn$</em>{0.8}$Ga$_{1.0}$</td>
<td>1</td>
<td>1435</td>
</tr>
<tr>
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<td></td>
<td>1430</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6: Measured melting temperatures for Ni$_{2-x}$Mn$_{1+x}$Ga ($X = -0.2, 0, 0.2, 0.8, and 1.0$)

### 4.4.3 Un-annealed samples

The three un-annealed samples that were subjected to DSC measurements had the composition: Ni$_{1.8}$Mn$_{1.2}$Ga, Ni$_{2}$MnGa and Ni$_{2.2}$Mn$_{0.8}$Ga.

These were measured using both the high temperature and low temperature DSC systems, with the predicted residual stress anomaly or ‘bulge’ clearly observed in two of the three alloys at the L2$_1$-B2 phase transition temperature (Figure 4.30).
Figure 4.30: Heat flux data for (a) Ni$_2$MnGa and (b) Ni$_{2.2}$Mn$_{0.8}$Ga, with a 2$^{nd}$-order polynomial baseline subtracted for the temperature range between 900 K and 1080 K.

The third alloy Ni$_{1.8}$Mn$_{1.2}$Ga did not show any phase transition during these heating cycles, but during later measurements the L$_2$-B$_2$ phase transition became clearer.

It is thought that the sharp peak, or drop off at the end of the DSC anomaly for un-annealed Ni$_{2.2}$Mn$_{0.8}$Ga and Ni$_{1.8}$Mn$_{1.2}$Ga, is a phase transition which is merged with the effects of the residual strain (Figure 4.31 below). This may be similar to the previously observed B$_2$-A$_2$ transition merging with the melting temperature for Ni$_2$MnGa (see section 4.3.4).
High Temperature Specific Heat Capacity Measurement of Ni$_{2-x}$Mn$_{1+x}$Ga

![Figure 4.31: Ni$_{2.2}$Mn$_{0.8}$Ga heat flux data with suggested residual strain ‘bulge’ (blue dotted line) and order/disorder phase transition peak (red dotted line).](image)

This bulge is not seen in the annealed samples and begins to reduce in the un-annealed samples after repeated heating and cooling cycles. Supporting the suggestion it is residual stress in the crystal lattice.

Using the above approach (of assuming the merging of the bulge and transition peak) to determine the phase transition temperature, the results for the un-annealed samples are very similar to those recorded for the annealed samples.

### 4.5 Measured Phase Diagram

The phase transition temperatures from the DSC measurements above produce the following phase diagram for Ni$_{2-x}$Mn$_{1+x}$Ga, X=-0.2. to 1, with composition plotted in terms of e/a, shown in Figure 4.32. Those areas missing data have been extrapolated from the measured results (dotted lines).
Figure 4.32: Measured phase diagram for Ni$_{2-x}$Mn$_{1+x}$Ga ($X = -0.2, 0, 0.2, 0.8,$ and 1.0).

The measured data for the L2$_1$-B2 phase transition compares well with published temperatures for this transition [142] (Figure below), a similar comparison of published data for melt temperature and B2-A2 phase transitions can be performed due to a lack of available data.
4.6 Analysis
To assist in understanding the nature of the phase transitions measured and to analyse the experimental results, a Bragg-William-Gorski [69] approximation has been performed using the equation shown in section 2.2.

4.6.1 L2₁-B2 phase transition
The lattice structure of the alloys at room temperature ranges from L2₁ for Ni₂.0Mn₁.0Ga to L2₁B (a modified L2₁ structure) for Ni₁.0Mn₂.0Ga. The lattice occupancies are shown below (Table 4.7).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Site Occupancies</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₂₁ (Ni₂MnGa Ordered)</td>
<td>Ni Ni Mn Ga</td>
</tr>
<tr>
<td>L₂₁B (NiMn₂Ga Ordered)</td>
<td>½Ni+½Mn ½Ni+½Mn Mn Ga</td>
</tr>
<tr>
<td>XA (NiMn₂Ga Ordered)</td>
<td>Mn Ni Mn Ga</td>
</tr>
</tbody>
</table>

*Table 4.7: Sub-lattice occupancies for L₂₁, L₂₁B and XA structures (See Figure 2.1) [167]*

The BWG approximation for ternary alloys of the form A₂BC presented in section 2.2 was developed for the alloys system Ni₂Mn₁+xGa₁-x [69], however with some modification is suggested that the equations can be adapted to model the phase transition of Ni₂-xMn₁+xGa.
The BWG analysis for the L2₁-B2 presented in section 2.2 assumes that the β and γ sub-lattices are essentially independent of the α₁ and α₂ lattices since the transition is between atomic species on the β and γ lattices (next-nearest neighbours). The atomic population of the α₁ and α₂ lattices have an effect on the interaction energy between the next-nearest neighbours (i.e. between β and γ sub-lattices) through their valance electron contribution.

The sub-lattice and atomic species occupying the lattice (when ordered) is assigned arbitrarily and the BWG approximation does not distinguish between the β and γ sites, therefore the modification of the phase transition temperature equation to use manganese concentration does not appear to invalidate the equation.

Since the BWG approximation equation for the L2₁-B2 phase transition is only concerned with next-nearest neighbour interactions between Mn and Ga on the β and γ sub-lattices, the bulk concentration of the Mn is not applicable in all cases as you cannot have more than 100% of the β sub-lattice occupied by Mn. To resolve this issue, the BWG L2₁ to B2 transition temperature equation has been modified to use Mn concentration on the α₁ and α₂ sub-lattices, rather than the bulk concentration. Assuming that in an ordered state the manganese preferentially orders on the β sites (next-nearest neighbour to a gallium atom), the atomic concentration of Manganese for Ni_{2-x}Mn_{1+x}Ga on the β site will be 1, for X>=0 and equal to the bulk concentration for X<0 (i.e < 1). Therefore the modified BWG L2₁-B2 transition temperature equation present for use with Ni_{2-x}Mn_{1+x}Ga, is:

\[ T_c(L2_1-B2) = \frac{24}{k} W_{Mn-Ga}(R_2)x_{Mn,\beta}(0.5-x_{Mn,\beta}) \]  

(4.3)

where

- \( W_{A-B}(R) \) = Interaction energy between atom species A and B at a distance of R
- \( R_2 \) = Next nearest neighbour separation
- \( x_{A,z} \) = Atomic concentration of atom species A on sub-lattice z
\( k_B \) = the Boltzmann constant

This equation assumes that Mn on the \( \alpha_1 \) and \( \alpha_2 \) sub-lattices are not involved in the order/disorder phase transition between the Ga and Mn atoms.

### 4.6.2 B2-A2 phase transition

The phase transition between B2 partially ordered and A2 completely disordered, for the BWG approximation is dependent on the nearest neighbour interactions only. It is proposed that unlike the \( L_{21} \)-B2 transition equations, the B2-A2 transition equations presented by Murakami [69] (See equation 2.12) can be used without modification for the \( \text{Ni}_{2-x}\text{Mn}_{1+x}\text{Ga} \) series of alloys. See Figure 4.34 for a comparison between the un-modified BWG approximation and the measured results.

