PREPARATION AND CHARACTERISATION OF THERMOELECTRIC MATERIALS

M.Sc. Thesis

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PREPARATION AND CHARACTERISATION OF THERMOELECTRIC MATERIALS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

by **PIYUSH KUMAR GAUTAM**



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JULY 2016



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **PREPARATION AND CHARACTERISATION OF THERMOELECTRIC MATERIALS** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF PHYSICS**, **Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2015 to July 2016 under the supervision of Dr. Preeti A. Bhobhe, Associate professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date PIYUSH KUMAR GAUTAM

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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Dedicated

to

Mrs. M. David

(Teacher)

ABSTRACT

The polycrystalline samples of $Mn_{50-x}CoGa_{25+x}$ and $Ga_{50-x}MnCo_{25+x}$ have been prepared using Tri-Arc melting technique. The phase purity of the prepared samples is confirmed by powder x-ray diffraction measurements followed by Rietveld analysis. Transport properties of the samples have been studied at low temperature using four-probe method and magnetic measurements were done using a SQUID magnetometer. Metallic behavior and magnetic phase transition is observed in all the samples. The magnetic phase transition is shifted from 710 K to 163 K with varying concentration x. Our result will specify how the band structure at Fermi level is related to thermoelectric properties of the samples which may help in designing Mn, Co based thermoelectric material and spintronic devices.

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Over the past few decades, there has been increased interest in the field of thermoelectrics (TE), due to the need for more efficient materials for electronic refrigeration and power generation [1, 1.2]. Some of the research efforts focus on minimizing the lattice thermal conductivity, while others try to find materials that exhibit large power factors. Due to the increased demand for alternative energy technologies to reduce our dependence on fossil fuels leads to important research in the field of high temperature energy harvesting via the direct recovery of waste heat and its conversion into useful electrical energy. Thus, the development of higher-performance TE materials is becoming ever more important.

Automotive industries are currently investigating means to develop electrical power from waste engine heat from the radiator and exhaust systems for use in next-generation vehicles. In addition, TE refrigeration applications include seat coolers for comfort and electronic component cooling. The deep space applications of NASA's Voyager and Cassini missions using radioisotope thermoelectric generators (RTGs) are well established [1.3]. A key factor in developing these technologies is the development of higherperformance TE materials, either completely new materials or through optimization and materials engineering of existing materials.

Thermoelectric refrigeration is an environmentally "green" method of small-scale, localized cooling in computers, infrared detectors, electronics, and optoelectronics as well as many other applications. However, most of the electronics and optoelectronics technologies typically require only small-scale or localized spot cooling of small components that do not impose a large heat load. If significant economical cooling can be achieved, the resulting "cold computing" could produce speed gains of 30–200% in some computer processors based on complementary metal oxide semiconductor (CMOS) technology. Cooling of the processors is perceived by many to be the fundamental limit to electronic system performance [1.4]. Thus, the potential payoff for the development of low-temperature TE refrigeration devices is great, and the requirement for compounds with properties optimized over wide temperature ranges has led to a much expanded interest in new TE materials. Recent utilization of Peltier coolers for the refrigeration of biological specimens and samples is an emerging TE application.

Currently the development and potential of bulk materials for TE applications is an active area of research. High-temperature bulk materials such as skutterudites, clathrates, **Heusler alloys**, and complex chalcogenides are being investigated. These materials possess complex crystal structures and exhibit properties that are favorable for potential thermoelectric materials. For example, skutterudites and clathrates are cage-like materials that have voids in which "rattler" atoms are inserted to significantly lower the thermal conductivity due to the rattling atoms ability to scatter phonons.

A discussion of thermoelectric effects and devices should start with one of the most fundamental TE phenomena, the Seebeck effect, or thermopower [1.6–1.8]. In the early 1800s, Seebeck observed that when two dissimilar materials are joined together and the junctions are held at different temperatures (*T* and *T*+ ΔT), a voltage difference (ΔV) develops that is proportional to the temperature difference (ΔT) [1.6]. The ratio of the voltage developed to the temperature gradient ($\Delta V/\Delta T$) is called the Seebeck coefficient α , an intrinsic property of the materials. The Seebeck coefficient is very low for metals (only a few $\mu V/K$) and much larger for semiconductors (typically a few hundred $\mu V/K$) [9]. A related effect the Peltier effect was discovered a few years later by Peltier, [10] who observed that when an electrical current is passed through the junction of two dissimilar materials, heat is either absorbed or rejected at the junction, depending on the direction of the current. This effect is due largely to the difference in Fermi energies of the two materials. These two effects are related to each other, as shown in the definition of the Peltier coefficient, $\Pi = \alpha T$. The rate at which the Peltier heat is liberated or rejected at the junction (Q_p) is given by Q_p $=\alpha IT$, where *I* is the current through the junction and *T* is the temperature in kelvin.

The potential of a material for TE applications is determined in large part by a measure of the material's figure of merit, *ZT*:

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} = \frac{\alpha^2 T}{\rho \kappa}$$
(1)

where α is the Seebeck coefficient, σ is the electrical conductivity, ρ is the electrical resistivity, and κ is the total thermal conductivity ($\kappa = \kappa_L$ + κ_E , the lattice and electronic contributions, respectively). The power factor, $\alpha^2 \sigma T(\text{or } \alpha^2 T/\rho)$ is typically optimized in narrow-gap semiconducting materials, through doping, to give the largest *ZT* [1.9]. High-mobility carriers are most desirable, in order to have the highest electrical conductivity for a given carrier concentration.



