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A Study Of The Martensitic Phase Transition In The Shape Memory Alloy Ni₂MnGa

by

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A Doctoral Thesis Submitted in partial fulfilment of the requirements for the award of the degree Doctor of Philosophy of Loughborough University United Kingdom

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ABSTRACT

A study of the martensitic phase transition in the shape memory alloy Ni₂MnGa has been carried out. Ni₂MnGa is one of the group of "shape memory effect" alloys which are currently exciting considerable interest. The origin of this effect in the compound is in the phase change which takes place on cooling through T=200 K from the cubic L2₁ Heusler structure to a tetragonal phase. Recently the results of band structure calculations have been used to conclude that in Ni₂MnGa the structural phase transition is driven by a band Jahn Teller distortion.

A polarised neutron diffraction study has been undertaken to determine the magnetisation distribution in the cubic and tetragonal phases. The aim of the experiment was to determine whether the phase transformation is driven by a repopulation of the d electrons into band of different symmetry. In fact this was found to be the case and the results represent the first direct observation of the band Jahn Teller mechanism.

A study of the way in which the transition takes place has been undertaken using unpolarised neutron diffraction from Ni₂MnGa single crystal.

The effect of electron concentration on the magnetic and structural properties of Ni₂MnGa has been investigated by substitute the Ga by other elements. Polycrystalline specimens of Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x, Ni₂MnGa_{1-x}In_x, Ni₂Mn_{1-x}V_xGa, Co₂Mn_{1-x}V_xGa, Cu₂Mn_{1-x}V_xGa were prepared using an argon arc furnace. A single crystal of Ni₂MnGa for use in the neutron experiments was grown using the Czochralski method.

Heusler alloys are properly described as ternary intermetallic compounds. Ni₂MnGa has the Heusler cubic (L2₁) structure with space group $Fm\overline{3}m$, and is ferromagnetic with Curie temperature of 376 K, and a magnetic moment of 4.71 μ_B largely confined to the Mn sites.

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Different techniques; such as X-ray diffraction, SQUID magnetometer measurements, DSC (Differential Scanning Calorimetry), the contactless measurement of the electrical resistivity and neutron diffraction measurements have been used on these samples.

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Dedication

To my Father and Mother who have given me inspiration and guidance. I am indebted to their care and affection who gave me much and took very little. To them I dedicate this thesis.

To my beloved wife Haseenah, sons Riyadh, Fathi and Yousef and daughters Abeer, Zainub and Heba for their love, support, understanding and all the sacrifices that they made, without which this thesis could not have been prepared. To all of them therefore, I dedicate the thesis.

Abu Riyadh

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CHAPTER ONE

GENERAL INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Intermetallic compounds exhibit a number of magnetic characteristics, which make them of interest. One of the present areas of interest in the field of magnetic materials was first initiated in 1903 by Heusler (Heusler, Starck et al., 1903), Normally one thinks that all 3d materials that order magnetically must contain one of the ferromagnetic elements namely iron, cobalt or nickel. Heusler first reported that Mn-Cu bronze could be alloyed with Sn, Al, As, Sb, Bi or B to produce ferromagnetic alloys even though none of the constituent elements is itself ferromagnetic.

This discovery stimulated numerous further investigations resulting in the discovery of many more ferromagnetic alloys and compounds containing non-ferromagnetic elements.

The Heusler alloys form an interesting group for magnetic study because they offer a possible means of investigating the effects of interatomic distances, atomic arrangement and atomic environment on the magnetic properties. These alloys have the L2₁ lattice structure and their chemical formula X_2YZ (X = Cu, Ni, Pd, etc. and Z = Al, Sn, Sb, Ga etc.).

It has been found that the magnetic properties of the alloys are directly related to the degree and type of chemical order present. It is thought that the magnetic properties of the alloys are closely related to their L2₁ structure. The majority of Heusler alloys have been shown to be ferromagnetic. However some alloys do display antiferromagnetic order (Webster and

Tebble, 1967; Doherty, Crangle et al., 1995). The structural and magnetic properties of several Heusler alloys have been reviewed by (Webster, 1969). Some Heusler alloys undergo structural phase transition (Suits, 1976) the origin of which is not yet understood.

Background

Martensitic phase transformation

The martensitic transformation is an important phenomenon, which controls the mechanical properties of metallic materials and has been studied extensively in the past. Initially the martensitic transformation was explained chiefly from the thermodynamical point of view. Subsequently, with advances in research techniques, the structures of various martensites were determined and the presence of substructures such as arrays of lattice defects was established.

A martensitic transformation is a first order phase transformation that occurs by co-operative atomic movements. The product of a martensitic transformation is martensite.

That a given structure is produced by a martensitic transformation can be confirmed by the existence of various characteristics, such as the diffusionless character, the surface relief, and the presence of many lattice imperfections. Such characteristics are therefore criteria for the existence of martensite (Nishiyama, 1978; Jena and Chaturvedi, 1992).

Shape-Memory Alloys

Metals are characterised by such physical qualities, ductility, malleability and conductivity. To these in the case of a new family of alloys, one can now add the anthropomorphic qualities of memory and trainability. The new alloys exhibit what is called the shape-memory effect. If such alloys are plastically deformed at one temperature, they will completely recover their original shape on being raised to a higher temperature. In recovering their shape the alloys

can produce a displacement or a force, or a combination of the two, as a function of temperature. Because of these novel and remarkable properties shape-memory alloys are helping to solve a wide variety of problems. Most recently the alloys have been exploited in mechanical and electromechanical control systems to provide, for example, a precise mechanical response to small and repeated temperature changes.

In order for an alloy to exhibit the shape-memory effect it must have a crystal structure that can transform into the configuration known as martensite when it is subjected to a certain temperature or stress and then shift out of it. Since the martensite transformation is essential for the shape-memory effect, alloys that exhibit memory are also known as mar-mem alloys. Alloys as diverse as iron-platinum, indium-cadmium, iron-nickel, nickel-aluminium and stainless steel have been observed to exhibit shape memory in varying degrees. A detailed review of shape-memory effect is given by (McDonald Schetky, 1979).

 Ni_2MnGa is one of a group of "shape memory effect" compounds which is currently exciting considerable interest since it is the only one which is found also to be ferromagnetic. The origin of the shape memory effect in Ni_2MnGa is in the martensitic transition which takes place on cooling through 200 K from the cubic L2₁ Heusler structure to a tetragonal phase. The transformation can be described as a simple contraction along one of the [100] directions of the cubic phase without any change in atomic positions. There is a strong deformation of the cell (c/a = 0.96) but a reduction of only <1% in cell volume. This phase transition is remarkable in that in spite of a strong deformation of the unit cell it is reversible and a single crystal can be cycled through it many times without breaking.

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Premartensitic Phase

The pre-martensitic state is an intermediate phase which precedes the martensitic transformation and is a result of a condensation of the TA₂ soft phonon mode with $q \neq 0$.

The progressive softening of the TA₂ phonon propagating in the [110] direction leads to a PM (Premartensitic) transition at $T_1 \approx 260$ K(Zheludev, Shapiro et al., 1996). The first indication to the existence of this phase was obtained in magnetoelastic measurements (Zheludev, Shapiro et al., 1995). Though the PM transition, unlike the MT (Martensitic transition) at a lower temperature, does not manifest itself in the magnetic susceptibility curves (Webster, Ziebeck et al., 1984), magnetostriction shows a distinct kink at T₁.

The best evidence for the existence of the PM phase is the behaviour of the transverse acoustic phonon $(\zeta_{\circ}, \zeta_{\circ}, 0)$, $\zeta_{\circ} = 1/3$ which produces elastic satellites [displacements along (110)]. At higher temperatures 265 K to 300 K the peak at $\zeta_{\circ} = 1/3$ is broad and relatively weak. As the temperature decreases below T₁ it becomes narrow and Bragg like. Its intensity increases dramatically and its q (wave vector) becomes defined by the experimental resolution rather than the shape of the dip in the phonon dispersion curve.

It could be expected that the formation of the PM phase which is characterised by a new (1/3,1/3,0) transverse modulation of the parent cubic structure, should be accompanied by a uniform distortion of the latter.

• Band Jahn-Teller mechanism

The conduction electron concentration is known to be a predominant factor in characterising the structural and magnetic properties of Heusler alloys, and it has also been invoked to account for this transition. However, similar phase transition in other Heusler alloys (Rh₂CoSn) have been ascribed to a band Jahn-Teller effect.

In the band Jahn-Teller mechanism, bands which are degenerate in the cubic system are no longer degenerate in the tetragonal phase. This enables the electrons to re-populate the lower energy bands. There will be a change in the degree of overlap associated with orbitals when the crystal deforms. Those orbitals overlapping in the direction of the crystallographic elongation will give rise to a narrow bandwidth compared to those in the direction of the contraction. Specifically for the 3d bands, the e_g narrow band orbitals are degenerate in the cubic phase, but for the tetragonal structure c/a< 1, the $3d_{3z^2-r^2}$ band will broaden and the $3d_{x^2-y^2}$ will narrow. This will give rise to a net transfer of 3d electrons into the $3d_{3z^2-r^2}$ band, as observed in the polarised neutron experiment, using the diffractometer D3 located on the hot source at the ILL in Grenoble.

Heusler alloys Crystallographic Structure

Heusler alloys are defined as ternary Intermetallic compounds, at the stoichiometric composition X_2YZ , which have the L2₁ structure as shown in figure (1.1).



Fig. (1.1) Heusler, L21 structure

The unit cell is comprised of four interpenetrating fcc sublattices A, B, C, D with origins at (0,0,0), (1/4,1/4,1/4), (1/2,1/2,1/2), and (3/4,3/4,3/4). Diffraction patterns for this structure have permitted Bragg reflections when the Miller indices are unmixed. This gives rise to three types of structure amplitudes:

I. h,k,i all odd:

$$F(111) = 4 \left| (f_{\rm A} - f_{\rm C})^2 + (f_{\rm B} - f_{\rm D})^2 \right|^{1/2}$$

II. h,k,l all even and h+k+l = 4n + 2

$$F(200) = 4 | (f_A - f_B + f_C - f_D) |$$

III. h,k,I all even and h+k+I =4n

 $F(220) = 4 | (f_A + f_B + f_C + f_D) |$

where f_A , f_B , f_C and f_D are the average scattering factors for the atoms in the respective sublattices.

The reflections for which h+k+l = 4n are the principal reflections, and are unaffected by the state of chemical order. The remaining two groups of reflections correspond to the order-dependent superlattice reflections.

For Heusler alloys, which have the site occupation indicated in fig. (1.1), the structure amplitudes for the three types of reflection reduce to:

$$F(111) = 4 |f_z - f_y|$$

$$F(200) = 4 |f_z + f_y - 2f_x|$$

$$F(220) = 4 |f_z + f_y + 2f_x|$$

The Heusler structure is formed essentially from the ordered combination of two binary B2 components XY and XZ, each of which may have the CsCI structure.

Magnetic properties

The majority of Heusler alloys order ferromagnetically and saturate in applied magnetic fields of less than 0.5 T at low temperatures. If the magnetic moment is confined to the Mn sites, as it often is in the alloys X_2MnZ , a value close to $4\mu_B$ is usually observed. Although they are metals, these Intermetallic compounds have localised magnetic properties and are ideal model systems for studying the effects of both atomic disorder and changes in the electron concentration on magnetic properties.

The most direct quantitative evidence for localised magnetic behaviour is provided by paramagnetic neutron scattering data. However, an indication may be obtained by comparing the ground state magnetic moment p_{\circ} with that extracted from the slope of the Curie-Weiss reciprocal susceptibility curve, i.e. $p_{eff}^2 = p(p+2\mu_B)$. A ratio of $p/p_{\circ} = 1.0$ is expected for localised systems where as for itinerant magnetism a ratio greater than one is expected.

If the transition metal atoms carrying the magnetic moment in Heusler alloys are in direct first neighbour contact, either as a result of atomic disorder or due to the presence of a second magnetic element, e.g. as in Co₂MnZ, there is then a tendency towards itinerant behaviour.

Extensive magnetic and other measurements have been made on several Heusler alloy series, including system such as $Pd_2MnIn_{1-x}Sn_x$ (Webster and Ramadan, 1977). It has been established that the s-p electron concentration is primordial in establishing the magnetic properties, affecting both the magnetic moment formation and the type of magnetic order.

Neutron diffraction and magnetic order

Most of the physical properties of Heusler alloys, in particular their magnetic properties, are critically dependent upon the chemical structure and ordering of the constituent elements. Neutron diffraction is uniquely capable of determining simultaneously both the chemical and magnetic structures of compounds, together with the magnitude and orientations of the magnetic moments.

1.2 Literature Review

An investigation by Hames (1960) showed that ferromagnetic alloy is found near the composition Ni₂MnGa. It was tentatively identified as having L2₁ (Heusler)-type structure (Hames, 1960). Neutron diffraction measurements by Webster (1968) confirmed that at room temperature Ni₂MnGa was highly ordered in the L2₁ structure and an investigation was carried out to show the effects of heat treatment on the degree of order. Also from neutron powder diffraction measurements at 77 K, Webster showed that there was a structural phase transition to a complex, tetragonally based structure, but lack of resolution prevented any detailed analysis (Webster, Ziebeck et al., 1984). The structural phase transition and magnetic properties in Ni₂MnGa have been investigated by Ooiwa et al. (1992) who reported that a magnetic moment on the Ni site was observed for the first time. Its magnitude which is induced by the molecular field from local Mn moment depends on structure and also on temperature. The results are consistent with recent theoretical results discussing the band Jahn-Teller effect (Ooiwa, Endo et al., 1992). Endo et al. (1992) investigated the structural phase transition from the L2₁ to the tetragonal structure, by magnetisation measurements and NMR using the Mn-55 resonance. The transition is suppressed with increasing X and Y, and disappears at X=0.1 and Y=0.4. The decrease of the Ni moment, which is determined for the first time in Ni₂Mn_{1-x}V_xGa, is closely related to the suppression of the transition (Endo, Ooiwa et al., 1992). Vasilev et al. (1993) measured the temperature dependence of the low-field magnetic susceptibility, the specific heat and the transverse sound velocity in single crystals of Ni₂MnGa compressed along (110) axis. The load was removed at liquid-nitrogen temperature. The dimensions and shape of the crystals are restored upon heating as the result of a sequence of first-order structural phase transitions. The new phases appear in Ni₂MnGa because of an anomalous instability of the crystal lattice of this compound with respect to atomic displacement along a [110] direction in the (110) plane (Vasilev, Kaaiper et al., 1993). Transmission electron cicroscopy (TEM) has been used by Cesari et al. (1997) to investigate the internal friction associated with the structural phase transformation in Ni₂MnGa. The observations have

shown that the anomalies associated with the phenomena are related to the structural transformations from the parent cubic phase (P) to an intermediate cubic modulated phase (I) and from the I phase to the martensitic one (M) (Cesari, Chernenko et al., 1997). Webster et al. measured the magnetisation of Ni₂MnGa, in a sample which transforms martensitically to a tetragonal structure below 202 K as shown in figure (2.1). The relative positions of the atoms are unchanged and the reduction in volume is only 0.015% (c/a=0.94).



Fig. (2.1) Ni₂MnGa Magnetisation at several applied fields vs. temperature.

The increase in magnetic hardness below 202 K is consistent with X-ray and neutron diffraction data indicating a tetragonal distortion below 202 K. The magnetic moment is essentially confined to the Mn atoms and is usually 4.13 $\mu_{\rm B}$ per formula unit(Webster, Ziebeck et al., 1984). The martensitic transition from a cubic to a tetragonal structure on cooling of Ni₂MnGa has been also investigated by Wirth et al. (1997), the martensitic transition temperature T_{M} , known to be 202 K for the nominal composition (Webster, Ziebeck et al., 1984), was expected to increase with increasing Ni content of the alloy (Wirth, LeitheJasper et al., 1997). For samples Ni₂(1+ δ)Mn(1+ δ)Ga(1- δ) with δ = 0, 0.046 and 0.10, respectively, the Curies temperature has been determined as 380 K independent of composition (Wirth, LeitheJasper et al., 1997). The T_M for the sample with $\delta = 0.10$ is single phase and remaining tetragonal up to the Curie temperature (Wirth, LeitheJasper et al., 1997). Ullakko et al. (1996) reported that strains of nearly 0.2% have been induced along [001] in unstressed crystals of Ni₂MnGa with a magnetic field of 8 KOe applied at 265 K. These strains are associated with the superelastic phase that is stable

below about 274 K (Ullakko, Huang et al., 1996). Kokorin et al. (1992) reported that three successive stress induced martensitic transformations are found in Ni₂MnGa; two of them $\beta'_1 \rightarrow \beta''_1$ and $\beta''_1 \rightarrow \beta''_1$ can not be realised by simple cooling. Once formed, the β''_1 and β''_1 phases are stabilised by cooling below the characteristic temperatures. The $\beta''_1 \rightarrow \beta''_1 \rightarrow \beta'_1 \rightarrow \beta_1$ sequences of phase transitions during heating results in complete shape recovery, where the β_1 phase is cubic with a = 5.824 Å, β'_1 phase is a tetragonal phase with a = b = 5.9 Å, c = 5.54 Å (Webster, Ziebeck et al., 1984), the β''_1 phase has orthorhombic symmetry with parameters a = 6.12 Å, b = 5.78 Å, c = 5.54 Å, c = 5.52 Å (Kokorin, Martynov et al., 1992).

The deformation behaviour of a Ni2MnGa single crystal uniaxially loaded in compression and tension along the $<100>\beta_1$ and $<110>\beta_1$ axes were investigated by Martynov et al. (1992). It was shown that three successive stress-induced structural transitions may be observed for specimens extended along $<100>\beta_1$ or compressed along the $<110>\beta_1$ direction, while only one transition was stress-induced in compression along the $<100>\beta_1$ axis. The crystal structure of stress-induced and thermal martensite was identified and related reversible deformation values for different loading geometry were estimated (Martynov and Kokorin, 1992). Chernenko et al. (1995) reported that several martensite phases in ferromagnetic Ni-Mn-Ga alloys were induced by combining uniaxial compression along the [110] axis and temperature. The intermartensitic transformations were observed during heating by Calorimetry, dilatometry and magnetic susceptibility measurement. During intermartensitic transformations, between modulated and unmodulated lattices, as well as during the final transformation to the parent phase, noticeable anomalous changes in the magnetic properties of the alloy were observed (Chernenko, Amengual et al., 1995). Fritsch et al. using single crystals of different composition have investigated the martensitic transformation by electron and low temperature X-ray diffraction as well as by differential scanning calorimetry. It was shown that the cooling-induced martensitic phases are long-periodic with a transverse modulation along the

(110) direction. Atomic shifts with periodicity of 5 and 7 atomic layers were observed in samples exhibiting a martensitic transformation at 180 K and 446 K, respectively. The transformation heats appeared to be different by a factor of 10 for both alloys (Fritsch, Kokorin et al., 1996). Chernenko et al. have also shown (1996), that Ni₂MnGa, under applied hydrostatic pressure produces shifts in the martensitic transformation temperatures (Chernenko and Lvov, 1996).

Kokorin et al. (1996) performed an investigations of the structural, elastic and thermal properties of the premartensitic state in Ni-Mn-Ga alloys. The state is interpreted as an intermediate phase which precedes the martensitic transformation and is a result of a condensation of the TA₂ mode with $q \neq 0$ (Kokorin, Chernenko et al., 1996). A system undergoing a two-step martensitic phase transition was studied by inelastic neutron scattering and neutron diffraction. Zheludev et al. (1996) observed several anomalies in the phonon dispersion curves in the parent cubic phase. The nearly complete softening in the $(\zeta, \zeta, 0)$ TA₂ branch results in a premartensitic first-order phase transition which involves a commensurate periodic distortion of the parent structure with the periodicity equal to that of the soft mode. A strong wave vector dependence of the coupling of periodic distortion to homogeneous strains leads to a further transformation to an incommensurate martensitic phase at lower temperatures (Zheludev, Shapiro et al., 1996). Stuhr et al. studied the low-energy phonons in the ferromagnetic and paramagnetic phases of Ni₂MnGa. The investigation showed a martensitic phase transformation with a transition temperature T_M of approximately 284 K, only about 80 K below the Curie temperature. The $(\zeta_i, \zeta_i, 0)$ TA₂ phonon branch shows a strong but incomplete softening at ζ_i approximately equal to 1/3 in the premartensitic phase when the temperature approaches T_M . The temperature dependence of the softening changes at the Curie temperature which can be explained by an additional contribution of the magnetisation to the Landau free energy (Stuhr, Vorderwisch et al., 1997). Kokorin et al. (1997) detected anomalies in the temperature behaviour of the physical properties of Ni₂MnGa in the temperature interval preceding the martensitic transformation, which is attributed to the TA₂ phonon mode condensation at

T =T_I > T_M (Kokorin, Chernenko et al., 1997). Segui et al. (1996) detected two successive anomalies in the temperature dependence of internal the friction (IF) and elastic modulus for certain off-stoichiometric Ni₂MnGa alloys both on cooling and heating between the parent and martensitic phases. According to transmission electron microscopy (TEM) observations, these anomalies are related to two structural transformations, namely $P \rightarrow I$ and $I \rightarrow M$ (I is an intermediate cubic phase obtained by [1/3 1/3 0] transverse displacement modulations of the parent P phase) (Segui, Cesari et al., 1996). Zheludev et al. reported a results of neutron scattering measurements on single crystals of Ni₂MnGa as a function of uniaxial stress and temperature. Emphasis was placed on the behaviour of the low-energy part of the $[\zeta\zeta 0]TA_2$ phonon branch and the associated pre-martensitic phase transformation. It has been shown that the uniaxial stress and temperature dramatically affected the $[\zeta\zeta 0]TA_2$ phonon dispersion branch when the anomalous dip shifts to higher ζ with increasing stress, but its position is temperature independent (Zheludev and Shpiro, 1996).

Fritsch et al. (1994) carried out measurements of the thermal diffuse X-ray intensity from a single crystal of Ni₂MnGa in the temperature range 180 to 250 K. Their results demonstrated the existence of a soft-mode behaviour in the high temperature phase of the Heusler alloy Ni₂MnGa. A significant decrease in the angular frequency of the TA-phonon with $q = (1/6)\tau_{110}$ is observed when the temperature approaches M_s (Fritsch, Kokorin et al., 1994). The phase transition has been extensively investigated by Zheludev et al. (1995,1996) particularly by inelastic neutron scattering, neutron diffraction and transmission electron microscopy which reveal the presence of precursor effects above T_M and an incomplete softening of the TA_2 phonon mode at a wave vector q of 0.33 (Zheludev, Shapiro et al., 1995; Zheludev, Shapiro et al., 1995; Zheludev, Shapiro et al., 1996). The observation of anomalies related to the TA₂-phonon mode Mañosa et al. (1997) through specific-heat, elastic constant, and magnetic susceptibility measurements, enabled them to correlate the TA₂ phonon mode with a softening of certain elastic constants particularly C' which is $1/2(C_{11} - C_{12})$ and is determined by the TA₂ phonon

(Manosa, Gonzàlez-Comas et al., 1997). Ultra sonic measurements carried out in a magnetic field at room temperature by Planes et al. revealed a strong dependence of the elastic constants, especially C' on applied field. These results suggest that the pre-martensitic transition may be driven by magnetoelastic interactions (Planes, Obradó et al., 1997). The temperature dependence of the electromagneto-acoustic conversion efficiency, low-field susceptibility, and propagation velocities of transverse and longitudinal sound waves have been investigated by Vasilév et al. (1990) in the Heusler alloy Ni₂MnGa. The results revealed anomalies at the Curie point (T_c = 374 K) and in the vicinity of the cubic-to-tetragonal phase transition ($T_M = 270-280$ K). The elastic moduli in the cubic phase of this compound have been determined (Vasilev, Kokorin et al., 1990). Worgull et al. (1996) employed an ultrasonic pulse echo technique to measure the elastic constants and their temperature dependence. These ultrasonic results differ from an earlier ultrasonic study and provide the first direct determination of the elastic constant C'. The elastic constants soften as the premartensitic transformation is approached. The behaviour of the elastic constants and the ultrasonic attenuation confirms the existence of the intermediate phase (Worgull, Petti et al., 1996)

The conduction electron concentration is known to be a predominant factor in characterising the structural and magnetic properties of the Heusler alloys Webster (1984), and it has also been invoked to account for the phase transition in Ni₂MnGa (Fujii). Fujii et al. (1989) calculated electronic structure of Ni₂MnGa for both cubic and tetragonal structures by KKR (Korringa-Kohn-Rostocker) method. From the density of states of the cubic and tetragonal structure for the Ni₂MnGa alloy, it was predicted that a band Jahn-Teller mechanism causes the lattice transformation in this alloy (Fujii, Ishida et al., 1989). Ooiwa and co worker (1992) carried out NMR measurements on Ni₂MnGa and concluded that their results were consistent with the band structure calculation (Fujii, Ishida et al., 1989), in which the band Jahn-Teller effect is the origin of the transition (Ooiwa, Endo et al., 1992). Similar phase transitions in other Heusler alloys (Rh₂CoSn) have also been ascribed to a

band Jahn-Teller mechanism originally proposed to account for the structural phase transitions observed in A15 compounds (Labbe and Friedel, 1966).

1.3 Objectives

Heusler alloys have the subject of many investigations since the discovery of the first ferromagnetic alloy. These alloys form an interesting group for studying ferromagnetism because they provide a means of investigating the effects of interatomic distances, atomic arrangement and atomic environment of the magnetic atoms on the occurrence of ferromagnetism. Most Heusler alloys retain the Heusler structure at low temperature, but Ni₂MnGa alloy transforms martensitically to a tetragonal structure below 202 K. This makes Ni₂MnGa Heusler alloy a good candidate for studying mechanisms giving rise to the structural phase transition.

The object of the research programme:

- The aim of the experiment is to investigate the change in distribution of the magnetic electrons between the cubic and tetragonal phases of Ni₂MnGa in order to test the hypothesis, based on band structure calculations, that the phase transition is driven by a band Jahn-Teller effect.
- A study of the way in which the transition takes place in the ferromagnetic Heusler alloy Ni₂MnGa.
- A study of the effect of electron concentration on the magnetic and structural properties of Ni₂MnGa by the substitution of Ga by other elements.

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CHAPTER TWO

SAMPLE PREPARATION

2.1 Sample Preparation

2.1.1 Introduction

The provenance of the materials was as follows. Table (2.1) shows some of the general properties of the pure elements used in the investigations (Brown and Forsyth, 1973; Kittel, 1976; Nordling and Österman, 1987; Goodfellow, 1996-97; David, 1996; Matthey, 1997-98).

2.1.2 Alloys

Polycrystalline specimens of Ni_2MnGa , $Ni_2MnGa_{1-x}Sn_x$, $Ni_2MnGa_{1-x}ln_x$, $Ni_2Mn_{1-x}V_xGa$, $Co_2Mn_{1-x}V_xGa$, and $Cu_2Mn_{1-x}V_xGa$ were prepared.

15g alloys were made by repeatedly melting in an argon arc furnace the appropriate quantity of constituent elements. The starting elements were purchased from Johnson Matthey in the form of rods, pieces, flakes, or shot. The final mass of each sample was always close to 15g with weight loss of less than 2.5% recorded in all cases. The purity of the elements was at least 99.9%. Resistivity sticks of 1x1.5x20 mm were then spark eroded out of each ingot. Some pieces were selected from the ingots to be used for specific heat and magnetisation measurements. Several large lumps were selected and crushed in a hardened steel pestle and mortar into a fine powder. The powder was then investigated using X-ray diffraction.

In tables (2.2), (2.3), and (2.4) are listed untreated "as cast" Heusler alloys which have been prepared using the arc argon furnace and these are

Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x; where x (%) = 5, 2.5, 2, 1, 0.5, 0.27, 0.26, 0.25, 0.167, and 0.125. Also a sample of Ni₂MnGa_{1-x}In_x has been prepared with different compositions where x (%)= 5, 2, 1, 0.5, 0.25, 0.125, 0.0833, and 0.067. Finally Ni₂Mn_{1-x}V_xGa, Co₂Mn_{1-x}V_xGa, and Cu₂Mn_{1-x}V_xGa as shown in table(2.4).