### 4.6.3 Unknown Phase Transition

The presence of the unknown peaks in the high temperature DSC data for the non-stoichiometric composition alloys has been suggested as either:

- an ordering of the Ni and Mn (on the \( \alpha \) for Ni-depleted and \( \beta/\gamma \) lattices for Ni-rich)
- a residual stress anomaly
- the presence of varying regions of composition in the sample

If the peak is due to an ordering transition then this transition could be modelled using the modified BWG approximation of the \( L_{21} \) to B2 transition (equation 2.11) but using the interaction between Ni and Mn at distance \( R \) (dependent on composition) and the concentration of the Mn on the sub-lattices in question. This modelling was performed and the results shown on Figure 4.34. However, the peak occurs at a very similar temperature for \( \text{Ni}_{1.8}\text{Mn}_{1.2}\text{Ga} \) and \( \text{Ni}_{2.2}\text{Mn}_{0.8}\text{Ga} \), suggesting the anomaly is more likely to be a compositional or residual stress issue. The fact that the peak is only observed in some (usually 1\(^{st}\) or 2\(^{nd}\) heating/cooling cycles) supports this suggestion, implying the slow heating and cooling of the sample is annealing the phenomenon.
4.6.4 Interaction energy between nearest and next-nearest neighbours

The calculation of the phase transition temperatures using the BWG approximation requires the knowledge of the interaction energy between the atomic species at the various lattice sites. This energy is defined as:

\[ W_{AB}(R) = V_{AA}(R) + V_{BB}(R) - 2V_{AB}(R) \]  \hspace{1cm} (4.4)

Where

- \( W_{AB}(R) \) = Interaction energy between atom species A and B at a distance of R
- \( R \) = Separation of the atoms
- \( V_{IJ}(R) \) = The bonding energy between atoms I and J at separation R

This interaction energy can be determined either experimentally from diffuse scattered X-ray or neutron diffraction [68] [7] or calculated from numerical simulation/modelling of the crystal/electronic structure [69],[70] The latter calculation can be performed analytically (e.g. Hartree-Fock approximation [69]) or numerically (e.g. density function theory (DFT), or cluster variation model (CVM)).

A Hartree-Fock approximation published in 2002 [69] presented a number of calculated interaction energies for Ni\textsubscript{2}Mn\textsubscript{1+x}Ga\textsubscript{1-x}, with a clearly defined e/a relationship.

\[ W_{IJ}(R) \propto f(e/\sigma) \]  \hspace{1cm} (4.5)

Assuming the bonding energy between the nearest and next-nearest neighbours is dependent on the e/a ratio for the alloy, the relationship derived from the study of Ni\textsubscript{2}Mn\textsubscript{1+x}Ga\textsubscript{1-x} should apply to the Ni\textsubscript{2-x}Mn\textsubscript{1+x}Ga alloys, under consideration in this thesis. This assumption seems justifiable as the Hartree-Fock approximation [69], upon which the interaction energies calculated in Table 4.7 are based, makes no reference to atomic occupancy on any particular sub-lattice, but instead used valence electron density and separation to determine the interaction energy [185].
Using the relationships derived from the Ni$_{2-x}$Mn$_{1+x}$Ga$_1$ study [69], the following interaction energies (shown in Table 4.8) were calculated for the next-nearest neighbour interactions between Mn-Ga and the nearest neighbour interactions between Ni-Mn, Ni-Ga, and Mn-Ga.

<table>
<thead>
<tr>
<th>Composition</th>
<th>e/a</th>
<th>WIJ(R), Interaction energy (x10$^{-3}$ eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Next-Nearest</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn-Ga</td>
</tr>
<tr>
<td>Ni$<em>{2.2}$Mn$</em>{0.8}$Ga</td>
<td>7.65</td>
<td>1.85</td>
</tr>
<tr>
<td>Ni$<em>{2.0}$Mn$</em>{1.0}$Ga</td>
<td>7.5</td>
<td>1.83</td>
</tr>
<tr>
<td>Ni$<em>{1.8}$Mn$</em>{1.2}$Ga</td>
<td>7.35</td>
<td>1.81</td>
</tr>
<tr>
<td>Ni$<em>{1.6}$Mn$</em>{1.4}$Ga</td>
<td>7.2</td>
<td>1.79</td>
</tr>
<tr>
<td>Ni$<em>{1.4}$Mn$</em>{1.6}$Ga</td>
<td>7.05</td>
<td>1.77</td>
</tr>
<tr>
<td>Ni$<em>{1.2}$Mn$</em>{1.8}$Ga</td>
<td>6.9</td>
<td>1.76</td>
</tr>
<tr>
<td>Ni$<em>{1.0}$Mn$</em>{2.0}$Ga</td>
<td>6.75</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Table 4.8: Calculated atomic interaction energies for Ni$_{2-x}$Mn$_{1+x}$Ga

In the thesis [69] containing the Hartree-Fock approximation for the Mn-Ga interaction energy no calculated value for the next nearest neighbour interaction for Ni-Mn was presented [69]. The relevant constants needed for the use of the H-F approximation equation for Ni-Mn were also absent [69]. Therefore an alternative calculation had to be performed to allow the BWG approximation of the unknown phase transition.

A simple alternative modelling approach for the calculation of the interaction energy using a screened coulomb potential (Debye-Huckel) approximation was used [185]. This approach treats the next-nearest neighbours (Mn and Ni on $\alpha_1$ and $\alpha_2$) as positively charged ions (atoms minus valance electrons), in a uniform electron gas (valance atoms), and at a distance $R_2$. 
The atomic ($R_2$) separation was determined for each alloy composition from interpolation of the published cubic lattice parameters for Ni$_{2.2}$Mn$_{0.8}$Ga, Ni$_2$MnGa, Ni$_{1.8}$Mn$_{1.2}$Ga and NiMn$_2$Ga. Previous published works have demonstrated that the lattice parameter changed monotonically with composition.

To validate this approximation for Ni-Mn next nearest neighbour interaction, the interaction energy for next-nearest neighbour Mn-Ga was determined, to allow comparison with the data in Table 4.8. The results of the calculation are below in Table 4.9.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$e/a$</th>
<th>Interaction energy ($\times 10^{-3}$ eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Next Nearest Neighbour</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni-Mn</td>
</tr>
<tr>
<td>Ni$<em>{2.2}$Mn$</em>{0.8}$Ga</td>
<td>7.65</td>
<td>1.06</td>
</tr>
<tr>
<td>Ni$<em>{2.0}$Mn$</em>{1.0}$Ga</td>
<td>7.50</td>
<td>1.06</td>
</tr>
<tr>
<td>Ni$<em>{1.8}$Mn$</em>{1.2}$Ga</td>
<td>7.35</td>
<td>1.05</td>
</tr>
<tr>
<td>Ni$<em>{1.6}$Mn$</em>{1.4}$Ga</td>
<td>7.20</td>
<td>1.05</td>
</tr>
<tr>
<td>Ni$<em>{1.4}$Mn$</em>{1.6}$Ga</td>
<td>7.05</td>
<td>1.04</td>
</tr>
<tr>
<td>Ni$<em>{1.2}$Mn$</em>{1.8}$Ga</td>
<td>6.90</td>
<td>1.04</td>
</tr>
<tr>
<td>Ni$<em>{1.0}$Mn$</em>{2.0}$Ga</td>
<td>6.75</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Table 4.9: Simple approximation of Ni-Mn next-nearest neighbour interaction energy, calculated using a simple screened coulomb potential model.
4.6.5 Results of analysis

Using the equations described above (Equation 2.11 and 2.12) and the interaction energies presented in the Table 4.8 and Table 4.9, the following phase transition temperatures were calculated: L2₁-B2 (disordered between Mn and Ga on β and γ sub-lattices), B2-A2 (complete disorder between all atoms on all sub-lattices) and a proposed L2₁-B2 type transition between Mn and Ni on the α₁ and α₂ sub-lattices. The results of the calculation are shown in Figure 4.34.

![Figure 4.34: BWG approximation and measure values of L2₁-B2 and B2-A2 phase transition temperatures for Ni₂₋ₓMn₁₊ₓGa (x=-0.2, 0, 0.2, 0.8 and 1.0)](image)

The calculated BWG L2₁-B2 phase transition temperatures, using the modified BWG approximation and the interaction energy based on e/a relationship from reference [69], follow the same shape as the measured data but with a difference of approximately 200 K. This difference between predicted and measured was also observed in the published study containing the e/a to interaction energy relationship [69] for the Ni₂₋ₓMn₁₊ₓGa alloys.
An improved fit to the measured data can be achieved by scaling the modelled L2₁-B2 curve by a constant factor, so that the measured phase transition temperatures and BWG approximations match for Ni₂MnGa (Figure 4.35). This scaling factor is equivalent to increasing the interaction energy between the Mn-Ga next-nearest neighbours, since for the transition temperature in the modified BWG equation is proportional to the interaction energy ($T_{L2₁-B2} \propto W_{A-B}(R)$). The results of the modified BWG equation using the scaled interaction energies are shown in Figure 4.35.