Fig 1.1 Figure of merit ZT shown as a function of temperature for several bulk TE materials [1.2].

From the application point of view the TE materials should meet certain requirement. TE materials should be non-toxic, cheap and earth abundant, mechanically and thermally stable. Also there should be high possibility of processable and reproducible high volume manufacturing. On this background Heusler compounds on account of their relatively low cost components, exceptional mechanical and thermal stability stands out to be good TE material [1.33]. On the other hand, they have been reported to have high electrical conductivity with moderate Seebeck coefficient which results into high power factor [1.34, 1.35]. Furthermore there is possibility to substitute small amount of elements to the parent compound without changing the original structure, allowing to tune the electronic properties leading to the change in electrical conductivity. These properties support the claim for Heusler alloys of being a potential candidate for a good TE material. Heusler alloys are discussed in detail in the next the section.

1.2 HEUSLER ALLOYS:

The family of Heusler compounds, named after Friedrich Von Heusler [1.11], incorporates a huge number of magnetic members exhibiting diverse magnetic phenomena like itinerant and localized magnetism, antiferromagnetism, helimagnetism, Pauli paramagnetism or heavy-fermionic behavior [1.12–1.19]. The first Heusler alloys studied were crystallizing in the $L2_1$ structure which consists of 4 fcc sublattices (see Fig. 2).Afterwards, it was discovered that it is possible to leave one of the four sublattices unoccupied ($C1_b$ structure). The latter compounds are often called half- or semi-Heusler compounds or simply Heuslers, while the $L2_1$ compounds are known as full-Heusler compounds.



Fig 1.2 Schematic representation of the various structures of the semiand full-Heusler compounds. In all cases the lattice is consisted of 4 interpenetrating f.c.c. lattices [1.32].

Heusler compounds form a remarkable class of materials with more than 1000 members and a wide range of extraordinary properties including half-metals, high temperature ferri- and ferromagnets, multiferroics, shape-memory alloys, and tunable topological insulators with a high potential for spintronics, energy technologies and magnetocaloric applications [1.32]. Exceptional tunability of Heusler materials allow to design almost any functionality. Whereas the Co₂-based Heusler compounds show high spin-polarization in tunnel junction devices and spin-resolved photoemission, the Mn-rich Heusler compounds attract much interest in the context of spin transfer torque, spin-Hall effect and rare earth free hard magnets. Many of the Mn₂-Heusler compounds crystallize in the inverse structure and are characterized by antiparallel coupling of magnetic moments on Mn atoms; the ferrimagnetic order and the lack of inversion symmetry leads to the emergence of new properties that are absent in ferromagnetic centrosymmetric Heusler structures, such as noncollinear magnetism, topological Hall effect. The first Heusler compounds, namely Cu₂MnSb, Cu₂MnAl and Cu₂MnSn, drew attention due to their ferromagnetism, though being formed by nonmagnetic elements [1.20, 1.21]. These first Heusler compounds, all contained Mn, which plays a unique role in this class of materials. The emergence of the unexpected ferromagnetism, which does not evolve straightforwardly from any of these elements, is an important distinction from other magnetic alloys.

1.2.1 Types of Structural Order in Heusler Compounds

The ordered X_2YZ Heusler compounds crystallize in the $L2_1$ structure (designation, see Fig. 3) with spacegroup Fm3m. The inorganic structure database (ICSD) notation is Cu₂MnAl type structure. The X element, typically the most electronegative transition metal, occupies the Wyckoff position 8c (1/4,1/4.1/4), Y, the less electronegative transition metal, is on 4b (1/2, 1/2, 1/2). In some cases, the Y element may also be a rare earth element or an alkaline earth metal. The Z atom, a main group element, is on 4a (0,0,0). There are two different types of nomenclature, either based on the electronegativity of the constituents, in this case, the most electropositive element is quoted first or, as in most cases, the X element is named first. The Heusler structure may be visualized as a superstructure of the CsCl lattice, in which the lattice parameter of the CsCl lattice is doubled in all three dimensions. This leads to a cell consisting of eight cubes with one atom in each center. The 16 atoms in this supercell may be divided in four groups consisting of four atoms. The atoms in the center of each cube are the X atoms, while the Y and Z atoms occupy the corners of the eight cubes. Each atom is face centered cubic ordered, leading to four interpenetrating face centered cubic lattices. In case of only half filled centers of the eight cubes, the $C1_b$ -Heusler structure with general formula XYZ is obtained ($C1_b$ designation, space group F43m). This structure is sometimes referred to as half-Heusler structure. Various variants of the $L2_1$ structure can be formulated, if the X, Y, and/or Z atoms are intermixed on the respective crystallographic positions, leading to different (local) symmetries and structure types

[22]. In the following, we will describe the most common types of structures:



Fig 1.3 Frequently occurring structure types for X₂YZ Heusler compounds [1.32].

B2-type structure

If the Y and Z atoms are randomly intermixed on their crystallographic positions, the *B*2-type structure is obtained in which the Y and Z sites become equivalent. This structure may also be described based on a CsCl lattice, and as a result of this intermixing, a CsCl lattice with X on the center of the cube randomly surrounded by Y and Z atoms is obtained (Fig. 3). The symmetry is reduced and the resulting space group is (*Pm3m*), ICDS notation is CsCl-type structure. All X atoms are on the 1*b* Wyckoff position and Z and Y atoms are randomly distributed on the 1*a* position.

A2-type structure

Complete disorder, viz., complete random intermixing on the Wyckoff 2a position, in the X₂YZ Heusler compounds between all sites results in the A2 type structure with reduced symmetry *Im*3*m*. The X, Y and Z sites become equivalent leading to a body-centered cubic lattice, also known as the tungsten (W) structure-type according to ICSD notation.