Name	Vanadium	Manganese	Cobalt	Nickel	Copper	Gallium	Indium	tin
Symbol	V	Mn	Co	Ni	Cu	Ga	ln	Sn
Atomic No.		25	27	28	29	31	49	50
Atomic Weight	50.942	54.938	58.933	58.71	63.54	69.72	114.82	118.69
Melting.Point°C	1900	1245	1495	1453	1083	29.78	156.17	231.9
Boiling.Point°C	3000	2150	2900	2730	2595	2403	2000	2270
Density g/cm ³	6.11	7.43	8.92	8.908	8.94	5.907	7.31	7.29
Purity %	99.95	99.985	99.998	99.97	99.9	99.9	99.95	99.9985
Lattice Type	bcc (A ₂)	Cubic	Hcp (A ₃)	fcc	fcc (A ₁)	cubic	Tetragonal	Tetragonal
Lattice Const.Å	3.04		a=2.51 c=4.07	3.524	3.61		3.25	6.49
Electron Config.	3d ³ 4s ²	3d ⁵ 4s ²	3d′4s²	3d ⁸ 4s ²	3d ¹⁰ 4s'	3d ¹ 4s ² 4p ¹	4d ¹⁰ 5s ² 5p ¹ 1	4d ¹⁰ 5s ² 5p ²

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Table (2.1) general properties of elements used

Chapter 2: Sample Preparation

No.	Sample name	% Of Sn	Weight loss %
1	Ni2MnGa	0	0.48
2	Ni ₂ MnGa _{0.95} Sn _{0.05}	5	1.03
3	Ni ₂ MnGa _{0.975} Sn _{0.025}	2.5	0.34
4	Ni ₂ MnGa _{0.98} Sn _{0.02}	2	0.50
5	Ni ₂ MnGa _{0.99} Sn _{0.01}	1	0.33
6	Ni ₂ MnGa _{0.995} Sn _{0.005}	0.5	0.17
7	Ni ₂ MnGa _{0.9973} Sn _{0.0027}	0.27	0.45
8	Ni ₂ MnGa _{0.9974} Sn _{0.0026}	0.26	0.48
9	Ni ₂ MnGa _{0.9975} Sn _{0.0025}	0.25	0.45
10	Ni2MnGa0.99833Sn0.00167	0.167	0.40
11	Ni2MnGa0.99875Sn0.00125	0.125	0.60

Table (2.2) shows $Ni_2MnGa_{1,x}Sn_x$ Heusler alloys of different compositions

Table (2.3) shows Ni₂MnGa_{1-x}In_x Heusler alloys of different compositions

Ni2MnGa1-xInx				
No.	Sample name	% Of In	Weight loss %	
1	Ni ₂ MnGa _{0.95} In _{0.05}	5	0.533	
2	Ni2MnGa _{0.98} In _{0.02}	2	0.553	
3	Ni2MnGa _{0.99} In _{0.01}	1	0.45	
4	Ni2MnGa _{0.995} In _{0.005}	0.5	0.29	
5	Ni2MnGa _{0.9975} In _{0.0025}	0.25	0.62	
6	Ni2MnGa _{0.99875} In _{0.00125}	0.125	0.54	
7	Ni2MnGa _{0.99917} In _{0.00083}	0.0833	0.24	
8	Ni2MnGa _{0.99933} In _{0.00067}	0.067	1.1	

Table (2.4) shows some Heusler alloys of different compositions

No.	Sample name	% Of V	Weight loss %
1	Ni ₂ Mn _{0.99} V _{0.01} Ga	1	0.27
2	Ni ₂ Mn _{0.90} V _{0.10} Ga	10	0.29
3	Co ₂ Mn _{0.99} V _{0.01} Ga	1	1.03
4	Cu ₂ Mn _{0.99} V _{0.01} Ga	1	2.21

2.1.3 Argon arc furnace

Polycrystalline 15g ingots were prepared using an argon arc furnace built in the department.

A schematic diagram of the furnace is shown in figure (2.1). The appropriate quantities of the constituent elements were placed in a cigar shaped trough in the copper hearth of the furnace.

The elements with the lowest melting point were placed in the bottom of the trough and those with the highest on the top, thus the fabrication of the ingot began by melting the constituent with the highest melting point. Once the elements had been arranged in the hearth of the furnace was closed and evacuated. It was then flushed with pure argon and evacuated several times before being filled with a reduced atmosphere (pressure = 0.2 bar) of argon. A DC generator was used to provide an arc between the electrode and the copper hearth.

Water cooling to the electrode and the hearth prevented overheating and hence damage. The electrode was mounted in a mechanical bellows, which allowed both vertical and lateral movement.

Prior to fabricating the ingot a piece of titanium was melted for several minutes. The molten titanium acted as a getter, removing any residual oxygen in the atmosphere. If the titanium remained shiny after the melt then it was clear that there had been negligible oxygen present. Once this was done the arc was directed on to the elements to form the specimen. After the ingot had been formed it was turned over several times and remelted in order to ensure homogeneity.



Fig. (2.1) Schematic diagram of the Argon arc furnace.


Fig. (2.2) Schematic diagram of Vacuum / Gas handling system of Argon arc furnace.

2.2 Single Crystal

A single crystal of Ni₂MnGa for use in the neutron diffraction experiments was grown using the Czochralski method (Brown, 1989) A BCG365 Bridgman/Czochralski/Float zone crystal growth systems manufactured by Barington&Company was used to grow the crystal (Brown, 1989).

2.2.1 Apparatus

Principal Features of the equipment are:

- Czochralski, Bridgman, RF Float zone and Kyropoulos crystal growth facilities.
- 1800°C RF operation in vacuum or inert atmosphere.
- Rapid heating and cooling cycles.
- Precise control of temperature gradients.
- Complete visibility within growth area.

Chapter 2: Sample Preparation

- Choice of work chamber size.
- Wide range of optional accessories.
- Contamination free growth area.

2.2.2 General Description

The BCG365 system is a versatile, low cost, precision crystal growth system, designed for use with Bridgman, Kyropoulos, Czochralski and RF Float zone crystal techniques.

Intended primarily for RF induction heating, resistance heated options are available as economical alternatives covering a lower range of temperatures but excluding the use of float zone techniques (Brown, 1989).

A choice of chamber sizes is also available, which make the system extremely versatile when combined with the choice of heating sources and the wide range of accessories.

The melt and growth area are contained within a double walled, water-cooled, temperature assembly mounted vertically from the rigid main frame assembly. All controls are contained in an individual console that may be fixed to the main frame or free mounted to a convenient location. A top plate secured to the main frame support by a precision adjustable slideway mechanism holds the upper end of the chamber. RF heating coil fixtures and the chamber lower base plate assembly is also rigidly mounted from the vertical main frame support.

Careful design of the chamber and furnace assemblies has provided for easy access to the crucible for charge loading and unloading. In addition, the transparent walls allow continuous visual assessment of the growth conditions throughout the run. This avoids the need for complex and costly temperature control equipment. These advantages combined with the short heating and cooling cycles, makes the system particularly useful for general alloy preparation and vacuum annealing.

Chapter 2: Sample Preparation

The equipment is supplied as a basic modular unit to which additional options may be added at any stage. This basic unit consists of the main frame assembly with its chamber support fixtures and Bridgman lowering mechanism, which allows a crucible or mould to be raised or lowered with respect to the heating source. The control console also forms part of the basic unit having removable blank panels to allow additional controls to be fitted when necessary.

When using the RF induction heating system, charge temperatures of up to 1800°C may be achieved (up to 3000°C if the float zone assembly is fitted). All the RF heated versions may be used with vacuum, inert, oxidising, or reducing atmospheres with compatible refractory materials for the chamber furniture. The RF experimental set-up is shown in figure (2.3) (Beaney, 1996), and figure (2.4) shows the vacuum crystal puller (Brice, 1965). The RF coils induce eddy currents in the carbon jacket, which heat the alumina crucible and, in turn, the melt.

Chapter 2: Sample Preparation



Fig (2.3) Experimental set-up of Crystal Growth System



Fig (2.4) Vacuum Crystal Puller

2.3 Czochralski Growth of Single Crystals

2.3.1 Introduction

The process described in this section is often referred to as crystal pulling, and usually involves pulling of a seed crystal from the melt. For a given material the process first described by Czochralski (1918) is the fastest melt growth method which produces crystals.

Crystal pulling is also the method which is likely to produce the highest quality crystal in the sense of the most perfect and homogeneous. At least half of all the high-quality crystals grown are pulled. In common with the other melt growth methods, pulling is applicable only to materials which melt congruently or near congruently, i.e. the compositions of the solid and the melt in equilibrium are similar (Brice, 1986).

2.3.2 The Production of Bulk Crystal

As might be expected, melt growth is widely employed for the preparation of congruently melting materials because of the high growth rates which can be used and the high crystalline perfection attainable with, for example, the Czochralski technique. However there are materials for which it cannot be applied and several other techniques such as hydrothermal, flux growth or closed tube vapour transport is then utilised.

The factors governing the choice of technique for the production of a bulk crystal of a given material are numerous but will hopefully become evident from consideration of the advantages and disadvantages of individual techniques. However some dominant factors can be listed (Hurle, 1979):

 Does the crystalline phase require melt congruently or incongruently or does it form by solid state transformation at some temperature below the liquidus temperature? If it does melt congruently or near congruently the possibility of melt growth is preferred. If it melts incongruently, solution or vapour growth should be used which would require much slower growth rate.

- Does the material evaporate or dissociate at the likely growth temperature? Melt growth of some crystals such as gallium nitride is precluded because of the enormous dissociation pressure which exists at the melting point and processes involving a much lower growth temperature must be found.
- Chemical reactivity of the crystal and the nutrient phase with the components of the growth apparatus is frequently a problem. For example, is there a suitable crucible material to contain the melt growth?
- In the case of single crystals compound the stoichiometry needs to be considered. In general the congruently melting composition will not be the stoichiometric one so that growth from the melt at the congruent point will not yield the stoichiometric solid.

2.3.3 Crystal Pulling (Czochralski Growth)

By far the most widely used and most rewarding method of liquid-solid single crystal growth of rare earth elements and, in particular, intermetallic compounds is pulling from melt by the Czochralski technique. The elements of pulling are illustrated in fig (2.5) (Hurle, 1979). Also, figure (2.6) shows the essential features of the Czochralski technique (Abell, 1989).

The basic method is simple:

- 1) The melt is raised to a temperature a little above the melting point. In a well designed system, temperature differences both radially and vertically are fairly small, so that the bulk of the melt is within say ± 20%C of its mean temperature, which for a high-thermal-conductivity material will be about 25°C above the melting point. For a low-conductivity material the mean melt temperature will be nearer to the melting point.
- 2) The seed crystal, rotating slowly, is brought slowly into contact with the melt surface, and allowed to come to thermal equilibrium. If the melt temperature

was at its optimum value, the seed melts slowly and at a decreasing rate so that the seed remains in contact with the melt. If the seed does not remain in contact, the melt temperature was too high. If visible crystal growth occurs, the temperature was too low and must be increased until all the grown material and a bit of the seed have melted.

- 3) After a short pause-typically 1 to 3 minutes-pulling is commenced at a slow rate. The new crystal should grow with a diameter, which is slightly, less than the seed diameter occurs.
- 4) The growth rate and rotation rates are increased to their final values. The diameter of the growing crystal should decrease. If a dislocation-free crystal is required, a long narrow neck is grown.
- 5) After completion of the neck, the melt temperature is lowered slowly. The diameter of the crystal increases. At a point determined by experience the lowering of the melt temperature is stopped and after a short time the crystal should attain its final diameter.
- 6) Growth is then terminated. In some cases this is done by sharply increasing the pulling rate so that the crystal breaks contact with the melt. A better procedure is to increase the melt temperature so that the crystal diameter decreases fairly slowly to zero. (Rapid changes can cause dislocation formation or even crack the crystal).

2.3.4 Growth of Ni₂MnGa

In order to maintain a constant diameter it is usual to increase or decrease the power input to the melt. An increase in power decreases the crystal diameter. Increasing either the growth rate or the seed rotation rate produces the same effect. However, either of these actions changes the amount of solute incorporated.

Ni₂MnGa single crystal was grown in the department using the Czochralski technique. The pulling rate of the crystal was 15 mmh⁻¹ and the rotation was 0.3 rpm. The crystal is 13 mm long and of 2 mm diameter.

Subsequent X-ray Laue photography indicated that the $(1\overline{1}0)$ axes was along the length of the crystal.



Fig (2.5) Schematic representation of a crystal puller



Fig (2.6) Schematic representation of the Czochralski technique: (a) seeded growth from a hot crucible; (b) random orientation growth by 'necking'; (c) induction heated cold crucible, and (d) tri-arc cold crucible.

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CHAPTER THREE

CRYSTALLOGRAPHIC: (X-ray Measurements)

3.1 Introduction

X-rays were discovered in 1895 by Wilhelm Konrad Röntgen in experiments with beams of energetic electrons. Unlike the ordinary light, these rays were invisible, but they travelled in straight lines and affected photographic films in the same way as light. On the other hand, they were much more penetrating than light and could easily pass through the human body, wood, thick layers of opaque materials etc. Röntgen immediately recognised the possible medical applications of these rays for making images of the tissues inside the human body.

The distance that X-rays can penetrate through a material depends on the density of the material. When X-rays pass through materials, they tend to be absorbed by the atomic electrons. Therefore materials of high density, such as lead, with a concomitant high density of electrons, strongly absorb and block X-rays (Ohanian, 1994).

3.2 Production of X-rays

X-rays, electromagnetic waves, are generated by the impact of energetic electrons on a metallic surface. Their generation can be understood by the familiar mechanism of the emission of radiation by acceleration of electric charges. When the fast-moving electrons collide with the atoms in the surface, they suffer sudden deceleration and radiate intense electromagnetic

waves of short wavelength. This kind of radiation is called Bremsstrahlung. They have been shown to form part of the electromagnetic spectrum with wavelength of the order of 1 A°. The precise spectrum of the X-rays emitted depends both on the material of the surface and on the energy of the electron beam (Brown and Forsyth, 1973; Ohanian, 1994).

3.3 Spectrum of X-rays emitted

The spectrum of X-rays obtained by bombarding a copper target with 35 K eV electrons is illustrated in figure (3.1) (Brown and Forsyth, 1973)



Fig (3.1) Spectrum of X-rays emitted by a copper target at 35 KeV excitation.

The spectrum consists of a broad band of continuous (white) radiation together with a number of discrete emission lines. Both parts of the spectrum can be understood in terms of quantum theory, the continuous radiation results from inelastic collisions between the material; energy lost in the collisions is emitted as X-radiation. The white spectrum has a well-defined minimum wavelength (maximum energy) which corresponds to a collision in which an electron loses the whole of its energy in a single process.

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Thus

$$\lambda_{\min} = \frac{hc}{eV_{\circ}}$$
 or $\lambda_{\min} = 12.34/V_{\circ}$ (3.1)

Where λ is in Å and V₀ in kV

It is found in practice that the maximum intensity of the white spectrum occurs at a wavelength approximately twice λ_{min} . The characteristic line spectrum of the target is emitted during the rearrangement of the orbital electrons of the target atoms as a consequence of the ejection of one or more of their inner electrons by the bombarding electrons. The K emission lines correspond to radiation emitted when electrons fall from the outer shells to fill holes in the K shell; the K_{α} line corresponds to an L-K transition and the K β_{I} line to an M to This is also true for the L and M shells, the α lines K transition. corresponding to transitions with a change of unity in the principal quantum number and the strongest β and γ lines to changes of 2 and 3 respectively. The selection rules for these transitions are such that the K α lines are a close doublet with the stronger component $K\alpha_1$ having twice the intensity of the weaker K α_2 component. As the atomic number of the target element increases, the energy difference between successive shells increases and hence the wavelength of the characteristic K lines is shortened.

Table (3.1) gives a list of the wavelengths of the K α and K β lines of some commonly used target materials (Brown and Forsyth, 1973).

Target	Wavelength (Å)				eta -Filter		
element	κα2	κα	$\overline{K\alpha}$	κ $β_1$	к		
					absorption	Element	Thickness
					edge		x 10 ⁻³ (cm)
Cr	2.2935	2.2896	2.2909	2.0848	2.070	V	1.7
Mn	2.1057	2.1017	2.1031	1.9101	1.896	Cr	1.7
Fe	1.9399	1.9360	1.9370	1.7565	1.743	Mn	1.8
Co	1.7928	1.7889	1.7902	1.6208	1.608	Fe	2.0
Ni	1.6617	1.6578	1.6591	1.5001	1.488	Со	2.0
Cu	1.5443	1.5405	1.5418	1.3922	1.380	Ni	2.2
Мо	0.7135	0.7093	0.7107	0.6322	0.620	Zr	11.3
Rh	0.6176	0.6132	0.6147	0.5456	0.533	Ru	7.3
Ag	0.5638	0.5594	0.5608	0.4970	0.486	Rh	7.7

Table (3.1) Data for some common target materials.

The filter thickness given is that required to reduce the intensity of the $K\beta$ line relative to the $K\alpha$ by a factor of 100.

3.4 Ranges of Radiation Used in Material Science

Radiation energy ranges continuously from very low to very high values e.g. 10^1 to 10^8 eV. The ranges of radiation can be categorised into four groups, according to their energy and to their mode of interaction with matter.

- 1. Very-high-energy radiation. With a lower limit of several MeV, they interact with the atomic nuclei by inducing nuclear reactions.
- High energy radiation. Their interaction extends to the inner electron shells of atoms, their energy ranging from about 1 KeV to a few MeV. It is the area of X-ray and of the so called high-energy electrons.
- 3. Low-energy radiation. Their interaction extends to the external electron shells of atoms, including the valence and the conduction bands of solids. Their energy ranges from about 10 eV to 1 KeV. It is the area of soft X rays and of low-energy electrons.

4. Very-low-energy radiation. Their interaction with atoms is limited to the valence and conduction bands and to the chemical bonds, with energies in the order of 1 eV or less. It is typically the range of light, ultraviolet and infrared radiation.

This classification in four groups of radiation is based on the localisation of the interaction at an atomic scale. Table (3.2) shows energy range of radiation commonly used in material science (Eberhart, 1991).

Energy (eV)	Electromagnetic	Matter waves	Classification
	waves		
10 ⁸			Very high energy
10 ⁷	γ-rays		
10 ⁶			
10 ⁵		High energy electrons	High energy
10 ⁴	X-rays		
10 ³			
10 ²	UV	Low energy electrons	Low energy
101			
1	Light		
10-1			
10 ⁻²	IR	Thermal neutrons	
10 ⁻³			
10 ⁻⁴			
10 ⁻⁵	Radio waves		Very low energy
10 ⁻⁶			
10-7			

Table (3.2) Energy range of radiation commonly used in material science

3.5 Apparatus

3.5.1 Experimental set-up

Measurements were made using standard Philips X-ray equipment with $CuK\alpha$ radiation. A broad focus PW2 103/100 copper radiation tube was used in conjunction with a PW1050/25 goniometer. The PW1050/25 can be employed in combination with various accessories for X-ray diffraction or X-ray Spectrometry such as counting components, sample holder.

In this instrument, both a hollow shaft, in which a specimen or a crystal holder assembly can be mounted, and a worm wheel, to which a counter probe arm can be attached, rotate in the same direction around an axis at speeds with a ratio 1 : 2. A high-precision worm, a wormwheel and precision-cut transmission gears are the main parts, which assure high resolution and great reproducibility.

The goniometer can be operated manually, or it is driven by a synchronous motor unidirectionally with increasing or decreasing angle or can move between two desired pre-set limits. A proportional detector PW1965/20/30 was connected to the counting equipment. The detector was fixed on the diffractometer 'axis' at constant angular velocity (Philips, 1950).

A schematic diagram of the diffractometer is shown in figure (3.2). The X-ray tube, with a supply voltage of 40 kV and supply current 20 mA, produced monochromatic radiation of wavelength $\lambda = 1.540562$ Å from the copper target. The sample was placed on a special sample holder, which was mounted at the centre of the goniometer. The start angle θ_i was selected and the counter was moved in steps of $\Delta 2\theta$ to a final angle $2\theta_f$. The diffracted radiation will be collected by the detector, thus all peaks within the specified range will be detected.

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The X-ray system is connected to a PC computer through interface unit, where the whole system can be controlled by a software package from Sietronics called Sietronics PW1050 diffractometer automation SIE 122D. Traces XRD analysis software is also provided. The diffraction pattern was displayed on a monitor and could be printed using Hewlett Packard Desk Jet 500C printer.



Fig (3.2) Schematic diagram of diffractometer apparatus.

The geometry of the diffractometer is shown figure (3.3).



Fig (3.3) Geometry of diffractometer

3.6 Sample Powder Preparation

Suitable powder was prepared by crushing pieces from the ingot using a steel pestle and mortar, resulting in a grain size of 250 μ m maximum. The powder specimens were pressed into specimen holder, in a form of a plate, (made from Aluminium), with a 1 mm depression. The dimensions were large enough so the incident beam could only interact with the sample powder and not the holder material.

3.7 Structure Determination

3.7.1 Introduction

The Heusler alloys are a series of ternary, intermetallic local moment materials; usually containing Mn. They order in either the L2₁ (Heusler)-type structure with composition X₂MnZ or in the Cl_b type structure with composition XMnZ, Z may be any of a large range of s-p elements making this an attractive system for systematic study. Typical Z site elements are In, Sn, Al, Ge or Ga. Common X site elements are Cu, Co, Ni, Pd, Pt or Rh.

The first ferromagnetic copper-manganese-based alloys were discovered by Heusler in 1903 (Heusler, Starck et al., 1903). The ferromagnetic alloy, Ni₂MnSn, is one of a series of intermetallic compounds known as Heusler alloys. Other examples of this kind of structure are Ni₂MnIn, Co₂MnGa, and Pd₂MnSb.

3.7.2 The Crystallographic Structure

The Heusler alloys structure may be visualised as a system of four interpenetrating fcc sublattices with atoms A, B, C, and D occupying the locations (0,0,0), (1/4,1/4,1/4), (1/2,1/2,1/2) and (3/4,3/4,3/4), respectively (Hames, 1960; Webster, Ziebeck et al., 1984). The crystallographic structure is cubic and corresponds to a space group $O_{\mu 3} - Fm\overline{3m}$ and is the prototype of

"Strukurbericht" $L2_1$ structure. The unit cell of such an arrangement is depicted in figure (3.4).



In Ni₂MnGa, Ni atoms may be considered to occupy A and C sites Mn B site and Ga D site respectively as shown in figure (3.4).

Table (3.3) summarises the magnetic and structural properties of the principal Heusler alloys (Pearson, 1958; Hames, 1960; Webster, 1969).

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		Lattice			$\mu_{_{00}}$
Alloy	structure	parameter	θ_{F}	θ_{N}	(Bohr
		(Å)	(K)	(К)	magnetons
)
Cu ₂ MnAl	L21	5.95	600		3.8
Cu ₂ MnIn	L21	6.2	520		4.0
Cu ₂ MnSn	L21	6.17	(530)	—	4.1
Ni₂MnGa	L21	5.85	379	<u> </u>	4.17
Ni ₂ MnIn	L21	6.068	323	<u> </u>	4.40
Ni ₂ MnSn	L21	6.052	344	—	4.05
Ni ₂ MnSb	L21	6.000	360		3.27
Co ₂ MnAl	B2	5.756	697	—	4.01
Co₂MnSi	L21	5.654	985		5.07
Co ₂ MnGa	L21	5.770	694		4.05
Co ₂ MnGe	L21	5.743	905		5.11
Co ₂ MnSn	L21	6.000	829		5.08
Pd₂MnAl	B2	6.165		240	4.4
Pd₂MnIn	L21	6.373		142	4.3
(slow-					
cooled)					
Pd₂MnIn	B2	6.373		150	4.3
(quenched)					
Pd ₂ MnSn	L21	6.380	189		4.23
Pd ₂ MnSb	L21	6.424	47		4.40

Table (3.3) A summary of the magnetic and structural properties of the principal Heusler

alloys.

3.7.3 X-ray Diffraction

f 'the atomic scattering factor' is a quantity used to describe the efficiency of scattering of a given atom in a given direction. It is defined as

f = (amplitude of the wave scattered by an atom)/

(amplitude of the wave scattered by one electron)

The atomic scattering factor depends also on the wavelength of the incident beam and a fixed value of scattering angle θ . For any atom scattered in the forward direction the scattering factor f=Z (atomic number), while as scattering angle increases f decreases and the scattered waves become more and more out of phase. Calculated values of f for various atoms as a function of $(Sin\theta)/\lambda$ are tabulated in appendix 12 (Cullity, 1978).

The scattered waves from each of the atoms in the unit cell are added. The amplitude of each wave is given by the appropriate value of f for the scattering atom considered and the value of $(Sin\theta)/\lambda$ involved in the reflection. The phase of each wave is given by (Cullity, 1978)

$$\phi = 2\pi (hu + kv + lw) \tag{3.2}$$

Where u, v, w are fractional co-ordinates of x/a, y/b, z/c respectively, a,b,c are the edges of the unit cell and h,k,l are Miller indices.

The scattered wave in a complex exponential form is given by

$$Ae^{i\phi} = fe^{2\pi i(hu+kv+lw)} \tag{3.3}$$

The structure factor, represented by a symbol F, is the collection of all the waves scattered by the individual atoms. It describes how the scattered beam is affected by the atomic arrangement, and is expressed in the following as

$$F_{hkl} = \sum_{n=1}^{N} f_n e^{2\pi i (hu_n + kv_n + lw_n)}$$
(3.4)

Where the summation is carried over all atoms of the unit cell. The absolute |F| gives the amplitude of the resultant wave in terms of the amplitude of the wave scattered by all atoms of a unit cell to that scattered by a single electron.

The structure factor is the single most important factor in determining the intensity of diffraction peaks, where the Bragg intensity of the beam diffracted by all the atoms in the unit cell is proportional to $|F|^2$.

3.7.4 Structure factors of Heusler alloys

The generalised structure, described earlier, is comprised of four interpenetrating fcc sublattices, upon substituting the co-ordinates in equation (3.4) yields

$$F_{hkl} = 4 \left[f_A + f_B e^{\pi i (h/2 + k/2 + l/2)} + f_C e^{\pi i (h+k+l)} + f_D e^{\pi i (3h/2 + 3k/2 + 3l/2)} \right]$$
(3.5)

where f_A , f_B , f_C and f_D are the average scattering factors for the A, B, C and D sites respectively.

Sublattices A, B, C and D give rise to none-zero Bragg reflections only when the Miller indices of the scattering planes are either all even, or all odd (Webster, 1969). Three types of Bragg reflection are produced with different fcc structure factors; the superlattice reflections F(111) for h,k,l all odd and F(200) for (h+k+l)/2 = 2n+1 and the order-independent principal reflection F(220) for (h+k+l)/2 = 2n, and are independent of chemical order. This means that they occur at the same positions and with the same intensities in the patterns of both ordered and disordered alloys. The other reflections are order dependent (Webster, 1969; Webster, Ziebeck et al., 1984). The structure factors are illustrated in the following manner

h, k, l all odd

$$F(hkl) = 4 \left[(f_A - f_C)^2 + (f_B - f_D)^2 \right]^{1/2}$$
(3.6)
e.g. (hkl) = (111), (311)

$$F(hkl) = 4[f_A - f_B + f_C - f_D]$$
(3.7)
e.g. (hkl) = (200), (222)

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$$F(hkl) = 4[f_A + f_B + f_C + f_D]$$
(3.8)
e.g. (hkl) = (220), (400)

The change in the positions of atoms causes a change in Bragg intensities. Determination of the nature of these changes is obtained by calculating the structure factors F for each atomic arrangement and by calculating the degree of chemical order.

In an ordered Heusler alloy X_2YZ for atoms occupy A, B, C and D sites, the structure factors can be written as

$$F(111) = 4 |f_y - f_z|$$

$$F(200) = 4 |2f_x - (f_y + f_z)|$$

$$F(220) = 4 |2f_x + (f_y + f_z)|$$
(3.9)

3.7.5 Lattice Parameter Determination

In order to determine the chemical structure of the Heusler alloys use is made of Bragg's law, (Cullity, 1978)

$$\lambda = 2d_{hkl}Sin\theta \tag{3.10}$$

Where λ is the X-ray wavelength impinging on the specimen, and d_{hkl} is the separation of the planes scattering the X-rays.

The plane spacing parameter, d, of a cubic unit cell and the Miller indices (hkl) is given by

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2}$$
(3.11)

What determines the possible diffracted beam direction, i.e., the possible angles 2θ , in which a given crystal can diffract a beam of monochromatic X-ray?. We obviously need a general relation which will predict the diffraction angle for any set of planes. This relation is obtained by combining equations (3.10) and (3.11) applicable to the particular crystal involved. Consequently in a cubic lattice reinforcement occurs at angles θ given by the equation

$$Sin^{2}\theta = \frac{\lambda^{2}}{4a^{2}}(h^{2} + k^{2} + l^{2})$$
(3.12)

This equation predicts, for a particular incident wavelength λ and a, all possible Bragg angles at which diffraction can occur from the planes (hkl). A diffraction pattern for the samples has been obtained and the peaks indexed according to the reflections expected from a face centred cubic lattice.

The correspondence between the calculated and measured reflections was good, confirming the fcc structure. For each reflection indexed hkl, a value of the lattice parameter a was calculated. The determination of the lattice parameter a depends only on the accuracy with which the angle θ is measured.