A similar scaling process for the unknown phase transition BWG curve, results in a good fit with the measured data for Ni₁.₀Mn₂.₀Ga and Ni₁.₂Mn₁.₈Ga, but not for Ni₁.₈Mn₁.₂Ga. If the BWG calculations for the unknown phase transition were repeated using bulk Mn concentration, and scaled to match the Ni₁.₀Mn₂.₀Ga result, the BWG data is a much better approximation of the measured results.

The significant difference between the measured temperatures of the unknown peak in the non-Ni₂MnGa compositions and the BWG approximation for sub-lattice concentrations (pink-dashed line), suggests that the unknown peak is not due to long-range order of the Ni and Mn atoms on next-nearest neighbour sub-lattices.

The BWG approximation using bulk concentrations is a better fit to the measured data however, this approximation predicts a ordering between Ni and Mn on adjacent next-nearest neighbour ($\alpha₁$ and $\alpha₂$) sub-lattices for stoichiometric Ni₂MnGa, which cannot happen as the Ni and Mn the occupy nearest-neighbour sub-lattices ($\alpha$ and $\beta$), with no disordering on the $\alpha₁$ and $\alpha₂$ lattices.

The failure of the BWG approximation to predict the unknown peak supports the supposition that the peak is due to residual stress in the lattice structure resulting from the non-stoichiometric compositions of the alloys or due to the varying regions of composition in the sample.
The BWG B2-A2 phase transition presented in Figure 4.34 shows the same discrepancy as seen in the previous study [69], with the calculated transition temperature approximately the correct value but not the correct shape. This discrepancy suggests that either the Hartree-Fock approximation used in the \(\text{Ni}_2\text{Mn}_{1-x}\text{Ga}_{1-x}\) study [69] is not correct for the nearest neighbour interactions or the BWG approximation (equation 2.12) for this phase transition is not appropriate.

The suggested error in the BWG approximation for the B2-A2 transition is supported by the fact that if the interaction energy between Ni-Mn and Mn-Ga are swapped in the BWG equation for the B2-A2 transition and the calculations repeated the resultant BWG approximation fits the measured data (See Figure 4.35). The BWG approximation, when modified using the above suggested substitutions resulting in better agreement between modelled and measured data is shown below:

\[
T_{c,\text{B2-A2}} = \frac{8}{k} \left\{ \left( x_{\text{Mn}} x_{\text{Ni}} W^{\text{Ni-Ga}}(R_i) + x_{\text{Mn}} x_{\text{Ga}} W^{\text{Mn-Mn}}(R_i) + x_{\text{Ni}} x_{\text{Ga}} W^{\text{Mn-Ga}}(R_i) \right)^2 \right\}^{-0.5} (4.8)
\]
High Temperature Specific Heat Capacity Measurement of Ni$_{2-x}$Mn$_{1+x}$Ga

![Diagram showing phase transitions and temperatures](image)

**Figure 4.35: BWG approximation modified results, for L2$_1$-B2, B2-A2 and unknown phase transition in Ni$_{2-x}$Mn$_{1+x}$Ga (unknown peak omitted from phase diagram as demonstrated it is not a phase transition).**

**4.7 Conclusion**

The measurement of the Curie temperature, L2$_1$-B2, B2-A2 and melt temperatures were made and the results followed the predicted trends with respect to e/a (decreasing in order/disorder transition temperature with decreasing e/a, due to decreasing magnetic moments from the Mn atoms).

The predicted L2$_1$-B2 phase transition temperature can be approximated reasonably well using a modified BWG approximation (equation 4.3), and the assumptions made (i.e. use of Mn concentration on $\beta$ sub-lattice, an interaction energy between Mn-Ga showing the same e/a relationship for Ni$_{2-x}$Mn$_{1+x}$Ga as for Ni$_2$Mn$_{1+X}$Ga$_{1-X}$) appear to be reasonable. However, the measurements and analysis in section 4.5 and 4.6 suggest that the interaction energy between next-nearest neighbours determined using the Hartree-Fock approximation [69] are not sufficiently accurate to produce an exact
correlation between the modelled and measured data without a scaling factor being introduced (Figure 4.34 and Figure 4.35). The calculation of the interaction energy needs to be investigated further and consideration extended to the inclusion of current electronic structure calculation and neutron diffraction data, or improved modelling of the interaction using numerical approaches such as Cluster Variation Modelling (CVM) or Density Function Theory (DFT) modelling.

The B2-A2 phase transition was more difficult to determine due to the transition temperature being very close to the melting point for most of the alloys measured. The modelling of the transition using BWG, produced values in the range of the measured results suggesting that the Hartree-fock approximation used to determine the interaction (partial ordering) energies was accurate under nearest-neighbour conditions. However, the BWG approximation equation presented by Murakami [69] failed to exactly match the measured data. A modified version of the B2-A2 BWG approximation (equation 4.7) produced a much better correlation between modelled and measured results across the entire composition range.

This discrepancy between the un-modified BWG approximation and the measured data may be a result of an error in the equation or an error in the understanding of the B2-A2 phase transition in Ni$_{2-x}$Mn$_{1-x}$Ga alloys. To confirm either of these options a new BWG approximation for four separate sublattices may need to be developed (or a full review of the Murakami BWG approximation [69]) so that the BWG approximation can be used for a full range of Ni$_{2-x}$Ga$_{1+x}$Ga$_{1+y}$ compositions. In addition a study of this structural transitions using neutron diffraction and further thermo-physical property measurements (e.g. specific heat).

The unknown peak in the DSC for the non-stoichiometric alloys is very unlikely to be an order-disorder phase transition between Ni and Mn on the $\alpha$ sub-lattices (demonstrated by the use of the BWG approximation), but is likely to be a residual stress anomaly caused by compositional variations.
away from $\text{Ni}_2\text{MnGa}$ or regions of inhomogeneity in the alloy sample (crystallographic inspection of the bulk sample could be used to demonstrate this or TEM).

Further study of the $\text{NiMn}_2\text{Ga}$ and just off-stoichiometric alloys using specific heat and neutron diffraction should be undertaken to confirm this interpretation of the unknown peak. In addition, modelling of the structure using DFT, CVM or Monte-Carlo simulation should be performed to determine the phase-stability of the material in this region, and the possible presence of the residual stress in the lattice.
High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga
5 Summary and conclusion
The development of the high temperature specific heat measurement (HTCP) system produced a usable and accurate system for the measurement of specific heat capacity between room temperature and 1350 K. The system used a linearly drifting baseline that reduced the duration of the measurement, while not impacting the resolution of the measurement. The introduction of the drifting baseline required the development of analytical techniques for the more complex measurement data.

The HTCP system has been shown to operate with samples ranging from 1 g to 50 g, resolving some of the concerns related to small sample specific heat measurement made in differential scanning calorimeters (DSC). The system also has scope for increased accuracy by reducing the linear heating rate, and using the system as a traditional adiabatic calorimeter.

Further work to develop the system and improve the accuracy would be advisable, with possible areas of development focusing on producing a more robust sample mounting configuration, improving the vacuum to further reduce heat loss from the sample and reducing the noise on the surface mounted temperature sensor (by replacing the thermocouple with a Pt100 platinum resistance thermometer). Additionally, systematically investigating the accuracy of the system for varying energy inputs and pulse durations would be advisable. An example investigation would be: a slow heat pulse , which would allow for the heater and sample to equilibrate. resulting in better thermocouple and post pulse regression data, but may result in increased heat loss from the sample.