X-type structure

The X-type structure is also sometimes referred to as inverse Heusler structure (space group F43m, ICSD notation is CuHg₂Ti structure). This type of structure is formed if the atomic number of the Y atom is higher than the number of the X atom. Half of X and all Z atoms form rock-salt lattice with the remaining X and Y atoms occupying the tetrahedral interstices, thereby forming a rock-salt lattice themselves. The difference to the $L2_1$ structure is highlighted by referring to the X structure as (X,Y)XZ compound.

Y-type structure in quaternary Heusler compounds

The Y-type structure is formed if each of the four interpenetrating fcc lattices of the former $L2_1$ type structure is occupied by a different atom. This type of structure is known as LiMgPdSn with space group F43m. Y-type quaternary compounds are formed e.g., in CoFeMnZ (Z = Al, Ga, Si, Ge) [1.23, 1.24].

1.3 FUNDAMENTALS OF MAGNETISM

The magnetic properties of a material arise from existence of a magnetic moment (μ) in the material even in the absence of an applied magnetic field and from induction of magnetic moment in response to an applied magnetic field. Classically, a magnetic moment is equivalent to a current loop [1.25].Quantum mechanically, the magnetic properties of a material owe their origin ultimately to the magnetic moment of the electrons and nucleons in the atoms of the material. The magnetic moment of the nucleons is three orders of magnitude smaller than that of the electrons [1.25] and is negligible for the kind of work described in the present thesis. The electronic magnetic moment has two sources. First is the magnetic moment associated with the intrinsic spin angular momentum (sometimes simply referred as spin) of the electron and designated as 'spin magnetic moment', and second is that arising from the orbital angular momentum of the electron around the nucleus of the atom and denoted as 'orbital magnetic momentum'. The spin and orbital components of magnetic moment of an electron are related to the respective angular momentum as $\mu = g J$. Here μ and J represent spin magnetic moment and spin angular momentum in case of spin of the electron. In case of orbital motion of the electron, μ represents orbital magnetic moment and *J* stands for orbital angular momentum. g is the gyromagnetic ratio and has different values for spin and orbital motion of the electron. The spin and orbital angular momenta combine to form a net angular momentum which gives rise to net magnetic moment to the atom. The magnetization (M) of the material is the net magnetic moment per unit volume. Sometimes, in the solid state, the orbital angular momentum does not contribute to magnetism because it is quenched under the environment of the neighboring atoms (designated as crystal field effect). Further, the completely filled electronic shells in the atom give rise to a diamagnetic response.

1.3.1 EXCHANGE INTERACTION

Quite often the magnetic moments (or spins) are able to interact with the neighbors and assume a specific orientation with respect to the neighboring moments. The driving force for aligning the different spins in a particular fashion arises from exchange interaction between the spins. The exchange interaction is of a quantum mechanical origin. It is a direct consequence of the Pauli Exclusion Principle and the Coulomb interaction for a system of electrons [1.25-1.27]. In the case of isotropic interaction, the interaction energy (exchange energy) between two spins s_i and s_j can be written as

$E_{ij} = -2 J_{ex} s_i s_j \cos\theta \tag{2}$

Where J_{ex} is the exchange parameter and f is the angle between the two spins. For a positive J_{ex} the parallel configuration of spins has a lower energy, while for a negative J_{ex} the anti-parallel configuration is lower in energy.

Ruderman-Kittel-Kasuya-Yosida (**RKKY**) interaction: In some cases the exchange interaction is mediated by conduction electrons. Localized magnetic moment on one atom spin-polarizes the conduction electrons. This spin polarization which has spatial oscillatory character and diminishes with distance couples magnetic atoms at a distance. This is known as the RKKY interaction. The resultant configuration of the two spins (of the magnetic ions) can be ferromagnetic or anti-

ferromagnetic depending on the separation between them. Heusler Alloys are mostly governed by this type of interaction.

1.3.2 TYPES OF MAGNETIC MATERIALS

Different relative orientation of the neighboring spins leads to various magnetic orders. Though there is a whole list of types of magnetic materials [1.28], only five basic types of magnetic materials are discussed below briefly.

(i) **Diamagnetic**: In some materials application of magnetic field induces a very small magnetic moment in the direction which is opposite to the applied magnetic field. This phenomenon is known as diamagnetism. This phenomenon arises from the completely filled atomic orbital (electronic magnetic moments sum to zero). Diamagnetism is present in all materials but is generally overshadowed by other magnetic order.

(ii) **Paramagnetic**: In paramagnetic materials there is a magnetic moment at atomic scale with no ordering at finite temperature leading to net zero magnetization in the absence of magnetic field. These magnetic moments have a tendency to align along the direction of the applied magnetic field leading to a finite magnetization in applied magnetic field. A paramagnetic system with localized magnetic moments obeys Curie's law which states that the magnetic susceptibility (χ) varies inversely as temperature. If a small applied magnetic field *H* gives rise to magnetization *M*. Then

$$\chi = \frac{M}{H} = \frac{C_{curie}}{T} \tag{3}$$

The proportionality constant C_{Curie} is material specific. From C_{Curie} the value of magnetic moment per moment carrier can be extracted. Inverse χ vs. temperature plot intercepts the temperature axis at zero (see Fig. 4). Conduction electrons in metals exhibit Pauli paramagnetism which shows a temperature independent magnetic susceptibility. (iii) Ferromagnetic: A ferromagnetic material has a spontaneous magnetization even in the absence of an applied magnetic field and there is a long range order of the magnetic moments at temperatures lower than $T_{\rm C}$ known as the Curie temperature of the ferromagnetic system. As already mentioned, the ferromagnetic ordering arises from the exchange interaction between the magnetic moments with a positive value of exchange constant. Temperature dependence of the susceptibility at temperatures above $T_{\rm C}$ follows the Curie-Weiss law

