SYNTHESIS AND CHARACTERIZATION OF MULTIFUNCTIONAL MAGNETIC ALLOY SYSTEMS IN BULK AND THIN FILM FORM

by

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Dedicated to
My Father

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and Characterization of Multifunctional Magnetic Alloy Systems in Bulk and Thin Film Form**" being submitted by **Mr. Saurabh Kumar Srivastava** to the Department of Physics, Indian Institute of Technology Delhi, for the award of the degree of '**Doctor of Philosophy**' is a record of the original bonafide research work carried out by him. He has worked under my supervision and guidance and has fulfilled the requirement for the submission of this thesis, which in our opinion has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other University for the award of any degree/diploma.

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ABSTRACT

Multifunctional alloys are those "smart" or "intelligent" materials for which more than one physical parameters vary with an externally applied stimulus; giving rise to utility of these materials for more than one purposes. In recent years, research in the field of novel multifunctional alloys has attracted growing interest among researchers. Heusler alloys are one of the important multifunctional alloys that are also magnetically ordered and have properties such as magnetic shape memory effect (MSME), magnetic superelesticity, magnetocaloric effect (MCE) and magnetostriction.

The thesis is focused on studies made on novel properties of off-stoichiometric full-Heusler alloy systems which could find applications in Magnetic shape memory effect and magnetocaloric effect. Investigation on off-stoichiometric Ni-Mn based systems by several research groups including ours revealed that the properties exhibited by Heusler alloys are very sensitive to the method of preparations, compositions and microstructure of the alloy. In order to further elucidate this point, in this thesis, we attempt to study Ni-Mn-Al / Ni-Mn-Ga off-stoichiometric alloys in single crystal, ribbon, and polycrystalline bulk forms. Exploratory studies on thin films of Ni-Mn-Al using electrodeposition technique are also a part of this thesis. The aim of the thesis is to investigate and understand the magnetic shape memory behaviour of Ni-Mn-Ga and Ni-Mn-Al system. The possibility of large magnetocaloric effect in Ni-Mn-Ga system has also been investigated. The specific objectives of the thesis are –

(i) Investigations on $Ni_{49}Mn_{29}Ga_{22}$ single crystal-

This is one of the most studied compositions since the discovery of large magnetic field induced strain (MFIS) in Ni-Mn-Ga by R. C. O'Handley and his group at

MIT, USA. Previous studies of electrical resistivity vs temperature on this crystal by our group indicated that along with martensite / austenite transformation near 340 K, the crystal shows two more intermartensitic transformations centred at 285 and 250 K, i.e. in total three martensite phases are present in this crystal. The literature on ferromagnetic shape memory Ni–Mn–Ga alloy system suggests that there is a strong interrelation of magnetic and structural subsystems in these alloys leading to unusual magnetoelastic and thermoelastic properties observed in them. Magnetic field induced rearrangement of martensite variants controlled by intervariant twinboundary motion decides the amount of magnetic field induced strain MFIS in the Ni–Mn–Ga alloys. The intermartensitic and low temperature magnetic transitions were not studied enough in Ni–Mn–Ga system in literature and it was needed to be well understood in order to better understand and control the magnetic field induced strains. To understand these low temperature transitions, higher harmonics of *ac* susceptibility measurement were made by us. Measurements of higher harmonics of *ac* susceptibility are thus established as excellent tool to identify the transformation temperature very accurately. In this thesis, fundamental and third order *ac*-susceptibility have been used to identify the transitions originating from different magnetic substructures that remain undetected by usual *dc*-susceptibility measurements. An anomaly identified at ~ 150 K by susceptibility measurements has been further explored by differential scanning calorimetry, temperature dependent x-ray diffraction, and transmission electron microscopy measurements. The results demonstrate that the magnetic subsystem in Ni-Mn-Ga is unstable at low temperatures not only for metastable modulated crystal structure but also for very stable modulated structure.