The experimental investigation of the high temperature phase transitions in the Ni$_{2-x}$Mn$_{1+x}$Ga alloys produced a phase diagram (Figure 4.30) that confirms the predicted trend for the Curie temperature. The modified Bragg-William-Gorski (BWG) analysis (see section 4.6 for discussion of the modification) of the order/disorder phase transitions, between the highly ordered L2$_1$ phase to the partially order-B2 phase, and between the partially order B2 phase to the
completely disorder A2 phase, showed that they followed the predicted e/a trends.

The original BWG analysis present by Murakami [69] produced calculated phase transitions that did not perfectly match the measured results. The nature of the differences between the measured and BWG phase transition temperatures, suggesting that:

1. For the L2\textsubscript{1}-B2 transition, the modified BWG approximation equation (Equation 4.3) is reasonable but the Hartree-Fock approximation used to calculate the next-nearest neighbour interaction is not accurate.
2. For the B2-A2 transition, the interaction energies seem to be correct for nearest neighbours pairs (as the BWG approximation produced values near the measured values) but the BWG approximation that was used may be in appropriate (as the shape of the BWG approximation was very different from the measured data).

The discrepancies between the modified BWG approximations and measured results for the L2\textsubscript{1} to B2 phase transition temperature have been seen in similar studies, suggesting that the L2\textsubscript{1}-B2 next-nearest neighbour interaction energy should be reviewed and improved, possibly using a numerical method such as density function theory (DFT), or Korringa, Kohn and Rostocker model (known as the KKR model).

The modification of the BWG approximation equations for the B2-A2 transition, improve the results of the modelled data suggesting that that either a review of the ternary alloy BWG approximation should be undertaken or a new BWG approximation for a four sub-lattice system (similar to Ni\textsubscript{2}MnGa sub-lattice configuration) should be developed. It may also be useful to further investigation this phase transition using specific heat measurements and structural investigation techniques (e.g. neutron diffraction), as this temperature region, of solidus to liquidus transitions, is very complex and can have an affect on the structure at lower temperatures.
6 **Further work**

Two key areas of further work have been highlighted by this project, they are:
- Further development of the HTCP system and measurement method.
- Further investigation of Ni$_2$MnGa alloys.

**Development of HTCP system**

The HTCP system developed as part of this thesis has potential for use in a number of material testing applications because of the unique sample size and temperature range. Existing methods require either very small or very large samples, and in the case of many materials (e.g. ceramics, composites, polymers, large grain alloys, graphite) production of material-representative samples that fit the size constraints can be difficult. Therefore, some effort should be put into further developing the technique to make it more reliable and automated (less reliant on user interpretation).

The new method of using a two body FEM analysis technique presented in this thesis shows promise as a computational analysis tool for heat pulse analysis. Research into this tool would prove useful not only for the HTCP technique, but also for lower temperature specific heat measurement and other measurement systems.

It might also be possible to extend the capability of the HTCP system to consider solidus/liquidus transitions (through the use of an alternative sample holder) or simultaneous $C_P$ and thermal conductivity measurement with the addition of more temperature sensors and a heated radiation shield.

**Ni$_2$MnGa alloys**

The results presented in this thesis have gone some way to providing a more complete phase diagram for Ni$_{2-x}$Mn$_{1+x}$Ga, in terms of high temperature order/disorder phase transitions. Further work should be undertaken to confirm/extend this area of the phase diagram for Ni$_2$MnGa and with the potential to confirm/disprove the possible unknown phase transition apparently observed in the DSC data for Ni$_{1.2}$Mn$_{1.8}$Ga and Ni$_{1.8}$Mn$_{1.2}$Ga.
Further investigation of order/disorder in compositions with depleted Ni, and excess Mn, is also of interest and should receive some attention given the work performed on Mn$_2$NiGa that showed that the atomic ordering in this composition was different from Ni$_2$MnGa. If this atomic ordering difference is confirmed then the questions to address is: Is there a composition between these two cases at which the atomic order will change?

The change in ordering and the treatment of order/disorder phase transitions could be continued either using the DSC/$C_p$ method used in this thesis or using high temperature diffraction. The advantage of diffraction is that the phase transition can be observed directly, however the DSC method is easier and cheaper to perform, and if the HTCP is developed further this could be used and would provide the enthalpy for the transition from which the interaction energies for the transition could be derived.

Further research is also needed to provide order/disorder phase transition data for other alternative Ni$_2$MnGa composition variations, e.g. Ni$_2$Mn$_{1+x}$Ga$_{1-x}$ or Ni$_{2-x}$MnGa$_{1+x}$, and composition with additional elements, e.g. Ni$_2$Mn$_{1-x}$GaFe$_x$. The recent interest in Ga$_2$NiMn as a SMA suggests investigation of the higher temperature phases for Ni$_{2-x}$MnGa$_{1+x}$ would be advantageous.

The development of the order/disorder phase transition portion of the phase diagram should not only be continued experimentally, but modelling and theoretical studies of the underlying mechanisms in the process should be undertaken. In particular, the interaction/interchange energy used to model order/disorder phase transitions (BWG) needs more research because, as shown in this work the available models for this property fall short of exactly matching measured data.
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High Temperature Specific Heat Capacity Measurement of Ni$_{2+X}$Mn$_{1-X}$Ga


“Toolbar FullProf Suite Program (2.05)”, Version July-2011, Copyright © 2011, J.Gonzalez-Platas and J.Rodriguez-Carvajal

Appendix A: Modelling

The modelling of thermal processes in the new HTCP system can be categorised as being of the following forms:

1. Analytical
2. Numerical

The first of these, the ‘Analytical’ method, is concerned with the solution of heat diffusion equations, the exact form of the equation is dependent on the situation being considered. However, the general form of the heat diffusion equation [3.6] is:

$$\rho C_p \frac{\partial T}{\partial t} = \kappa \nabla^2 T + q(x,t) \tag{A.1}$$

The advantage of this is that it produces exact solutions to heat diffusion problems. However, modelling of real thermal processes makes this initial equation very complex and difficult to solve. Therefore, due to the in-ability of the analytical modelling to model the heat pulse accurately enough for data analysis, analytical modelling has only been used for:

1. Simple thermal transfer problems: dampening effects of radiation shield on furnace fluctuations.
2. Validation of the numerical finite element models.
3. To model the heating of a sample using an external or internal heater, for a comparison mounting techniques.

The seconds category of models is numerical, and these are models based on simple equations using a large number of iterations to model thermal processes. The advantage of this is the simplicity of setting up the model even for highly complex thermal processes. The disadvantage of the technique is that in order to achieve a high level of accuracy a large amount of processing time is required. However, this technique is used for the majority of the heat pulse models, using simplified models.

The modelling approaches are discussed in detail below.
A.1 Analytical modelling

A number of online libraries containing solutions to the heat-flux equation (equation A.1), for various geometries and barrier conditions. The best solution type for the problems being considered as part of the high temperature specific heat measurement system (HTCP) are those based on Green’s functions.

Please see reference A.1 for a full discussion of the Green’s function solution to the thermal diffusion problems. The solutions used in the modelling below also come from this source [A.1].

A.1.1 Furnace fluctuations:
During commissioning it was noted that during isothermal conditions (furnace held at a set temperature) the sample temperature exhibited an oscillation. This oscillation was of sufficient magnitude to make specific heat analysis impossible. This oscillation was due to the fluctuation in furnace temperature about the furnace set point temperature due to the PID settings on the controller not being correct.

As similar fluctuation was observed in drifting baseline heat pulse measurement, and at high temperature this fluctuation in sample temperature began to interfere with \( C_p \) analysis.