Flat Sample Surface (g_{II})

The effect of any X-ray diffraction apparatus in modifying a pure diffraction maximum can be analysed by employed the superposition theorem (Klug and Alexander, 1970). According to this theorem the profile of the observed maximum, $h(\in)$, will be the convolution (Faltung) of the pure diffraction profile, $f(\in)$, and the weight function of the apparatus, $g(\in)$:

$$h(\epsilon) = \int_{-\infty}^{+\infty} g(\zeta) f(\epsilon - \zeta) d\zeta$$
(3.13)

The quantity $h(\in)$ is known as "fold" of $g(\in)$ and $f(\in)$. The function g expresses the sum total of the apparatus effects upon the pure function which is being measured. The variable \in measures the angular deviation of any point from the theoretical scattering angle, $2\theta^{\circ}$; this and the auxiliary variable ζ have the same dimensions as 2θ .

The weight function , $g(\in)$, of a spectrometer can also be regarded as composed of the following specific instrumental functions:

- g_I X-ray source profile.
- g_{II} flat rather than curved sample surface.
- g_{III} vertical divergence of the beam.
- g_{IV} absorption of the beam by the sample.
- g_V width of the receiving slit.
- g_{VI} misalignment function.

If the forms of these functions are known, the total instrumental profile, g can be synthesised.

In the physical sense, all these factors may be thought of as contributing simultaneously to the observed diffraction profile. For both the old and the new spectrometer designs, the function g_{II} takes the form

$$g_{II} = |\epsilon|^{-1/2}$$
 (3.14)

with the angular limits $\in = 0$ and

$$\epsilon_{\rm m} = -(\gamma^2 \cot \theta)/114.6 \text{ degrees}$$
 (3.15)

Compared with the other instrumental factors, the flat-sample effect is minor except at very small Bragg angles or when the horizontal beam divergence, γ , is large. This is particularly true when the source is viewed longitudinally, in which case γ can be as much as 3 or 4° without impairing the resolving power appreciably. It should be noted that below $2\theta = 90^\circ$ the functions g_{II} , g_{III} ,

and g_{1V} all shift the point of maximum intensity in the same direction, namely, toward lower Bragg angles (negative \in). In spectrometers without soller slits these three functions continue to distort the line profiles toward lower angles in the angular range above 90°, but the magnitude of the effect decreases rapidly to zero as 20 approaches 180° (Klug and Alexander, 1970).

Tables (3.4), (3.5) and (3.6) show the calculated values of lattice spacing for Ni_2MnGa , $Ni_2MnGa_{1-x}Sn_x$ series, $Ni_2MnGa_{1-x}ln_x$ series, $Ni_2Mn_{0.99}V_{0.01}Ga$, $Ni_2Mn_{0.99}V_{0.01}Ga$ and $Cu_2Mn_{0.99}V_{0.01}Ga$ at room temperature.

The variation of lattice constant a with tin content for untreated Ni₂MnGa is shown graphically in figures (3.5) and (3.6). Also the variation of the lattice parameter a with Indium content in Ni₂MnGa is shown in figures (3.7) and (3.8).

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			Lattice Parameter
Alloy	% of Sn	Average a Å	for (220) Plane
Ni₂MnGa	0	5.839	5.829
Ni2MnGa0.95Sn0.05	5	5.847	5.856
Ni ₂ Mn _{0.975} Sn _{0.025}	2.5	5.855	5.824
Ni₂MnGa _{0.98} Sn _{0.02}	2	5.838	5.822
Ni ₂ MnGa _{0.99} Sn _{0.01}	1	5.831	5.826
Ni₂MnGa _{0.995} Sn _{0.005}	0.5	5.828	5.844
Ni ₂ MnGa _{0.9973} Sn _{0.0027}	0.27	5.840	5.829
Ni ₂ MnGa _{0.997} Sn _{0.0026}	0.26	5.817	5.816
Ni ₂ MnGa _{0.9975} Sn _{0.0025}	0.25	5.827	5.829
Ni ₂ MnGa _{0.99833} Sn _{0.00167}	0.167	5.840	5.841
Ni ₂ MnGa _{0.99875} Sn _{0.00125}	0.125	5.835	5.859

Table (3.4) Lattice Parameter of Ni₂MnGa and Ni₂MnGa_{1-x}Sn_x Alloys.

Table (3.5) Lattice Parameter of Ni₂MnGa_{1-x}In_x series Alloys.

			Lattice Parameter
Alloy	% of In	Average a Å	for (220) Plane
Ni ₂ MnGa _{0.95} In _{0.05}	5	5.850	5.851
Ni ₂ MnGa _{0.98} In _{0.02}	2	5.833	5.831
Ni ₂ MnGa _{0.99} In _{0.01}	1	5.839	5.851
Ni ₂ MnGa _{0.995} In _{0.005}	0.5	5.852	5.869
Ni ₂ MnGa _{0.9975} In _{0.0025}	0.25	5.821	5.831
Ni ₂ MnGa _{0.9933} In _{0.00067}	0.067	5.843	5.849
Ni ₂ MnGa _{0.99875} In _{0.00125}	0.125	5.831	5.854
Ni ₂ MnGa _{0.99917} In _{0.00083}	0.083	5.825	5.849

Table (3.6) Lattice Constant of $Ni_2Mn_{1-x}V_xGa$, $Co_2Mn_{0.99}V_{0.01}Ga$ and $Cu_2Mn_{0.99}V_{0.01}Ga$.

			Lattice Parameter
Alloy	% of V	Average a Å	for (220) Plane
Ni ₂ Mn _{0.99} V _{0.01} Ga	1	5.826	5.846
Ni ₂ Mn _{0.90} V _{0.10} Ga	10	5.820	5.824
Co ₂ Mn _{0.99} V _{0.01} Ga	1	5.817	5.816
Cu ₂ Mn _{0.99} V _{0.01} Ga	1		



Fig (3.5) The variation of the lattice parameters with tin content for untreated Ni₂MnGa alloy.



Fig (3.6) The variation of the lattice parameters for (hkl) = (220) with tin content for untreated Ni_2MnGa alloy.



Fig (3.7) The variation of the lattice parameters with Indium content for untreated Ni₂MnGa alloy.



Fig (3.8) The variation of the lattice parameters for (hkl) = (220) with Indium content for untreated Ni₂MnGa alloy.

3.7.6 X-ray Diffraction results of Heusler Alloys

All measurements were carried out at room temperature. X-ray powder diffraction patterns of Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x, Ni₂MnGa_{1-x}In_x, Ni₂Mn_{1-x}V_xGa, and Co₂Mn_{1-x}V_xGa are shown in figures (3.9) to (3.14).

The aim of this investigation was to show whether the addition of Tin or Indium elements to the Ni₂MnGa alloy had an affect on the lattice parameter. The lattice constant was calculated for Ni₂MnGa sample using the Bragg equation, and the average value was found to be 5.824 Å while at the principal reflection (220), the value of a was 5.829 Å. Webster obtained a value of 5.825 Å for the lattice constant of a similar alloy. A refinement program named Fullprof also used to analyse the diffraction pattern of the Ni₂MnGa alloy, the purpose of this method is to fit a calculated diffraction profile to the measured diffraction profile. The refined lattice constant for Ni₂MnGa was found to be 5.818 Å. The refined diffraction profile is shown in figure (3.10).

The variation of the average lattice parameters and the lattice parameters for (hkl) = (220) with the Tin content are illustrated graphically on figures (3.5) and (3.6). Both graphs show a change of the lattice constant but it is not consistent where the values are increasing and decreasing due to the a mount of Tin. A similar result were obtained by replacing the content of Tin element with Indium and this is illustrated on figures (3.7) and (3.8).

From the characterisation of all X-ray diffraction patterns it was found that the patterns are consistent with the compounds crystallising in the face centred cubic $L2_1$ structure.

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All diffraction patterns showed some extra peaks, it turned to be part of the aluminium sample holder peaks.

There is a common feature between all diffraction patterns that is (200), (311), (222), (331) and (420) peaks are very tiny and sometimes it was very difficult to pinpoint the correct value of 2θ angles for these peaks.

On some diagrams for the samples containing 2.5%, 0.5%, 0.27% and 0.26% of Sn Reflection (220) showed a split, sometimes it was tiny and on some other patterns was large it might be due to $k\alpha_2$ line. The (400) reflection on all patterns showed a single shoulder and sometimes a double one. Also the intensity of the (422) reflection increases and decreases with the variation of the content of Tin or Indium in the Ni₂MnGa alloy, this also the case for the (220) reflection which turned to be the most intense reflection on all diffraction patterns. The (220) reflection has an extra peak in some diffraction patterns this peak is not indexable.

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Fig. (3.9) X-ray diffraction Pattern of Ni₂MnGa at room temperature.



Fig. (3.10) The refined diffraction profile of Ni₂MnGa at room temperature.



Fig. (3.11) X-ray diffraction pattern at room temperature of (a) Ni₂MnGa_{0.95}Sn_{0.05} and (b) Ni₂MnGa_{0.975}Sn_{0.025}.



Fig. (3.11) X-ray diffraction pattern at room temperature of (c)Ni₂MnGa_{0.98}Sn_{0.02} and (d) Ni₂MnGa_{0.99}Sn_{0.01}.



Fig. (3.11) X-ray diffraction pattern at room temperature of (e) Ni₂MnGa_{0.995}Sn_{0.005} and (f) Ni₂MnGa_{0.9973}Sn_{0.0027}.


Fig. (3.11) X-ray diffraction pattern at room temperature of (g) Ni₂MnGa_{0.9974}Sn_{0.0026} and (h) Ni₂MnGa_{0.9975}Sn_{0.0025}.



Fig. (3.11) X-ray diffraction pattern at room temperature of (i) Ni₂MnGa_{0.99833}Sn_{0.00167} and (j) Ni₂MnGa_{0.99875}Sn_{0.00125}.

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Fig. (3.12) X-ray diffraction pattern at room temperature of (a) Ni₂MnGa_{0.95}In_{0.05} and (b) Ni₂MnGa_{0.98}In_{0.02}.



Fig. (3.12) X-ray diffraction pattern at room temperature of (c) Ni₂MnGa_{0.99}In_{0.01} and (d) Ni₂MnGa_{0.995}In_{0.005}.



Fig. (3.12) X-ray diffraction pattern at room temperature of (e) Ni₂MnGa_{0.9975}In_{0.0025} and (f) Ni₂MnGa_{0.99875}In_{0.00125}.



Fig. (3.12) X-ray diffraction pattern at room temperature of (g) Ni₂MnGa_{0.99917}In_{0.00083} and (h) Ni₂MnGa_{0.99933}In_{0.00067}.



Fig. (3.13) X-ray diffraction pattern at room temperature of (a) Ni₂Mn_{0.99}V_{0.01}Ga (b) Ni₂Mn_{0.90}V_{0.10}Ga.



Fig. (3.14) X-ray diffraction pattern at room temperature of $Co_2Mn_{0.99}V_{0.01}Ga$.

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CHAPTER FOUR

MAGNETIC MEASUREMENT

4.1 Introduction

Ferromagnetism, antiferromagnetism, and ferrimagnetism are magnetic phenomena, which differ essentially from the diamagnetism and paramagnetism, since they are based on the interaction between the magnetic moments. These effects belong therefore to the class of cooperative phenomena. The theory of ferromagnetism (antiferromagnetism, ferrimagnetism) can be divided into two parts (Wagner, 1972). On the one hand, we have the subject of spontaneous magnetisation (saturation magnetisation). The second part comprises all effects caused by the magnetic anisotropy of the crystals: for example, the theory of the technical magnetisation curve, which deals with the adjustment of the individual uniformly magnetised domains in an external field and thus the problems of hysteresis, the theory of domain structure, the Bloch walls representing the transition region between two domains, and magnetostriction.

When a substance is placed in a magnetic field H, this field will induce inside the substance a field B which is given by

$$\mathbf{B} = \mathbf{H} + 4\pi \mathbf{M} = \mu \mathbf{H} \tag{4.1}$$

here M is the magnetisation of the substance and μ is the permeability. The magnetisation is due to the external field H. To a good approximation M is a linear function of H and we can put

$$M = \chi H$$
 . (4.2)

where χ is the magnetic susceptibility. Susceptibility is parameter characteristic of the substance considered, which, in general, depends on its temperature. According to sign and order of magnitude of χ substances are subdivided into three large classes (Wagner, 1972):

- a) $\chi < 0$ Diamagnetic substances
- b) $\chi > 0$ Paramagnetic substances
- c) $\chi = \infty$ Ferromagnetic substances

Group (a) is largest as almost all organic molecules belong to it, as well as all noble gases, several metals such as the noble metals, bismuth, zinc, mercury, and non-metals such as sulphur, iodine, silicon (Bates, 1963). The second group comprises all substances which posses a permanent magnetic moment, such as the transition elements and their compounds, as well as the rare earths, and the alkali metals. A few substances belonging to group b are ferromagnetic below a certain characteristic temperature, the Curie point, these substances represent group c, which also comprises the antiferromagnetic and ferrimagnetic substances. The property of being ferromagnetic (antiferromagnetic, ferrimagnetic) is linked with definite crystalline structures so that this class comprises only solids.

(a) Ferromagnetism

Iron, cobalt, nickel (and various alloys of these materials) are termed ferromagnetic materials. Ferromagnetic materials are the most magnetically active substances, and so they have very high magnetic susceptibilities, ranging from 1000 up to 100000. These materials are made of atoms with permanent dipole moments, and when these materials form solids by exchanging electrons to make chemical bonds, something special happens. If the atoms are of the right type and if the bond lengths are right, the electrons discover that they can place the system in a state of lower energy by having neighbouring atomic dipole moments aligned with each other. If the entire sample were to be made of aligned dipoles, however, a strong magnetic field would be created, and this would be a state of high energy. So

the system compromises. It makes microscopic regions in which billions of dipoles are aligned, satisfying the demands of most of the electron bonds. But the alignment directions of the separate regions are random throughout the sample, making a very weak net magnetic field. These regions are called magnetic domains, and their behaviour gives ferromagnetic materials their distinctive properties. When this happens these materials becomes paramagnetic.

For example, if a ferromagnetic material is heated to too high temperature, it ceases to be ferromagnetic. The reason is that above a certain critical temperature, called Curie temperature, the thermal motion of the atoms is so violent that the electrons in the bonds are no longer able to keep the dipole moment aligned.

The domains also make permanent magnets possible. If a ferromagnetic sample is placed in a strong magnetic field, the domains can be forced to coalesce into large domains aligned with the external field. When the external field is removed, the electrons in the bonds maintain the alignment and the magnetism remains. This means that the ferromagnetic materials can remember their past magnetic history. This property of magnetic memory is called hysteresis.

By applying a large magnetic field to separate the magnetic and nuclear scattering contributions, Felcher et al investigated the magnetic moment distribution in the Heusler alloy Cu₂MnAI. They were able to show that the alloy was chemically highly ordered and that within the accuracy of the experiment the entire moment of the molecule could be attributed to the Mn atom. Webster 1967 has confirmed that in most Heusler alloys containing Mn the magnetic moment is confined to the Mn sites and usually ~ 4 Bohr magneton per atom. Hence, it has been established that the magnetic moments are confined to the Mn sites except in those alloys which contain cobalt in which the magnetic moment is shared with the Co atoms (Webster, 1969), and that the chemical ordering of the atoms is an important condition for magnetic order.

Heusler alloys containing group III elements tend to exhibit partial or complete B2 disorder arising from interchange between atoms on the Y and Z sites. Group IV elements tend to stabilise the Heusler structure. In addition to influencing the crystallographic structure, the electron concentration is of paramount importance in establishing the long-range magnetic order. This is especially so in those Heusler alloys in which only the manganese atoms carry a moment and their separation $a/\sqrt{2}$, ~ 4.5 Å, on their f.c.c. sublattice is too large for direct d-d coupling to occur. The electron concentration affects not only the strengths of the exchange coupling, but also the sign, alloys containing group III elements tending towards antiferromagnetism and those containing group IV elements to ferromagnetism (Webster, Ziebeck et al., 1984).

In the Ni₂MnZ series, where Z is Al, Ga, In, Sn or Sb, only Ni₂MnAl (Ziebeck and Webster, 1975) orders in the B2 structure and is antiferromagnetic. All other alloys are highly ordered in the Heusler L2₁ structure and are ferromagnetic. The magnetic moment per manganese atom at 4.2 K are similar and broadly consistent with theoretical predictions if it is assumed that the manganese atoms contribute one electron to the conduction band. On raising the temperature to the paramagnetic region the moment remains effectively constant, as would be expected for a localised moment system.

Since the electron concentration plays such an important role both in stabilising the Heusler structure and in defining the type and the strength of the magnetic order, it is probable that it is also instrumental in driving the structural phase transition at 202 K in Ni₂MnGa (Webster, Ziebeck et al., 1984).

(b) Diamagnetism

A diamagnetic material is one whose atoms have no permanent dipole moment. When they are placed in a strong magnetic field, Lenz's law acts on the orbiting electrons and causes an atomic dipole moment to appear directed oppositely to the direction of the magnetic field. The effect is very weak but its effect, is to cause repulsion where other forms of magnetism give attraction. Because this effect opposes the applied field, the susceptibilities of such materials are negative, and because the effect is weak the magnitude of the susceptibilities are small, say in the range -10^{-5} to -10^{-4} erg Oe⁻²g⁻¹.

(c) Paramagnetism

A paramagnetic material is one whose atoms do have permanent dipole moments, but a cooperative state is not formed. If a magnetic field is applied to such a material, the dipole moments try to line up with the magnetic field, but are prevented from becoming perfectly aligned by their random thermal motion. Because the dipoles try to line up with the applied field, the susceptibilities of such materials are positive, but are rather small say in he range 10^{-5} to 10^{-3} erg $Oe^{-2}g^{-1}$.

4.2 Magnetic properties of solids

4.2.1 Magnetic dipole strength

According to Ampere's law, the magnetic moment of a current loop is the product of the loop area and the current (in emu). Thus for an orbiting electron in a circular path of radius r and angular frequency ω (Blackmore, 1969), the magnetic dipole moment is

$$\mu_{or} = -er^2\omega / 2c \tag{4.3}$$

Now the relationship between ω and r for an electron in motion about an atom is constrained by the quantum limitation that the orbital angular momentum must be a multiple of \hbar . This requires that the magnetic moment associated with orbital motion must be a multiple of the Bohr magneton

$$\mu_{B} = (e\hbar / 2mc) = 9.27 \times 10^{-21} \, erg \, / \, gauss \tag{4.4}$$

The angular momentum associated with the spin of an electron can be characterised by a spin quantum number $s = \pm 1/2$. This spinning motion has an associated magnetic moment, which is written as

$$\mu_{sp} = g s \mu_B \tag{4.5}$$

where g is the spectroscopic splitting factor, or g-factor. Since g = 2.0023 for a free electron, the magnetic moment of a spinning electron is almost exactly one Bohr magneton.

The total angular momentum for a multi-electron atom is obtained by vector addition of the components of orbital and spin angular momentum. In this scheme, the individual orbital quantum numbers combine vectorially to give a gross orbital angular momentum for the electronic system of the atom which is

$$\hbar \mathbf{J} = \hbar \mathbf{L} + \hbar \mathbf{S} \tag{4.6}$$

The manner in which electrons are assigned to various quantum states within a partially filled subshell is determined by the Pauli principle and by Hund's rules. A magnetic atom has a partially filled sub-shell and thus has some unpaired electrons; such an atom has a non-vanishing permanent magnetic moment, as required for Paramagnetism, ferromagnetism, antiferromagnetism, or ferrimagnetism.

The total magnetic moment of an atom or ion can be written as

$$\vec{\mu} = \mu_{\rm B} \left(\mathbf{L} + 2\mathbf{S} \right) \tag{4.7}$$

This moment precesses around the direction of \mathbf{J} , so using the terminology of Landé the momentum can be written as

$$\mu = g \mu_B J \tag{4.8}$$

Here

$$g = 1 + \frac{J(J+1) + S(S+1) - (L+1)}{2J(J+1)}$$
(4.9)

is the Landé splitting factor for an electron system in which the orbital and spin systems are coupled in the Russell-Saunders manner.

4.2.2 The forms of permanent dipole response

For different kinds of magnetic behaviour which involve permanent dipoles in solid are illustrated in figure (4.1) (Blackmore, 1969).



Fig. (4.1) shows the low temperature ordering of neighbouring dipoles, and the consequent behaviour of spontaneous magnetisation and susceptibility, for A, paramagnetism, B, antiferromagnetism, C, ferromagnetism and D, ferrimagnetism

a) Paramagnetic behaviour occurs when the magnetic moments of the various atoms are uncorrelated in the absence of a magnetic field. Of course the dipoles tend to become aligned in a magnetic field, and the magnetisation is governed by something similar to a Langevin function. In this case the weak-field susceptibility is still of the Curie law type

$$\chi = C/T \tag{4.10}$$

b) For an antiferromagnetic solid at low temperatures the total energy of the crystal in the absence of an external magnetic field is lowest when dipoles of opposing magnetic moment alternate. This arrangement is very stable at low temperatures, and the susceptibility in an applied field is small. When the temperature rises, the efficiency of this dipole-dipole interaction decreases and the susceptibility increases until the spins become "free" at the Néel temperature T_N to respond to a field. For still higher temperatures the behaviour is paramagnetic, and the susceptibility follows a modified Curie law

$$\chi = \frac{C}{T + \theta} \tag{4.11}$$

In this model θ must be of the same order of magnitude as T_N.

c) A ferromagnetic solid is ordered with parallel spins below the Curie temperature T_{c_1} a situation which results in a spontaneous magnetisation M_s . The magnitude of this bulk polarisation decreases to zero at the Curie point, and the paramagnetic susceptibility for the disordered spin system at higher temperatures obeys the Curie-Weiss law

$$\chi = \frac{C}{T - T_c} \tag{4.12}$$

d) The low temperature ordering in a ferrimagnetic material is similar to that of an antiferromagnetic material, but the two opposing spin systems have magnetic moments of unequal magnitude, and a net spontaneous magnetisation results as the lowest energy state of the system. This magnetisation declines to zero magnitude when the solid is warmed to the Curie point T_f, and the behaviour once again becomes paramagnetic at higher temperatures.

4.3 Magnetic Order

4.3.1 Introduction

At low temperature it is observed that many materials possess a finite magnetisation in the absence of an applied field. This spontaneous magnetisation is due to alignment of the permanent dipole moments and indicates that each dipole is aware of the direction in which other dipoles are pointing. This awareness results from the interactions between the moment. The transition to a state in which the dipoles are aligned represents an increase in the degree of order within the solid and thus a decrease in entropy. The simplest type of magnetic order is ferromagnetic order in which all the moments contribute equally to the spontaneous magnetisation. The ordering in antiferromagnets is such that there is no spontaneous magnetisation because half the dipoles are aligned in one direction and the other half in the opposite direction. In ferrimagnets there are oppositely directed moments which do not cancel and thus there is a net spontaneous magnetisation.

The magnetic interaction between the dipoles is too small to be responsible for magnetic ordering. To demonstrate this we estimate the magnetic interaction between two moments of magnitude μ_B a distance r = 3 Å apart; the field B at one moment due to the other is of the order $\mu_a \mu_B / 4\pi r^3$ so that the interaction energy can be estimated (Hook and Hall, 1991) as

$$\Delta E \sim \mu_B B \sim \frac{\mu_* \mu_B^2}{4\pi r r^3} \sim 3 \times 10^{-25} J \sim 2 \times 10^{-6} eV$$

This energy is equal to K_BT at a temperature of order 0.03 K. Random thermal disorder would be sufficient to destroy alignment of magnetic moments by this mechanism above this temperature. Many ferromagnets retain a spontaneous magnetisation at temperatures of order 1000 K, indicating a much stronger interaction. The only possibility is that the interaction results from the electrostatic interactions of the electrons with each other and with the nuclei in the solid; exchange provides a mechanism where

by the electrostatic interaction energy of two electrons can depend on the relative orientation of their magnetic moments.

4.3.2 The exchange interaction

For the interaction between neighbouring atomic magnetic moments in ferromagnets, Weiss (1907) introduced the molecular field theory which it was assumed that the effect of neighbouring moments could be represented by an internal field proportional to the intensity of magnetisation I. For an external field H the total effective field on a magnetic moment can be written as

$$H_e = H + cI \tag{4.13}$$

where c is the molecular field constant. This theory was considered the basis of the Curie-Weiss law for paramagnetic susceptibility

$$\chi = \frac{C}{T - \theta} \tag{4.14}$$

where χ is the susceptibility at temperature T, $\theta = T_c$ is the Curie temperature and C is a constant.

Heisenberg (1928) showed that a Weiss molecular field of the correct order of magnitude could originate as a result of the quantum mechanical exchange interaction between electrons from neighbouring atoms. The exchange energy, E between two spins S_i and S_j was expressed (Webster, 1969)

$$\mathbf{E} = -2\mathbf{J}_{\mathbf{i}\mathbf{i}}\mathbf{S}_{\mathbf{i}} \cdot \mathbf{S}_{\mathbf{i}} \tag{4.15}$$

where J_{ij} is the exchange integral for the spins i and j. If only exchange interactions between nearest neighbour are considered then the exchange energy for a given atom i with its j neighbours is

$$E = -2J_e \sum_j S_i \cdot S_j$$
(4.16)

where J_e is the exchange integral, assumed isotropic.

By carrying out the summation J_e may in principle be related to the Curie temperature θ . If all the spins are identical the summation yields the relation

$$\theta = 2ZJ_{e}S(S+1)/3k \tag{4.17}$$

where Z is the number of nearest neighbours and k is Boltzman constant. θ is the paramagnetic Curie temperature obtained from extrapolation of the paramagnetic χ^{-1} Vs T curve, but in this approximation it may be assumed to be equal to the ferromagnetic Curie temperature θ_{F} .

If the exchange integral J_e is negative, rather than positive as in the ferromagnetic case, then coupled spins will tend to antiparallel alignment and antiferromagnetism will result below a critical temperature, θ_N the Néel temperature. Above θ_N the moments are disordered, as in a ferromagnet above its Curie temperature, and the susceptibility is given by the Curie-Weiss law, but with $\theta = -\theta_N$.

In the above discussions it has been assumed (Webster, 1969) that the magnetic moments may be regarded as localised and that coupling is via a direct Heisenberg exchange interaction between neighbouring moments.

In transition metals the electrons responsible for ferromagnetism are believed to be those which derived from 3d states of free ions and are unscreened from neighbouring atoms in solids, which means the magnetic moments originate in the incomplete 3d shells, and a direct exchange would require sufficient overlap of the 3d wave-functions to provide an interaction of the appropriate magnitude and sign. In Heusler alloys the shortest distance between Mn sites is ~ 4.2 Å, $a/\sqrt{2}$, which is too great for the required overlap to occur.

CHAPTER 5: Measurements of the Specific Heat Capacity

An alternative method known as the collective electron theory has been put forward to account for the magnetic properties of metals. This assumes that the 3d and 4s electrons in the transition metals are sufficiently perturbed to permit itinerant behaviour. If the exchange coupling happens to favour parallel alignment of the 3d electrons for example, then the energies of those aligned paralleled to the given direction will be lowered, and those aligned antiparallel will be raised with respect to the Fermi level. This changing of energies results in an equal number of spins in the two directions and therefore a net spontaneous magnetisation corresponding to a non integral number of Bohr magnetons per atom.

Several attempts have been made to construct theories that will combine both the localised and collective electron theories in order to solve the problem of co-operative magnetic phenomena using models intermediate between the two. Zener (1951) in his model it was assumed that the 3d electrons remain localised whilst the 4s electrons form an energy band. This would mean that any direct exchange between the 3d shells of neighbouring atoms is assumed to be antiferromagnetic, and the 3d spins are coupled strongly to the spin of the conduction electrons and this type of interaction is ferromagnetic. The type of magnetic order that prevails is dependent upon the relative magnitudes of the various types of coupling. In 1953 Zener and Heikes applied the theory to the Heusler alloys that had been known with some qualitative success.

The RKKY Interaction

The original Zener theory turned out to be oversimplified but it drew attention to the fact that indirect exchange interactions might contribute to the internal field.

What is commonly known as the RKKY interaction is a mechanism for magnetic coupling between localised magnetic moments in metals. lt depends on the ability of conduction electrons to interact magnetically with the local moments and to propagate the polarisation between different magnetic atoms. The complete theory of s-d interaction has been developed by Ruderman-Kittel-Kasuya-Yosida (RKKY). In this theory the polarisation of the conduction electrons is represented by a long-range oscillatory function. The periodicity of the oscillations, which correspond to ferromagnetic and antiferromagnetic coupling, depends upon the conduction electron concentration. The RKKY interaction has been very successful in explaining the magnetic properties of the rare earth metals. The experimental evidence has suggested that in the rare earth metals the exchange must be long-range and oscillatory in real space, and the incomplete 4f shells are considered to be highly localised inside closed outer shells. However in the transition metal alloys the situation has been found to be more complicated as the 3d electrons are not localised and screened to the same extent as for the rare earth metal.

