STRUCTURAL AND MAGNETIC PROPERTIES OF HEUSLER ALLOYS

GURU DUTT GUPT

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
MARCH 2024

STRUCTURAL AND MAGNETIC PROPERTIES OF HEUSLER ALLOYS

by

GURU DUTT GUPT

Department of Physics

submitted

in fulfillment of the requirements of the degree of the Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI
MARCH 2024

Dedicated to

My parents and my family for their love, care, and affection

DECLARATION BY THE CANDIDATE

I, **Guru Dutt Gupt**, hereby declare that the thesis entitled ***"Structural and Magnetic Properties of Heusler Alloys"*** is my original work conducted under the supervision of Prof. Rajendra S. Dhaka and has been approved by the Student Research Committee (SRC) at the Department of Physics, Indian Institute of Technology Delhi, New Delhi, India. Furthermore, I confirm that this work has not been submitted and will not be submitted to any other institute or university for any degree or diploma. I assure compliance with the ethical code of conduct prescribed by the institute. I have duly acknowledged and credited all materials, theoretical analysis, data, figures, and text taken from other sources by appropriately citing them in the thesis. Further, I confirm that I have not used any artificial intelligence (AI) based software for writing any part of the thesis.

Signature _____

Name of the candidate: Guru Dutt Gupt
Entry Number: 2016PHZ2022
Department of Physics
Indian Institute of Technology Delhi
Hauz Khas, New Delhi – 110016, India.
Date:

CERTIFICATE OF THE SUPERVISOR

This is to certify that **Guru Dutt Gupt's** thesis, ***"Structural and Magnetic Properties of Heusler Alloys,"*** submitted to the Department of Physics, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Physics, is an original record of his research work. He worked under my supervision and guidance to complete the requirements for submitting this thesis, which I feel reached an acceptable standard. He fulfilled the requirements for submitting the thesis, which, to the best of my knowledge, was of sufficient quality. The thesis results have not been submitted, in part or entirely, to any other university or institute for the award of any degree or diploma.

Signature_____

Prof. Rajendra S. Dhaka
Associate Professor
Department of Physics
Indian Institute of Technology Delhi
Hauz Khas, New Delhi – 110016, India.
Date:

ACKNOWLEDGEMENT

Foremost, I pray to the Almighty for bestowing upon me blessings, knowledge, well-being, and unwavering strength throughout my Ph.D. expedition and the successful completion of this thesis. This Ph.D. odyssey has been a treasure trove of experiences. I acknowledge that this accomplishment would have been unattainable without my supervisor, Prof. Rajendra Singh Dhaka, for his unwavering support and invaluable guidance. I extend my heartfelt gratitude to him for affording me the incredible opportunity to work within his research group and providing the necessary research infrastructure for my endeavors. Again, I thank him for agreeing to convert from an M.Tech (Solid State Material) to a Ph.D. program, after completing one year. His consistent mentorship, unwavering encouragement, collaborative spirit, and insightful suggestions have been instrumental in steering me toward the successful culmination of this thesis. I extend my deepest appreciation during this journey, which presented its share of challenges and fluctuations, including agreements and disagreements, with Prof. Dhaka's steadfast dedication, discipline, and punctuality, which consistently motivated and inspired me to progress in my research work.

I am deeply thankful to the members of the Students Research Committee (SRC) at the Indian Institute of Technology Delhi: Prof. Sujeet Chaudhary (Chairperson), Prof. Pranaba Kishor Muduli (Departmental expert), and Prof. Hemant Kumar Kashyap (outside departmental expert), for their valuable suggestions and guidance during the semester presentation throughout my Ph.D. journey. I also would like to thank my teachers who taught me during the coursework of Ph.D. and provided insightful and meticulous knowledge of the basics of science, which helped me a lot in the research.