(ii) Detailed studies of structural, transport and magnetic properties of $Ni_{52+x}Mn_{26-x}Al_{22}$ ($1 \leq x \leq 5$) melt spun ribbons –

It is known that Ga is very brittle and hence for further studies on MSME effects, Ga is replaced by Al in the studies reported in this thesis. The preparation of the samples is also changed to a more user-friendly, practical application oriented melt-quenched ribbon forms. Alloys of Ni-Mn-Al system are interesting not only as potential high temperature shape memory alloys, but also as alloys which exhibit different crystal structures of martensite. The mechanical properties of Ni-Mn-Al are also superior to the Ni-Mn-X alloys in terms of practical applicability. Earlier work on detailed investigation on polycrystalline Ni-Mn-Al buttons by our group revealed that the ease of processing parameters and transition occurring around room temperature are some features that warrant future research in Ni-Mn-Al alloys. In this thesis studies on Ni-Mn-Al is continued in ribbon and thin film forms due to a growing interest in these forms attributed to the ease of processing parameters involved and their practical applicability. Structural, transport and magnetic properties of $Ni_{52+x}Mn_{26-x}Al_{22}$ ($1 \leq x \leq 5$) melt spun ribbons have been studied in detail. Possibility of Ni-Mn-Al as high temperature shape memory alloy has been established in $x = 5$ sample.

(iii) Study of Magnetocaloric properties of $Ni_{2.29}Mn_{0.89}Ga_{0.82}$ alloy –

An attempt has been made to look at the other multifunctional property of Heusler alloy that is Magnetocaloric effect (MCE) in the above mentioned Ni-Mn-Ga composition. In recent years, ferromagnetic Ni-Mn based Heusler alloys have received much attention as new and cheaper magnetic substances that are able to exhibit large magnetocaloric efficiency. The composition studied in this thesis is based on the available phase diagram of Ni-Mn-Ga off-stoichiometric alloys by Khovaylo *et al.* The composition $Ni_{2.29}Mn_{0.89}Ga_{0.82}$ shows magnetic and structural transition around 330 K. Detailed calorimetric studies on $Ni_{2.29}Mn_{0.89}Ga_{0.82}$ composition is carried out in this thesis.

(iv) Investigation on Ni-Mn-Al thin films –

Electrodeposition of binary and ternary magnetic alloys has been established as a fast and economical method of deposition of thin films which offers selectivity of the deposition area on a particular film. Controlling the composition of ternary alloys in desired stoichiometric ratio in electrodeposited films has been a challenging task. In this thesis deposition of thin films of Ni-Mn-Al by electrodeposition method has been attempted. The thesis explores the possibility of both co-deposition and layer by layer deposition methods for depositing Ni-Mn-Al thin films. The effect of changing deposition parameters on the quality of the film is also studied.

The thesis has been divided into seven chapters; details of which are as follows:

I. Chapter 1 (Introduction): contains overview of the work done so far on magnetic shape memory alloys in bulk and thin film form and magnetocaloric effect in Heusler alloys. Since both MSME and MCE discussed in this thesis are related to martensitic transformation phenomenon, a detailed account of solid state phase transformations including martensite to austenite transformation, are discussed. Related phenomenon of twin boundary motion is also discussed in this chapter. The chapter also discusses the role of magnetic entropy and parameters involved in magnetic refrigeration.

II. Chapter 2 (Experimental details and characterization techniques): This chapter contains the details of alloy, ribbons and thin film processing methods; along with the experimental details on various measurements and characterization techniques used in the present study. The samples are characterized by following characterization techniques.

a. Structural Characterization: X-ray diffraction (XRD) and Transmission electron microscopy (TEM)

b. Electrical Properties: Resistivity versus temperature (ρ-T) measurements.

c. Magnetic properties: Magnetization versus temperature (M-T), Magnetization versus Field (M-H) and Magnetization versus time (M-t) measurements.

d. Magnetic Field Induced Strain (MFIS) measurements.

III. Chapter 3 (Investigations on Ni-Mn-Ga single crystal) : Magnetic anomaly observed at low temperature (~ 150 K) has been explored by *ac* susceptibility measurements, differential Scanning calorimetry (DSC), temperature dependent XRD and transmission electron microscopy (TEM) measurements. It has been shown that the anomaly is observed in a non-modulated tetragonal structure and has purely magnetic origin. The results demonstrate that the magnetic subsystem in Ni-Mn-Ga is unstable at low temperatures not only for metastable modulated crystal structure, but also for very stable nonmodulated tetragonal structure. Results of fundamental and third order *ac* susceptibility measurements demonstrate that higher harmonics of *ac*-susceptibility is an excellent tool to identify transition / anomalies originating from different magnetic substructures that remain undetected by usual *dc* susceptibility measurements.