4.4 Arrott plots

The investigation of magnetic properties with the help of Arrott plots, i.e. plots of M^2 versus $\mu_o H/M$, has proved to be a useful tool in the analysis and description of magnetic materials. The basis of Arrott plots is a Landau description of the magnetisation, for which the free energy takes the form (Neumann and Ziebeck, 1995)

$$F = F_{\circ} + \frac{1}{2}AM^{2} + \frac{1}{4}BM^{4} - \mu_{\circ}M \cdot H$$
(4.18)

where A and B are coefficients in a series expansion of the free energy F in powers of the magnetic moment M. $\mu_{o}H$ is the external magnetic field and F_o comprises all contributions that are independent of the magnetic moment M. The coefficient A is temperature dependent and is related to the magnetic susceptibility χ (T) via χ (T) = 1/A(T). The coefficient B is taken to be temperature independent.

The free energy may be minimised with respect to M for any external magnetic field H, hence we get

$$M^{2} = \frac{1}{B} \frac{\mu_{\circ}H}{M} - \frac{A}{B}$$
(4.19)

Arrott plots are obtained by plotting the values of M(H) and (H) as a function of M^2 versus $\mu_{o}H/M$. According to the above equation this should result in a straight line. However, for the experimental investigations the Arrott plots are often found to result in curved lines. A detailed account for the Arrott plots can be found in (Brommer and Franse, 1990)

4.5 Measurement of Magnetisation

The magnetisation of ferromagnetic specimens may be measured in three main ways (Crangle, 1991): the induction method, the force method, and methods based on the detection of the dipole field of a magnetised specimen.

4.5.1 The SQUID System

SQUID stands for Superconducting Quantum Interference Device. It is a highly sensitive instrument used to measure magnetic moments down to 10⁻⁸ emu. It mainly consists of a Superconducting ring with a small insulating layer known as the weak link as shown in figure 4.2 (Babateen, 1994). Its resolution reaches down to 10⁻¹⁴T. The flux passing through the ring is quantised once the ring has gone Superconducting but the weak link enables the flux trapped in the ring to change only by discrete amounts. Quantised changes in flux occur as a result of tunnelling by electrons through a Josephson weak link in the SQUID ring. These quantised changes are used by the instrument to calculate the magnetic moment of the sample.



Fig. (4.2) SQUID magnetometer.

The Quantum Design Magnetic Property Measurement System or MPMS is a sophisticated analytical instrument configured especially for the study of the magnetic properties of small experimental samples over a broad range of temperatures and magnetic fields. Automatic control and data collection are provided by an HP computer and two independent subsystem controllers. Most of the gas control and other ancillary functions in the system are also automated.

The cryogenic probe integrates a 5.5 Tesla [1 Tesla for MPMS₂] superconducting magnet with a SQUID detection system and a high-performance temperature control system to provide rapid precision measurements over a temperature range of 1.9 to 400 Kelvin [4.5 to 350 Kelvin for MPMS₂] (Quantum Design, 1990).

4.5.2 SQUID Magnetometer

The single junction SQUID device has been used very effectively for years as an ultra-high sensitivity magnetometer. When an RF magnetic field of symmetric shape and of such an amplitude that ± 1 flux quantum is impressed upon the SQUID, it will produce a measurable RF power absorption from the driving oscillator. If the device is also subjected to an external magnetic field, the induced opposing circulating current will bias the SQUID preferentially in one current to greatly exceed the one flux quantum critical current compared with the opposite polarity. One then amplitude modulates the RF at a lower frequency and synchronously detects the amplitude modulation. If the SQUID is biased at a maximum or a minimum, the synchronous detector will produce an output at twice the modulation frequency. If, however, the bias field is not at the symmetry point, an error signal at the modulation frequency will be produced whose amplitude depends upon the displacement of the field from the symmetry point and of positive or negative phase, depending upon which direction the "error" is from the null point. This error is used to generate a correction field to return the SQUID back to zero. By this means one can detect externally imposed fields

to a small fraction, approximately 10⁻⁵, of a flux quantum. In order to improve field sensitivity, one commonly uses a large-area Superconducting pickup coil to capture the weak external field, and then to transformer-couple the resulting small current into the SQUID. In this fashion field sensitivities of 10⁻¹¹ gauss (10⁻⁷ Tesla) have been achieved (Lynn, 1990).

4.5.3 Experimental Set-up

The experimental set-up of the MPMS is shown in figure 4.3. The system has five major physical components.

- The HP computer with the installed MPMS control system software. This unit communicates with the two MPMS subsystem controllers via the IEEE-488 Bus interface protocol.
- 2) The electronic control console is comprised of the 1822 MPMS controller, the 1802 R/G bridge, the MPMS gas control system and vacuum pump, the Superconducting magnet power supply, and the microstepping sample transport controller.
- 3) The liquid helium dewar mounted in its cabinet.
- 4) The MPMS cryogenic probe which includes the temperature control module (TCM) integrated with MPMS Superconducting magnet and SQUID detection system.
- 5) The sample transport mechanism which is mounts on the top of the TCM, and three sample rod assembles for mounting samples.



Fig. (4.3) The MPMS system components

System Components

- 10. Dewar
- 1. Sample rod
- 2. Sample rotator
- 3. Sample transport
- 4. Probe
- 5. Helium level sensor
- 6. Superconducting solenoid
- 7. Flow impedance
- 8. SQUID capsule
- 9. Dewar cabinet

- 11. HP printer
- 12. Magnet power supply
- 13. Model 1802 Temperature controller
- 14. Console cabinet
- 15. Power distribution unit
- 16. Model 1822 MPMS controller
- 17. Gas/Magnet control unit
- 18. HP Vectra computer
- 19. Monitor

4.5.3 Measurement Steps

After putting the sample inside the tube, the following procedure was followed to insert the sample into the instrument before making a measurement (Quantum Design, 1990):

- 1) The sample is drawn into a protective glass sleeve by pulling the support tube up through the slide-seal, then the sliding clamp is adjusted so that the bottom of it was 128 cm above the centre of the sample. This will put the sample in the centre of the pickup coil when the support tube is inserted into the probe through the sample transport.
- 2) The airlock is vented by using the "Vent Sample Space" touch key and inserting the slide-seal housing into the socket in the sample transport.
- 3) The airlock valve is purged automatically.
- 4) Now we go into the Collect Data menu in the MPMS control system and with the touch key we press Go To bottom. This will move the transport to the bottom of its travel. Once the sample drive is positioned at the bottom limit of its travel, we slide the sample tube all the way into the probe until the slide clamp engages the mounting shoe on the sample transport. Now set the desired length and number of readings for the intended measurement, and select a suitable sensitivity range for the SQUID detection system or enable the "Autoranging" function. A quick scan of the sample should be run to verify whether the sample is correctly mounted and positioned properly with respect to the pickup coils.
- 5) After the sample is properly positioned, touch the soft key at the bottom of the Collect Data menu, to initiate a complete measurement using the measurement parameters displayed at the left side of the menu. The results of the measurement can be plotted out.
- 6) When the measurement has been completed, the sample may be removed by loosing the two Knurled screws on the mounting shoe then rotating the clamp and sliding the support tube up until the sample is safely above the airlock valve. The airlock valve may then be closed and the sample removed.

4.6 **Results and Discussion**

Magnetisation measurements in applied fields of up to 5 T have been carried out over the temperature range 2 – 300 K using a SQUID and from 100 K to 300 K, magnetisation measurements in applied fields up to 5 T have been carried out using a SQUID magnetometer. Polycrystalline samples of Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x and Ni₂MnGa_{1-x}ln_x with tin concentration of 2, 1, 0.5 and 0.25, and for indium concentrations of 5, 2, 1 and 0.5 were measured along with a single crystal of Ni₂MnGa, within the temperature range 100 K to 300 K and in applied field up to 1.5 T.

The magnetisation measurements for polycrystalline and single crystal Ni₂MnGa are shown in figures 4.1, 4.2 and 4.3. Figure 4.4 shows a plot of moment as a function of applied field at constant temperature (213K). Figures 4.5, 4.6, 4.7 and 4.8 show the magnetisation measurements as a function of temperature for the tin doped samples of Ni₂MnGa_{0.98}Sn_{0.02}, Ni₂MnGa_{0.99}Sn_{0.01}, Ni₂MnGa_{0.995}Sn_{0.005} and Ni₂MnGa_{0.9975}Sn_{0.0025} respectively. Figure 4.9a shows the magnetisation measurements as a function of temperature for Ni₂MnGa_{0.95}In_{0.05}. Figures 4.9b and 4.9c show a plot of magnetisation isothermals and Arrott plots respectively for the same sample. For the Ni₂MnGa_{0.98}In_{0.02} sample the magnetisation result is shown in figure 4.10a, the magnetisation isothermals in fig. 4.10b and Arrott plots in 4.10c. Finally, figures 4.11 and 4.12 show the magnetisation as a function of temperature for Ni₂MnGa_{0.99}Sn_{0.01} and Ni₂MnGa_{0.995}Sn_{0.005} polcrystalline samples in applied fields of 0.1 and 0.2 T.

A summary of the measured transition temperature, (upon cooling and heating) and magnetic moment / fu in Bohr magneton is presented in table 4.1.

Sample	%Sn	Transition temp.(K)		Applied	Magnetic moment
		Cooling	Heating	Field (T)	/Formula unit (µ _в)
(Single Crystal)	0	205.96	220.58	0.5	
Ni₂MnGa					
(Polycrystalline)	0	175.03	187.79	0.5	
Ni₂MnGa	× 1				
Ni₂MnGa _{0.98} Sn _{0.02}	2	N/A	N/A	0.5 - 5	3.34
Ni₂MnGa₀.99Sn₀.₀1	1	N/A	N/A		2.76
Ni₂MnGa₀.995Sn₀.005	0.5	N/A	N/A		3.65
Ni ₂ MnGa _{0.9975} Sn _{0.0025}	0.25	179.99	201.90		3.97
%In					
Ni ₂ MnGa _{0.95} In _{0.05}	5	N/A	N/A	0.5 - 5	4.049
Ni₂MnGa _{0.98} In _{0.02}	2	N/A	N/A		3.244
Ni₂MnGa _{0.99} Sn _{0.01}	1	N/A	N/A		
Ni ₂ MnGa _{0.995} Sn _{0.005}	0.5	N/A	N/A		

Table (4.1) The measured transition temperature and magnetic moment per formula unit for Ni₂MnGa (single crystal), Polycrystalline Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x and Ni₂MnGa_{1-x}Sn_x.



Fig. (4.1) Magnetisation against temperature for Ni₂MnGa Polycrystalline sample at a field of 0.5 T.



Fig. (4.2) Magnetisation as Function of temperature for Ni₂MnGa single crystal in a field of 0.5 T applied parallel to $[1\overline{1}0]$.



Fig. (4.3) Magnetisation as function of temperature for Ni₂MnGa single crystal



Fig. (4.4) Moment as a function of field for Ni₂MnGa single crystal at 213K the field was applied along $\begin{bmatrix} 1 & 1 \\ 0 \end{bmatrix}$



Fig. (4.5) Magnetisation as a function of temperature at various applied field for Ni₂MnGa_{0.98}Sn_{0.02}.



Fig. (4.6) Magnetisation of Ni₂MnGa_{0.99}Sn_{0.01} as a function of temperature at various applied field.



Fig. (4.7) Magnetisation of Ni₂MnGa_{0.995}Sn_{0.005} as a function of temperature at various applied field



Fig. (7.8) magnetisation of $Ni_2MnGa_{0.9975}Sn_{0.0025}$ as a function of temperature at various applied field.



Fig. (4.9a) Magnetisation of Ni₂MnGa_{0.95}In_{0.05} as a function of temperature at various applied field



Fig. (4.9b) Magnetisation Isothermals for Ni₂MnGa_{0.95}In_{0.05}



Fig. (4.9c) Ni₂MnGa_{0.95}In_{0.05} (Arrotts plots)



Fig. (4.10a) Magnetisation of $Ni_2MnGa_{0.98}In_{0.02}$ as a function of temperature at various applied field.



Fig. (4.10b) Magnetisation Isothermals for Ni₂MnGa_{0.98}In_{0.02}.



Fig. (4.10c) Ni₂MnGa_{0.98}In_{0.02} (Arrotts plots)


Fig. (4.11) Magnetisation as a function of temperature at various applied field for Ni₂MnGa_{0.99}In_{0.01}.



Fig. (4.12) Magnetisation as a function of temperature at various applied field for Ni₂MnGa_{0.995}In_{0.005}.

The results from the magnetisation measurements, on Ni₂MnGa polycrystalline sample as shown in fig. 4.1 clearly identify a magnetic phase transition at around 175.03 K during the cooling cycle and around 187.79 K upon heating, in an applied field of 0.5 T. This was confirmed by resistivity measurements which identified a phase transition around 154 K and 199.75 K upon cooling and heating respectively. Magnetisation measurements were carried out on a series of polycrystalline samples , where Ga was substituted partially by tin and indium in the alloy Ni₂MnGa. For the samples which contain tin the results of magnetisation as a function of temperature in various applied fields as presented in figures 4.5, 4.6 and 4.7 showed a typical behaviour of a ferromagnet and did not reveal any significant features in the

temperature interval 100 - 300 K. However, measurements undertaken between 100 and 300 K on the Ni₂MnGa_{0.9975}Sn_{0.0025} polycrystalline revealed a magnetic phase transition at around 179.99 K upon cooling and 201.9 K upon heating. Specific heat and resistivity measurements for samples taken from the ingot identified a similar phase transition.

Subsequent magnetic measurements were carried out on polycrystalline alloy which has a partial substitution of indium on the Ga sites. The result is indicated for $Ni_2MnGa_{0.95}In_{0.05}$, $Ni_2MnGa_{0.98}In_{0.02}$, $Ni_2MnGa_{0.99}In_{0.01}$ and Ni₂MnGa_{0.995}In_{0.005} in various applied fields. Figure 4.9a shows a typical ferromagnetic behaviour pattern, however for applied fields of 0.5 and 1 T, there is a slight change at around 200 K but it can-not be identified as a phase transition. It is possible that the magnetisation was increasing due to the increasing applied field. From fig. 4.9b, it may be seen that the magnetic isotherms change very little up to 295 K the maximum temperature available in the measurements suggesting that the Curie temperature is substantially higher. Arrotts plots reveal that the isotherms in the high field region are characterised by straight lines. A similar argument could be used for the $Ni_2MnGa_{0.98}In_{0.02}$ sample, where the results are shown in figures 4.10a, 4.10b As indicated in figures 4.11 and 4.12 magnetisation and 4.10c. measurements as a function of temperature at various applied field again show typical ferromagnetic behaviour.

Magnetisation measurements were also carried out in the temperature range 100 to 300 K on a single crystal of Ni₂MnGa using a squid magnetometer. The field was applied parallel to the $[1\overline{10}]$ axis of the crystal and the results showed that in a low field , (0.5 T), a jump in the magnetisation occurs at 220.58 K during heating. On cooling from 300 K in the same field the discontinuity in magnetisation occurs at 205.96 K clearly indicating the presence of hysteresis in the transition (fig.4.2). For a field of 1.5 T there is very little evidence of any discontinuity in the magnetisation associated with the structural phase transition as shown in fig. 4.3.

Resistivity measurements and magnetisation measurements have hysteresis associated with them which would be consistent with a first order phase transition.

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CHAPTER FIVE

Measurement of Specific Heat Capacity

5.1 Differential Scanning Calorimetry (DSC)

5.1.1 Introduction

The specific heat of Ni_2MnGa , $Ni_2MnGa_{1-x}Sn_x$ and $Ni_2MnGa_{1-x}In_x$ alloys in the range (100 - 298)K has been measured using a DSC manufactured by Mettler Instrument.

When a phase transition occurs, the change in heat content and the thermal properties of the sample is indicated by a peak in its differential thermal analysis output. If the reaction proceeds at a rate varying with temperature, i.e., possess as an activation energy, the position of the peak varies with heating rate if other experimental conditions are maintained fixed. This provides a straightforward method to investigate the activation energies involved in the phase transitions.

The differential scanning calorimeter was used to gather thermodynamic data on the samples. Thermal analysis measures the difference in heat flow to the sample and an inert atmosphere with respect to temperature. This allows the thermal changes in the sample to be detected; phase changes take in or emit heat energy whilst taking place, and the DSC allows these to be measured and calculated.

The specific heat at constant pressure, $C_{p.}$, of a sample can be determined as a function of temperature by the CP method. This function can either be presented graphically or presented in tabular form.

The heat flow to the sample, measured at constant heating rate, is directly proportional to the specific heat of the substance. In order to obtain precise values of C_p , a correction must be applied for additional heat flow arising from the difference in weight of the sample pan and reference pan. With the help of a preliminary blank experiment the correction is automatically made. The masses of both sample and blank pan (with the same reference pan) enter into the calculation as does the C_P function for aluminium. At the same time the blank correction compensates for any asymmetry in the measuring system.

Experiments were carried out using Mettler TA3000 system with DSC30 model measuring cell over the temperature range 100K to 298K.

5.2 Measuring Principle

Figure 5.1 shows a sectional view of the differential scanning calorimeter (DSC) measuring cell (Mettler, 1984).



Fig. (5.1) Sectional view of the DSC measuring cell.

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As shown in figure (5.1) a sample and a blank reference are heated or cooled at a constant rate. When a sample goes through a transition, an endothermic or exothermic reaction occurs. DSC's measure the energy (heat flow) required to keep the sample and reference at the same temperature.

It is clear from figure 5.1 that the heat flow \dot{H} to the sample, (\dot{H} in order to express that the heat flow is the change in sample enthalpy), is equal to the difference between the two heat flows \dot{Q}_s and $\dot{Q}r$.

Where \dot{Q}_s sample heat flow and \dot{Q}_r reference heat flow.

$$\dot{H} = \dot{Q}_{s} - \dot{Q}_{r} \tag{5.1}$$

According to the thermal analogue of Ohm's law $\dot{Q} = (T_2 - T_1)/R_{th}$, i.e., the heat flow is proportional to the driving force (temperature difference $T_2 - T_1$) and inversely proportional to the thermal resistance R_{th} . When this is applied to the DSC cell it follows that:

$$\dot{H} = \dot{Q}_{s} - \dot{Q}_{r} = \frac{T_{c} - T_{s}}{R_{th}} - \frac{T_{c} - T_{r}}{R_{th}}$$
 (5.2)

For reasons of symmetry, the two T_c 's and the two R_{th} 's are identical. It follows that

$$\dot{H} = -\frac{T_s - T_r}{R_{th}}$$
(5.3)

In order to avoid problems with signs, an effect is defined as exothermic or endothermic and the sign is omitted.

<u>Enthalpy</u>: The integration of a DSC signal over the thermal zero line yields the enthalpy function of the sample. The change of the enthalpy comprises the overall heat change resulting from possible transitions and from the specific heat, or from the latent heat.

A process in which the enthalpy of a body increases is called endothermal as heat is drawn from the surroundings. Obviously the exothermic is a process where heat is given up to the surroundings.

Temperature difference, $\Delta T = T_s - T_r$, is measured with a thermocouple as its electrical signal is directly proportional to the difference in temperature between the hot and the cold junctions (over the temperature range used): $\Delta U = \Delta T \cdot S$:

S is the so-called slope or sensitivity of the thermocouple, expressed in micro volt per Kelvin. As the temperature difference, $\Delta T_s - \Delta t_r$, is measured by the sensor thermocouple, it follows from the thermocouple equation, $\Delta U = \Delta T \cdot S$

$$\dot{H} = \frac{\Delta U}{R_{\rm th} \cdot S}$$
(5.4)

As the two terms in the denominator are functions of the actual temperature, they can be combined as the calorimetric sensitivity: $E = R_{th}$ 'S, which can be divided into a temperature dependent (relative) term E_{rel} and a temperature independent term E_{in} , specific to the measuring cell being used: $E = E_{rel} \cdot E_{in}$. Thus it follows that the heat flow to the sample is:

$$\dot{H} = \frac{\Delta U}{E_{In} \cdot E_{rel}}$$
(5.5)

The temperature dependence of E_{rel} is contained in the TA processor, (TA processor is the central unit of every TA3000 system configuration), as a hard programmed polynomial: $E_{rel} = A+BT+CT^2$, where A, B and C are the specific sensor parameters.

 E_{in} is determined by calibrating the DSC using the known heat of fusion of indium with the DSC measuring cell set to "medium sensitivity" using the standard sensor.

The primary signal is converted once per second with equation 5.5 to the DSC signal \dot{H} for the on-line plot on the printer/plotter and for the analogue output.

No account is taken in the derivation of equation 5.5 of the fact that heat capacities as well as resistances are associated on the path of the heat flow. The original heat flow is calculated in all off-line evaluations, is plotted on the printer/plotter and used for partial and total integrals.

5.3 Theory of DSC Reaction Kinetic and Applied Kinetics

5.3.1 Basic equations of Reaction Kinetics

Based on investigations (on the work) of Willhelmy in 1850, the rate of chemical reaction $\dot{\alpha}$ or $d\alpha/dt$ can be expressed as a function of the degree of conversion, α , using the kinetic equation as follows:

$$\dot{\alpha} = K(1-\alpha)^n \tag{5.6}$$

where

 $\dot{\alpha}$ = rate of reaction in s⁻¹

 $K = reaction rate constant in s^{-1}$

 α = degree of conversion (which grows from 0 to 1 during the reaction)

n = order of reaction

In calorimetric measurements, α is the ratio of enthalpies up to a given degree of conversion (Δ H) and total enthalpy of reaction (Δ H_T), i.e.

$$\alpha = \frac{\Delta H}{\Delta H_T} \tag{5.7}$$

which is equivalent to the ratio of areas under the DSC curve corresponding to a given conversion.

5.3.2 Reaction Temperature

In 1884 Arrhenius worked out an empirical relation for the temperature dependence of the reaction rate.

In equation (5.6), according to the Arrhenius relationship, the K parameter is a temperature dependent, hence the equation is written as

$$K = A e^{-E_A / RT} \tag{5.8}$$

where

A = reaction rate constant at infinite temperature (pre-exponential factor s⁻¹) E_A = activation energy in J mol⁻¹ T = temperature in Kelvin R = gas constant = 8.31 J mol⁻¹ K⁻¹

Taking logarithms of equation 5.8

$$\ln K = \ln A - \left(\frac{E_A}{R} \cdot \frac{1}{T}\right)$$
(5.9)

This is a linear function of $\ln K$ versus 1/T, the so called "Arrhenius plot" as shown in figure 5.2





To obtain the temperature dependence of the reaction rate, we combine equations 5.6 and 5.8 as

$$\dot{\alpha} = d\alpha/dt = Ae^{-E_A/RT}(1-\alpha)^n \tag{5.10}$$

At constant heating rate B = dT/dt, equation 5.10 can be written in the following form

$$\frac{d\alpha}{dT} = A(1-\alpha)^n e^{-E_A/RT} / B$$
(5.11)

Determination of parameters A, E and n is based on the solution of equations (5.10) and (5.11).

5.4 Sample Preparation

The purpose of sample preparation is to reduce the thermal resistance to the DSC sensor. Thus temperature gradients with sample and consequent "blurring" of the DSC signal are avoided (Mettler, 1984).

Small pieces of a sample can be chipped or cut out from the ingot, and powders also provide ideal samples. The solid piece is then laid flat in the bottom of the pan using tweezers. Frequently a pan lid, moulded as shown in figure (5.3), is sufficient to ensure that the sample is automatically pressed down on to the bottom of the pan when it is sealed.



Fig. (5.3) Pan sample holder

To weigh the sample the pan and the lid were tared, the sample was then placed in the pan, which was closed and the net weight read on the balance.

In general, the sample pan was measured against a reference pan in all DSC measurements. Apart from the sample, the reference pan should be as similar as possible in weight and shape to the sample pan. Normally an empty pan with perforated lid is used as a reference to a void distortion at temperatures above 250 °C. As the pan can be used repeatedly it is recommended that two holes are pierced in the lid in order to identify it.

After opening the DSC cell, the sample pan is placed in the left hand measurement position so that the centre pin of the pan is located in the hole surrounded by the 5 thermocouples. The reference pan is inserted in the right hand measurement position.

5.5 Experimental

5.5.1 DSC Measurements

The Mettler TA3000 system shown in figure (5.4) was used to study the phase transition temperature and determination of the specific heat of Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x and Ni₂MnGa_{1-x}In_x in the temperature range 100 K to 298 K.

The system shown consists of a DSC30 cell (cryofurnace covering temperature range -175 °C to 600 °C), a liquid nitrogen reservoir, a TC10A TA processor to control the furnace being used and to perform the calculations, as well as a printer for the output of results. Inert gas (argon) was used to purge gas and vapour products formed during analysis from the cell. The measurement cell is thus protected from corrosive gases. The purge gas also removes atmospheric oxygen in order to avoid unwanted oxidation of the sample.



Fig. (5.4) The Mettler TA3000 System.

- (a) Power cable for furnace
- (b) Power cable for DSC30 cell
- (c) Signal cable for DSC30
- (d) Connecting cable to printer/plotter
- (e) Connecting cable to microbalance.
- (f) Mains cable for printer/plotter
- (g) Mains cable for TC10A
- (h) Mains cable formicrobalance
- (I) Hand or foot transfer key

Thermal events in the sample appear as deviations from the DSC baseline in either an endothermic or exothermic direction depending upon whether more or less energy has to be applied to the sample relative to the reference material. In DSC, endothermic responses are usually represented as being positive, i.e. above the baseline, corresponding to an increased transfer of heat to the sample compared to the reference.

Samples ~ 90 mg to 175 mg were cooled down or heated in an inert argon atmosphere (with a flow rate 80 to $100 \text{ cm}^3/\text{min}$) at a heating or cooling rate of 5 K/min with a temperature range of -173 °C to 25 °C. Samples were sealed in aluminium pans, with usually a hole punched through the lid to allow any vapour to escape.

5.5.2 Results

The screening method is principally used for any initial thermoanalytical study of a substance. It is generally applied over a wide temperature range at medium to high heating rate. Data obtained during the experiment are then available for the various numerical evaluations as they are stored entirely in the TA processor. The DSC curve recorded in this measurement is now available in the data memory for evaluation.

The DSC curve obtained by the screening method can now be evaluated using various methods available in the TA processor.

The peak temperature of the initial transition exotherm was measured, and DSC thermograms from Ni₂MnGa alloy is shown in figure (5.5). Figure (5.6) shows the transition peaks for Ni₂MnGa_{0.9975}Sn_{0.0025} alloy upon cooling and heating the sample. The phase transition of these alloys with their enthalpy change ΔH are shown in table (5.1). Figure (5.7) shows the peak temperatures in the DSC thermograms for the Ni₂MnGa_{0.99917}In_{0.00083} alloy for both cooling and heating. The results for the DSC measurement on the Ni₂MnGa_{1-x}In_x series are given in Table (5.2).

CHAPTER 5: Measurements of the Specific Heat Capacity



Fig. (5.5) DSC thermograms for Ni₂MnGa at a heating and cooling rate of 5 K/min.



Fig. (5.6) DSC thermograms for Ni₂MnGa_{0.9975}Mn_{0.0025} at a heating and cooling rate of 5 K/min.



		Transition Te	<u>тр.Т_М (К)</u>	Enthalpy (∆H)
Alloy	%Sn	<u>Cooling</u>	<u>Heating</u>	JG ⁻¹
		(298 - 108)K	(108 - 298)K	
Ni₂MnGa	0	209.4	224.1	3.5849 cooling Exo
				4.2059 Heating Endo
Ni ₂ MnGa _{0.95} Sn _{0.05}	5	NA	NA	NA
Ni₂MnGa _{0.975} Sn _{0.025}	2.5	NA	NA	NA
Ni ₂ MnGa _{0.98} Sn _{0.02}	2	NA	NA	NA
Ni₂MnGa _{0.99} Sn _{0.01}	1	NA	NA	NA
Ni₂MnGa₀.995Sn₀.5	0.5	NA	NA	NA
Ni ₂ MnGa _{0.9973} Sn _{0.0027}	0.27	NA	NA	NA
Ni ₂ MnGa _{0.9974} Sn _{0.0026}	0.26	NA	NA	NA
Ni ₂ MnGa _{0.9975} Sn _{0.0025}	0.25	175	199.6	1.3090 cooling Exo
				1.6792 Heating Endo
Ni ₂ MnGa _{0.99833} Sn _{0.00167}	0.167	NA	NA	NA
Ni ₂ MnGa _{0.99875} Sn _{0.00125}	0.125	NA	NA	NA

Table (5.1) DSC measurement for Ni_2MnGa and $Ni_2MnGa_{1-x}Sn_x$ series.

Table (5.1) DSC measurement for $Ni_2MnGa_{1-x}In_x$ series.