Given the large temperature range of the testing, correcting the furnace controller PID settings was impractical. Instead a radiation shield was installed around the sample to dampen the effects of the furnace fluctuations. So that the correct size (or number/configuration) of radiation shielding could be determine, the heat transfer mechanism (between furnace and sample) was modelled.

The modelling of the furnace fluctuations dampening through the radiation shields required the use of a solution to the thermal diffusion equation for a 1D heat transfer through a medium \( L \) thick (with thermal diffusivity \( \alpha \)), with
High Temperature Specific Heat Capacity Measurement of Ni$_{2+y}$Mn$_{1-x}$Ga

radiation heat flux boundary condition. The solution to this from reference A.1 is:

$$ T(x,t) = \alpha \int_{\tau=0}^{t} 4 \varepsilon \sigma T_0^3 \, dT_{\text{Furnace}}(\tau) G(x,t|L,\tau) \, d\tau $$  \hspace{1cm} (A.2a)

$$ G(x,t|x',\tau) = \frac{2}{L} \sum_{m=1}^{\infty} \exp \left[ -\frac{\beta_m^2 \alpha(t-\tau)}{L^2} \right] \left[ \beta_m \cos \left( \frac{\beta_m x}{L} \right) + B_1 \sin \left( \frac{\beta_m x}{L} \right) \right] $$

$$ \times \left[ \beta_m \cos \left( \frac{\beta_m x'}{L} \right) + B_1 \sin \left( \frac{\beta_m x'}{L} \right) \right] \left[ \beta_m^2 + B_1^2 \right] \left[ 1 + 2 \left( \beta_m^2 + B_1^2 \right) \right] + B_1^4 $$  \hspace{1cm} (A.2b)

$$ B_1 = B_2 = \frac{hL}{k}, \quad h = 4 \varepsilon \sigma T_0^3 $$  \hspace{1cm} (A.2c), and (A.2d)

And the Eigen values of $\beta_m$ determined with:

$$ \tan(\beta_m) = \frac{\beta_m (B_1 + B_2)}{\beta_m^2 - B_1 B_2} $$  \hspace{1cm} (A.2e)

Using this equation to model the fluctuation of the inner face of the radiation shielding (opposite side to furnace fluctuation), using a furnace fluctuation of ±0.5 K with a period of 40 seconds, for various radiation shield thicknesses. The results of the modelling are shown in Figure A.1.

![Temperature fluctuation graph](image)

Figure A.1: Internal face temperature versus time for the radiation shield model, for alumina screens of thickness= 0.5mm, 1.0mm, 2.0mm and 3mm.
This modelling showed that the use of the 3 mm alumina shield would greatly reduce the effects on sample temperature of the furnace fluctuations which are caused by incorrect PID settings on the furnace controller. The dampening effect provided by the 3.0 mm alumina radiation shield would clearly improve the noise (fluctuation) on $C_p$ pulse measurement.

**A.1.2 Sample heat pulse measurements:**
The analytical modelling of the heat pulse was performed using the same procedure as above but using a Greens function solution for solid finite cylinder, with internal heat generation and radiative heat loss boundary condition. [A.1]

This single body analytical model [A.1] is used to confirm the FEM modelling results. Analytical solutions for multi-body systems (e.g. heater-sample, or heater element-heater body-alumina cement-sample) but the results only confirmed the FEM system and were of no use in heat pulse analysis, due to their dependence on too many thermal properties (e.g. thermal conductivity of the sample, thermal conductivity and specific heat of heater element, etc.). Therefore, the results of the multi-body analytical modelling has not been presented here.

**A.1.3 Heater mounting configurations**
The effect of the mounting of the sample in the HTCP system on the thermal behaviour has been considered in two possible forms, either with the sample mounted on a heater or with the heater inserted internally in the sample.

While the first of these is the easiest to construct and much easier to produce viable sample for, it has been suggested that the heat loss from the sample would be much larger with a contact heater when compared to an internal heater.

This modelling has been created to demonstrate the differences between “heat pulses” produced using the two different sample mounting techniques.
The modelling has been achieved by assuming that the sample and heater are the same material, therefore allowing the use of a simple model to map the heat diffusion through a sample. The two different heater configurations are achieved by keeping all other modelling equations the same (Equations A.2b-e) but the modification of Equation A.2a to include a heat generation term.

\[
T(x,t) = \frac{\alpha}{k} \int_{\tau=0}^{t} \int_{x'=0}^{L} q(x',\tau)G(x,t|x',\tau)d\tau.dx'
\]  

(A.3)

Where \(q(x',t)\) is the heater power supplied a point \(x'\), at time \(\tau\).

For the comparison of the heater mountings the dimension of the external heater and internal heater can be assumed to be identical heaters with identical samples but with the heater power term in equation A.3 different. See equation A.4 and figure A.2a and b for a schematic of the model configuration. Figures A.2c, d, e and f show the result of the modelling detailed above.

<table>
<thead>
<tr>
<th>(q(x,t))</th>
<th>(q(x,t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q(x,t) = \begin{cases} Q &amp; x \leq a \ni 1 &amp; t \leq t_0 \ 0 &amp; x &gt; a \ni 0 &amp; t &gt; t_0 \end{cases} )  (A.4a)</td>
<td>(q(x,t) = \begin{cases} Q &amp; \frac{L-a}{2} \leq x \leq \frac{L+a}{2} \ni 1 &amp; t \leq t_0 \ 0 &amp; \text{otherwise} \ni 0 &amp; t &gt; t_0 \end{cases} ) (A.4b)</td>
</tr>
</tbody>
</table>

External heater | Internal heater
The results of the modelling discussed above is shown below, in Figure A.2

(a) Schematic of the external heater model
(b) Schematic of the internal heater model

(c) Temperature versus time data for the three contact heater models
(d) Temperature versus time data for the three internal heater models

(e) Internal temperature profiles for the three contact heater models at t=100 seconds
(f) Internal temperature profiles for the three internal heater models at t=100 seconds

Figure A.2: Results of modelling the two sample mounting techniques.

The three different runs in the modelling represent:

Run 1: stable baseline, with no radiative heat loss at 300 K.
Run 2: stable baseline, with radiative heat loss at 300 K
Run 3: stable baseline, with radiative heat loss at 1100 K
Post pulse regression analysis (Section 3.4.3, for explanation) of the above modelling results (to determine specific heat) produces ‘dT’ data for the three models using the two different sample mounting techniques of:

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T₀ = 300 K, ε = 0.0)</td>
<td>(T₀ = 300 K, ε = 0.3)</td>
<td>(T₀ = 1100 K, ε = 0.3)</td>
</tr>
<tr>
<td>Contact heater</td>
<td>3.72</td>
<td>3.66</td>
</tr>
<tr>
<td>Internal heating</td>
<td>3.72</td>
<td>3.66</td>
</tr>
</tbody>
</table>

Table A.1: Results of post regression analysis of the modelled data as used for the comparison of the sample mounting technique.

The table above suggests that at room temperature the heat loss from a sample mounted using either method would be the same, but at elevated temperatures the ‘external heater’ method of sample mounting loses heat more rapidly than the ‘internal heater’ method. The high rate of heat loss is the cause of the difference between the two samples.

The difference between the two results (‘internal heater’ and ‘contact heater’) at 1100K is approximately 1.5%. It can be assumed that the difference between the two results is a consequence of the input heat being directly lost to the environment due to the exposed surface of the heater. If this is the case, the above modelled data suggests that the use of a contact heater would result in poor HTCP specific heat measurements.

In practice heat loss directly from an external heater would be significantly higher than suggested above, because this model assumes that 100% of one side of the heater is in contact with the sample. Unless a very well fitting heater were constructed for each sample under proper testing conditions the contact heater could be wider than the sample. This implies that not only the exposed surface of the heater is larger but also that there is additional exposed surface on the sample side of the heater. All this would increase the direct heat loss from the heater.
A.2 Numerical modelling of the heat pulse

The modelling of the heat pulse has been attempted using both a “finite difference” method and a simplified finite element method (FEM). However, for more complex modelling the presence of interfaces between two different materials (i.e. the alumina heater element and the metallic sample) and the addition of more complex heat loss scenarios tends to cause instabilities for the finite difference analysis. As a result all numerical modelling has been performed using a simplified FEM technique.