IV. Chapter 4 (Investigations on $Ni_{52+x}Mn_{26-x}Al_{22}$ ($1 \leq x \leq 5$) polycrystalline rapidly quenched melt spun ribbons): Structural, transport and magnetic properties of $Ni_{52+x}Mn_{26-x}Al_{22}$ ($1 \leq x \leq 5$) melt spun ribbons have been discussed in detail in this chapter. With increasing x, systematic changes were found in structural, resistivity and magnetization behavior in these melt-spun ribbons. The martensitic transition temperature T_0 (= $(M_s + A_f)/2$) increases from 277 K for x = 1 to 446 K for x = 5. The thesis suggests possible composition for high temperature shape memory effect in x = 5 sample.

The x-ray diffraction pattern at room temperature shows cubic B2 structure for $1 \leq x \leq 3$ samples. For x = 4, 5 the structure is tetragonal at room temperature. Calorimetric studies suggest that samples $1 \leq x \leq 3$ are in high temperature austenite phase in the ambient condition of room temperature, whereas, x = 4, 5 samples are in low temperature martensite phase at room temperature. Temperature dependent x-ray diffraction (300 K$\leq T \leq$ 475 K) has been performed to elucidate the evolution of phase for the representative x = 5 sample. Above room temperature the tetragonal phase starts disappearing and the evolution of B2 austenite phase was clearly observed in this sample with increasing temperatures. The martensite to austenite transition for x = 5 sample was found to be at around 446 K. The room temperature crystal structure of x = 5 sample was also confirmed by transmission electron microscopy (TEM).

Resistivity versus temperature for all samples shows semiconducting behaviour below room temperature and a metallic behaviour above room temperature. The semiconducting to metallic transition occurs at around room temperature for all the samples. It is interesting to note that for x = 5 sample the sudden change in resistivity behavior, signifying the transition from semiconducting to metallic form, occurred in its martensitic state. This is contrary to the conventional belief that the resistivity of Ni-Mn-Al alloys in martesititc phase behaves as in a semiconductor, whereas in the austenite phase it is typically of metals. The change of resistivity behaviour in the martesite phase itself indicates the possibility of magnetic origin of this behaviour. Although the underlying mechanism of this behaviour is not completely clear at present, assuming that the Neel temperature of Ni-Mn-Al is ~ 300 K, the observed behaviour can be attributed to a spin-density wave formation.

V. **Chapter 5 (Investigations on Ni-Mn-Ga polycrystalline alloy):** Magnetocaloric properties of $Ni_{2.29}Mn_{0.89}Ga_{0.82}$ have been studied. It has been shown that an optimum shape of magnetic entropy change versus temperature $\Delta S_m(T)$ curve results in large refrigeration capacity (RC) of ~ 100 J/kg in an applied field of 5T, around 319 K.

VI. **Chapter 6 (Thin Films of Ni-Mn-Al):** Thin films of Ni-Mn-Al have been attempted using 3-electrode electrodeposition system by application of different routes of preparation.

1. Co deposition of Ni-Mn-Al from sulphate and chloride baths has been attempted by mixing the solutions in proper ratio, adjusting deposition potential. It has been shown that due to the large variation in standard deposition potential of Ni and Al, this method proves to be difficult for this particular ternary alloy composition.
2. Layers by layer deposition – Two approaches were taken

(i) Repetition of bimetallic layers - bi-metallic Ni-Mn and Ni-Al films are deposited one above the other. Repetition of Ni-Mn and Ni-Al layes was done 3 times to obtain the final films.

(ii) Repetition of Layer by layer deposition of elements -Deposition of Al followed by Ni and then Mn. Repetition of Al/Ni/Mn layers were done 3 times to obtain the final films.

Details of techniques involved and effect of varying deposition parameters are also discussed in this chapter.

V **Chapter 7 (Conclusions and future scope):** summarizes the complete research work of the thesis and highlights the important conclusions drawn from the present research work. Suggestions for further research in this area are also a part of this chapter.

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