$$\chi = \frac{M}{H} = \frac{C_{curie}}{T - \theta_p} \tag{4}$$



Fig 1.4 (a) Magnetic susceptibility (χ) vs. temperature (*T*) plot at $T > \theta_p$ for paramagnet ($\theta_p = 0$), ferromagnet ($\theta_p > 0$) and antiferromagnet ($\theta_p < 0$) (from Ref. 1.6). Here θ_p is the paramagnetic Curie temperature. (b) $1/\chi$ (*T*) plot for the three cases. In paramagnet, ferromagnet and antiferromagnet, intercept on the temperature axis is at zero, positive and negative value respectively.

Where θ_p is the paramagnetic Curie temperature and its value depends on the strength of the exchange interaction and number of neighbors. Inverse χ vs. temperature plot intercepts the temperature axis at θ_p (see Fig. 4).

(iv) Antiferromagnetic: When the exchange parameter is negative, neighboring magnetic moments are aligned anti-parallel and the resultant order is known as the antiferromagnetic order. Very often in an antiferromagnetic material there are two sub-lattices with equal magnetic moments pointing in opposite directions. Each of the sub-

lattices has a spontaneous magnetization even in the absence of an applied magnetic field just like a ferromagnet. The two sub-lattices order antiferromagnetically at temperature lower than T_N known as the Neel temperature. At $T>T_N$ the two sub-lattices show paramagnetic behavior and the temperature dependence of susceptibility at $T>T_N$ follows

$$\chi = \frac{M}{H} = \frac{C_{curie}}{T + \theta_p} \tag{5}$$

Comparing with the Curie-Weiss law in a ferromagnet (see eqn. 4), this gives a negative paramagnetic Curie temperature $\theta_p = -\Theta$ in the present case. Inverse χ vs. temperature plot intercepts the temperature axis at negative value (see Fig. 4). This gives a method to differentiate between paramagnetic, ferromagnetic and antiferromagnetic materials as shown in Fig.4 [1.25].

(v) Ferrimagnetic: In some cases two the sub-lattices with antiferromagnetic order, do not have equal magnetic moments. Then contrary to the case of an antiferromagnet, the net magnetization is not zero. Such a magnetic order is known as the ferrimagnetic order. The net magnetic moment can have very different temperature dependences depending on the temperature dependences of the magnetic moments of the two sub-lattices. Such systems do not follow the

Curie-Weiss law [1.25].

1.4 Phase transitions

A phase of a material is defined as a region of spatially uniform macroscopic properties like density, atomic arrangements, crystal structure, chemical composition, magnetic order etc. A material can exist in different phases at different values of the control variable (temperature/pressure/magnetic field etc.). The transition from one phase to the other is termed as a phase transition.

1.4.1 Classification of phase transitions

When a material undergoes a phase transition from a high temperature phase to a low temperature phase, the free energies of both the phases are equal at a temperature $T_{\rm C}$ (known as the thermodynamical phase transition temperature), but certain order of the derivative of the free energy with respect to a control variable may differ. The order of the phase transition is defined by the lowest order of the derivative of free energy which is discontinuous across the phase transition [1.29-1.31]. If G_1 and G_2 are the free energies of the phases on the two sides of a thermodynamical phase transition temperature, then a phase transition will be of nth order if

$$\frac{\partial^{n} G_{1}}{\partial T^{n}} \neq \frac{\partial^{n} G_{2}}{\partial T^{n}} \qquad \text{and} \quad \frac{\partial^{m} G_{1}}{\partial T^{m}} \neq \frac{\partial^{m} G_{2}}{\partial T^{m}} \quad \text{for } 0 \leq m < n$$

m and n both being integers.

Some of the derivatives of free energy are given below.

Entropy
$$S = -\left(\frac{dG}{dT}\right)_P$$

Volume $V = -\left(\frac{dG}{dT}\right)_T$
Magnetisation $M = \left(\frac{dG}{dH}\right)_{T,P}$
Heat Capacity $C = T\left(\frac{dS}{dT}\right) = -T\left(\frac{d^2G}{dT^2}\right)$
Susceptibility $\chi = \left(\frac{dM}{dH}\right) = -T\left(\frac{d^2G}{dH^2}\right)$
Isothermal compressibility $K_T = -\frac{1}{V_0}\left(\frac{dV}{dP}\right)_T = -\frac{1}{V_0}\left(\frac{d^2G}{dP^2}\right)_T$

The discontinuous change in the first derivative of free energy i.e. volume, entropy, magnetization etc., across the phase transition qualifies the phase transition as first-order (Fig. 5(c)). On the other hand a continuous first-order derivative and a discontinuous second-order derivative (e.g. heat capacity, susceptibility and compressibility) qualify the phase transition as second-order (Fig. 5(d)). In a first-order phase transition, a discontinuity of entropy leads to latent heat (L_Q) of the phase transition amounting to $L_Q = T_C \Delta S$ where $\Delta S = [S_2 - S_1]_{Tc}$ is the difference in entropy between the two phases at T_C . All the higher order phase transitions do not have a latent heat. However, experimentally it has been found that in most of the phase transitions

which do not have a latent heat, the heat capacity either diverges or exhibits a cusp.