I acknowledge the Department of Physics at IIT Delhi for granting access to XRD, PPMS EVERCOOL-II, and AFM facilities. Additionally, I acknowledge the Central Research Facility (CRF) at IIT Delhi for performing the measurements such as HR-XRD, FESEM, EDX, and SQUID.

I express gratitude to Dr. B. Schwarz at Karlsruhe Institute of Technology, Germany, for providing the magnetic and specific heat data. I am thankful to Dr. P. D. Babu at BARC Trombay Mumbai for the magnetic measurements and for giving me valuable time to discuss the result that assists in understanding the magnetism and data interpretation. I would like to thank Prof. Clemens Ulrich and Dr. James Hester for providing the temperature-dependent neutron diffraction facility and insightful discussions that aided in data interpretation and Dr. Yousef Kareri for helping in the measurements at the University of New South Wales, Sydney, Australia.

I acknowledge the Ministry of Human Resource and Development for the fellowship that supported my research at IIT Delhi. Financial support from IIT Delhi through seed grant with

Reference No. BPHY2368 and SERB-DST through the Early Career Research (ECR) Award to Prof. R. S. Dhaka (Project Reference No. ECR/2015/000159) for the pulsed laser deposition, which was pivotal to the work presented in this thesis. The high-temperature furnace, acquired through the grant of DAE Young Scientist Research Award to R. S. Dhaka (Project Sanction No. 34/20/12/2015/BRNS), provided by BRNS, deserves gratitude. The INSA-DFG program, Fellowship No. Int/DFG/2019, facilitated high-temperature specific heat measurements as part of the international exchange of scientists program between India and Germany. The core research grant from SERB-DST (Project Reference No. CRG/2020/003436) is deeply appreciated for its financial backing. Neutron diffraction measurements at UNSW, Australia, were facilitated by the Department of Science & Technology (DST), India, through the Indo-Australia early and mid-career researchers (EMCR) fellowship to RSD, administered by INSA (sanction order no. IA/INDO-AUST/F-19/2017/1887). Additionally, I thank to Prof. M. Miryala and Prof. M. Murakami for providing the opportunity to visit the lab at Shibaura Institute of Technology, Japan, through the Sakura Science Program.

I am grateful to my colleagues and labmates, both past and present, who have formed a close-knit community during this Ph.D. journey. Their contributions, discussions, suggestions, and camaraderie have been invaluable during the ups and downs of this lengthy voyage. Thanks go to Dr. Mahesh Chandra, Dr. Vishal Maurya, Dr. Rishabh Shukla, Dr. Priyanka, Dr. Ajay Kumar, Dr. Jayjit Mukherjee, Jayashree Pati, Simran Sapra, Manisha Srivastava, Manish Kumar Singh, Ajay Kr Yadav, Madhav, Dr. Vikas Narayan Thakur, Dr. Sandeep Kumar, Ramcharan Meena, Dr. Pravin Dwivedi, Dr. Narendra Jakhar, Priyanka Yadav, Sudhanshu Gupta, Anmol Shukla, Dr. P. SenthilKumar, Mahantesh Khetri, Meenal Aggrawal, Hemanshu Dua, Gazal Gupta, Pooja Rani, Aakash Kaushik, Anurag Sharma, Kamlesh Kumar, Surepalli Suraj, and Ananya. They have not only been colleagues but also a supportive family throughout these years. I extend special thanks to Dr. Mahesh Chandra, Dr. Vishal Maurya, Dr. Rishabh Shukla, Dr. Ajay Kumar, Ajay Kumar Yadav, and Dr. Narendra Jakhar for the unforgettable moments shared during my Ph.D. journey. I don't want to forget to thank them who helped me for staying and continuing my research after five years of my Ph.D., named as Ajay kr Yadav, Dr. Ravi Kumar, Manish and Madhav. Further, I am profoundly grateful to my friends, seniors, and juniors at IIT Delhi, who helped alleviate stress and provided support at various stages of my Ph.D. expedition. Among them, Rishabh Shukla, Ravi Kumar, Yashir Khan, Nanhe Kumar Gupta, Chandan Vishwakarma, and Gaya Prasad and outside IIT Delhi: Rajeev, Arjun, Neeraj, Ajay, Uday Pratap, and Yadavendra stand out for their unwavering encouragement and assistance, helping me navigate challenging phases.