		Transition Temp.T _M (K)		Enthalpy (∆H)
Alloy	%in	Cooling	<u>Heating</u>	JG ⁻¹
		(298 - 108)K	(108 - 298)K	
Ni ₂ MnGa _{0.95} In _{0.05}	5	NA	NA	NA
Ni ₂ MnGa _{0.98} In _{0.02}	2	NA	NA	NA
Ni ₂ MnGa _{0.99} In _{0.01}	1	NA	NA	NA
Ni ₂ MnGa _{0.995} In _{0.5}	0.5	NA	NA	NA
Ni ₂ MnGa _{0.9975} In _{0.0025}	0.25	NA	NA	NA
Ni ₂ MnGa _{0.99875} In _{0.00125}	0.125	NA	NA	NA
Ni ₂ MnGa _{0.99933} In _{0.00067}	0.067	NA	NA	NA
Ni ₂ MnGa _{0.99917} In _{0.00083}	0.0833	196.8	210.5	3.0232 cooling Exo
				3.4102 Heating Endo

Figures (5.8) to (5.13) show the variation of the specific heat as a function of temperature for Ni₂MnGa, Ni₂MnGa_{0.9975}Sn_{0.0025}, Ni₂MnGa_{0.99917}In_{0.0083} alloys respectively.



Fig. (5.8b) Variation of specific heat as a function of temperature for Ni₂MnGa (heating)



Fig. (5.10a) Variation of specific heat as a function of temperature for Ni₂MnGa_{0.9975}Sn_{0.0025} (cooling)



Fig. (5.10b) Variation of specific heat as a function of temperature for $Ni_2MnGa_{0.9975}Sn_{0.0025}$ (heating)



Fig. (5.11) Variation of specific heat as a function of temperature for Ni₂MnGa_{0.9975}Sn_{0.0025} (cooling and heating curves)



Fig. (5.12a) Variation of specific heat as a function of temperature for Ni₂MnGa_{0.99917}In_{0.00083} (cooling)



Fig. (5.12b) Variation of specific heat as a function of temperature for $Ni_2MnGa_{0.99917}In_{0.00083}$ (heating)



Fig. (5.13) Variation of specific heat as a function of temperature for Ni₂MnGa_{0.99917}In_{0.00083} (cooling and heating curves)

5.5.3 Discussion

It has been established that Ni₂MnGa orders ferromagnetically below 378 K and undergoes a structural phase transition at 200 K (known as Martensitic transition) (Webster, 1969; Webster, Ziebeck et al., 1984).

DSC measurement for Ni₂MnGa alloy upon cooling the sample from 298 K to 100 K showed a phase transition at 209.4 K as indicated in figure 5.5. However on heating the sample from 100 K to 298 K the phase transition peak appeared at 223.6 K as shown in figure 5.5, demonstrating hysteresis in the phase transition as expected for a first order transition.

A series of measurements were then carried out on Ni₂MnGa_{1-x}Sn_x alloy where x = 5, 2.5, 2, 1, 0.5, 0.27, 0.26, 0.25, 0.127 and 0.125. Starting with 5% of Sn the peak disappeared totally and the DSC measurement showed a flat spectrum, as did the other samples for x > 0.25. During cooling the DSC measurement on Ni₂MnGa_{0.9975}Sn_{0.0025} (0.25% Sn), indicated a phase transition at 175 K as shown in figure 5.6. After heating the sample from 100 K to 298 K the phase transition occurred at 199.6 K as shown in figure 5.6. It was noticed that the peak in this case is broader than that of the stoichiometric sample.

With 0.25% doping of Sn the phase transition moved to the lower temperatures, with a shift of 34.4 k for cooling and 24 K for heating. The enthalpy change (Δ H) in Ni₂MnGa alloy is 3.5849 J/G through the cooling cycle and 3.7614 J/G through the heating cycle, however the values of the enthalpy changes are 1.3090 J/G and 1.6792 J/G for Ni₂MnGa_{0.9975}Sn_{0.0025}. Compared with the values of Ni₂MnGa the later values are much lower.

DSC measurements have also been carried out on a series of Ni₂MnGa_{1-x}In_x alloys, where x = 5, 2, 1, 0.5, 0.25, 0.125 and 0.0833. It was not possible to detect any phase transition for x > 0.0833. For x = 0.0833 the measurements showed a broad peak during cooling and the heating cycles as shown in figure 5.7. Upon cooling the phase transition occurs at 196.8 K and at 210.5 K for heating. Here also the peaks have moved to lower temperatures with a shift of 12.6 K and 13.1 K in position of the peaks observed for Ni₂MnGa. The change in the enthalpy (Δ H) for this sample is 3.0232 J/G and 3.4102 J/G for cooling and heating respectively.

As the absorbed energy is stored as enthalpy inside the substance, the heat capacity is also a measure of how much the enthalpy of a body increases when it is heated through 1 Kelvin, hence the specific heat defines how much energy is needed to heat 1 gram or 1 mole of substance by 1 Kelvin

The heat flow to the sample, measured at constant heating rate, is directly proportional to the specific heat of the substance. The specific heat at constant pressure, C_P , of a sample was determined as a function of temperature.

As a result of measuring the specific heat of Ni₂MnGa during the cooling cycle from 298 K to 100 K, it was found that the average specific heat below the phase transition peak in the range of 163 K to 197 K is (129.32 \rightarrow 142.68) J MOL⁻¹ K⁻¹. Above the phase transition in the range of 263 K to 287 k the

CHAPTER 5: Measurements of the Specific Heat Capacity

average value of the specific heat (143.09 to 153.55) J $MOL^{-1} K^{-1}$. The figures show that the value of the specific heat of the sample past the transition peak has been increased, which may be that due to the change that took place during the phase transition. On the other hand by heating the sample from 100 K to 298 K, the peak shifted from 209.4, (cooling), to 224.1 K, (heating), and on the range from (183 K to 208 K) below the phase transition the average value of the specific heat is on the range of (117.79 to 122.78) J $MOL^{-1} K^{-1}$ and a above the phase transition, where the range was from (245 K to 283 K) the average value of the specific heat is (13.66 to 131.22) J $MOL^{-1} K^{-1}$. On both cases there is an increase in the specific heat but it is much higher for cooling than that where the sample was heated.

By adding 0.25% of Tin to Ni₂MnGa alloy and measuring the specific heat during the cooling cycle, it was found that at the range of (159K to 162K), below the phase transition, the average value of the specific heat is (119.33 \rightarrow 119.2) J MOL⁻¹ K⁻¹ and at the range of (185 K to 201 K), above the phase transition, the average value of the specific heat is (128.00 to 129.18) J MOL⁻¹ K⁻¹ and above the transition region, where the range is (178K to 189K) the average value is (117.34 \rightarrow 127.04) J MOL⁻¹ K⁻¹.

We could see from the results of both Ni₂MNGa and Ni₂MnGa_{0.9975}Sn_{0.0025}, the average values of the specific heat of the first sample are higher than the second, upon cooling and heating them.

It was not possible to calculate the average value of the specific heat for the third sample, because it is impossible to determine any region below and above the transition region.

As we can see from tables 5.1 and 5.2 the DSC measurements did not show any transition, it is possible that the transition is out of range of the instrument.

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CHAPTER SIX

ELECTRICAL RESISTIVITY MEASUREMENTS

6.1 Introduction

The electrical resistivity of conductive materials is an important property which can provide detailed information concerning magnetic and structural phase transitions. The investigations here have been confined to the ferromagnetic Heusler series Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x, and Ni₂MnGa_{1-x}In_x. In ferromagnetic metals the electrical resistance is primarily caused by scattering of the conduction electrons by phonons and by spin waves. (Goodings, 1963).

The measurement of the electrical resistivity as a function of temperature is a standard method which is employed for the detailed investigation of phase transitions. According to Ohm's law (Ashcroft and Mermin, 1976), the magnitude of a current I flowing through a wire is proportional to the potential difference $V = \Phi_2 - \Phi_1$ along the wire, where Φ_1 and Φ_2 are the electrical potential at the ends of the wire. The factor of proportionality is the resistance of the wire

$$V = IR \tag{6.1}$$

The electrical resistance R of a wire or a sample depends on its dimensions, but it is independent of the size of the current or the potential difference. The resistance itself is not a material constant because it depends on the dimensions of the sample.

The material constant which can be extracted from the resistance measurements is ρ the specific electrical resistivity. It is usually denoted as the electrical resistivity. It does not depend on the geometry of the sample. Within the Drude model the electrical resistivity ρ , as a material-parameter, is

defined to be the factor of proportionality between the electric field \vec{E} at a point \vec{r} in the metallic sample and the current density \vec{i}

$$\vec{E}(\vec{r}) = \rho \vec{j}(\vec{r}) \tag{6.2}$$

If $\vec{E} \parallel \vec{j}$ for all directions of \vec{E} then the resistivity ρ is a scalar. Otherwise ρ is given by a matrix which reflects the directional dependence of the current. The current density is a vector-field. Its magnitude corresponds to the amount of charge (per unit time) crossing a unit area which is oriented perpendicular to the direction of the flow. For a uniform current density which flows through an isotropic wire characterised by a constant cross-section A, the current density is given by:

$$\mathbf{j} = \mathbf{J}/\mathbf{A} \tag{6.3}$$

where I is the total current. The potential difference along the wire of length ℓ is given by:

$$V = E\ell \tag{6.4}$$

Thus equation 6.2 becomes

$$V = \frac{\rho\ell}{A}I$$
(6.5)

Hence the resistance of a wire is given by:

$$R = \rho \frac{\ell}{A}$$
(6.6)

Hence, from equation 6.6, the resistance R of a metallic material depends on the geometry of the sample and the specific resistivity ρ is a material constant characterising its electrical properties.

6.2 Temperature Dependence of Resistivity

The resistivity of a material depends on temperature. In metals, the resistivity increases with increasing temperature, whereas in semiconductors the reverse is true. Certain materials have the property that their resistivity drops suddenly to zero at very low temperatures. Such materials are called superconductors, because, with zero resistivity, they offer no resistance to electric current (Cutnell and Johnson, 1992).

The vibrational energy of the lattice increases with temperature; that is to say, the number of phonons increases. As a result the number of electron collisions with phonons increases with increasing temperature. For many materials and limited temperature ranges it is possible to express the temperature dependence of the resistivity (Cutnell and Johnson, 1992; Crummett and Western, 1994) as follows:

$$\rho = \rho_{\circ} \left[1 + \alpha (T - T_{\circ}) \right]$$
(6.7)

where ρ and ρ_{\circ} are the resistivities at temperature T and T_o, respectively. α has the unit of reciprocal temperature, (depending on the material), and is the temperature coefficient of resistivity. The scattering of electrons in magnetic solids is complicated, involving several mechanisms which may give rise to both elastic and inelastic (spin-flip) components (Wijn, 1981).

Since the resistance R is proportional to ρ we can use the resistance as a thermometer:

$$R = R_{\circ} \left[1 + \alpha (T - T_{\circ}) \right]$$
(6.8)

where R_{\circ} is the resistance at a reference temperature T = 0 and R is the resistance at T. In the previous equation an approximation has been made,

where ℓ, ρ, α and A all change slightly with temperature, therefore the approximation is good only for a limited range of temperature.

For larger temperature ranges, a power series (polynomial) can be used to express the actual change in R as the temperature T varies. Thus we can write:

$$R_{T} = R_{\circ} \left[1 + \alpha T + \beta T^{2} + \gamma T^{3} + \cdots \right]$$
(6.9)

The coefficients of the various terms are determined by taking the actual resistance at many temperatures and fitting the data to a curve described by this equation, using the coefficients as variables to attain the best fit.

At low temperatures magnons are an important source of scattering, and for a local moment system give rise to a T^2 dependence. As the temperature is raised the spin-disorder scattering becomes increasingly important (Wijn, 1981).

6.3 Electrical Resistivity Measurements Techniques

Resistivity measurements of metals have been used in material characterisation, spot-weld evaluation, case depth measurement, fault sizing, as well as in the monitoring of material property transformation (Ross and Kim, 1990).

There are various ways of measuring the electrical resistivity experimentally; the conventional method, the two-point and the four-point probe methods, and Contactless methods.

The conventional method

Here the electrical resistivity of a sample, in the form of rod for example is, attached to current and voltage leads as shown in figure 6.1. If the geometry of the sample is known the electrical resistivity ρ can be calculated. This method is applicable for a sample with a resistance much higher than the resistance of the connection wires.



Fig. (6.1) Basic circuit for resistivity measurement.

Two-Point Probe method

This method is based on the measurement principle of applying a current and measuring the potential difference between two points. In this case the contacts for the current and the voltage are applied at two points.

• Four-point Probe Technique

One technique used for measuring the resistivity of metal and alloys is four-point probe technique. This technique is also the most common method for measuring the temperature-dependent resistivity of low resistance materials such as high T_c superconducting samples (Ross and Kim, 1990).

The four-point probe set-up consists of four equally spaced contacts eg. tungsten metal tips with finite radius. Each tip is supported by springs on the other end to minimise sample damage during probing. A high impedance current source is used to supply current through the outer two probes; a voltmeter measures the voltage across the inner two probes to determine the sample resistivity as shown in figure 6.2 (Bridge, 1997). Typical probe spacing s ~ 1mm.



Fig. (6.2) Schematic of 4-point probe configuration.

The four-terminal method is required for low resistivity materials (Callarotti and Alfonzo, 1972). For bulk samples where the sample thickness t >> s, the probe spacing, it can be shown that the resistivity is given by the expression (Bridge, 1997):

$$\rho = 2\pi s(V/I) \tag{6.10}$$

For a thin sample, the resistivity is given by (Ross and Kim, 1990) as:

$$\rho = tF(V/I) \tag{6.11}$$

where t is the sample thickness, V is the measured voltage, I is the applied current, and F is a correction factor. In the case of a rectangular parallelepiped, F is a function of the ratio of the sample's width to length.

Difficulties with the four-point probe technique may include unreliable probe contacts, sensitivity to noise from thermally-induced voltages, and sensitivity to the radius of the current probes (Ross and Kim, 1990). Problems with thermo electric currents can be overcome using A.C. techniques or by reversing the current.

Contactless Resistivity Measurement Technique

It is well known that electrical resistivity can be measured without attached leads by means of induced eddy currents. This method has been developed by (Bean, DeBlois et al., 1959).

The basic idea is as follows: if a magnetic field is applied suddenly to a sample (conductor) (either switched on or off), eddy currents are induced to flow through the sample. Due to Lenz's rule the eddy currents flow in such a manner that a magnetic field is induced in the opposite direction to that of the applied field. Hence the applied field is not able immediately to penetrate into the whole of the sample. Rather the penetration is delayed due to the induced magnetic field. Due to the electrical resistivity of the sample the attenuation of eddy currents results in a decrease of the induced field within a short period of time. As a result, the applied magnetic field diffuses into the material (Schippan, 1997).

The value of the electrical resistivity ρ of a material can be experimentally obtained by determining the penetration rate of the magnetic field (Bean, DeBlois et al., 1959; Callarotti and Alfonzo, 1972; Delaney and Pippard, 1975). In the experiments the sample, a rod of circular cross section, is wound locally with a small secondary pickup coil and the sample and the pickup coil are inserted in a larger magnetising solenoid. No electrical contacts to the sample are required. Thus all experimental problems due to the use of contacts are eliminated. A step function of current is applied through the magnetising coil, and the resulting voltage is caused by the penetration of flux into the sample rod and so can be used to measure the diffusivity and hence the resistivity (Bean, DeBlois et al., 1959).

A variety of contactless measurements techniques are described in a paper by (Delaney and Pippard, 1975). An overview of some contactless methods are given by (Wejgaard and Tomar, 1974; McRae, Maréché et al., 1980). Special applications include the

measurement of ρ for semiconductors are described (Chen, 1989) or the measurement of the thickness of conducting shell (Callarotti, Schmidt et al., 1972).

The contactless measurement of electrical resistivity ρ is discussed for samples with a cylindrical geometry by (Schippan, 1997).

6.4 Instrumentation

The contactless method for measuring the electrical resistivity is based on an applied magnetic field and the notion of a change of flux inside the sample material. The technique involves two basic coil systems, one for the applied homogeneous field and a second coil to measure the change of flux inside the sample. A cylindrical sample is placed inside a large solenoid (the primary coil) to which a step function current pulse is applied in order to produce a rapid change in the magnetic field. A smaller secondary coil is closely wound around the sample and measures the decay of the magnetic field associated with the eddy currents, as the flux penetrates the enclosed material. The rate of decay gives the magnetic diffusivity and hence the electrical resistivity of the sample. The experimental set-up is shown in figure 6.3 (Schippan, 1997).



Fig. (6.3) Schematic diagram of Contactless Resistivity measurement System.

The system consists of four main parts (Schippan, 1997):

- 1) Primary (Driver) coil and secondary (pick-up) coil
- 2) Temperature measurement
- 3) Data recording
- 4) Data analysis and software

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6.4.1 The Driver Coil and the Pick-up Coil

• The (Primary) driver coil

Figure 6.4 shows the arrangement of the coil system (Schippan, 1997). The coil holder was made from non-magnetic plastic material (Darvic). For the coil, a copper wire is used with a diameter of 0.5 mm. Two pick-up coils are used as shown in figure 6.4; this gives a possibility to compare two samples or to measure two samples at once.

• The (Secondary) Pick-up coil

The functionality of the pick-up coil is illustrated in figure 6.5, using an equivalent circuit (Schippan, 1997). Electrical connections and cables are characterised by a capacitance C, a resistance R of the wire and an inductance L of the empty coil system. The voltage U(t) is recorded by an oscilloscope, the input resistance of the oscilloscope is 1 M Ω and therefore its influence on the circuit can be neglected.



Fig. (6.4) Schematic drawing of the coil system.
The magnetic field of the driver (primary) coil is given by:

$$\hat{B}_{a} = 4\pi\mu\mu_{a}nI \tag{6.12}$$

and

$$n = N/\ell \tag{6.13}$$

where N is the number of turns and ℓ the length. Typical values used are 1 - 10 mT, N = 370, ℓ = 205 mm, and I_{max}= 0.7 A (maximum current). The coil is driven by an amplifier with a square pulse signal. The signal for the amplifier is taken from the calibration signal of the oscilloscope which is also used for triggering.



Fig. (6.5) Circuit diagram for the Pick-up coil system.

6.4.2 Temperature Measurement

For the temperature measurement a silicon diode is used in the four point configuration. This set-up compensates for the resistivity of the wires. The diode is driven by an applied voltage in forward direction using a constant current of $I_{diode} = 10 \ \mu$ A. The sensor is located at the top of the pick-up coil close to the sample. The voltage is measured by a digital voltmeter (DVM) which is controlled by the computer via a GPIB (General Purpose Interface Bus). A program written in C language converts the voltage into absolute temperature. The absolute temperature is determined to an accuracy of $\Delta T = \pm 1 \ K$.

6.4.2.1 The Heater

The change of temperature will go through an adiabatic process which means that the system changes from an equilibrium state to another via a sequence of equilibrium states. In this experiment the temperature range is from 77.4 K to room temperature. The coil system is covered by a copper tube with heating wires. There are three heating coils as shown in figure 6.6. The copper tube is thermally insulated from the surrounding. For good thermal insulation the whole set-up is under vacuum. The heating voltage is 20-40 V, and the maximum heating speed is 1 K/min..



Fig. (6.6) Heating System.

6.4.3 Data Recording

An oscilloscope is used to measure the signal coming from the pick-up coil and a digital voltmeter (DVM) measures the voltage of the temperature sensor. Both devices are controlled by a computer via GPIB interface technique (Schippan, 1997).

6.4.4 Data Analysis

The signal from the pick-up coil is a damped oscillation with frequency $\tilde{\omega}$ and damping constant β . For analysing the signal the method of Fourier transform (FT) is commonly used. The advantage of using this method is the possibility of simultaneously estimating the damping constant and the resonance frequency. In the experiment the oscillations are recorded and stored by the oscilloscope and the driver program calculates the direct Fourier transform. An explanation of the data analysis has been put forward by (Schippan, 1997).

6.5 Results and Discussion

The specimens investigated were in the form of rectangular sticks. These sticks were originally made for a four point probe electrical resistivity set-up. Due to the increased sensitivity of the contactless resistivity method, interest was subsequently focused on this technique. The technique readily enabled the thermal variation of the resistivity to be established. However, due to the different size of the specimens and the fact that the calibration sample had cylindrical geometry, it was not possible to determine the absolute magnitude.

Over the temperature range used, namely 300 to 80 K upon cooling and 80 to 300 K upon heating, the resistivity measured as a function of temperature has been on the Heusler alloys Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x, and Ni₂MnGa_{1-x}In_x, where for Sn percentages of 5, 2.5, and 0.25 have been used whereas for In percentages of 5 and 1 were used. Other compositions have been used, for example 2, 1, 0.5, 0.27, 0.26, 0.167, and 0.125 % of Sn as a substitute for Ga. In addition 2, 0.5, 0.25, 0.125, 0.0833, and 0.067 % of In were used as a substitute for Ga.

The results of the electrical resistivity versus temperature for the Ni₂MnGa, Ni₂MnGa_{0.95}Sn_{0.05}, Ni₂MnGa_{0.975}Sn_{0.025}, and Ni₂MnGa_{0.9975}Sn_{0.0025} are shown in figures 6.7, 6.8, 6.9, and 6.10. Figures 6.11, and 6.12 also show the measurement of the electrical resistivity as a function of temperature for Ni₂MnGa_{0.95}In_{0.05} and Ni₂MnGa_{0.99}In_{0.01} alloys. In all measurements, cooling and heating curves, hysteresis loops are observed.

Table (6.1) shows the transition temperatures for Ni_2MnGa , $Ni_2MnGa_{1-x}Sn_x$ and $Ni_2MnGa_{1-x}In_x$ series.

Alloy	% Sn	Transitio	Sample Geometry		
		Cooling			heating
		(300 - 80)	(80 - 300)		
Ni₂MnGa	0	154.30	199.75	cylinder rod	
Ni ₂ MnGa _{0.95} Sn _{0.05}	5	82.16	122.02	thick stick	
Ni ₂ MnGa _{0.975} Sn _{0.025}	2.5	110.79	141.10	thick stick	
Ni ₂ MnGa _{0.9975} Sn _{0.0025}	0.25	167.18	203.12	thick stick	
	% In				
Ni ₂ MnGa _{0.95} In _{0.05}	5	118.54	164.39	thick stick	
Ni ₂ MnGa _{0.99} In _{0.01}	1	144.01	173.95	thick stick	

Table (6.1) Transition temperature for cooling and heating.

Figure 6.13 shows the result of the transition temperature as a function of percentage of Sn as a substitute for Ga in Ni₂MnGa alloy. Figure 6.14 shows the transition temperature versus percentage of In as a substitute for Ga in the same alloy.

Table (6.2) shows measured transition temperature, (cooling and heating), obtained by magnetisation, specific heat and resistivity measurement methods.

Sample	%Sn	%In	Magnetisation		Specific heat		Resistivity	
-			T _c (K)	T _h (K)	T _c (K)	T _h (K)	T _c (K)	T _h (K)
(Polycrystalline)	0	0	175.03	187.79	(209.4	224.10) _{Sn}	(154.00	199.75) _{Sn}
Ni₂MnGa	5	5	N/A	N/A	N/A	N/A	(82.0	122.02) _{Sn}
							(118.54	164.39) _{Sn}
	2.5	N/A	N/A	N/A	N/A	N/A	(110.79	141.10) _{Sn}
	2	2	N/A	N/A	N/A	N/A	N/A	N/A
	1	1	N/A	N/A	N/A	N/A	(144.01	173.95) _{Sn}
	0.5	0.5	N/A	N/A	N/A	N/A	N/A	N/A
	0.27	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	0.26	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	0.25	0.25	(179.99	201.90) _{Sn}	(175.0	199.60) _{Sn}	(167.18	203.12) _{Sn}
	0.167	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	0.125	0.125	N/A	N/A	N/A	N/A	N/A	N/A
	N/A	0.067	N/A	N/A	N/A	N/A	N/A	N/A
	N/A	0.0833	N/A	N/A	(196.0	210.50) _{In}	N/A	N/A
(Single crystal)								
Ni₂MnGa	0	0	205.96	220.58				

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Table (6.2) A summary of transition temperatures obtained by Magnetisation, specific heat and resistivity methods for Ni₂MnGa (polycrystalline and single crystal),Ni₂MnGa_{1-x}Sn_x and Ni₂MnGa_{1-x}In_x alloys.

A.



Fig. (6.7a) Resistivity measurement as a function of temperature for Ni₂MnGa (cooling)



Fig. (6.7b) Resistivity measurement as a function of temperature for Ni₂MnGa (heating)



Fig. (6.7c) Hysteresis loop for cooling and heating as a result of resistivity measurement of Ni₂MnGa



Fig. (6.8a) Resistivity measurement as a function of temperature for $Ni_2MnGa_{0.95}Sn_{0.05}$ (cooling).



Fig. (6.8b) Resistivity measurement as a function of temperature for Ni₂MnGa_{0.95}Sn_{0.05} (heating).



Fig. (6.8c) Hysteresis loop for cooling and heating as a result of resistivity measurement of Ni₂MnGa_{0.95}Sn_{0.05}.



Fig. (6.9a) Resistivity measurement as a function of temperature for $Ni_2MnGa_{0.975}Sn_{0.025}$ (cooling).



Fig. (6.9b) Resistivity measurement as a function of temperature for $Ni_2MnGa_{0.975}Sn_{0.025}$ (heating).



Fig. (6.9c) Hysteresis loop for cooling and heating as a result of resistivity measurement of Ni₂MnGa_{0.975}Sn_{0.025}.



Fig. (6.10a) Resistivity measurement as a function of temperature for $Ni_2MnGa_{0.9975}Sn_{0.0025}$ (cooling).



Fig. (6.10b) Resistivity measurement as a function of temperature for $Ni_2MnGa_{0.9975}Sn_{0.0025}$ (heating).



Fig. (6.10c) Hysteresis loop for cooling and heating as a result of resistivity measurement of Ni₂MnGa_{0.9975}Sn_{0.0025}.



Fig. (6.11a) Resistivity measurement as a function of temperature for Ni₂MnGa_{0.95}In_{0.05} (cooling).



Fig. (6.11b) Resistivity measurement as a function of temperature for $Ni_2MnGa_{0.95}In_{0.05}$ (heating).



Fig. (6.11c) Hysteresis loop for cooling and heating as a result of resistivity measurement of Ni₂MnGa_{0.95}In_{0.05}.



Fig. (6.12a) Resistivity measurement as a function of temperature for Ni₂MnGa_{0.99}In_{0.01} (cooling).



Fig. (6.12b) Resistivity measurement as a function of temperature for Ni₂MnGa_{0.99}In_{0.01} (heating).



Fig. (6.12c) Hysteresis loop for cooling and heating as a result of resistivity measurement of Ni₂MnGa_{0.99}In_{0.01}.



Fig. (6.13a) transition temperature Vs % of Sn in the alloy Ni₂MnGa (cooling).



Fig. (6.13b) transition temperature Vs % of Sn in the alloy Ni₂MnGa (heating).



Fig. (6.13c) transition temperature Vs % of Sn in the alloy Ni₂MnGa (cooling & heating).



Fig. (6.14a) transition temperature Vs % of In in the alloy Ni₂MnGa (cooling).



Fig. (6.14b) transition temperature Vs % of In in the alloy Ni₂MnGa (heating).



Fig. (6.14c) transition temperature Vs % of In in the alloy Ni₂MnGa (cooling & heating).

The results of measuring the resistivity of the Heusler alloy Ni₂MnGa as a function of temperature is shown in figures (6.7a) and (6.7b). A change of ρ occurs around 150.30 K on cooling and at 199.75 K upon heating respectively. Combining the cooling and heating curves yields a hysteresis loop (figure 6.7c).

Previous neutron scattering measurements and magnetisation investigations on a similar sample, (Webster et al.) have shown a change in magnetic properties around 210 K (Webster, Ziebeck et al., 1984). Substitution of Ga by a 5% of Sn leads to a shift in the transition temperature, whereupon cooling a change in p occurs around 82 K while the change was observed at 122 K on the heating. The transition was shifted by 72 K on cooling and by 78 K on heating as shown in figures 6.8a and 6.8b, both changes occurred below 154 K, which was observed for Ni₂MnGa. By changing the composition, eg. where 2.5% of Sn was substituted for the Ga, it is shown in figures 6.9a and 6.9b that a transition occurred around 110.79 K upon cooling the alloy and around 141.79 K on heating. In this case a shift of 43 K and 57 K for cooling and heating respectively was observed, compared with 154.30 K and 199.75 K for Ni₂MnGa. Finally by substituting the Ga by 0.25% of Sn, the resistivity measurement as a function of temperature showed a big change, where on cooling the change occurred around 167.18 K while it was around 203.12 K on heating. There is slight difference between this composition and the Ni₂MnGa in terms of the transition temperatures.

When In is used instead of Sn to form a new composition by substituting the Ga atom by 5% and 1% of In, the results in figures 6.11a, 6.11b, 6.12a, and 6.12b again show a change in the structure around 118.54 K (cooling), 164.39 K (heating), 144.01 K (cooling), and 173.9 K (heating) respectively. Looking at the compositions $Ni_2MnGa_{0.95}Sn_{0.05}$, and $Ni_2MnGa_{0.95}In_{0.05}$ we see that although the compositions are similar, the transition temperatures occurred at a lower region for 5% of Sn compared to 5% of In.