Fig 1.5 Free energy as a function of temperature (*T*) across (a) a firstorder phase transition and (b) a higher order phase transition. Here $T_{\rm C}$ is the thermodynamical phase transition temperature. Temperature dependence of entropy (*S*) is also shown for (c) a first-order phase transition and (d) a higher order phase transition [31].

Chapter 2

EXPERIMENTAL TECHNIQUES

Three samples of combination of Mn, Co and Ga in stoichiometric ratio of 2:1:1 were being prepared by arc melting technique. The samples were then sealed in vacuum quartz tube and were put into furnace for annealing. The samples were cut into three parts for x-ray diffraction, resistivity and thermo-power measurement respectively. The experimental techniques used for the preparation and characterization of the samples are discussed below.

2.1 ARC MELTING

In an arc melting furnace, an electrical arc is used to melt the constituent elements for making an alloy.



Fig 2.1 Tri arc furnace 5TA model [2.1]

The arc melting furnace consists of mainly two parts: (i) a hearth with cups of one electrical polarity and (ii) electrodes with opposite polarity. Elements to be melted are placed in a cup of the hearth and the electrodes are used to strike the arc for melting the material. Temperatures in excess of 2000°C can be attained in such a furnace. We have used an assemble form of the Tri arc furnace of similar form shown in the figure [2.1]. The material to be melted is placed in the cup of the hearth. A small piece of titanium is also placed in a small separate cup of the hearth. The hearth is inserted into the tapered hole in the bottom of the furnace and clamped into position. The furnace is then evacuated by a mechanical pump, followed by backfilling high purity inert argon gas. A suitable current is then set in the power supply. First, the piece of titanium is melted by striking arc to remove any possible oxygen impurity from the argon gas. Then the arc is struck on the material to be melted under the continuous flow of argon gas. The stingers are moved around and over the material in order to obtain a uniform and homogeneous melt. The specimen is turned over and remelted several times to ensure the homogeneity of the sample. Then the arc is turned off by gradually decreasing the current from the power supply [2.1].

2.2 DIFFUSION PUMP

The samples obtained from arc-melting were sealed in quartz ampoule under high vacuum (10⁻⁵ mbar) to prevent any surface oxidization during annealing. The high vacuum is created using a Diffusion Pump (Fig2.2) based vacuum system consisting of two parts (i) Mechanical forepump (Rotary pump): to create initial pressure of order 10⁻⁵ mbar, because diffusion pump cannot discharge directly into atmosphere. (ii) Diffusion

pump: to create high vacuum and discharge to forepump.



Fig 2.2 Diffusion Pump [2.12]

ANNEALING AND ICE QUENCHING

In order to relieve the stresses and obtain better homogenization the samples sealed in quartz ampoule were kept in furnace at 1073 K for seventy two hours. The samples were then quenched in ice-cold water. The quenching to room temperature was done to trap and maintain the highly ordered structural form stable only at high temperature, thus preventing any structural transformation that may take place while slow cooling.

2.3 POWDER X-RAY DIFFRACTION (XRD):

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice [2.2, 2.3]. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample.

The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law $(2d_{hkl} \sin\theta = n\lambda)$ [2.4].



This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. A set of lattice planes is denoted with Miller indices (*hkl*) where *h*, *k*, *l* are the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes [2.3]. Here d_{hkl} is the spacing between the (*hkl*) lattice planes, λ is the wavelength of x-ray and *n* is an integer. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 200 angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification. Typically, this is achieved by comparison of d-spacing with standard reference patterns. All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays

are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this. X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K α and K β . K α consists, in part, of K α 1 and K α 2. K α 1 has a slightly shorter wavelength and twice the intensity as K α 2. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. Kaland Ka2 are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for singlecrystal diffraction, with CuK α radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation [2.4], constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ . The instrument used to maintain the angle and rotate the sample is termed a goniometer.

2.4 ENERGY DISPERSIVE ABSORBTION X-RAY ANALYSIS (EDAX):

This technique is useful in determination of the elemental composition of material. The principle behind this technique is that atoms of each element have a unique electronic structure with characteristic binding energies of electrons in different electronic levels [2.5, 2.6]. When atoms within the material interact with the high energy electron beam, it can either excite the electrons from the inner levels of the atom or eject the electrons out from the atom, thus creating a vacancy in a particular electronic level. An electron in some higher energy level fills this vacancy and the difference in energy is released in the form of electromagnetic radiation.



Fig 2.4 Schematic of x-ray emission [2.6]

The schematic of this process is shown in figure (2.4) above. The energy of the emitted radiation is in x-ray range for the innermost K level. The energy of this x-ray is characteristic of the atom and can be used as fingerprint of the particular atom [2.5]. The number of x-ray photons and the energy of the same are measured with an energy dispersive analyzer. The information from the analyzer is used for quantitative analysis of elemental composition of the material.

2.5 ELECTRICAL RESISTIVITY MEASUREMENT

Resistivity measurement contains information about the scattering mechanism of the charge carriers in the material [2.7, 2.8]. Temperature dependence of resistivity can differentiate between a conductor and semiconductor/insulator. Further, it can help identify the characteristics of the scattering mechanisms involved, viz. impurity, phonon etc. Resistivity measurement can be used to deduce the "order" of a phase transition like 1st order martensitic transition which generally is accompanied with a large change in electron scattering and hence large change in resistivity or 2nd order magnetic transition that results in decrease in resistance due to setting up of magnetic order in the system.