I want to extend my heartfelt appreciation to my well-wishers for their presence and cooperation throughout this journey, which has been immensely meaningful. Special thanks are reserved for Ms. Manisha Upadhyay for her continuous and unwavering support, affection, and motivation during these years.

I would like to express my warm gratitude adequately towards my beloved family members: Vidywati Devi (Mother), Shyam Narayan Gupt (Father), my fiancee Manisha Upadhyay, my sisters Arti, Malti, and Shanti, Shivdutt (Brother), Gayatri Upadhyay, Bhaskar Upadhyay, Tarkeshwar, Madhulika, Jaya, Alok, Gautam, Shivam, Niranjan and my extended family members. Also, I would like to thank Ajay, Rajababu, Ramashray, and Abhay. Their unending love, unwavering support, and continuous encouragement have been the cornerstone of my Ph.D. journey.

Last but not least, I owe profound gratitude to all those close to me who contributed in numerous ways, making this journey possible.
I heartily dedicate this thesis to my beloved family.
Guru Dutt Gupt

ABSTRACT

In the present era of technology, materials science plays a crucial and indispensable role in developing numerous advanced technologies across various sectors, including health, computing, defense, and many more. It is intriguing to note that magnetic materials belonging to a distinct class of materials, exhibit a wide range of applications. The properties displayed by magnetic materials are strongly influenced by factors such as the crystal structure, spin order, and interaction. These characteristics can be thoroughly explored and examined using diffraction techniques like x-ray diffraction (XRD), powder neutron diffraction (ND), and magnetic properties such as dc and ac magnetization and transport properties measurements. In the area of magnetic materials, Heusler alloys have emerged as the most promising candidates in contemporary research due to their high magnetic moment and high Curie temperature (above room temperature). This is primarily used for applications in various fields such as spintronics, thermoelectricity, shape memory alloys, and many more. The unique properties and versatility of Heusler alloys make them highly attractive for further exploration and utilization in cutting-edge technological advancements. In this context, we prepared Heusler alloys and investigated their structural and magnetic properties by performing various experiments varying the temperature and magnetic field.

In this thesis, the structural and magnetic properties of $Ni_2Cr_{1-x}Mn_xAl$ (x = 0, 0.25, 0.5) Heusler alloys have been investigated using x-ray diffraction and magnetic susceptibility (χ–T) (dc and ac), and isothermal magnetization measurements at low temperatures and high magnetic fields, respectively. The Rietveld refinement of x-ray diffraction patterns attribute the coexistence of both phases of cubic ($L2_1$) and tetragonal ($L1_0$) structures, respectively. The analysis of χ–T data show an irreversible behavior with the paramagnetic effective magnetic moment (μ_{eff}) of about 1.6 μ_B/f.u. for the $x = 0$ sample. Interestingly, the χ–T curves of the $x = 0.25$ and 0.5 samples show the broad bifurcation between zero-field-cooled and field-cooled, which reveals the coexistence of ferromagnetic (FM) and antiferromagnetic (AFM) type magnetic interactions with increase of μ_{eff} = 2.3 and 3.3 μ_B/f.u., respectively. The inverse χ curves are fitted using modified Curie-Weiss law, which indicates the enhancement of FM ordering with Mn substitution, possibly due to the exchange interaction between Mn–Mn atoms. The detailed analysis of magnetic isotherms using the modified Langevin model confirms the SPM cluster embedded in the FM/PM matrix above the blocking temperature. Notably, suppressing the bifurcation and shift in the magnetization towards low temperature by applying the magnetic field may suggest the presence of spin glass behavior. This is further investigated by analyzing ac–χ data and determining spin relaxation time using the Vogel–Fulcher law and a critical-scaling approach to confirm the cluster glass-like behavior for both the $x = 0.25$ and 0.5 samples. Moreover, the low temperature-specific heat capacity presents anomalous behavior with an increase in the Sommerfeld coefficient.