Three models have been produced, all for cylindrical samples. The models can be described as follows:

1. Single body
2. Multi-body - two bodies
3. Multi-body – more than two bodies

All models use the same basic modelling technique but with slight variations.

A.2.1 Single body Modelling

The numerical modelling of transient heat effects for the purpose of the HTCP system has been performed using a simplified finite element modelling (FEM) technique. This involves simplifying the sample and heater to a series of nodes which transfer heat energy between each other, in accordance with standard heat transfer principles. A node is a point approximation of the sample/heater (or a portion of the sample/heater). An iterative approach can be used to determine the temperature of that point at a given time t. To improve the accuracy of the model heat loss from that point (heat loss and transfer to other nodes) and heat generated in that node need also to be addressed.

A simple example of a single body (node) has been taken to be represents by cubic sample, which is 10mm x 10mm x10mm made of molybdenum ($\rho = 10525$ kg.m$^{-3}$, $C_p = 238$ J.kg$^{-1}$.K$^{-1}$, and $k = 78$ W.m$^{-1}$.K$^{-1}$) at 300 K (at t=0...
seconds). Heat is generated in the sample at a rate of 1 Watt. The temperature of the sample after one second would be:

\[
T(t = 1) = T_0 + \frac{dP \cdot t}{C_p \cdot m} = 300 + \frac{1}{238 \times 10.525 \times (10^{-3})^3} = 300.399\,K
\]  

(A.5)

where \(T_0 = 300\,K\) is the initial temperature of the sample, \(C_p\) = specific heat of the sample, \(m = \) mass of the sample \((W \times L \times D \times \rho)\), and \(dP\) = the rate of heat generation in the sample.

With no heat loss from the sample, after one second of heating the sample temperature would have changed by 0.399 K, after another one second \((t=2\) seconds\), the sample would have changed by another 0.399 K. This implies that the temperature of the sample at time \(t\) could be expressed as:

\[
T(t) = T_0 + \frac{dP \cdot t}{C_p \cdot m}
\]  

(A.6)

If, however, there is heat loss, this equation is no longer accurate. The fact that all heat lost is temperature dependent prevents the simple addition of a heat loss term to the above equation.

\[
T(t) = T_0 + \frac{dP \cdot t}{C_p \cdot m} - \frac{F(T(t))}{C_p \cdot m}
\]  

(A.7)

Where \(F(T(t))\) = the heat loss function for the model \((in\,Watts)\).

To determine the sample temperature at time \(t\) numerically, it is necessary to split the time between zero and time \(t\) into a number of finite elements \((duration\,of\,each\,element = dt)\), and then calculate the thermal processes that take place during the much shorter period of time:

\[
T(n) = T(n - 1) + \frac{dP \cdot dt}{C_p \cdot m}
\]  

(A.8)
Since the duration of each finite element is very short the heat loss variation (due to temperature changes in the node) is much smaller. Thus it is possible to assume that the heat loss during the finite element step is constant. The constant heat loss from the sample for each specific time step is determined by using the temperature of the node at the beginning of that time step:

\[
T(n) = T(n-1) + \frac{dP dt}{C_p m} = \frac{F(T(n-1))dT}{C_p m}
\]

(A.9)

The temperature profiles for these three models (no heat loss, constant heat loss and FEM heat loss) can be seen in figure A.3 below. The data for this graph was calculated assuming only radiation heat loss from the surface of the sample into an environment at 300K. The emissivity was assumed to be 0.2.

Figure A.3: Modelled temperature profile of a cubic sample with internal heat generated at 1 Watt, with no heat loss, constant heat loss, and FEM heat loss.

This is the basis for the single body model, with manipulation of heat loss factors depending on the conditions. The modelling of the heat pulse of the HTCP sample has both heat loss due to radiation and heat loss due to solid conduction from the sample due the wires connecting to the sample heater. The equation for a single body model is shown below:
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\[ T(n) = T(n-1) + \frac{dP}{C_p m} \left( \frac{kA_{wire}(T(n-1) - T_{ambient})}{L_{wire}} + \sigma E A_{sample}(T^4(n-1) - T_{ambient}^4) \right) dt \tag{A10} \]

Where \( A_{wire} \) = cross sectional area of the heater connection wires, \( L_{wire} \) = length of the heater connection wires, \( A_{sample} \) = surface area of the sample and \( T_{ambient} \) = the ambient temperature around the sample.

A.2.2 Multiple body modelling

The simple single body model above does not produce any internal temperature data for the sample, nor does it consider any effects due to the sample and heater being made of different materials. For the modelling to consider these processes it is necessary to split the sample into a number of nodes in the same way that time was split in the single body model. The segments of the original sample can then be treated as above but with heat transfer between the separate nodes, in addition to the heat loss from the surface of the sample.

This splitting of the sample into more than one node then allows for modelling of internal gradients in the sample, and increasing the number of nodes increases the accuracy and smoothness of modelling internal gradients. Figure A.5 below shows internal gradients for a 1D heat generation problem, for one two and ten node models of the same system, which has no heat loss and internal heat generation at x<3.

(a) (b)

Figure A.5: FEM modelling of (a) the sample temperature profile versus time, and (b) versus position in the sample at t=1.0 seconds, for FEM modelling
using the ‘single body mode’, the ‘two body model’ and the ‘multiple body model’.

As a guide the time interval for the FEM modelling was always determined using the equation below. This prevented the models from becoming unstable.

\[ dt < \frac{1}{2} \frac{dx^2}{\alpha} \quad (A.11) \]

**A.2.3 Modelling real heat pulses**

The modelling the heat pulse in the sample has been performed for a cylindrical sample, using concentric tube and rod shaped nodes. The sample heater is assumed to be a line heater in the centre of the sample with the heat diffusing out through the sample in a radial direction.

It should be noted that due to the cylindrical nature of the sample model the cross-sectional areas between samples will vary depending on where in the sample the nodes is, meaning that the inner surface of each node will be different to the outer surface.

The physical properties of each node are subsequently determined as follows:

**Node position:**

\[ r_{\text{center}}(n) = n dr, \quad r_{\text{LHS}}(n) = (n - \frac{1}{2}) dr, \quad r_{\text{RHS}}(n) = (n + \frac{1}{2}) dr \quad \text{(A.12a), (A.12b), (A.12c)} \]

**Node cross-sectional area (in direction of heat diffusion)**

\[ A_{\text{LHS}}(n) = 2 \pi r_{\text{LHS}}(n) L, \quad A_{\text{RHS}}(n) = 2 \pi r_{\text{RHS}}(n) L \quad \text{(A.13a), (A.13b)} \]

**Node end area (top and bottom of the node, perpendicular to the diffusion)**

\[ A_{\text{end}}(n) = \pi \left( r_{\text{RHS}}^2 - r_{\text{LHS}}^2 \right) \quad \text{(A.14)} \]

**Node volume**

\[ V(n) = L \pi \left( r_{\text{RHS}}^2 - r_{\text{LHS}}^2 \right) \quad \text{(A.15)} \]
The exact modelling equation for each node depends on the model type and position in the sample, but each node has heat loss due to one or more of the following processes:

1. Heat loss due to ‘outer’ surface radiation:

   This is radiation heat loss in the direction of the modelling. Only one node per model will experience this type of heat loss.

   $$ F_{\text{surface}}(n,i) = \varepsilon \sigma A_{\text{RHS}}(n) \left( T_{i-1}^4(n) - T_{\text{ambient}}^4 \right) $$ (A.16)

2. Heat loss due to ‘end’ surface radiation:

   This is radiation heat loss from the ends of the sample. All nodes in a model have this heat loss.

   $$ F_{\text{end}}(n,i) = 2 \varepsilon \sigma A_{\text{RHS}}(n) \left( T_{i-1}^4(n) - T_{\text{ambient}}^4 \right) $$ (A.17)

3. Conductive heat loss:

   This is the heat loss from the sample due to the wires connecting the sample heater. This will only be used on nodes representing the sample heater portion of the model.

   $$ F_{\text{wire}}(n,i) = \frac{k_{\text{wire}} A_{\text{wire}}}{L_{\text{wire}}} \left( T_{i-1}^4(n) - T_{\text{ambient}}^4 \right) $$ (A.18)

It should be noted that not all nodes have to represent portions of the sample with the same thickness. For example the ‘two body’ model has the interface between the nodes at 1mm. This represents the radius of a real sample heater. This means that the thickness of the second node is up to eight times the radius of the heater node, depending on the size of the sample.