Fig 2.5 Electrical resistivity measurement techniques: (a) Two-probe technique and (b) Four-probe technique

There are two widely known methods of resistivity measurement (a) Two-probe method [see Fig2.5 (a)] – when two probes are used to send current as well to measure voltage signal across the sample. The resistance measured in this method has contributions from the lead resistance and contact resistance along with the sample resistance. This puts serious limitations on the method in cases where either the sample resistance is comparable to the lead resistance (metallic samples) or contact resistance is appreciable. (b) Four –probe method [Fig2.5 (b)]:

The limitations of two probe method is overcome by connecting two extra leads on the sample for voltage signal measurement known as four probe technique. The voltage signal in this four-probe technique has contribution from the sample only, and there is no contribution from lead resistance or contact resistance.

2.6 DIFFERENTIAL SCANNING CALORIMETRY (DSC):

Differential scanning calorimetry (DSC) measures the energy absorbed (endotherm) or produced (exotherm) as a function of time or temperature. It is used to characterize melting, crystallization, resin curing, loss of solvents, and other processes involving an energy change. Differential scanning calorimetry may also be applied to processes involving a change in heat capacity, such as the glass transition. In DSC analysis, the sample is placed in an aluminum pan, and the sample pan and an empty reference pan are placed on small platforms with in the DSC chamber. Thermocouples are used as sensor below the pans.



Fig 2.6 (a) DSC Setup [2.13]

DSC measurements can be made in two ways: by measuring the electrical energy provided to heaters below the pans necessary to maintain the two pans at the same temperature (power compensation), or by measuring the heat flow (differential temperature) as a function of sample temperature (heat flux). The DSC ultimately outputs the differential heat flow (heat/time) between sample pan and the empty

reference pan. Heat capacity may be determined by taking the ratio of heat flow to heating rate. Thus, $C_p = (q/t)/(\Delta T/t) = q/\Delta T$

Where C_p is the material's heat capacity, q is the heat flow through the material over a given time, and ΔT is the change in temperature over that same time.



Fig2.6 (b) DSC Thermograph [2.13]

The glass transition temperature (T_g) is also an important characteristic of non-crystalline and semi-crystalline materials, but T_g is a particularly significant property of many common polymers. At a temperature below T_g , amorphous and semi-crystalline materials tend to be hard and brittle because the polymer chains (in case of amorphous sample) are locked in a tangled, coiled position. Generally the glass transition point depends on the processing of the material, as well as that material's natural characteristics such as structure, bonding, and molecular weight. Since it takes energy to break these bonds, the glass transition appears on a DSC curve as an endothermic process. In DSC, the T_g can be found by a permanent decrease in baseline heat flow, and T_g is usually taken as the inflection point in the curve.

The **crystallization temperature** (T_c) is another important transition that occurs in some polymeric materials. At the crystallization

temperature, the polymer loses its random chain arrangement, intermolecular bonds form, and the polymer molecules become more ordered. Formation of bonds during crystallization is an exothermic process, so an increase in heat flow (a peak on the DSC curve) accompanies the crystallization process. Generally, the T_c is found by finding the onset point of the crystallization curve. Note that many amorphous polymers never undergo crystallization.

Melting occurs when your material changes phase from a solid to a liquid. When a material starts to melt, its intermolecular bonds absorb energy and begin to loosen and break. Since melting involves absorption of energy, it is an endothermic process and appears on the DSC curve as a large, temporary decrease in heat flow. Once the material has completely melted, the heat flow returns to its original baseline value. The melting temperature is generally measured at the onset point of the melting curve.

Curing of a polymer occurs when individual chains form strong bonds to other chains, a process that is sometimes referred to as "crosslinking." Like crystallization, this process of chain ordering and bond formation is exothermic. The curing temperature is generally given as the onset of the curing peak on the DSC curve.

2.7 MAGNETISATION:

Magnetic moment per unit volume is called magnetisation. To measure the magnitude of magnetic moment we find out magnetisation. Experimentally it can be done in two ways.

- (1) Isothermally with change in magnetic field.
- (2) At constant magnetic field with change in temperature.

Furthermore there are techniques which involve direct and indirect measurement of magnetic moment. Indirect techniques for magnetisation measurement include Hall Effect, Faraday Effect, Nuclear Magnetic Resonance (NMR) and other techniques. Direct techniques for measurement of magnetisation involve two methods. (a) Force technique. (b) Flux technique. Force technique involves the measurement of force on the sample. Flux technique involves measurement of magnetic flux or change in magnetic flux linked with the sample [2.9]. Faraday balance, torque magnetometer are few examples of force technique. Vibrating Sample Magnetometer (VSM), Superconducting Quantum Interference Device (SQUID)

Magnetometer are examples of flux technique.

SQUID

The SQUID is basically a superconducting sensor which operates below the transition temperature (Tc) of the superconducting materials used for fabrication of the device. The basic phenomena governing the operation of SQUID devices are flux quantization in superconducting loops and the Josephson Effect [2.10, 2.11].



Fig 2.7 (a) Flux quantization. (b) Non-hysteretic *I–V* characteristic of a resistively shunted Josephson junction [2.10].

Flux quantization refers to the fact that the total flux linked with a superconducting loop is always constrained to be an integral multiple of a flux quantum (Φ_0).

$$\Phi_{tot} = \Phi_{ext} + LI = n\Phi_0$$

where Φ_{ext} is the externally applied magnetic flux, *L* the selfinductance of the superconducting loop, *I* the screening current induced in the superconducting loop because of the application of the external magnetic flux and *n* is an integer. The Josephson Effect refers to the ability of two weakly coupled superconductors to sustain at zero voltage a supercurrent associated with the transport of Cooper pairs, whose magnitude depends on the phase difference between the two superconductors.