Chapter 6: Electrical Resistivity Measurements

It was shown that substitution of part of the Ga by Sn or In in the alloy Ni₂MnGa has an effect on the transition temperature. If we consider the transition of Ni₂MnGa as a basis, the results showed that there is a large shift of up to 78 K. We know that conduction electron concentration (e/A) is larger for Sn than In. To find out which of the elements has more effect on these changes we plotted the transition temperature as a function of the percentages of the Sn and the In atoms as shown in figures 6.13 and 6.14 respectively. The results showed that 9.5% of Sn was needed to suppress the transition, upon cooling, and about 12% upon heating, while for In atoms 23.5% was needed for the transition to disappear during cooling and 31% during heating. In conclusion we could say it takes more In than Sn to suppress the transition. It seems that the electron concentration is more important than the size of the atom. It was shown by Webster et al. that electron concentration plays an important role in stabilising the Heusler structure and in defining the type and the strength of the magnetic order; it is probable that it is also instrumental in driving the structural phase transition (Webster, Ziebeck et al., 1984).

Resistivity, magnetisation and specific heat measurements have all confirmed existence of a structural phase transition. However, the results obtained from different measuring methods, showed that the measured values are not consistent with each other as, shown in table 6.2, for the polycrystalline Ni₂MnGa, while for 0.25% concentration of tin in the alloy, the measurements showed that the measured values are more or less in agreement. For the Ni₂MnGa single crystal the obtained results came from magnetisation measurements only, so it can not be compared with the other results.

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CHAPTER SEVEN

NEUTRON SCATTERING

7.1 Introduction

The neutron is a highly effective probe for the investigation of condensed matter. The use of neutron scattering in studying condensed matter phenomena is well-established, and can be routinely employed.

To identify the various advantages of neutron scattering we recall the most important characteristics of the neutron and the neutron-atom interaction.

Neutrons have properties which combine to make neutron scattering a suitable technique for the investigation of condensed matter:

- It has no charge, which means its interactions with matter are confined to short-range nuclear forces.
- They can penetrate into the bulk of a solid sample without having to overcome a coulomb barrier due to electrostatic forces.
- The neutron has an intrinsic magnetic moment.

There are two different interactions between a neutron and the atoms of a crystal which give rise to significant scattering; these are the neutron-nuclear interaction and the interaction between the neutron magnetic moment with the magnetic moment of unpaired electrons in magnetic atoms.

The wavelength of a thermal neutron is of the order of 1Å, which means that the arrangements of atoms in crystalline solid will act as a diffraction grating for neutrons. Neutrons are therefore suited for the investigation of the crystallographic structure of atoms in solids. Furthermore, the kinetic energy of thermal neutrons is of the order of 25 meV, which is a typical thermal

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energy for many excitation in solids. Furthermore, since the neutron has mass, momentum transfers can be undertaken, enabling elementary excitations to be studied throughout the Brillouin zone.

The neutron has a magnetic moment (1.913 nuclear magnetons) and spin ½ which means that neutrons interact with the unpaired electrons in magnetic atoms. Elastic scattering from this interaction provides information on the arrangement of electron spins and the density distribution of unpaired electrons. Inelastic magnetic scattering gives the energy and wavevector dependence of magnetic excitations and in general permits a study of time-dependent spin correlation in the scattering system.

There are two different interactions between a neutron and the atoms of a crystal which give rise to significant scattering; these are the neutron-nucleus interaction and the interaction between the neutron magnetic moment and magnetic dipole of the atom:

- The neutron-nucleus interaction is a strong interaction so that the potential of the neutron near the nucleus will be very different from its potential outside it, and the Born approximation should not be expected to hold. The neutron-nucleus interaction is a very short range one as it extends only over the nuclear radius, namely a radius of the order of 10⁻¹² cm or less (Sacchetti, 1992).
- The magnetic moment in an atom may have contributions from both electron spin and electron orbital angular momenta; both of these will contribute to the interaction with the neutron spin magnetic moment which gives rise to neutron-magnetic scattering. However in many cases, particularly for the first series transition elements, the net orbital magnetic moment is small because of orbital quenching (Brown and Forsyth, 1973).

This magnetic dipole interaction has a longer range than the nuclear interaction but is weak because of the small size of the moments involved. The atomic magnetic moments are often about two to three μ_{B} (1 μ_{B} =9.3x10⁻²⁴ J m² Wb⁻¹).

Compared with inter-atomic distances and thermal excitations in crystals, the neutrons produce interference effects when scattered from condensed matter systems which allow the determination of either the crystallographic structures via the nuclear interaction, or magnetic structures via the magnetic interaction. Neutron scattering gives information not only about the ordered state but also in the paramagnetic phase by measuring the magnetic correlation (Ouladdiaf, 1995). Reviews of the theory of neutron scattering may be found in numerous texts, e.g. Squires(1978), Bacon(1975), Lovesey(1987), Price and Sköld(1986), etc. Table (7.1) shows some fundamental properties of the neutron.

m _n = 1.008664924u			
$= 1.643 \times 10^{-24} g$			
s = 1/2			
$\mu_n = 1091304275\mu_N$			
$q_n = (-0.4 \pm 1.1) \times 10^{-21} e$			
$r_n = 0.11 \pm 0.02 \text{ fm}$			
d _n =(-0.7 ± 0.4)x10 ⁻²¹ e Cm			
$\alpha = (1.2 \pm 1.0) \times 10^{-3} f^3 m$			
λ (Å)			
30 < λ <2.8			
2.8 < λ <0.9			
0.9 < λ <0.4			

Table (7.1) Fundamental properties of the neutron.

7.2 Neutron Scattering Theory

7.2.1 The Interaction between neutrons and Condensed Matter

We consider a scattering process, where atoms in a solid target are bombarded by a beam of neutrons. Upon interacting with the solid these neutrons will be scattered and subsequently detected. The neutrons scattered by the target will give the cross-section as a function of the scattering angle, or alternatively as a function of the energy transfer of the scattered neutrons in the case of inelastic scattering. Experimentally, nuclear scattering arises from an interaction between the neutrons and the nuclei of the ions which make up the solid.





Fig. (7.1) Schematic diagram of a neutron experiment.

Suppose that a beam of neutrons, characterised by a wave vector **k**, falls on to the sample. The scattered neutrons can be measured with a neutron detector placed at an angle 20 with respect to the direction of the incident beam, i.e. in direction \mathbf{K}' . Returning to the schematic scattering experiment in figure (7.1), we see that the neutron wave vector **k** suffers a change in direction and magnitude during the scattering experiment. This implies a change in the neutron momentum, which must be exchanged with the sample

(Sköld and Price, 1986). The momentum transferred to the sample is conventionally described in terms of the corresponding wave vector \mathbf{Q} , and the law of momentum conservation is written as

$$\mathbf{Q} = \hbar \left(\mathbf{k} - \mathbf{k}^{\prime} \right) \tag{7.1}$$

where \mathbf{k} and \mathbf{k} are the initial and final wave vector for the neutron respectively as shown in figure (7.2).



Fig. (7.2) Definition of scattering vector.

If the incident neutron is travelling with velocity \mathbf{v}_i and the scattered neutron is travelling with velocity \mathbf{v}_f , then the momentum $\hbar \mathbf{Q}$ may be taken up by the scattering atom and subsequently shared with the rest of the sample. This can be written in a form

$$\hbar \mathbf{Q} = \mathbf{m} \mathbf{v}_{\mathbf{i}} - \mathbf{m} \mathbf{v}_{\mathbf{f}} \tag{7.2}$$

Where m is the mass of the neutron.

From equation (7.2) the energy transfer can be defined as

$$\hbar\omega = \frac{1}{2}mv_{i}^{2} - \frac{1}{2}mv_{f}^{2}$$
(7.3)

or

In general the magnitude of k will change as well as its direction, and so energy is also exchanged with the sample. The law of energy conservation can be written as

$$\hbar\omega = \mathbf{E} - \mathbf{E}' = \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{\hbar^2 \mathbf{k}'^2}{2m}$$
(7.4a)

$$\Delta E = \frac{\hbar^2}{2m} (k^2 - k'^2)$$
 (7.4b)

where ΔE is the energy transferred to the sample and the two terms on the right hand side represent the incident and scattered neutron energies.

If E = 0 and $|\mathbf{k}| = |\mathbf{k}'|$ then the scattering is elastic. On the other hand, for $E \neq 0$ the scattering is inelastic. For inelastic scattering, the neutron is losing or gaining energy through its interaction with the sample.

7.2.2 Scattering Cross-section

Consider a beam of thermal neutrons, all with the same energy E or wavelength, incident on a target. The geometry of the scattering experiment is shown in figure (7.3).



Fig. (7.3) Geometry of scattering problem.

The interaction of a monochromatic beam of neutrons incident upon a target may be defined in terms of a quantity known as the scattering cross-section σ . This can be denoted in three ways:

 If the incident beam is characterised by a uniform flux Φ, then the total scattering cross-section can be defined as

$$\sigma = \frac{N}{\Phi} \tag{7.5}$$

where N is the total number of neutron scattered/unit time (neutrons scattered in all directions) and Φ is the flux of the incident neutrons (number of neutrons/cm²/sec).

 If the neutrons scattered into the solid angle dΩ in the direction θ,Φ, then the differential neutron cross-section, which is angle dependent and integrated over the energies, is given by

 $\frac{d\sigma}{d\Omega} = (number of neutron scattered per unit time/unit solid angle) / \Phi d\Omega$ (7.6)

The partial differential cross-section is defined by

 $\frac{d^2\sigma}{d\Omega dE'} = (number of neutrons scattered / unit time / unit solid)$ $angle with final energy between E' and E' + dE')/<math>\Phi d\Omega dE'$ (7.7)

7.2.2.1 The Differential Cross-section for Elastic Scattering

To obtain an expression for the differential cross-section which is appropriate for elastic scattering, i.e. no energy is transferred to or from the target sample,

we consider the differential scattering cross-section $\left(\frac{d\sigma}{d\Omega}\right)$, representing the sum of all processes in which the state of the neutrons changes from k to k'. From equation (7.6) we have

$$\frac{d\sigma}{d\Omega} = \frac{1}{\Phi} \sum_{k'} W_{k \to k'}$$
(7.8)

where Φ is the flux of the incident neutrons and $W_{k\to k'}$ is the number of transitions per unit time from the state k to the state k' To calculate the differential cross-section for this case we need to know the probability of a transition from the plane-wave state defined by the wave vector k to the plane-wave state defined by the wave vector k'. This probability is given by a fundamental result in quantum mechanics, known as Fermi's golden rule (Merzbacher, 1970).

This is

$$\sum_{k'} W_{k \to k'} = \frac{2\pi}{\hbar L^3} \rho_{k'} \left| \left\langle k' | V | k \right\rangle \right|^2 \tag{7.9}$$

where the neutron and the scattering system are considered to be in a large box of volume L³, $\rho_{k'}$ is the density of the final unperturbed scattering states and V is the interaction potential that causes the transition, in this case the interaction between the incident neutron and the scattering system. The incident flux is given by

$$\Phi = \frac{\hbar \mathbf{k}}{L^3 \mathrm{m}} \tag{7.10}$$

Hence, from equations (7.8), (7.9) and (7.10), the neutron cross-section can be written as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\mathbf{k}'}{\mathbf{k}} \left(\frac{\mathrm{m}}{2\pi\hbar^2}\right)^2 \left| \langle \mathbf{k}' | \mathbf{V} | \mathbf{k} \rangle \right|^2 \tag{7.11}$$

7.2.2.2 The Differential Cross-section for Inelastic Scattering

We need now to calculate the partial cross-section for inelastic scattering. For this type of scattering the energy of the scattered neutron differs from that of the incident neutron. If E and E' are the initial and final energies of the neutron, and E_{λ} and $E_{\lambda'}$ are the initial and final energies of the scattering system, then with the conservation of energy

$$E + E_{\lambda} = E' + E_{\lambda'} \Rightarrow \frac{\hbar^2 k^2}{2m} + E_{\lambda} = \frac{\hbar^2 k'^2}{2m} + E_{\lambda'}$$
(7.12a)

or

$$\mathbf{E}' - \mathbf{E} = \mathbf{E}_{\lambda} - \mathbf{E}_{\lambda'} \tag{7.12b}$$

We denote the initial and final states of the scattering system by $|\lambda\rangle$ and $|\lambda'\rangle$ respectively, with corresponding energies E_{λ} and $E_{\lambda'}$. The cross-section 7.11 is then

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathbf{k},\lambda'}^{\mathbf{k},\lambda} = \frac{\mathbf{k}'}{\mathbf{k}} \left(\frac{\mathrm{m}}{2\pi\hbar^2}\right)^2 \left| \left\langle \mathbf{k}\lambda' \right| \mathbf{V} \left| \mathbf{k}\lambda \right\rangle \right|^2$$
(7.13)

Now we could define a partial differential cross-section for scattering process, in which the incident neutron state $|\mathbf{k}\rangle$ changes to $|\mathbf{k}'\rangle$ and the state of scattering system changing from $|\lambda\rangle$ and $|\lambda'\rangle$, as

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega\mathrm{d}E'}\right) = \frac{\mathrm{k}'}{\mathrm{k}} \left(\frac{\mathrm{m}}{2\pi\hbar^2}\right)^2 \left|\left\langle \mathbf{k}'\lambda'\right|\mathbf{V}|\mathbf{k}\lambda\right\rangle|^2 \delta(\hbar\omega + \mathrm{E}_{\lambda} - \mathrm{E}_{\lambda'})$$
(7.14)

where
$$\hbar \omega = \frac{\hbar}{2m} (k^2 - k'^2) = E - E'$$
 (7.15a)

and $\int \delta(\hbar\omega + E_{\lambda} - E_{\lambda'}) dE' = 1$ (7.15b)

The δ -function represents the energy distribution of scattered neutrons.

To obtain the total partial differential cross-section for all possible scattering process, we need to sum over all final states λ' and average it over all initial states λ , which occur with probabilities P_{λ} . For polarised neutron scattering the summation has to be carried out over all initial and final spins states σ and σ' of neutron and the probability distribution of the polarisation of the incident neutrons is P_{σ} . Hence the double differential cross-section is (Sköld and Price, 1986)

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega\mathrm{d}E'} = \frac{\mathrm{k}'}{\mathrm{k}} \left(\frac{\mathrm{m}}{2\pi\hbar^{2}}\right)^{2} \sum_{\lambda,\sigma} \mathrm{P}_{\lambda} \mathrm{P}_{\sigma} \sum_{\lambda',\sigma} \left|\langle \mathbf{k}'\sigma'\lambda' | \mathbf{V} | \mathbf{k}\sigma\lambda \rangle\right|^{2} \delta(\hbar\omega + \mathrm{E}_{\lambda} - \mathrm{E}_{\lambda'})$$
(7.16)

Equation 7.16 is termed as the "master formula" for neutron scattering and is the basis for interpretation of all experiments carried out in this field.

7.2.3 The Interaction Potential V

V is the interaction potential between the neutron and the scattering system (sample). The potential interaction $V(\bar{r})$ is composed principally of two parts:

- Nuclear interaction potential V_n: interaction between the neutrons and the nuclei of the ions which make up the solid, which yields the nuclear scattering contribution.
- Magnetic interaction potential V_M: interaction between the magnetic moment of the neutron with the spin and orbital magnetic moment of the unpaired electrons in the solid.

For an unpolarised neutron beam, the interference between these two interactions vanishes and the cross-section is the sum of a nuclear part and a magnetic part. In the case of elastic scattering, there is no energy transfer and the δ -function vanishes (Ouladdiaf, 1995).

Nuclear Scattering (The nuclear interaction Potential Vn

The nucleon-nucleon interaction between the incident neutron and the scattering system nuclei leads to a nuclear potential of a very short range $(10^{-13} - 10^{-14} \text{ cm})$ in comparison with the thermal neutron wavelength. It is isotropic and within the first Born approximation. Its strength can be parameterised or characterised by one parameter, the scattering length b, which depends on the atomic type, the isotope and the relative orientation of the nuclear spin.

The Fermi pseudo potential is used to calculate the scattering potential of a rigid array of scattering centres of position R_i and scattering length b_i ; this is given by

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m} \sum_{i} b_i \delta(\mathbf{r} - \mathbf{R}_i)$$
(7.17)

where \mathbf{r} and \mathbf{R}_i are the instantaneous positions of the neutron and the nucleus, respectively and m is the mass of the neutron.

Evaluating the average of equation 7.17 over the neutron wave functions we get (Sköld and Price, 1986).

$$\langle \mathbf{k}' | \mathbf{V} | \mathbf{k} \rangle = \frac{2\pi\hbar^2}{m} \sum_{i} \mathbf{b}_i \int d\mathbf{r} \, e^{-\mathbf{k}' \cdot \mathbf{r}} \delta(\mathbf{r} - \mathbf{R}_i) e^{i\mathbf{k} \cdot \mathbf{r}}$$
 (7.18a)

or

$$\langle \mathbf{k}' | \mathbf{V} | \mathbf{k} \rangle = \frac{2\pi\hbar^2}{m} \sum_{i} b_i e^{i\mathbf{Q} \cdot \mathbf{R}}$$
 (7.18b)

where $\mathbf{Q} = \mathbf{k} - \mathbf{k'}$ is the scattering vector.

Then the master formula, equation 7.16 gives

$$\frac{d\sigma}{d\Omega dE'} = \frac{1}{N} \frac{k'}{k} \sum_{\lambda,\sigma} P_{\lambda} P_{\sigma} \left| \sum_{\lambda',\sigma'} \sum_{i} b_{i} \left\langle \sigma' \lambda' \right| e^{iQ \cdot R_{i}} \left| \sigma \lambda \right\rangle \right|^{2} \delta(\hbar\omega + E_{\lambda} - E_{\lambda'}) \quad (7.19)$$

For Unpolarised beams both spin states are equally probable, hence σ and σ' can be omitted from equation 7.19 and the formula becomes

$$\frac{d\sigma}{d\Omega dE'} = \left(\frac{1}{N}\right) \frac{k'}{k} \sum_{\lambda} P_{\lambda} \sum_{\lambda'} \left| \sum_{i} b_{i} \left\langle \lambda' \right| e^{i\mathbf{Q} \cdot \mathbf{R}_{i}} \left| \lambda \right\rangle \right|^{2} \delta(\hbar\omega + E_{\lambda} - E_{\lambda'})$$
(7.20)

The Magnetic Scattering (The Magnetic interaction Potential V_M

Magnetic scattering of neutrons takes place because of the interaction of the magnetic moment of the neutron with the individual magnetic moment \vec{m}_j of the unpaired electrons of the target atoms, and it is a pure dipole-dipole interaction.

The magnetic interaction potential can be written as

$$V_{\rm M}(\mathbf{r}) = -\vec{\mu}_{\rm n} \cdot \vec{\mathrm{H}} \tag{7.21}$$

The magnetic field H has a contribution from the magnetic dipole (spin contribution) and the momentum of the electrons that gives rise to a current (orbital contribution). The operator corresponding to the magnetic dipole moment of the neutron is denoted by

$$\hat{\mu}_n = -\gamma \mu_N \hat{\sigma} \tag{7.22a}$$

$$\mu_{\rm N} = \frac{e\hbar}{2m_{\rm p}} \tag{7.22b}$$

where μ_N is the nuclear magneton, m_p is the mass of the proton, the coefficient $\gamma = 1.9132$ and $\hat{\sigma}$ is the Pauli spin operator for the neutron. Similarly the operator corresponding to the magnetic dipole moment of the electron is denoted by

$$\hat{\mu}_{e} = -2\mu_{B}\hat{S}_{e} \tag{7.23a}$$

$$\mu_{\rm B} = e\hbar/2m_{\rm e} \tag{7.23b}$$

where μ_B is the Bohr magnetron, m_e is the mass of the electron and S_e is the spin angular momentum operator for the electron in units of \hbar .

The coupling between the neutron dipole moment and the magnetic moment of unpaired electrons (the magnetic interaction potential) as determined by their spin and orbital moments can be expressed as:

$$V_{M}(\mathbf{r}) = -\bar{\mu}_{n} \left(\operatorname{Curl} \frac{\bar{\mu}_{e} x \hat{\mathbf{r}}}{r^{2}} - \frac{2\mu_{B} \hat{\mathbf{p}}_{e} x \hat{\mathbf{r}}}{\hbar^{2} r^{2}} \right)$$
$$= -\mu_{N} 2\mu_{B} \vec{\sigma} \cdot \left(\operatorname{Curl} \frac{\hat{\mathbf{s}} x \hat{\mathbf{r}}}{r^{2}} + \frac{1}{\hbar} \frac{\hat{\mathbf{p}}_{e} x \hat{\mathbf{r}}}{r^{2}} \right)$$
(7.24)

where $\,\hat{p}_e\,$ is the angular momentum of the electron with spin $\,\hat{s}\,.$

The scattering cross-section from a sample containing many unpaired electrons is obtained by substituting equation 7.24 in the master formula of equation 7.16. The matrix elements $\langle \mathbf{k}' \sigma' \lambda' | \mathbf{V} | \mathbf{k} \sigma \lambda \rangle$ now have to be evaluated.

First, it can be shown (Sköld and Price, 1986), that the matrix elements between the plane wave states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$ are given by

$$\langle \mathbf{k} | \mathbf{V} | \mathbf{k} \rangle = 4\pi \gamma \mu_N 2 \mu_B \vec{\sigma} \cdot \mathbf{D}_\perp (\mathbf{k} - \mathbf{k}')$$
 (7.25)

where \mathbf{D}_{\perp} is the magnetic interaction operator

$$\mathbf{D}_{\perp}(\mathbf{Q}) = \sum_{i} \left[\hat{\mathbf{Q}} \cdot \left(\mathbf{s}_{i} \mathbf{x} \hat{\mathbf{Q}} \right) + \frac{i}{\hbar \mathbf{Q}} \left(\mathbf{p}_{i} \mathbf{x} \hat{\mathbf{Q}} \right) \right] e^{i\mathbf{Q} \cdot \mathbf{r}_{i}}$$
(7.26)

 \mathbf{s}_i is the angular spin momentum operator of the electron.

Second, we evaluate the matrix elements over the neutron spin states $|\sigma\rangle$ and $|\sigma'\rangle$. For unpolarised neutrons, the matrix elements of products of the neutron spin operator $\bar{\sigma}$ satisfy the conditions

$$\sum_{\sigma} P_{\sigma} \sum_{\sigma'} \left| \left\langle \sigma' \middle| \sigma_{\alpha} \sigma_{\beta} \middle| \sigma \right\rangle \right|^{2} = \delta_{\alpha\beta}$$
(7.27)

where α and β label the co-ordinate axis.

Now the master formula becomes

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega\mathrm{d}E'} = \frac{1}{\mathrm{N}_{\mathrm{M}}} \left(\frac{\mathrm{k}'}{\mathrm{k}}\right) (\gamma \,\mathrm{r_{o}})^{2} \sum_{\alpha} \sum_{\lambda} P_{\lambda} \sum_{\lambda'} \left\langle \lambda \right| \, \mathbf{D}_{\perp\alpha}^{+} \left| \lambda \right\rangle \left\langle \lambda' \right| \mathbf{D}_{\perp\alpha} \left| \lambda \right\rangle \delta(\hbar\omega + \mathbf{E}_{\lambda} - \mathbf{E}_{\lambda'}) \quad (7.28)$$

where $r_{o} = \frac{e^2}{m_e c^2} = 0.28179 \times 10^{-12} m$ is the classical radius of the electron and

 N_M is now the number of magnetic ions.

7.2.4 Coherent and Incoherent Scattering

It has been assumed that all the nuclei in a crystal are the same (Newport, Rainford et al., 1988). This may not be true, even if it is a crystal of a single element, for two reasons. Firstly there may be more than one isotope in the crystal, which will scatter neutrons differently, in general. The second factor arises from the fact that the neutron has a spin, as do nuclei, in the main. The nuclear spins in a material are usually totally disordered, and the way in which the neutrons are scattered by the nuclei depends on the relative orientation of their spin. Thus the neutrons see an array of scattering centres of random strengths, due to the spin dependent part of the interaction.

Two types of scattering can be distinguished, namely *coherent scattering* and *incoherent scattering*. We will see that the diffraction from the lattice divides up, a part "coherent" which represents diffraction from a lattice of nuclei with the average scattering length \overline{b} , and a part "Incoherent" which is the sum of scattering from individual nuclei which depends on the spread (variance) in scattering lengths. Furthermore, the coherent scattering occurs when the scattered waves from atoms in different spatial positions interfere, and hence the neutron wave functions have to be added taking into account their phase difference.

A scattering system which is a single element may consists of a mixture of several different isotopes each with a well-defined abundance or relative frequency ω . These isotopes will each have their own characteristic values of the scattering length b, and the isotopes will be distributed randomly among the atomic positions for a given element.

The coherent scattering yields Bragg peaks (which are highly q dependent) and coherent inelastic scattering (which is q dependent, in general), but the incoherent elastic scattering is much less dependent on q, appearing between the Bragg peaks. This difference is useful in separating effects due to

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individual nuclei from collective effects. The sum of the total incoherent scattering and the coherent inelastic scattering is often called "diffuse scattering".

The average value of the scattering length b for the system is given by (Johnson, 1986)

$$\overline{\mathbf{b}} = \sum_{i} \omega_{i} \mathbf{b}_{i} \tag{7.29}$$

and the average value of b² is

$$\overline{b}^2 = \sum_i \omega_i b^2_i$$
(7.30)

This effect will produce coherent and incoherent nuclear isotopic scattering (disorder scattering), the cross-section of which are

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega}\right)_{\mathrm{coh}} \propto \left\langle \mathrm{b} \right\rangle^2 \tag{7.31a}$$

and

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\Omega\mathrm{d}\omega}\right)_{\mathrm{incoh}} \propto \left|\left\langle\overline{\mathrm{b}}^2\right\rangle - \left\langle\overline{\mathrm{b}}\right\rangle^2\right| \tag{7.31b}$$

For nuclear scattering the total double differential cross-section can be written as:

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{coh} + \left(\frac{d^2\sigma}{d\Omega\omega}\right)_{ncoh}$$
(7.32)

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In addition to the isotopic incoherent scattering (resulting from disorder amongst the various isotopes) incoherent scattering can also arise if the spin of the nucleus is non-zero. A neutron of spin $\frac{1}{2}$ may combine with a nucleus having spin I, to form one of two compound nuclei, having spins of (I + $\frac{1}{2}$) and (I - $\frac{1}{2}$) respectively. Each of these compound nuclei will have an associated scattering length, labelled b₊ and b₋. The coherent and incoherent scattering resulting from this process are:

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{coh} \propto (W_+b_+ + W_-b_-)^2$$
(7.33)

and

$$\left(\frac{d^{2}\sigma}{d\Omega d\omega}\right)_{incoh} \propto \left(W_{+}b_{+}^{2} + W_{-}b_{-}^{2}\right) - \left(W_{+}b_{+} - W_{-}b_{-}\right)^{2}$$
(7.34)

The weighting factor of each spin is given by (Bacon, 1975)

$$W_{+} = (I+1)/(2I+1)$$
(7.35)

$$W_{-} = (I)/(2I+1)$$
 (7.36)

7.3 Polarised and Unpolarised Neutrons and Polarisation

analysis

To specify completely the physical state of a beam of neutrons, we must give both its momentum and spin state. Up to now the spins of incident neutrons were taken to be randomly orientated, i.e. unpolarised. However, if incident neutrons whose spins have some preferred axis are used, i.e. the beam is, to some degree, polarised, more information will be gained about the nature of the scattering process. In such a scheme two new co-ordinates will be introduced in the scattering process, the polarisation of the incident beam and the polarisation of the scattered beam. Now we need to know how the crosssection for the scattering process depends on the polarisation of the incident neutrons, and how we can relate the polarisation of the scattered neutrons to the properties of the target system. In some instances the scattered neutrons are unpolarised. Thus, in this instance, polarisation is created in the scattering process and this polarisation must be intimately connected with the physical properties of the target system sensed by the neutrons. The use of polarised incident neutrons, or just the analysis of the polarisation of the scattered beam, results in a marked decrease in the measured intensity, usually by at least an order of magnitude. Until now, polarised neutrons have mainly been used in elastic scattering experiments, but high-flux reactors make inelastic magnetic scattering experiments possible with polarised neutrons.

Generally we can see that the cross-section for the scattering of polarised neutrons will be independent of the polarisation if there no preferred axis in the target system itself. Thus, pure nuclear scattering is independent of polarisation because nuclear spins are always randomly orientated at most temperatures of interest (Marshall and Lovesey, 1971). Because a ferromagnet does have a preferred axis (when the domains are aligned by an external magnetic field) the cross-sections are as before, but a new term due to interference between nuclear and magnetic scattering appears. Also, in the polarisation of neutrons inelastically scattered by a ferromagnetic target

system a polarisation is created, the orientation of which depends on whether it is associated with a scattering process in which an elementary excitation is created or annihilated (Marshall and Lovesey, 1971).