The modelling equations for the sample are:

For node 1 (representing the heater):

$$ T_{\text{heater}}(1,i) = T(1,i-1) + \frac{dP \cdot dt}{C_p \cdot m} - \frac{k A_{\text{RHS}}(T(1,i-1) - T(2,i-1))}{dr} \frac{(F_{\text{end}}(1) + F_{\text{surface}}(1)) \cdot dt}{C_p \cdot m} $$ (A.19)

For the n\textsuperscript{th} node, representing the outer node of the sample (the N\textsuperscript{th} node):

$$ T_{\text{surface}}(N,i) = T(N,i-1) - \frac{k A_{\text{RHS}}(T(N,i-1) - T(N-1,i-1))}{dr \cdot C_p \cdot m} \frac{(F_{\text{end}}(N) + F_{\text{surface}}(N)) \cdot dt}{C_p \cdot m} $$ (A.20)

where N = the total number of nodes in the sample.
For all other nodes the modelling equation is

\[ T(n,i) = T(n,i - 1) - \frac{kA_{net} \cdot (T(n,i - 1) - T(n - 1,i - 1))}{drC_p, m} - \frac{kA_{net} \cdot (T(n,i - 1) - T(n + 1,i - 1))}{drC_p, m} \cdot \frac{F_{net}(N)dt}{C_p, m} \]  \hspace{1cm} (A.21)

The modelling of the heat pulse using the numerical method (FEM) can only be performed on real pulses using the ‘single body model’ and the ‘two body model’. The “multiple body model” could not be used successfully for the analysis of real pulse data due to the amount of data needed and the resulting processing time.

In addition, since all calculations performed for the FEM analysis in the HTCP system use Microsoft Excel spreadsheets, the number of time elements needed for the duration of the a pulse data file (>1000 seconds) became too large to handle and caused a number of program crashes. This problem increased when the modelling was converted to conform to the cylindrical model form and with the inclusion of more complex heat loss scenarios.

The modelling of the real heat pulses using the ‘single body model’ is performed by determining the change in the measured sample temperature (by removing a baseline from the measured platinum resistance thermometer, or PtRT, sample temperature) and then fitting the modelled data to it. The single body model is constructed using the measured sample temperature at the beginning of the heat pulse and the measured power supplied to the sample heater. The fitting of the model to the real data is achieved by the manipulation of the specific heat used in the model along with the model’s heat loss coefficients (figure A.6).

The ‘two body model’ works in a slightly different fashion. To begin with the sample is broken into two differently sized sections. One section represents the heater and one the sample. In order to improve the fit of the modelled data to real data it was assumed that there was some thermal resistance between the sample heater and the sample. This slow transfer of heat between the
sample and heater accounts for the spike in the measured sample temperature (PtRT) during the heating phase of the data. The thermal resistance between the two nodes is described by using a suitable value of the thermal conductivity of the sample or heater. This coefficient along with the sample specific heat and the heat loss coefficients are used to tune the model to improve the fit with the measured data.

The ambient temperature for the model used for the fit to the real data is taken as either the measured shield temperature or as a regression line fit to the pre-pulse measured sample temperature data (PtRT) offset by a small temperature to bring it more in line with the measured shield data (figure 3.64, see section “3.4.3 Finite Element modelling analysis” for a discussion of this process). Figure A.6 below shows an example of the fitting of modelled data to a real HTCP measurement pulse.

![Graph showing modelling of a real HTCP pulse measurement with a 'single body model' and a 'two body model'.](image)

Figure A.6: Modelling of a real HTCP pulse measurement with a ‘single body model’ and a ‘two body model’.
A.2.4 Comparison of the Fem and analytical models

To demonstrate that the FEM model works correctly as an approximation of the real temperature response of a typical sample during a heat pulse a comparison of the two body FEM models used in HTCP data analysis with a similar model determined analytically has been performed (see figure A.7).

The comparison below (figure A.7) shows the modelled behaviour of a stainless steel sample at a stable temperature of 300K. The sample experiences 1 Joules of energy input (heat pulse duration 100 seconds). The sample is a cylinder of diameter 8mm and length 15mm. The heat loss from the sample is solely by radiation from the surface with an emissivity of 0.3. To simplify the fitting process it is assumed that the sample is made up of one material (steel) even in the two-body model.

The thermal properties of the sample are defined as:

\[ C_P = 450 \, J.\,kg^{-1}.K^{-1} \]
\[ \rho = 7885 \, kg.m^{-3} \]
\[ K = 16.4 \, W.m^{-1}.K^{-1} \]
As can be seen all three models agree during the post pulse period of the pulse. However, the ‘two-body model’ is slightly different during the heating stage. This is due to the fact that the ‘two-body model’ was designed for situations where there is a thermal resistance between the sample and the heater. This inbuilt resistance causes a delay between the heat transfer between heater and sample during heating. During the cooling stage the much larger thermal mass of the sample results in the sample being the dominant signal, therefore bringing the ‘two body model’ in line with the other models.

The strong agreement between the numerical model and the standard model (taken from reference A.1), verifies that the simple FEM modelling developed for heat pulse analysis is function correctly and nominally producing accurate modelled data.
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Appendix B: Uncertainty of measurement

The combined Uncertainty Of Measurement (UOM) for specific heat measurements made using the HTCP was determined in accordance with UKAS uncertainty guidelines M3003 [B.1], equation below:

\[ C_{\text{measured}} = \frac{1}{m} \frac{dQ}{dT} \]  
\[ \frac{\delta(C_{\text{measured}})}{C_{\text{measured}}} = \sqrt{\left( \frac{\delta(dQ)}{dQ} \right)^2 + \left( \frac{\delta(m)}{m} \right)^2 + \left( \frac{\delta(dT)}{dT} \right)^2} \]  

Where

- \( C_{\text{measured}} \) = measured specific heat capacity
- \( M \) = mass of sample, plus heater and mounting cement
- \( dT \) = change in sample temperature due to \( dQ \)
- \( dQ \) = energy supplied to sample during the heat pulse

and \( d(X) \) = the uncertainty on measurand \( X \).

The measured specific heat is the specific heat of the sample material and the addenda combined. The addenda consists of the sample heater and mounting cement (used to attached the heater to the sample). Therefore the specific heat of the sample material is defined as:

\[ C_{\text{sample}} m_{\text{sample}} = C_{\text{measured}} m_{\text{total}} - C_{\text{addenda}} m_{\text{addenda}} \]  

Thus, the uncertainty of the sample specific heat is dependent not only on the measurands in equation B.1 and B.2 but also the uncertainty on the thermal and physical properties of the addenda (heater and cement):

\[ \frac{\delta(C_{\text{sample}})}{C_{\text{sample}}} = \sqrt{\left( \frac{\delta(C_{\text{measured}} m_{\text{measured}})}{C_{\text{measured}} m_{\text{measured}}} \right)^2 + \left( \frac{\delta(C_{\text{addenda}})}{C_{\text{addenda}}} \right)^2 + \left( \frac{\delta(m_{\text{addenda}})}{m_{\text{addenda}}} \right)^2} \]  

B.1 Uncertainty on sample mass.