$I = I_0 \sin \delta \phi$

Where I_0 is the maximum current the junction can sustain without developing any voltage and is known as the critical current of the Josephson junction, and $\delta\phi$ the phase difference between the two weakly coupled superconductors. When two superconductors are separated by a thin oxide barrier (tunnel junction), thus causing tunneling effect which leads to the Josephson Effect.

Chapter 3

RESULTS AND DISCUSSION

3.1 XRD RESULTS

Figure 3.1(a) shows the powder XRD patterns of the three samples Co₂MnGa, Mn₂CoGa and Ga₂MnCo at the room temperature, recorded using Cu K_{α} source. To make a comparison, we calculated the XRD profiles for these three compositions and the same are shown in Fig. 3.1(b).From the comparison of the measured and calculated patterns, it is obvious that owing to the high background in the measured data, the structure of the three alloys cannot be confirmed. Moreover, similar atomic numbers of Co and Mn makes it difficult for X-rays to distinguish between the two atoms and adds further to the complexity of the problem. Infact the (hkl) peaks appears to be of a body centered cubic (BCC) structure. The high background in the recorded XRD profile is due to the high absorption of x-rays by the elemental composition of the alloys. To overcome these issues and to determine the right crystal structure adopted by these three compositions, we recorded the XRD profile using a Molybdenum (Mo) source of X-rays [see figure 3.1(c)].



Fig 3.1(a) Measured XRD patterns of the samples



Fig 3.1(b) Calculated XRD patterns of the samples



Fig 3.1(c) Measured XRD patterns for Mo target

Figure 3.1(c) shows the XRD patterns of all three samples obtained using Mo source. The immediate observation is reduction in the background and appearance of sharp intense peaks with well-defined peak positions and *hkl* values. Generally, the distinction between a simple Heusler and inverse Heusler structure is made on the basis of presence or absence of (111) and (200) peaks. From the XRD profiles presented above, it is confirmed that Co₂MnGa and Ga₂MnCo forms simple Heusler while Mn₂CoGa forms inverse Heusler. Secondly, it can be seen from the XRD data that the peak for the same hkl value of all the three samples have different 20 values as shown in the inset diagram of figure 3.1 (b).The calculated lattice parameter through Rietveld analysis for Mn2CoGa, Ga2MnCo and Co2MnGa is 5.929 Å, 5.897 Å and 5.848 Å respectively. The decrease in lattice parameter also agrees with the decrease in ionic radii of order Mn>Ga>Co with values 0.645 Å>0.62 Å>0.61 Å.

3.2 RESISTIVITY RESULTS

Figure 3.2 shows the resistivity data of Co_2MnGa which has constant value as the temperature is increased from 2K to ~30K. This is expected as it is well known from basic free electron theory that it is

imperfection in lattice due to defects, impurities and dislocation that are responsible for such residual resistivity in all materials. This was first explained by Matthiessen and is known after him as Matthiessen's rule for residual resistivity. On further heating, the resistivity of the sample increases gradually with temperature showing the metallic nature of the sample. The resistivity data is fitted with a simple expression for metals, $\rho(T)=\rho_0+\rho_e T+\rho_p T^2$. Where ρ_0 = residual resistivity due to electron-electron scattering, ρ_p = resistivity due to electron-phonon scattering. The curve fits in a large range of temperature (75K to 390K) which confirms the metallic nature of the sample.



Figure 3.2 Resistivity vs. temperature plot for Co₂MnGa. The symbols represent measured data points and the line represents the fit.

Next, we plot the resistivity vs temperature variation of Mn_2CoGa in Figure (3.3). Here too, we observe a residual resistivity (upto ~40K) followed by simple metallic resistivity only beyond 150K. Above 250 K we observe distinct deviation from the $\rho(T) = \rho_0 + \rho_e T + \rho_p T^2$ behavior. Moreover, a change in slope of the resistivity curve is observed in the vicinity of ~320K. This change in slope could be due to magnetic or

structural phase transitions that are common in such materials and will be discussed in the following sections.



Fig 3.3 Resistivity vs. temperature plot for Mn₂CoGa

Figure (3.4) shows the resistivity data of Ga₂MnCo. As the temperature is increased from 2K, resistivity first decreases and then increase with a minimum around 25K. Normally, such resistivity minima can be associated with disorder in the disorder scattering of conduction electrons. In the present case, the disorder can originate from sitedisorder or site vacancies or could be purely magnetic in nature. Further the temperature range for fitting is further decreased and only for temperature range 75K to 150 K can be fitted with metallic type behavior. This also agrees with the decrease in carrier concentration of the samples in the order of their valence electrons; Co (9 e) > Mn (7 e)) > Ga (3 e). The graph shows a shift from linear increase in resistivity value above 180K, which starts to flatten above 250K. This Flattening of the resistivity is unusual but interesting, which is investigated further through DSC and Magnetisation measurement for the confirmation of any structural and/or magnetic transition occurring in this temperature range.



Fig (3.4) Resistivity vs. temperature plot for Ga₂MnCo

3.3 DIFFERENTIAL SCANNING CALORIMETRY (DSC) RESULTS

Mn₂CoGa and Ga₂MnCo showed some anomalous signatures in terms of slope change in the high temperature region of resistivity measurements, to ascertain the nature of these anomalies; Differential Scanning Calorimetry was conducted on these two samples. DSC curve obtained for Mn₂CoGa is shown in the figure (3.5). The data recorded while warming the sample, shows a downward curve in the temperature range 300K to 320K, confirming an endothermic reaction. In Heusler alloys, this kind of endothermic feature is associated with some structural site ordering. Thus, the change in slope seen in resistivity data can be understood to be of structural origin.