Further, the investigation of the nuclear and magnetic structures in Heusler alloys has been performed using the temperature-dependent powder neutron diffraction on the polycrystalline inverse Heusler alloys $Cr_2Co_{(1-x)}Cr_xAl$ (x = 0, 0.2). The nuclear and magnetic structures are revealed by the Rietveld refinement of powder neutron diffraction patterns in the temperature range 100–900 K, where the magnetic structure is obtained below 750 K temperature using the space group $I\bar{4}m2$ and wave vector (k = (0, 0, 0)). The inverse tetragonal structure is confirmed and consistent over the large temperature range from 100–900 K of the $x = 0$ sample. Interestingly, the transition temperature (730±5 K) is obtained with the fitting of the ordered magnetic moment as a function of the temperature using empirical power law $M(T) = M_0\,(1 - T/T_C)^{\beta}$ and intensity of the (110) peak mimics the magnetization behavior by decreasing the intensity as increasing the temperature. The spin configuration of the microscopic magnetic structure suggests the fully compensated ferrimagnetic behavior where the magnetic moments of Cr2 are antiparallel with respect to the Cr1, and Co moments. Moreover, the observed anomaly in the lattice parameters at 730±5 K suggests that the distortion in the crystal structure may play an important role in the magnetic phase transition.

Generally, some types of disorder are found in Heusler alloys; however, a few alloys show the ordered structure. Therefore, we have prepared the quaternary Heusler alloy, and in-depth analysis has been performed on the structural and complex magnetic interaction across the phase transition using the x-ray diffraction and magnetic data as a function of temperature and magnetic field of the quaternary $CoFeV_{0.8}Mn_{0.2}Si$ Heusler alloy, respectively. The Rietveld refined XRD pattern suggests that the sample is found to crystallize in a single-phase cubic Y-type structure belonging to the space group $F\bar{4}3m$ (no. 216). The ferromagnetic nature is obtained from the thermo-magnetization, recorded in the temperature range 300–700 K having the ferromagnetic transition temperature ≈446 K, which is found from the derivative of field-cooled data. The saturation magnetization is found to be 2.2 μ_B/f.u. at 5 K, concur nearly with the Slater–Pauling rule, a prerequisite for half-metallic nature. The values of asymptotic critical exponents (β, γ, and δ) and the T_C are extracted through detailed analytical analysis including the Modified Arrott plot, the Kouvel-Fisher (K–F) method, and the Widom scaling relation. Interestingly, the estimated values of $\beta = 0.369$ and $\gamma = 1.445$ closely approximate the theoretical values of the 3D Heisenberg model and validate the second-order thermodynamic phase transition across the T_C. The obtained exponents lead to the collapse of renormalized isotherms, represented by the relationship between the magnetization (m) and the applied magnetic field (h), into two distinct branches above and below the T_C, which validates the reliability of the analysis. Furthermore, these exponents suggest that the spin interaction follows a decay pattern of $J(r) \sim r^{-4.99}$, indicating a short-range magnetic ordering akin to the itinerant-electron 3D Heisenberg model.