The uncertainty on the sample mass is determined from the uncertainty of the measured mass, and any weight loss experienced by the sample during a HTCP measurement run. Equation B.5 below is the formula for determining the UOM for sample mass:
The uncertainty of 0.001 g is the uncertainty on the balance used to weight the sample, this term is included twice due to the uncertainty of the second sample mass measurement made post HTCP measurement.

The measured $dm$ value is determined post HTCP measurement, but with the heater element still cemented in place. It is assumed that the change in sample+addenda mass during the HTCP measurement comes only from mass loss from the sample. The value of $dm$ is dictated by how much mass that sample looses/gains during a measurement, such changes in mass are assumed to be due to oxidation of the sample or drying of the sample.

### B.2 Uncertainty on addenda mass.

Since the mass of the addenda (heater and mounting cement) must be determined once the heater has been fixed in place inside the sample, a direct measurement of the addenda mass cannot be made. Instead the mass of the addenda is determined from the mass of the sample and addenda minus the mass of the sample (weighed prior to addenda being attached).

Therefore the uncertainty on the addenda mass is due to the uncertainty on the sample mass (before the heater and mounting cement are added) and the uncertainty on the sample + addenda mass.

$$m_{\text{addenda}} = m_{\text{total}} - m_{\text{sample}}$$  \hspace{1cm} (B.6)

$$\frac{\delta(m_{\text{addenda}})}{m_{\text{addenda}}} = \sqrt{\left(\frac{0.001g}{m_{\text{total}}}\right)^2 + \left(\frac{0.001g}{m_{\text{sample}}}\right)^2}$$ \hspace{1cm} (B.7)

### B.3 Uncertainty on addenda specific heat

The uncertainty on the specific heat capacity of the addenda is due to solely to the uncertainty on the measured data that the addenda $C_P$ is calculated.
from. Since the addenda is assumed to be 100% alumina the standard \( C_P \) data for Alumina has been used for the addenda specific heat. The UOM on the standard data is: \( \pm 5\% \) [B.2].

### B.4 Uncertainty on input energy

The uncertainty on the input energy comes from the uncertainty on the power supplied to the heater element, and the duration the heater is on.

\[
dQ = VI dt
\]

\[
\frac{\delta(dQ)}{dQ} = \sqrt{\left(\frac{\delta(V)}{V}\right)^2 + \left(\frac{\delta(I)}{I}\right)^2 + \left(\frac{\delta(dt)}{dt}\right)^2}
\]

With \( \delta(I) \) and \( \delta(V) \) being the resolution of the measured data (\( \pm 0.001\)mA and \( \pm 0.001\)mV) respectively. The uncertainty on duration \( \delta(dt) \) is the resolution on the time base of the measured data, this is the time between two recorded data point in the data file, which is equal to 1.7 seconds. Therefore the UOM for \( dQ \) can be written as:

\[
\frac{\delta(dQ)}{dQ} = \sqrt{\left(\frac{0.001mA}{I}\right)^2 + \left(\frac{0.001mV}{V}\right)^2 + \left(\frac{1.7}{dt}\right)^2}
\]

### B.5 Uncertainty on \( dT \)

The uncertainty on \( dT \) is dependent on the analysis technique used to determine \( dT \).

For FEM modelling analyses of data produced using the new high temperature specific heat measurement system (HTCP), \( C_P \) is determined directly with no need to determine \( dT \), and the uncertainty assigned to this technique has been set at 10\%. The value of 10\% has been assigned to the results from the FEM approach since a deviation of more than 15\% results in a noticeable change in the modelled heat pulse, and the user performing the analysis would repeat to produce a better fit between the modelled and measured data. The value of 10\% is considered conservative enough to
cover the uncertainty on fitting and the other UOMs associated with the technique (e.g. input energy, sample mass, etc).

For heat pulse analysis of the HTCP data the low resolution of the technique has been shown to have a uncertainty of ±20% on numerical method and ±30% on the graphical method. This value was assigned after repeat analysis using this technique of the same set of data, to investigate the repeatability of the heat pulse analysis approach, after multiple analyses the standard deviation on the results was 10%, increasing the uncertainty to include the 97% confidence interval [B.1], the UOM was assigned a value of ±20% for the numerical approach and ±30% for graphical approach (see section 3.4.3).

The post pulse regression analysis technique (Section 3.4.3) does require the measurement of dT and since it is based on a least square fit of the post pulse data, an analytical UOM would be difficult to determine. Instead a graphical UOM has been developed.

The graphical method of dT UOM assessment is performed as follows:

**Step 1:** Determine the nominal dT value; using a least squares fits approach, to fit a n\(^{th}\) order polynomial to the \(\ln(dT)\) data by defining the range over which the regression will be performed and the order of polynomial being fit.

**Step 2:** The UOM is then determined by varying the regression range by ±10% and determine the dT value for the eight (Table C.1) modified regression lines. Figure C.1 shows the variation of dT with modified post pulse regression range.

<table>
<thead>
<tr>
<th>Regression Name</th>
<th>Start of regression range</th>
<th>End of regression range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal dT</td>
<td>(T_S)</td>
<td>(T_E)</td>
</tr>
<tr>
<td>Variation 1</td>
<td>(T_S)</td>
<td>(T_E + 10%)</td>
</tr>
<tr>
<td>Variation 2</td>
<td>(T_S)</td>
<td>(T_E - 10%)</td>
</tr>
<tr>
<td>Variation 3</td>
<td>(T_S + 10%)</td>
<td>(T_E)</td>
</tr>
</tbody>
</table>
High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga

<table>
<thead>
<tr>
<th>Variation</th>
<th>$T_S + 10%$</th>
<th>$T_E + 10%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variation 2</td>
<td>$T_S + 10%$</td>
<td>$T_E - 10%$</td>
</tr>
<tr>
<td>Variation 3</td>
<td>$T_S - 10%$</td>
<td>$T_E$</td>
</tr>
<tr>
<td>Variation 4</td>
<td>$T_S - 10%$</td>
<td>$T_E + 10%$</td>
</tr>
</tbody>
</table>

Table B.1: Post pulse regression range for dT determination and UOM assessment.

Figure B.1 Example of the variation of dT regression curves with varying regression range.

Step 3: From the list of eight variations in dT select maximum or minimum deviation, unless the variation curve is clearly in error as seen in Variation 6 curve above. If the measured curve were off by this much then the operator would re-analyse to produce a better curve, and since this approach is looking for the uncertainty on the measurement such a large deviation would be corrected.
For the data in Figure C.1 the dT variation for the four curves is shown in Table B.2:

<table>
<thead>
<tr>
<th>Regression line</th>
<th>Measured dT</th>
<th>Deviation from Nominal value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal</td>
<td>0.249</td>
<td>0.00%</td>
</tr>
<tr>
<td>Variation 1</td>
<td>0.247</td>
<td>-1.02%</td>
</tr>
<tr>
<td>Variation 2</td>
<td>0.248</td>
<td>-0.47%</td>
</tr>
<tr>
<td>Variation 3</td>
<td>0.247</td>
<td>-0.90%</td>
</tr>
<tr>
<td>Variation 6</td>
<td>0.296</td>
<td>18.77%</td>
</tr>
</tbody>
</table>

Table B.2: Example deviation from Nominal value for UOM calculation

### B.6 Summary

A combination of the above approaches allows for the determination of the UOM on any measured \( C_P \) value.

The use of a combination of the above approaches should be used for the UOM determination for the measured \( C_P \) values of any HTCP pulse measurement.

### B.7 References:


High Temperature Specific Heat Capacity Measurement of Ni$_{2+x}$Mn$_{1-x}$Ga