Fig (3.6) shows the DSC graph of Ga_2MnCo , recorded during warming of sample. An endothermic-exothermic peak seems to occur in succession with changing temperature as feature can be seen in the graph. Such feature represents simultaneous occurrence of a first and second order transition, indicating some site and magnetic spin order – disorder phase change occurring in the temperature range (240K to 280K). As the change in differential heat takes place over a wide temperature it also confirms the second order phase transition. Change in the slope of resistivity of Ga_2MnCo observed in the same temperature. Recording the magnetization as a function of temperature can help understand this feature better.



Fig (3.6) DSC curve of Ga₂MnCo

3.4 MAGNETISATION VS TEMPERATURE RESULTS

Magnetisation vs temperature was recorded in an applied field of 100 Oe for Co₂MnGa, in zero field cooled (ZFC) and field cooled warming (FCW) mode. The M-T data of the sample confirms its ferromagnetic nature [figure (3.7)]. The ordering temperature is also quite high, ~ 710 K. However, the large bifurcation between ZFC and FCW curves results from incomplete transformation of ferromagnetic to paramagnetic phase, due to temperature limitations of the measuring instrument. Records present in literature state the ferromagnetic ordering temperature of Mn₂CoGa to be greater than 750 K. As the maximum operating temperature of the magnetometer used by us is about 700 K, we did not record the data for Mn₂CoGa.



Fig (3.7) Magnetisation vs Temperature graph of Co₂MnGa

The figure [3.8 (a)] shows the magnetisation results for Ga₂MnCo, recorded with an applied field of 100 Oe. A sudden increase in magnetisation value during initial fall in temperature hints towards setting up of ferromagnetic order. On lowering the temperature further the magnetisation value starts decreasing suggesting rise of antiferromagnetic order in the sample. To see if the latter order vanishes with application of higher magnetic field, M-T data was recorded with an applied field of 500 Oe [see in figure 3.8 (b)]. This data also shows the similar trend, but with broadening of the width of

peak-like feature. To obtain a more understanding of the magnetic order the Magnetisation vs Field (M vs H) data is recorded at different temperatures.



Fig 3.8 (a) Magnetisation graph of Ga₂MnCo (100 Oe)



Fig (3.8 a) M v/s. T measured for Ga₂MnCo

Figure [3.9 (a)] shows M vs H plot for Ga₂MnCo recorded at 175_K, 80_K and 50_K, while the figure [3.9 (b)] shows M vs H plot at 5K. The linear relation between M and H at 175_K confirms its paramagnetic nature. The magnetization values at fields 80_K and 50_K shows its FM behavior but the magnetization does not saturates even for field as high as 7 T which confirm the competing FM-AFM

interaction at low temperature. The magnetization data at 5_K also confirms that the sample has competing interaction. The coercive width at this temperature is larger than at higher temperature, this explains the difference between ZFC and FCW at 5K.



Fig 3.9 (a) M vs H graph at 175 K, 80 K and 50 K



To calculate the paramagnetic transition temperature, $1/\chi$ vs T graph is plotted and fitted for the line given from Curie-Wiess Law $(\frac{1}{\chi} = \frac{1}{c}T - \frac{\theta}{c})$ for Ga₂MnCo as given in figure (3.10). The transition temperature (θ)

is determined by extending the line plotted for the paramagnetic region. Temperature θ is the point of intersection of line and the temperature axis. The value for curie constant C is determined by taking inverse of the slope of the line. From the value of C, the effective magnetic moment (μ_{eff}) of the sample is determined by the formula C= N_A μ_{eff} /3k_B (where N_A is Avogadro constant, k_B is Boltzmann constant). The calculated value of θ =163.24K and μ_{eff} =0.76 μ_{B} .



Fig 3.10 1/x vs T graph of Ga₂MnCo

Thermopower measurements of the samples are not taken due to shifting of experimental setups and related problems. Hence in the time being the anomalous behavior shown by Ga₂MnCo is investigated by doping of Mn with Cu and Cr. This is discussed in detail in the next chapter of Future Scope. Thus thermopower measurements and analysis will be the future plan for this thesis.

Chapter 4 FUTURE SCOPE

Magnetic interaction in Heusler Alloys is governed by RKKY type interaction. The magnetic interaction depends on the separation between the magnetic spins. Thus the unexpected behavior shown by Ga₂MnCo can be due to site-disorder between some Mn at Ga atoms, the exact position of which cannot be detected from simple powder XRD profile. To investigate this anomalous magnetic behavior Mn is doped by a non-magnetic element (Cu) and an element (Cr) with magnetic moment different from that of Mn.

Figure 3.11 (a) and figure 3.11 (b) shows the powder XRD results of $Ga_2Mn_{1-x}Cu_xCo$ for x= 0, 0.25, 0.50, 0.75 and $Ga_2Mn_{1-x}Cr_xCo$ for x= 0, 0.25, 0.75 respectively. All the samples crystallize into BCC lattice, confirmed by Rietveld analysis of the XRD data.



Fig 4.1 XRD plot of Ga₂Mn_{1-x}Cu_xCo



To check and study thoroughly the assertion made for the anomalous behavior of Ga_2MnCo , investigation of the samples through resistivity measurements, magnetisation measurements could not be taken due to time limit of this project. So taking all the measurement mentioned for the samples besides taking thermopower measurements for all the samples will be the future plan.

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