Furthermore, the use of polarised neutrons and polarisation analysis is extremely important in allowing the separation of the magnetic component of scattering resulting from the electronic spins, from the scattering due to all other sources.

The spin state of a neutron is defined relative to a direction known as the polarisation direction (taken to be the z axis in Cartesian co-ordinates).

The spin state of the neutron can then be denoted by u and v with respect to this direction. Conventionally, u is the "spin-up" state with eigenvalue +1 for the operator σ_z , and v is "spin-down" state with eigenvalue -1. Providing neutrons are detected without specification as to their spin direction, and are given an initial direction of polarisation to create a reference, this gives rise to four cross-sections, which will be called spin-state cross-sections, corresponding to the following neutron spin transitions (Squires, 1978).

$$u \rightarrow u, v \rightarrow v, u \rightarrow v, v \rightarrow u$$

The process $u \to u$ and $v \to v$ involve no change of the neutron's spin and are called non-spin-flip cross-section, whilst $u \to v$ and $v \to u$ involve a change of the neutron's spin and are known as spin-flip cross-sections. Any cross-section $k \to k$ ' for unpolarised neutrons is related to the corresponding spin-state by

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega\mathrm{d}\omega}\right)_{\mathbf{k}\to\mathbf{k}'} = \frac{1}{2}\cdots$$
 (sum of four spin-state cross-sections)
Expression for $d^2\sigma/d\Omega dE'$ is given by (Squires equation 7.26) as

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E'}\right)_{\sigma\lambda\to\sigma'\lambda'} = \left(\gamma r_{\circ}\right)\frac{k'}{k} \left|\left\langle\sigma'\lambda'\right|\underline{\sigma}\cdot\mathbf{Q}_{\perp}\left|\sigma\lambda\right\rangle\right|^2 \delta(\hbar\omega + E_{\lambda} - E_{\lambda'})$$

Using the properties of the Pauli spin operator σ , four partial atomic scattering amplitudes can be defined:

$$U^{uu} = b + Q_{\perp z} + I_z$$
 (7.37a)

$$U^{\nu\nu} = b - Q_{\perp z} - I_z \tag{7.37b}$$

$$U^{uv} = \left(Q_{\perp x} + iQ_{\perp y}\right) + \left(I_{\perp x} + iI_{\perp y}\right)$$
(7.37c)

$$U^{vu} = (Q_{\perp x} - iQ_{\perp y}) + (I_{\perp x} - iI_{\perp y})$$
(7.37d)

These partial scattering amplitudes describe only the coherent scattering process. Using equations (7.37a) to (7.37d) the following conclusions can be made (Johnson, 1986):

- a) Coherent nuclear scattering of amplitude b is always non-spin-flip (uu or vv) scattering.
- b) Isotopic disorder scattering which is incoherent, is also non-spin-flip scattering.
- c) The nuclear spin disorder scattering is of two types: the component of nuclear spin I_z which is parallel to the polarisation direction produces non-spin-flip scattering, whilst the components I_x , I_y which are perpendicular to the polarisation direction give spin-flip-scattering.
- d) The magnetic scattering is also non-spin-flip if the relevant spin components are parallel to the direction of the neutron polarisation. However, if the spin components responsible for the scattering are perpendicular to the polarisation direction, then the polarisation of the neutron will change and the scattering will be spin-flip. This statement is true for all types of scattering; incoherent, coherent, elastic or inelastic.

In the case when neutrons with both u and v spin states are detected experimentally (as in the case when unpolarised neutrons are used), the measured partial differential cross-section for moments aligned along the z direction becomes (assuming there is no nuclear spin scattering):

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega} = \mathrm{b}^2 + 2\mathrm{b}\mathrm{Q}_{\perp z} + \mathrm{Q}^2_{\perp z} + \mathrm{Q}^2_{\perp y} + \mathrm{Q}^2_{\perp x}$$
(7.38)

If the scattering system is an ordered ferromagnetic crystal, then this coherent scattering cross-section represents the scattering associated with Bragg peaks, and the differential cross-section becomes:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = b^2 + 2bp\hat{q}\cdot\hat{\lambda} + pq^2 \tag{7.39}$$

where $\hat{\lambda}$ is a unit vector in the direction of the spin of the incident neutron and \hat{q} , the magnetic interaction vector. p is an effective magnetic scattering amplitude and for a spin moment only, can be written as:

$$p = \left(\frac{e^2\gamma}{2mc^2}\right)gsf$$

where g is the Lande splitting factor, s is the spin and f is the form factor.

Alternatively, if the atomic moment arises from both spin and orbital contributions, then P becomes:

$$\mathbf{P} = \left(\frac{\mathrm{e}^2 \gamma}{2\mathrm{mc}^2}\right) \mathrm{gjf}$$

In a ferromagnetic or ferrimagnetic material the nuclear and magnetic scattering densities have the same periodicity, hence both nuclear and magnetic effects contribute to neutron scattering in the same Bragg reflections (Brown, 1989). If the nuclear structure factor is N and the magnetic structure factor Q, then the scattered intensity for neutrons polarised parallel to Q is proportional to

$$\left(N + |\mathbf{Q}|\right)^2 \tag{7.40}$$

and that for neutrons polarised anti-parallel to Q is proportional to

$$\left(N - |\mathbf{Q}|\right)^2 \tag{7.41}$$

the ratio R between the intensities for the two spin states is

$$R = \frac{N^2 + 2NQ + Q^2}{N^2 - 2NQ + Q^2}$$
(7.42)

If N and Q are both real and the beam is completely polarised parallel to Q equation (7.42) simplifies to

$$R = \frac{1+2\gamma+\gamma^2}{1-2\gamma+\gamma^2}$$
(7.43)

where $\gamma = \frac{|\mathbf{Q}|}{\mathbf{N}}$

When, as is often the case $\gamma \ll 1$

$$R \sim 1 + 4\gamma \tag{7.44}$$

Equation (7.44) demonstrates the sensitivity of polarised neutron diffraction to weak magnetic scattering: the difference of the flipping ratio from unity varies

directly with γ , whereas the ratio of the reflection intensities with and without magnetic scattering varies as $1 + \gamma^2$. It is therefore particularly advantageous to use the polarised beam technique when the magnetic scattering is weak (Brown, 1993).

Measurement of the ratio R (the flipping ratio) allows determination of the magnetic structure factor as a fraction of the nuclear one. Since by using this technique the magnetic structure factor is obtained from a simple ratio measurements, it is possible to achieve rather high precision as, many of the systematic errors which plague absolute intensity measurements cancel out. This way of obtaining precise values for magnetic structure factors from flipping ratio measurements is the basis of classical polarised neutron diffraction (Brown, 1989).

7.4 Instrumentation for Neutron Diffraction

7.4.1 The Neutron Source

High-flux reactor

The high-flux reactor at the ILL operates at a thermal power of 58 MW using a single fuel-element. There are hot, thermal and cold neutrons available at different beam-tubes. The single fuel-element sits in the centre of a tank of 2.5 m diameter containing the heavy water moderator.

Cooling and moderation is by heavy water circulation passing through heat exchangers. The moderator partly reflects the thermalised neutron towards the fuel element. Biological shielding is provided by a light water swimming pool-type assembly surrounding the reflector tank and encased in dense concrete. Table (7.2) shows essential data of the High-Flux Reactor at Grenoble (Ibel, 1994).

Thermal Power	58.4 MW
Max unperturbed thermal flux in the reactor	1.5x10 ¹⁵ / cm ² .s
Max perturbed thermal flux in the beam	1.2x10 ¹⁵ / cm ² .s
tubes	
Coolant flow in fuel element	2400 m ³ /h
Coolant pressure (outlet)	4 bar
Coolant temperature (outlet)	50 °C
Average consumption of ²³⁵ U	30 %

Table (7.2) Essential data of the High-Flux Reactor at Grenoble.

Neutron Fluxes available

The thermal neutron flux, in equilibrium with the heavy water moderator (300 K), has a peak in the Maxwellian distribution at 1.2 Å. For certain beams and guide tubes this is modified by the inclusion of special moderators.

The length of the guides (up to120 m) allows the installation of many instruments which benefit from a high thermal or cold neutron flux and a low background.

- Hot source (10 dm³ of graphite at 2400): It enhances the neutron flux at wavelengths below 0.8 Å.
- Vertical cold source (20 dm³ of liquid deuterium at 25 K): It enhances the neutron flux wavelengths above 3 Å (4.5e 14 n/cm².sec).
- Horizontal cold source (6 dm³ of liquid deuterium at 25 K): It enhances the neutron flux at wavelengths above 3 Å (8e 14 n/cm².s)

Figure (7.4) shows typical energy spectra of neutrons produced by two common types of source: a neutron reactor and a pulsed spallation source (Sköld and Price, 1986).



Fig.(7.4) Wavelength-dependent neutron spectra from (a) 2000 K graphite, (b) 300 K D_2O and (c) 25 K liquid D_2 moderators at the Institut Laue-Langevin ((ILL) high-flux reactor.

7.4.2 The Polarised Neutron Diffractometer

Figure (7.5) shows a schematic drawing of a polarised neutron diffractometer (Brown, 1989).



Fig. (7.5) Schematic drawing of a polarised neutron diffractometer.

Neutrons from a reactor source are polarised and monochromated by a magnetised crystal in a shielded drum. To act as a polariser, the Bragg reflection used to select the monochromatic neutrons must have the property that its nuclear and magnetic structure factors are the same. For such a reflection the reflectivity of neutrons polarised parallel to Q is large, while that for anti-parallel polarisation goes to zero. Once polarised the neutron passes towards the sample through magnetic guides which maintain a small (~0.01T) field parallel to the polarisation direction to prevent depolarisation of the beam by stray fields. Some suitable reflections are given in table 7.3 (Sköld and Price, 1986). A device for flipping the neutron spins is inserted in the path between monochromator and sample. The spin flipper must have the property that when activated it inverts the neutron polarisation. The sample is mounted on a two-circle diffractometer equipped to allow the application of a vertical magnetic field.

The detector can move in a defined direction up to 20°, thus enabling data in non-zero layer lines to be detected.

Material	Reflection	d Spacing (Å)	
Co _{0.92} Fe _{0.08}	200	1.6	
Cu ₂ MnAI	111	3.43	
⁵⁷ Fe	110	2.03	

Table (7.3) Some polarising monochromators.

7.4.3 Single Crystal Diffractometers

- D3 polarised hot-neutron normal-beam diffractometer for magnetic density determination.
- D9 hot neutron four-circle diffractometer.

Single crystal diffraction is a powerful method for the investigation of structural details in condensed matter. Hot neutrons are required to uncover the finest details of the nuclear structure, while the use of spin polarised neutrons enable the various scattering components to be separated. (nuclear polarisation, magnetic and electronic scattering).

The Four-Circle Diffractometer

For every hkl reflection to be measured, the crystal has to be correctly oriented relative to the incoming beam and relative to the detector in order to fulfil the Bragg condition.

The crystal is mounted in an Euler Cradle, A characteristic of the four circle diffractometer, (three angles: ω , γ , ϕ , as shown in figure 7.6) which is able to bring any vector of the reciprocal lattice in a reflection position in the horizontal plane. The detector remains in the horizontal plane and collects the intensity, while the crystal is rotated around the vertical axis ω scan or $\omega/2\theta$ scan) in order that the reflection nodes cross the Ewald sphere (Schweizer, 1991; Ouladdiaf, 1995).

In such case the integrated intensity of a Bragg reflection is given by

$$I_{\rm int}(2\theta) = \frac{N}{v_{\rm o}} \frac{\lambda^3}{8\pi \, Sin\theta} \, |F|^2 A \tag{7.45}$$

where *N* is the number of unit cell in the crystal, v_{\bullet} the volume of one of the unit cells, *F* the structure factor of the Bragg reflection which is measured and *A* the absorption factor.

The Lorentz factor $1/\sin 2\theta$ expresses how the integration of the δ -function in the reciprocal lattice is transformed in an integration in the (ω , χ , 2 θ) experimental angles.



Fig. (7.6) Eurilian Cradles.

The Lifting Counter Diffractometer

The technique allows a more elaborate sample environment around the crystal, such as cryostat, furnace or magnetic field. In such an arrangement the only rotation of the crystal is around the vertical axis (ω), but the detector which moves around two axes (γ in the horizontal plane and v in the vertical plane) can be lifted above the horizontal plane to collect the intensity. The intensity in this case can be written as

$$I_{\rm int}(2\theta) = \frac{N}{v_{\circ}} \frac{\lambda^3}{Sin\gamma} |F|^2 A$$
(7.46)

These diffractometers can be used to find

- mean atomic positions. From these it can be found how the atoms are bound together to form molecules, and how the molecules are stacked.
- local atomic distributions. This gives information about the timeaveraged thermal motion or the local atomic disorder.
- magnetic structures and magnetic moment distributions.

Structural data of this kind are required for a large number of systems, ranging from organic molecules to high temperature superconductors. Often studies are made as a function of temperature, pressure and magnetic field which may lead to important modifications of the crystal structure.

D9 at ILL is ideally suited for structural determination. Structural data from D9 is also used to help in the analysis of magnetic structure.

The polarised neutron diffractometer D3 at ILL is used for magnetisation density determination.

7.5 D3: Polarised hot-neutron normal-beam diffractometer

D3 is a single-crystal diffractometer with a polarised incident neutron beam. Figure (7.7) shows a general view of D3 set-up.

In practice, the diffractometer is set at a Bragg peak of an already-known crystalline structure. Then, by simply reversing the beam polarisation, the diffractometer performs a highly sensitive measurement of a spin-dependent nuclear-magnetic-interference amplitude term which is present in the Bragg scattering of polarised neutrons from a small single-crystal specimen magnetised in a field.

A device for flipping the neutron spins is inserted in the path between monochromator and sample. The spin flipper must have the property that when activated it inverts the neutron polarisation. Measurements are made by setting the diffractometer so that the required Bragg reflection is scattering its maximum intensity into the detector. The flipping ratio is then obtained from the ratio of the intensities, corrected for the background, recorded with the spin flipper off and with it on.

The diffractometer uses neutrons from the hot source with wavelengths as short as 0.4 Å. It is, therefore, possible to measure magnetic structure factors up to Sin $\theta / \lambda \text{ Å}^{-1}$, a large enough value to include any details nature provides in the smallest magnetic ions.

D3 uses readily exchangeable CoFe and Cu₂MnAl (Heusler alloy) polarising monochromators within removable shielded cassettes in symmetric Laue geometry. Wavelength change in an on-line operation, including the insertion of the appropriate resonant harmonic filter. This is particularly useful when extinction or multiple scattering are present. The beam polarisation depends slightly on the wavelength the monochromator and the in-pile moderator.

Collimation (channel A or B) used: it is 90% at its lowest and reaches 99% at its best. Polarisation reversal is made with a "Cryoflipper". The secondary axis is set on an ILL "Tanzboden" floor, mechanically attached to the monochromator exit port. Normal beam geometry with lifting detector is used and, therefore, the large cryomagnet is kept vertical. The detector support arm and the sample adjustment table are non-magnetic so that a cryomagnet with large stray fields can be used. A pneumatic half-shutter system in front of a 5 cm diameter single ³He detector facilitates the determination of the exact orientation matrix for the crystal.



Fig. (7.7) A general view of the normal beam polarised neutron diffraction D3.

Most measurements carried out on D3 require the sample to be at low temperature and in an intense magnetic field, therefore a 4.6 T cryomagnet is dedicated to the instrument. A precision temperature controller and a cryomagnet controller are interfaced to the instrument computer which can set [H, T] variables on-line. An airtight chamber attached to the top of the cryostat makes it possible to insert air-sensitive samples without any contact with the atmosphere.

The instrument is extensively automated. Figure (7.8) shows a detailed schematic diagram for D3 diffractometer.



Fig. (7.8) Layout of D3 diffractometer.

Positioning, measurement, data storage and transfer are under control of a computer. The software acquisition system provide the user with many simple commands

Data can readily be analysed on the ILL computing system of programs making use of the Cambridge Crystallographic Subroutine Library (CCSL). These provide quick reduction, sorting and averaging of the various data sets already collected. Resulting magnetic structure factors are then Fourier

transformed for direct visualisation of the atomic magnetisation density maps, (Maximum Entropy using Memsys Code) and then used to refine physical models for the magnetic electrons. Table (7.4) shows some properties of D3 instrument.

Beam tube	H4, hot neutron source			
Polarising monchromators				
Take-off-angle $7^{\circ} < 2\theta_{\rm M} < 45^{\circ}$				
High-Flux, low resolution	Cu ₂ MnAl (111), d = 3.362 Å			
Less-Flux, better resolution	Co _{0.92} Fe ₈ (200), d = 1.771 Å			
Flux sample at I = 0.843Å	CoFe: 1x10 ⁶ n cm ⁻² s ⁻¹			
	Heusler: 4.6x10 ⁶ n cm ⁻² s ⁻¹			
Polarisatio	n reversal			
Cryoflipper	Wavelength independent			
Sampl	e size			
Maximum diameter	11 mm			
Maximum length (height)	20 mm			
Sample en	vironment			
Temperature	1.50 K < T < 300 K			
Electromagnet	0.01 T < H < 1.2 T			
Cryomagnet	1.50 T < H < 4.6 T			
Detector				
Angular ranges	-135° < g < +5°			
	-185° < w < +185°			
	-5° < n < +22°			

Table (7.4) Characteristics of D3 Polarised neutron diffractometer.

7.6 D9: Hot Neutron four-circle Diffractometer

Figure (7.9) shows an overall view of D9. The 2-stage displex cryorefrigerator is mounted on the Eulerian Cradle.

The diffractometer D9 is used for precise and accurate measurements of Bragg intensities up to very high momentum transfer. The resolution allows routine recording of extended data sets for the detailed study of atomic disorder and atomic thermal motions.

The wavelength of the neutrons is among the shortest available at any reactor. The monochromator is a Cu crystal in transmission geometry using the (220) planes, but a horizontally focused Be-monochromator is being developed. The instrument is placed on a Tanzaboden floor allowing a continuous choice of wave-lengths in the range from 0.35 to 0.85 Å. In order to suppress $\lambda/2$ contributions, several resonance filters are available (0.48, 0.55, 0.70, and 0.84) Å.

The sample-holder is an Euler Cradle with offset zero-axis. A small twodimensional area detector is available for studies of satellites and twinning. It covers 32x32 pixels of $(0.25^{\circ})^2$, and programs are available for intensity integration using this system.

Measurement of one Bragg reflection normally takes a few minutes, and recording of a full set of data a few days. If the crystal is studied as a function of temperature, pressure or other variables, the total measurement time is about a week. Table (7.5) shows some properties of D9 instrument.



Fig. (7.9) An overall view of hot neutron four-circle diffractometer D9.

Cu (220)				
13° — 56°				
(0.25 — 0.85) Å				
Eulerian Cradle				
-20° < 2q < 140°				
-10° < w < 48°				
-30° < c < 200°				
-180° < f < 180°				
0.6x0.6 cm ²				
> 10 ⁷ n cm ⁻² s ⁻¹				
ctor				
ixel size 32 x 32 pixels				
2 x2 mm ²				
0.25 x 0.25 deg ²				
64 x 64 mm ²				
Sample environment				
20 K				
850 °C				
1000 °C				
2 K				

Table (7.5) Characteristics of D9 hot neutron four-circle diffractometer.

7.7 Experimental Results and Discussions

7.7.1 D3 Polarised Neutron Diffraction

Polarised neutron diffraction, using the D3 single crystal diffractometer, was used to investigate the change in distribution of the magnetic electrons between the cubic and tetragonal phases of Ni₂MnGa in order to test the hypothesis of a band Jahn-Teller mechanism.

The relationship between electronic properties and crystal structure is of fundamental importance for the understanding of solids. Detailed model calculations (Labbe and Friedel, 1966) have been provided to account for structural phase transitions in A15 superconductors. In these calculations, the lattice distortion essentially removes the degeneracy of the d bands in the vicinity of the Fermi level, thus causing a repopulation by the electrons and a

lowering of the free energy. This mechanism, which has been called a band Jahn-Teller effect, has recently been proposed for other metallic systems (Fujii, Ishida et al., 1989), e.g. Ni₂MnGa, which undergoes a Martensitic phase transition at ~ 200K (Webster, Ziebeck et al., 1984). Martensitic phase transitions are themselves of particular interest, since they are of second order and arise from the condensation of certain phonon modes. Since Ni₂MnGa is ferromagnetic, a detailed investigation of the spin density distribution above and below the ferromagnetic transition temperature can be carried out using polarised neutrons. In this way any re-population of electrons can be quantified and the appropriateness of the band Jahn-Teller mechanism assessed.

Ni₂MnGa is a ferromagnetic Heusler alloy which has a Curie temperature of 378 ± 4K and an fcc L2₁ structure with lattice parameter a = 5.822 Å, as shown in (fig.3. Chapter Three) (Webster, Ziebeck et al., 1984). There is a phase change on cooling through $T_t = 200K$ from the cubic L2₁ Heusler structure to a tetragonal modification of the same structure. The two phases have different magnetic anisotropy, and their magnetisations differ in weak fields but converge in strong fields around 5T. The saturation magnetisation at low temperatures is $3.7\mu_B$ per Ni₂MnGa formula unit. There is a severe distortion of the unit cell in the transition (c/a = 0.957) but the atomic volume changes by less than 0.5% and the phase change takes place reversibly without shattering the crystal. The aim of the experiment was to investigate the change in distribution of the magnetic electrons between the cubic and tetragonal phases of Ni₂MnGa in order to test the hypothesis, based on band structure calculations, that the phase transition is driven by a band Jahn-Teller effect.

Initially the crystal was oriented with its length along the [110] axis, vertically on the polarised diffractometer D3 at the ILL. On cooling through the phase transition the cubic (220) reflection split into two reflections separated by the angle v (the inclination of the detector), one above and one below the cubic position. This shows that only two of the three possible tetragonal twins are present: those whose tetragonal c-axes are parallel to the cubic [100] and

[010] axes. The twin whose c-axis would have been perpendicular to both the long axis and the field direction was not formed. With this arrangement of twins it is not possible to measure a significant number of multiple reflections which are equivalent under cubic symmetry but distinct in the tetragonal phase. To try to change the twin populations the crystal was demagnetised by heating it above T_c and cooling in zero magnetic field. Its previous finite magnetic remanance disappeared but there was no apparent change in twin population. With this crystal orientation the magnetism did not appear to play a major part in determining the twin distribution. Eventually the crystal was mounted with its long axis horizontal and a [113] axis parallel to the field. With this orientation a reasonable fraction of the full set of the tetragonal phase reflections was accessible, although the scattering geometry was not ideal. Flipping ratios were measured with $\lambda = 0.84$ Å for both the cubic and tetragonal phases, at T = 230K and T = 100K respectively for all reflections with $\sin\theta/\lambda < 0.64$ Å⁻¹. A set of strong reflections was measured at the shorter wavelength $\lambda = 0.42$ Å at both temperatures to check for extinction.

Analysis of the data suggests that there is a disorder amounting to some 18% between the Mn and Ga atoms. The moments determined for each site in the cubic phase at 230K are Mn 2.93(4), Ni 0.43(2) and Ga 0.13(4). There are significant differences in the tetragonal phase between the magnetic scattering of reflections belonging to multiplets which are equivalent under cubic symmetry. Figure (7.10) shows a Fourier section illustrating the difference in the magnetisation distribution in the cubic and tetragonal phases. The most significant feature is the positive feature on the Mn site extended along the tetragonal c-axis, suggesting that in the cubic to tetragonal transition the $3d_{3z^2-r^2}$ will broaden and the $3d_{x^2-y^2}$ will narrow. The consequent repopulation of the $3d_{3z^2-r^2}$ band at the expense of the $3d_{x^2-y^2}$ is what has been observed in the experiment.

In the band Jahn-Teller mechanism, bands which are degenerate in the cubic system are no longer degenerate in the tetragonal phase. This enables the electrons to re-populate the lower energy bands. In contrast to the normal Jahn-Teller effect associated with Cu²⁺ or Mn³⁺ ions in which the energy bands are split in the band model, there is a modification in the width of the energy levels. There will be a change in the degree of overlap associated with orbitals when the crystal deforms. Those orbitals overlapping in the direction of the crystallographic elongation will give rise to a narrower bandwidth compared to those in the direction of the contraction. Specifically for the 3d bands, the e_g narrow band orbitals are degenerate in the cubic phase, but for the tetragonal structure c/a < 1, the 3d_{3z²-r²} band will broaden and the 3d_{x²-y²} band will narrow. This will give rise to a net transfer of 3d electrons to the 3d_{3z²-r²} band, as observed in the experiment.



Fig. (7.10) A Fourier section perpendicular to $[\overline{1}10]$ through the origin. The coefficients are the differences between the magnetic scattering in the tetragonal and cubic phases the latter being scaled to compensate for the increase in total magnetisation on cooling from 230 to 100K. The contours are at equal intervals of $0.027\mu_B\text{Å}^{-3}$, negative contour are shown as dashed lines.

7.7.2 D9 The Unpolarised neutron study

Ni₂MnGa is one of the group of "shape memory effect" alloys which are currently exciting considerable attention. The origin of this effect in Ni₂MnGa is in the phase change which takes place on cooling through T = 200K from the cubic L2₁ Heusler structure to a tetragonal phase. The transformation can be described as a simple contraction along the <100> directions of the cubic phase without any change in the atomic positions. There is a strong deformation of the cell (c/a \approx 0.96) but a reduction of only <1% in the cell volume (Webster, Ziebeck et al., 1984).

A study of the way in which the transition takes place has been undertaken using neutron diffraction from a single crystal. The D9 diffractometer which receives neutrons from the hot source at ILL Grenoble was used because it was particularly suited to this experiment.

Martensitic phase transformation is a displacive, diffusionless first-order transformation from a symmetric high temperature parent phase to a low symmetry Martensitic structure (Nishiyama, 1978).

Associated with the phase transition are phonon anomalies in the parent phase. In bcc structure, the $[\zeta\zeta 0]$ TA₂ mode with displacements along $[1\overline{1}0]$ softens.

Inelastic neutron scattering experiments have been used to study a single crystal of the Ni₂MnGa shape-memory ferromagnetic Heusler alloy in a wide temperature range above the martensitic phase transformation at $T_M = 220$ K. These reveals significant softening of the [$\zeta\zeta 0$] TA₂ phonon at a wave vector $\zeta = 0.33$ (Zheludev, Shapiro et al., 1995).

Figures (7.11a) and (7.11b) show some representative spectra measured at different temperature which reveals the decrease of the phonon energy as the temperature approaches T_M . Phonon dispersion curves measured at 370 and 270K are shown in figure (7.11a). The most prominent feature is the wiggle in

the $[\zeta\zeta 0]$ TA₂ branch, which deepens with decreasing temperature, resulting in a distinct minimum at ζ =0.33 below 300K. The way the dip evolves is shown in figure (7.11b).



Fig. (7.11a) Partial acoustic phonon dispersion curves measured for Ni₂MnGa at 270 and 370K.



Fig. (7.11b) Temperature dependence of the anomaly in the $[\zeta\zeta 0]TA_2$ branch.

Figures (7.11a), (7.11b) and fig. (7.12) (Stuhr and Vorderwisch, 1994) have been used to calculate $v_s = \omega/\kappa$ (velocity of sound) in a region, where $q \rightarrow 0$, and hence to calculate the elastic constants; c_{11} , c_{12} and c_{44} for TA₂, TA and LA.



Fig. (7.12) Transverse phonon (open circles), longitudinal phonons (closed circles) and magnons (crosses) in (0 ζ 0)-direction.

Table (7.6) shows the equations which have been used to calculate υ_{s} and the elastic constants.

	Wave propagation along [100] direction	
Longitudinal	$v_{s} = (c_{11}/\rho)^{1/2}$	
Transverse	$\upsilon_{\rm s} = (c_{44}/\rho)^{l/2}$	
	Wave propagation along [110] direction	
Longitudinal	LA (c _L): $\omega^2 \rho = 1/2 (c_{11} + c_{12} + 2c_{44})k^2$	
Transverse	$TA_1 \qquad \omega^2 \rho = c_{44} k^2$	
	TA ₂ (c'): $\omega^2 \rho = 1/2 (c_{11} - c_{12})k^2$	
	Wave propagation along [111] direction	
Longitudinal	LA (c' _L): $\omega^2 \rho = 1/3(c_{11} + c_{12} + 4c_{44})$	
Transverse	TA (c' _T): $\omega^2 \rho = 1/3(c_{11} - c_{12} + c_{44})$	
Where $v_s = \omega/\kappa$,	$c_{L} = 1/2(c_{11} + c_{12} + 2c_{44}), c' = 1/2(c_{11} - c_{12})$	
density $\rho = 8.14$	g/cm^{3} and a = 5.824 Å.	

Table (7.6) Equations used for calculation sound velocity and elastic constant

Table (7.7) shows our calculation of the single crystal (Ni₂MnGa) elastic constants, using inelastic neutron scattering measurements of the single crystal (Zheludev, Shapiro et al., 1995). A density of 8.14 g/cm³ was used in the calculation. The values of c_{11} , c_{44} were obtained from the equations listed in table (7.6) and c_{12} obtained using equation $c_{12} = c_{L} - c' - c_{44}$.