To study the bulk properties of Heusler alloy in thin film form, we have successfully grown an epitaxial thin film of Co_2CrAl Heusler alloy on the single crystalline MgO(001) substrate

using a pulsed laser deposition system. The x-ray diffraction pattern in θ-2θ mode showed the film growth in single phase B2-type ordered cubic structure with the presence of (002) and (004) peaks and the film oriented along the direction of the MgO(001) substrate. The ϕ scan along the plane (220) confirms the four-fold symmetry and the epitaxial growth relation found to be $Co_2CrAl(001)[100]||MgO(001)[110]$. The thickness of about 12 nm is extracted through the analysis of x-ray reflectivity data. The isothermal magnetization (M–H) curves confirm the ferromagnetic (FM) nature of the thin film having significant hysteresis at 5 and 300 K. From in-plane M–H curves, the saturation magnetization values are determined to be 2.1 μ_B/f.u. at 5 K and 1.6 μ_B/f.u. at 300 K, which suggests the soft FM behavior in the film having the coercive field $\approx$522 Oe at 5 K. The thermo-magnetization (M–T) measurements at 500 Oe magnetic field show the bifurcation between field-cooled and zero-field-cooled curves below around 100 K. The normalized field-cooled magnetization curve follows the T^2 dependency, and the analysis reveals the Curie temperature around 335$\pm$11 K. Moreover, the decrease in the resistivity indicates semiconducting behavior with the temperature and has a negative temperature coefficient of resistivity (5.2×10^{-4} /K) in the film.

सार

प्रौद्योगिकी के वर्तमान युग में, पदार्थ विज्ञान एक महत्वपूर्ण और अपरिहार्य भूमिका निभाता है स्वास्थ्य सहित विभिन्न क्षेत्रों में कई उन्नत तकनीकों को विकसित करने में, कंप्यूटिंग, रक्षा, और भी बहुत कुछ है। यह ध्यान रखना दिलचस्प है कि चुंबकीय सामग्रियों के एक विशिष्ट वर्ग से संबंधित सामग्रियां, अनुप्रयोगों की एक विस्तृत श्रृंखला प्रदर्शित करती हैं। चुंबकीय सामग्रियों द्वारा प्रदर्शित गुण ऐसे कारकों से काफी प्रभावित होते हैं , जैसे क्रिस्टल संरचना, स्पिन क्रम और इंटरैक्शन। एक्स-रे विवर्तन (XRD), पाउडर न्यूट्रॉन विवर्तन (ND), और चुंबकीय गुण, डीसी और एसी चुंबकत्व और परिवहन गुण माप जैसी विवर्तन तकनीकों का उपयोग करके इन विशेषताओं को गहनता से खोजा और जांचा जा सकता है। चुंबकीय सामग्री के क्षेत्र में, हेस्लर समसामयिक अनुसंधान में, मिश्रधातुएँ उच्च चुंबकीय क्षण और उच्च क्यूरी तापमान (कमरे के तापमान से ऊपर) सबसे आशाजनक उम्मीदवार के रूप में उभरी हैं। इसका उपयोग मुख्य रूप से विभिन्न क्षेत्रों जैसे स्पिंट्रोनिक्स, थर्मोइलेक्ट्रिसिटी, आकार मेमोरी मिश्र धातु और कई अन्य क्षेत्रों में अनुप्रयोगों के लिए किया जाता है। हेस्लर मिश्र धातु की अद्वितीय गुण और बहुमुखी प्रतिभा उन्हें आगे की खोज के लिए अत्यधिक आकर्षक बनाती है और अत्याधुनिक तकनीकी प्रगति के लिए उपयोग करते हैं| इस संदर्भ में, हमने हेस्लर मिश्र धातुओं को तैयार किया और तापमान और चुंबकीय क्षेत्र को बदलने वाले विभिन्न प्रयोग कार्य करके उनके संरचनात्मक और चुंबकीय गुणों की जांच की।