	CL	C44	c´	C ₁₁	C ₁₂	CL	Ст́
10 ¹² dyn/cm ²							
TA[100]		0.87					
TA[100[1.09					
LA[100]				2.61			
TA ₁ [110]		0.584					
TA ₂ [110]							
TA ₂ [110]			0.081				
LA[110]	3.13		0.163				
LA[111]						3.77	
TA[111]							0.49
					2.18		

Table (7.7) Single-crystal elastic constants obtained from equations on table (7.5).

The measured velocities, for propagation in the [110] direction, associated with the three independent elastic constants $c_L = \frac{1}{2} (c_{11}+c_{12}+2c_{44})$, c_{44} and $c' = \frac{1}{2}(c_{11}-c_{12})$ are shown in table (7.8). The velocities determined by an earlier ultrasonic study and the velocities obtained from the inelastic neutron-scattering experiments are also shown. All velocities are at 300K (Worgull, Petti et al., 1996).

The single-crystal elastic constants, calculated from the velocities shown in table (7.8), are listed in table (7.9). A density of 8.13 g/cm³ was used in the calculation. The values of c_{11} and c_{12} were obtained from the directly measured values of c_L , c_{44} and c' using relations $c_{11} = c_L + c' - c_{44}$ and $c_{12} = c_L - c' - c_{44}$. Values of c_{11} , c_{44} and c_{12} , listed in the EMG (electromagnetic generation) (Worgull, Petti et al., 1996).

Table (7.8) The ultrasonic velocities for longitudinal and two shear modes at 300K, neutron scattering studies, and from electromagnetic generation of ultrasound (EMG).

	VL	V ₄₄ 10 ⁵ cm/s	V
Study			
Present	5.54	3.56	0.740
Neutron	5.23	3.94	0.772
EMG 5.46		3.36	2.77

Table (7.9) Single-crystal elastic constants at 300K obtained from the velocities shown in table (7.8) and the density $\rho = 8.13 \text{ g/cm}^3$.

	CL	C44	c´	C11	C ₁₂	
10 ¹² dyn/cm ²						
Study						
Present	2.50	1.03	0.045	1.52	1.43	
EMG	2.42	0.92	0.63	2.13	0.87	

In a previous experiment using polarised neutron in D3 it was found that there was a significant redistribution of magnetic electrons in the transformation. It was also found that the transformation takes place in stages, and that there is considerable hysteresis. The present experiments on D9 were undertaken to gain further information about the way in which the transformation takes place. The small multidetector on D9 enables the distribution of the scattering around any Bragg reflection to be determined in some detail.

Some preliminary rapid heating and cooling cycles were made to establish the temperature range of the transition and the angular width of scans required to accept most of the diffracted intensity. Several reflections of the form {hhl}, {h00} and {hhh} were chosen, and ω scans of width 5 degrees centred on the reflection positions in the high temperature cubic phase were carried out in bisecting geometry. When the instrument geometry permitted, the reflections

were scanned at two different positions in the rotation around the scattering vector, as widely spaced as possible.

Finally a set of twenty scans through the position of Bragg peaks of the high temperature cubic phase was measured at temperature intervals 1K between 235K and 200K, first cooling and then heating.

Precursor phenomena in the parent phase

A precursor effect where acoustic anomalies, phonon dispersion curves, and diffuse elastic scattering in the parent phase give an indication of the eventual Martensitic structure. For example in a number of bcc materials the ($\zeta\zeta$ 0) TA₂ mode with displacement along ($\overline{110}$) softens at a certain wave vector ζ_{\circ} which is close to a reciprocal-lattice vector of the low temperature structure. This has been demonstrated in extensive studies of Ni-Ti, Ni-Al and Au-Cd.

Phonon dispersion curves were determined from inelastic neutron scattering (Zheludev, 1995; Zheludev, 1995) along the high-symmetry directions [ζ 00], [ζ ζ 0], [ζ ζ ζ] and [2ζ ζ ζ] using constant-q. The most striking feature, however, is the strong temperature dependence of the [ζ ζ 0](110) TA₂ branch. Figure (7.11b) shows the dispersion curve which has a wiggle at $\zeta_{\circ} = 1/3$ at room temperature, which develops into a distinct minimum as the temperature is decreased.

The softening of the TA₂ phonon is incomplete. In the limit $\zeta \rightarrow 0$ the [$\zeta \zeta 0$]TA₂ mode corresponds to the zener elastic constant c['] = (c₁₁ - c₁₂), which is known to be reduced in bcc materials, and show an anomalous decrease as T \rightarrow T_M in Ni₂MnGa.

Associated with the dip in the [$\zeta\zeta 0$] TA₂ phonon dispersion curve is a quasielastic diffuse "central peak", which shows up in [$\zeta\zeta 0$] transverse scans in the vicinity of 1/3[110] fig (7.11b). Its intensity increases steadily as the frequency of the corresponding TA₂ phonon decreases. Its shape in q-space

roughly coincides with that of the dip in the dispersion manifold and its q-width is T-independent at $T > T_1$ ($T_1 = 265$ K). The energy width of the peak is resolution limited: just like the phonon anomaly, it is localised in a narrow valley along [110]. All this suggests that the diffuse peak is defect-induced and is directly related to the reduction of vibrational frequencies (Zheludev, 1995).

In accordance with the original soft mode theory of Cochran (Zheludev, Shapiro et al., 1995), fig (7.13) shows the temperature dependence of the TA₂ soft mode frequencies in Ni₂MnGa. $(\hbar\omega)^2$ decreases linearly with temperature. The absence of complete phonon softening has been accounted for by assuming anharmonic coupling of the periodic lattice distortion.



Fig. (7.13) $(\hbar\omega)^2$ Vs T for the [$\zeta\zeta 0$] TA₂ mode at $\zeta = 0.325$.

A thermodynamic, or phenomenological, theory that is used extensively to describe phase transitions is the Landau free energy theory (Burns, 1985). It is based on the idea of an order parameter. An order parameter measures the extent of the departure of the atomic (or electronic) configuration in the less symmetric phase from that in the more symmetric (high temperature) phase. The appearance of an order parameter at T_c breaks the symmetry of the high temperature phase, the order parameter is zero above T_c and nonzero below T_c. In ferroelectric order-disorder transitions the order parameter would be some measure of the amount of long-range ordering of the permanent dipole.

For displacive transitions the order parameter could be some measure of the displacement of certain ions from their high temperature equilibrium positions. For most ferroelectrics of either the order-disorder or displacive type, the spontaneous polarisation P_s can be taken as the order parameter.

The diffusionless phase transitions in Ni₂MnGa may be described by Landautype phenomenological free energy functional (Krumhansl and Gooding, 1989; Krumhansl, 1992). The theory should be able to account for: (a) a firstorder phase transition at T₁ with complete phonon softening, resulting in a periodic distortion of the cubic phase with the wave vector of the soft mode, (b) the MT at T_M which involves both a tetragonal distortion and a new superstructure, and (c) the fact that the perstructure in the MT phase has a different periodicity from that of the "softest" ($\zeta_{\circ}\zeta_{\circ}0$) phonon and is incommensurate with the tetragonal lattice. For this, the theory should make use of a suitable set of order parameters, including the amplitudes of periodic ($\zeta, \zeta, 0$) distortions of the parent structure $\eta(\zeta)$ (Zheludev, Shapiro et al., 1996).

In a great majority of cases the transition is dominated by one member of a small set of anomalously "soft" distortive modes, which because of great anisotropy occupy only narrow regions of the phonon-dispersion Brillouin zone. This suggests writing a Landau-type free energy in terms of only a few order parameters, i.e., static expectation of amplitudes or phases of the distortive modes (Krumhansl and Gooding, 1989). Consider a model free energy for a single-component order parameter η ,

$$F = \frac{A}{2}\eta^2 + \frac{B}{3}\eta^3 + \frac{C}{4}\eta^4 + \cdots$$

If B is negative, A and C positive, for certain values of the parameters a firstorder transition is possible, from F = 0 at $\eta = 0$ to some finite value of η where F is also zero. A is approximately the quasiharmonic force constant, B and C are third- and fourth- order generalised force constants.

(Fritsch, Kokorin et al., 1994) have shown that measurements of the thermal diffuse x-ray intensity from a single crystal of Ni₂MnGa in the temperature range 180 to 250K showed a Martensitic phase transition. It is accompanied by a strong soft-mode behaviour in the transverse acoustic phonon branch with q along the [110] direction and polarisation along [110] in the high temperature phase. An acoustic examination of the high-temperature phase (Vasilyev, Kokorin et al., 1990) has revealed that the [$\eta\eta$ 0] transverse acoustic mode (displacements are along the [110]) direction exhibits an anomaly for T \geq M_s in the limit $\eta \rightarrow 0$. Such behaviour corresponds to a decrease of the elastic constant c' = $\frac{1}{2}(c_{11} - c_{12})$ when approaching the transition. Thus the result of (Fritsch, Kokorin et al., 1994) demonstrates the existence of a soft mode behaviour in the high-temperature phase of the Heusler alloy Ni₂MnGa, (T = 250K). A significant decrease in the angular frequency of the TA-phonon with q = (1/6) τ_{110} , where τ is the reciprocal lattice vector, is observed when the temperature approaches M_s.

Inelastic neutron scattering and neutron diffraction were used to study a single crystal of the Ni₂MnGa shape memory Heusler alloy in a wide temperature range covering the parent phase ($T>T_1 = 260K$), a premartensitic phase $(T_1 > T > T_M)$, and a Martensitic $(T < T_M = 220K)$ phase region. Several anomalies in the phonon dispersion curves in the parent phase were observed. The premartensitic phase involves a transverse modulation of the parent cubic structure with a simple periodicity of (1/3,1/3,0). The approximately tetragonal lattice of the low-temperature martensite is distorted by transverse modulations with incommensurate wave vectors ($\zeta_{M}, \zeta_{M}, 0$), The observed phenomena are attributed to electron-phonon ζ_M =0.43. interactions and anharmonic effects (Zheludev, Shapiro et al., 1996). An investigation performed by (Kokorin, Chernenko et al., 1996) of the structural and physical properties of the premartensitic state which is realised in lowtemperature Ni-Mn-Ga alloys. This state is interpreted as an intermediate phase of the TA₂ soft mode with $q \neq 0$. This kind of mode condensation is assumed to manifest itself through the volume increase of the lattice cell of the initial cubic high-temperature phase. The minima of the thermal

expansion coefficient and elastic modulus at the P-I transformation, (where the intermediate phase I is intermediate between the high-temperature parent phase P and the Martensitic phase M), are associated with the anomalous increase in the mean square displacements of atoms at temperatures where the TA₂ soft-mode frequency is anomalously small.

Recently (Planes, Obradó et al., 1997) presented a model that accounts for the first order phase transition between the bcc and the intermediate phases. The first order character has been experimentally demonstrated by the measurement of a latent heat and by the magnetic field dependence of the transition temperature. In the model, the first order transition occurs as a consequence of a magnetoelastic coupling. Such a coupling has been experimentally observed. Hence, the premartensitic transition must be considered as a magnetically driving precursor effect announcing the MT by the modification of the dynamical response of the bcc parent lattice. Within a general framework, the results presented here provide show that coupling of a secondary field (magnetic in this case) to incipient degree of freedom, can fundamentally affect the characteristics of a phase transition.

(Worgull, Petti et al., 1996) in recent ultrasonic measurements, determined the elastic constants c_{44} , c_L and c'. All three elastic constants soften as the premartensitic transformation temperature is approached, and the ultrasonic attenuation also increases dramatically as the intermediate phase transition is approached. The behaviour of the elastic constants and the ultrasonic attenuation is consistent with inelastic neutron scattering results and confirms the existence of the intermediate phase. Recent neutron studies (Zheludev, Shapiro et al., 1995) show that phonon anomalies occur in the phonon dispersion in the parent cubic phase. Softening is observed in the TA₂ branch of a wave vector $\zeta_{\circ} \approx 0.33$ in Ni₂MnGa. The phonon softening is incomplete, the phonon soften results is a premartensitic intermediate transformation at a temperature 265K. A study of a single crystal by (Zheludev, Shapiro et al., 1995) on the temperature dependence of the inelastic scattering of the [$\zeta\zeta_0$] TA₂ phonon branch shows that for $\zeta \rightarrow 0$, the mode corresponds to the elastic constant c' = $\frac{1}{2}(c_{11} - c_{12})$, which is known to be anomalously low in bcc metals.

Recently (Manosa, Gonzàlez-Comas et al., 1997) determined the elastic constant at room temperature; that is c_{11} , c_{44} , $c_L [= (c_{11}+c_{12}+2c_{44})/2]$ and $c' [= (c_{11}-c_{12})/2]$. The evolution of the elastic constants with temperature is shown in figure (7.14). A noticeable decrease of the two shear elastic constants c_{44} and c' occurs at the phase transition. It is specially remarkable for c', for which the a mount of softening at the transition point is around 60%. The amount of softening found for c' is very similar to that reported for the phonon frequency at q=0.33. The larger softening of c' results in an important increase of the elastic anisotropy (c_{44}/c') at the phase transition. On the other hand, the longitudinal elastic constants do not exhibit anomalous behaviour: both c_{11} and c_L increase as temperature is reduced.



Fig. (7.14) Relative changes of the elastic constants as a function of temperature. C_{11} , c_L , and c_{44} have been obtained by the pulse-echo method. c' has been obtained by the through transmission method.

Analysis of the D9 measurements

(a) Cooling from T=235K to T=200K

The patterns of diffracted intensity observed during the transition are quite complicated. Figure (7.15) shows the position and shape of diffracted peaks observed around the 220 position at T=235K and at T=206K on cooling and at T=200K. At T=235K (figure 7.15a) there is just a single peak from the cubic phase 220 reflection; at T=200K there two peaks which can be associated with 202 or 022 reflections from the tetragonal phase. These are the limiting cases. At T=206K at least seven distinct peaks can be discerned. During heating there is hystereis and the progression is simpler.



Fig. (7.15): The distribution of scattered intensity around the cubic 220 reflection in Ni₂MnGa whilst cooling (a) 240K (b) 206K (c) 200K.

The full body of the scans have been analysed starting with the "prewash" program (Fujii, 1987). This program extracts peaks from a multidetector scan which have heights greater than a predetermined level (ten times the standard deviation of the background was chosen) and which are correlated over a specified number (ten were chosen) of contiguous frames (that is, steps in ω) in the multidetector scans. The information about the peaks so selected was processed to obtain the approximate integrated intensities and the central positions of all the peaks containing more than about two per cent of the total intensity in the scan. Spurious information about very weak apparent reflections was thus excluded. Analysis of these data allows the d spacings of the contributing reflections and the orientation of their scattering vectors to be found. Thus the various peaks were associated with individual

regions (called domains) within the crystal and the lattice parameters, and the orientations of each temperature for cooling and were determined. The final analysis given below is referred to the {220} set of reflections. There was crystallographic consistency between the different reflections from each domain. The orientation of the scattering vector of each peak was calculated in terms of its rotation from the scattering vector direction of its parent reflection in the cubic phase, about two axes perpendicular to this direction and to one another. These rotations, together with the absolute values of the d spacings, allowed the peaks in the scans of different reflections and at different temperatures to be associated with one another and with particular tetragonal domains. The fraction of the volume of the crystal associated with each of the domains was calculated from the relative intensities of the contributing peaks.

(b) Heating from T=200K to T=235K

The patterns obtained during slow heating were different and simpler. The seven-fold pattern of peaks illustrated in figure (7.15b) did not occur. The pattern of a two peaks-like figure (7.15c) persisted up to T=216K. At T=219K a third peak started to appear. It remained as a single peak from T=220K upwards, albeit somewhat extended at first, until it became identical to the single peak first observed at T=235K.

Six domains were sufficiently well-resolved in several scans for their orientation, cell dimensions and quantities to be determined.

Domain 1 corresponds to regions that remain cubic. Their cell dimensions do not change appreciably during cooling. Eventually, at about T=204K, they disappear altogether. These are called *Type 1*.

Domains 2, 3 and 5 are intermediate domains only observed during cooling. They are tetragonal but with c/a ratios closer to unity than type 3. These are type 2. The range temperature over which they occur is smaller than for the other types.

Domains 4 and 6 are domains for which the c/a ratio is furthest from unity. They have the fully developed tetragonal structure. Their first appearance during cooling was at T=220K and they persisted to T=200K. These are *Type3.*

Figure (7.16) shows how the lattice parameters of the three types vary with temperature. Within each type there is relatively little variation of lattice parameters with temperature but the values for each type are characteristic.



Fig. (7.16) Lattice parameters of the different domain types identified in Ni₂MnGa on heating and cooling through the cubic to tetragonal phase transition.

A model is being developed to try to relate the stepwise nature of the transformation, the lattice parameters and the orientations of the different domains to shear processes of the type described by Batterman and Barrett (Batterman and Barrett, 1966). It is supposed that the particular shears which occur are those favoured by local strains in the crystal. This may explain why only two of the many possible tetragonal domain orientations are present in this crystal at and probably below T=200K.

Zheludev et. al. used inelastic neutron scattering to study a single crystal of Ni₂MnGa, where they observed, though incomplete, a softening in the $[\zeta\zeta 0]TA_2$ phonon branch at a wave vector $\zeta_{\circ} \approx 0.33$. The most prominent feature is the wiggle in the $[\zeta\zeta 0]TA_2$ branch, which deepens with decreasing temperature, resulting in a distinct minimum below 300K as shown in figure

(7.11b). They pointed out that this mode, for $\zeta \rightarrow 0$, corresponds to the elastic constant c['] = $\frac{1}{2}(c_{11} - c_{12})$.

We used figures (7.11a), (7.11b) and (7.12) to calculate the sound velocities in the limit $\zeta \rightarrow 0$ and small ω hence we calculated elastic constants c_{11} , c_{44} , c_L and c' for the inelastic neutron measurements, but our values do not agree with the values obtained by an ultrasonic pulse echo technique (Worgull, Petti et al., 1996; Manosa, Gonzàlez-Comas et al., 1997).

It has been shown by (Manosa, Gonzàlez-Comas et al., 1997) that the variation of the elastic constant with temperature lead to a noticeable decrease of c_{44} and c' around q = 0.33, but these values do not change as $q \rightarrow 0$. Zheludev and Manosa shown that c' changes around q = 0.33, where phonon dispersion curves show anomaly in the [$\zeta\zeta 0$] TA₂ branch, but not as $q \rightarrow 0$.

The present results show that the formation of domains, due to the unpolarised neutron study, have an effect on softening as $q \rightarrow 0$. The precursor effects, premartensitic and the diffuse scattering have only a small effect on softening as $q \rightarrow 0$.
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CHAPTER EIGHT

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

8.1 Conclusions

As stated in chapter one, this study aimed at exploring the way in which the structural phase transition takes place in the ferromagnetic Heusler alloy Ni₂MnGa, and at investigating the effect of electron concentration on the magnetic and structural properties of Ni₂MnGa by the substitution of Ga by other elements. By use of spin polarised neutron diffraction the change in the distribution of magnetic electrons between the cubic and tetragonal phases was investigated, in order to establish the mechanism which gives rise to the phase distribution.

The chemical and magnetic structures of the alloy Ni₂MnGa have been investigated in detail by other workers using magnetic, X-ray and neutron diffraction techniques. In summary, it was confirmed that at room temperature Ni₂MnGa was highly ordered in fcc L2₁ Heusler structure with a lattice parameter of 5.825 Å and space group $Fm\overline{3}m$. The alloy is ferromagnetic with a Curie temperature of 376 K and a magnetic moment of 4.17 μ_B per formula unit. On cooling below 202 K it undergoes a Martensitic transformation from the cubic phase to the tetragonal phase with c=5.66 Å, a=5.920 Å and c/a=0.940.

Magnetic measurements in applied fields up to 15 KOe indicated behaviour typical of a homogeneous soft ferromagnet, down to 202 K. However, at 202 K there was an abrupt change in the field dependence of the magnetisation, as shown in fig. 2.1. Below 202K it was found difficult to saturate the sample.

Polycrystalline samples of Ni₂MnGa were prepared by the repeat melting of appropriate quantities of the starting elements in an argon arc furnace. The structural characterisation of the compound was carried out. X-ray powder diffraction measurements, obtained at room temperature using copper radiation, indicated a single phase, which formed in the L2₁ structure. The calculated values for the lattice constants of all samples are tabulated in tables 3.1, 3.5, and 3.6. Ni₂MnGa has a = 5.824 which is very close to the value obtained by other workers. The Fullprof refinement program used to analyse the diffraction patterns gave a value of 5.818 Å for this sample. An investigation was carried out to find out whether the partial substitution of Ga by tin, indium or other elements in the alloy Ni₂MnGa has an effect on the lattice parameter. The result of the calculated values of the lattice parameter from the X-ray diffraction showed slight change from the value of the lattice constant of Ni₂MnGa. X-ray diffraction patterns for all samples are shown in chapter three. In addition to the strong cubic reflections, several much weaker peaks were present on all diffraction patterns. Fullprof analysis showed that some of these peaks are not indexable as part of the cubic structure. Samples containing 2.5%, 0.5%, 0.27%, and 0.26% of tin showed split on (220) reflection; this could be due to $K\alpha_2$ line. Also it has been observed that the (400) reflection showed a single shoulder in some cases and a double shoulder in all patterns.

Magnetisation measurements carried out using a SQUID magnetometer within the temperature range from 2 K to room temperature and in applied fields of up to 5 T on polycrystalline samples of Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x, and Ni₂MnGa_{1-x}In_x indicated a ferromagnetically ordered state. When Ni₂MnGa was cooled from 300 K to 100 K then heated from 100 k to 300 K, with applied field of 500 gauss, the magnetisation measurements showed a change in magnetic structure upon cooling and heating. This was also the case for Ni₂MnGa single crystal. The magnetisation measurements have a hysteresis associated with them.

The possibility of a change of the structural phase transition of the Heusler alloy Ni₂MnGa by the substitution of Ga with other elements e.g. Sn or In was initially investigated by using the Differential Scanning Calorimeter (DSC).

When a phase transition occurs, the change in heat content and the thermal properties of the sample is indicated by a peak in its differential thermal analysis output. The specific heat at constant pressure, C_P, of a sample can be determined as a function of temperature. The heat flow to the sample. measured at constant rate, is directly proportional to the specific heat of the substance. The specific heat of Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x, and Ni₂MnGa_{1-x}In_x alloys in the range 100 K to 300 K has been measured, and the measurements indicate a phase transition during cooling and heating at 209.4 K and 224.1 K for Ni₂MnGa respectively. By substituting the Ga with 0.25% of tin, the scan showed a phase transition at 175 K upon cooling and 199.6 K upon heating, yielding a shift of ~ 34 K for cooling and ~ 25 K for heating. For 5, 2.5, 1, 0.5, 0.26, 0.167, and 0.125% of tin in Ni₂MnGa_{1-x}Sn_x, the scan did not reveal any significant changes in the temperature range 298 - 108 K, either for cooling or heating. It is possible that the transition is outside the range of the instrument. When the In was used, at 5, 2, 1, 0.5, 0.25, 0.125, 0.067%, as a substitute for Ga, once again the scan did not reflect any changes; where as for 0.0833% of In the measurement showed a weak phase transition upon cooling and heating at 196.8 K and 210.5 K respectively. A shift of ~ 13 K and ~ 14 were observed Ni₂MnGa and Ni₂Mn_{0.99917}In_{0.00083} samples.

For a more detailed understanding of the phase transition, and to see whether the electron concentration affected the phase transition in Ni₂MnGa, it was decided to substitute the Ga for In. This does not change the electron concentration but the size of atom. This enabled the influence of the size effect in affecting the phase transition. The replacement of Ga by tin increases the electron concentration by 1 electron. To study these effects in detail, resistivity measurements were carried out to investigate the structural phase transition using the contactless resistivity measurements technique.

CHAPTER 8: Conclusions and Recommendations for Further Work

The investigations were confined to the Heusler alloy series Ni₂MnGa, Ni₂MnGa_{1-x}Sn_x, and Ni₂MnGa_{1-x}In_x. The results have identified a structural phase transition at 150.30 K on cooling and at 199.75 K upon heating for Ni₂MnGa. Substitution of Ga by a 5, 2.5, and 0.25% of tin showed a structural phase transition at 82K, 110.79 K, 167.18 K respectively upon cooling, while during heating the transitions were identified at 122 K, 141.79 K, and 203.12 K respectively. When the Ga was substituted by 5 and 1% of In, a phase transitions were observed at 118.54 K and 144.01 K on cooling, 164.39 K and 173.9 K on heating respectively.

It is well established that the type and the strength of the magnetic order of the Pd₂MnZ system depends upon the electron to atom ratio; e.g. the compound containing Sn is ferromagnetic whilst the In compound is antiferromagnetic. It is probable that this is also instrumental in driving the structural phase transition.

Resistivity, magnetisation and specific heat measurements have all identified a structural phase transition, although the temperature at which it occurs differs, depending on the property being measured. Looking at the transition temperature as a function of the concentration of tin and the indium indicated that 9.5% of Sn was needed to suppress the transition, upon cooling, and about 12% upon heating, while for indium atoms 23.5% was needed for the transition to disappear during cooling and 31% during heating. In conclusion, it requires more indium than tin to suppress the transition. Hence, it seems that the electron concentration is more important than the size of the atom.

Resistivity measurements and magnetisation measurements have a hysteresis associated with them which would be consistent with a first order phase transition. A study of the way in which the transition takes place has been undertaken using neutron diffraction and Ni₂MnGa single crystal. The investigation was carried out by using D9 diffractometer. The result of cooling from T = 235 K to T = 200 K showed a complicated diffraction pattern. At T = 235 K there is just a single peak associated with the (220) reflection in the

CHAPTER 8: Conclusions and Recommendations for Further Work

cubic phase where as at T = 200 K there are two peaks which can be associated with (202) or (022) reflections from the tetragonal phase. At T =206 K at least seven distinct peaks can be discerned. Thus the various peaks were associated with individual domains within the crystal and the lattice parameters and the orientation of each domain at each temperature on cooling and heating were determined. On heating from T = 200 K to T = 235K, the patterns obtained during slow heating were different and simpler. During heating there is hysteresis and the progression is simpler.

A model is being developed to try to relate the stepwise nature of the transformation, the lattice parameters and the orientations of the different domains to shear processes of the type described by other workers. It is supposed that the particular shears which occur are those favoured by local strains in the crystal. This may explain why only two of the many possible tetragonal domain orientations are present in this crystal at and probably below 200 K.

A polarised neutron diffraction study was undertaken to determine the magnetisation distribution in the cubic and tetragonal phases. Polarised neutron flipping ratio measurements were carried out using the polarised neutron diffractometer D3. It was found that there was a significant redistribution of magnetic electrons in the transformation. It was also found that the redistribution of the magnetisation density was consistent with the band Jahn Teller mechanism. It concluded that the microscopic mechanism giving rise to the structural phase transition is associated with the redistribution of electrons, and is not a soft mode mechanism as proposed by other workers. In the soft mode mechanism, as pointed out by other workers, elastic constants are observed to be strongly temperature-dependent. This has been attributed to the soft mode behaviour, but it cannot be the case since elastic constants do not change as $\zeta \rightarrow 0$, where the soft mode occurs at finite q = 0.33 and therefore the elastic constants do not see the softening of the lattice.

8.2 Recommendations for Further Work

- It is proposed to repeat the essential parts of the experiment with new crystals of a different origin which have been carefully annealed and then in some case subjected to controlled deformation.
 Experiments are being undertaken where the crystal is squashed along its axis, perpendicular to its axis, to see if this affects the domain population. We also hope to discover to what extent the orientation and the number of intermediate tetragonal domains depends on such treatment.
- Soft mode behaviour needs to be investigated in more detail to try to understand why lattice constants are affected whereas in fact the phonons are not changing velocity. This appears to be a common feature in many Martensitic phase transitions and therefore needs to be resolved.
- Further measurements in the vicinity of the wave vector characterising the phonon softening are required, using a monochromator of better resolution, in order to quantify this behaviour. It is also necessary to repeat the measurement as a function of temperature in order to observe how the behaviour changes in the transition to low temperature tetragonal phase. Ni₂MnGa is one of the few ferromagnets which undergoes a Martensitic phase transition, and from the polarised neutron measurements, we have been able to identify it to be an excellent system for studying the wave vector dependence of the magnetic-lattice coupling mechanism and its temperature variation.
- The contactless resistivity measurement technique proved to be good for measuring the electrical resistivity as a function of temperature. A study of the transition temperature as a function of tin and indium concentration in Ni₂MnGa was limited by the fact that the contactless resistivity apparatus was only capable of measuring data down to a temperature of ~ 78 K. It has already been shown that the suppression of transition with high percentage of Sn and In

was below this value. Further study of this could be achieved with suitable apparatus that can measure resistivity down below 4.2 K.

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