इस थीसिस में, $Ni_2Cr_{1-x}Mn_xAl$ (x = 0, 0.25, 0.5) हेस्लर मिश्र धातुओं के संरचनात्मक और चुंबकीय गुणों को एक्स-रे विवर्तन और चुंबकीय संवेदनशीलता (χ-T) (डीसी और एसी) और आइसोथर्मल चुंबकीयकरण का माप क्रमशः कम तापमान, और उच्च चुंबकीय क्षेत्र पर उपयोग करते हुए जांच की गई है। एक्स-रे विवर्तन पैटर्न का रिटवेल्ड शोधन इसका श्रेय देता है की क्रमशः घन ($L2_1$) और चतुष्कोणीय ($L1_0$) संरचनाओं के दोनों चरणों का सह-अस्तित्व है। χ-T डेटा का विश्लेषण, x = 0 नमूने के लिए लगभग 1.6 μ_B/f.u. के प्रभावी चुंबकीय क्षण (μ_{eff}) के साथ एक अनुत्क्रमणीय व्यवहार दिखाता है। दिलचस्प बात यह है कि x = 0.25 और 0.5 का χ-T वक्र नमूने शून्य-फ़ील्ड-कूल्ड और फ़ील्ड-कूल्ड के बीच व्यापक विभाजन दिखाते हैं, जो क्रमशः μ_{eff} = 2.3 और 3.3 μ_B/f.u. की वृद्धि के साथ लौहचुंबकीय (एफएम) और प्रतिलौहचुंबकीय (एएफएम) प्रकार चुंबकीय अंतःक्रियाओं के सह-अस्तित्व को प्रकट करता है। व्युत्क्रम χ वक्र संशोधित क्यूरी-वीस नियम का उपयोग करके फिट किया गया है, जो इंगित करता है Mn प्रतिस्थापन के साथ एफएम ऑर्डर में

वृद्धि, संभवतः Mn-Mn परमाणुओं के बीच परस्पर विनिमय अंतःक्रियाओं के कारण है। संशोधित लैंगविन मॉडल का उपयोग करके चुंबकीय समताप रेखाओं का विस्तृत विश्लेषण अवरुद्ध तापमान के ऊपर एफएम/पीएम मैट्रिक्स में एम्बेडेड एसपीएम क्लस्टर की पुष्टि करता है। विशेष रूप से, चुंबकीय क्षेत्र को लागू करके कम तापमान की ओर द्विभाजन और चुंबकीकरण में बदलाव को दबाने से स्पिन ग्लास व्यवहार की उपस्थिति का सुझाव मिल सकता है। इसे आगे एसी-χ-डेटा का विश्लेषण करके और वोगेल-फुलचर कानून और क्रिटिकल-स्केलिंग दृष्टिकोण का उपयोग करके स्पिन विश्राम समय का निर्धारण करके दोनों x = 0.25 और 0.5 नमूनों के लिए क्लस्टर ग्लास जैसे व्यवहार की पुष्टि करने के लिए जांच की जाती।

आगे, हेसलर मिश्र धातुओं में परमाणु और चुंबकीय संरचनाओं की जांच तापमान पर निर्भर पाउडर न्यूट्रॉन विवर्तन का उपयोग पॉलीक्रिस्टलाइन इनवर्स हेस्लर मिश्र धातुओं $Cr_2Co_{(1-x)}Cr_xAl$ (x = 0, 0.2) पर किया गया है। परमाणु और चुंबकीय संरचनाओं को तापमान सीमा 100-900 K में पाउडर न्यूट्रॉन विवर्तन पैटर्न के रिटवेल्ड शोधन द्वारा प्रकट किया जाता है, जहां स्पेस समूह I-4m2 और तरंग वेक्टर (k = (0, 0, 0)) का उपयोग करके चुंबकीय संरचना को 750 K तापमान से नीचे प्राप्त की जाती है। व्युत्क्रम चतुष्कोणीय संरचना की पुष्टि की जाती है और x = 0 नमूने के बड़े तापमान सीमा 100-900 K पर सुसंगत होती है। दिलचस्प बात यह है कि संक्रमण तापमान (730±5 K) आदेशित चुंबकीय क्षण की फिटिंग के साथ प्राप्त किया जाता है इम्पेरिकल शक्ति नियम $M(T) = M0(1 - T/TC)^{\beta}$ का उपयोग करके तापमान का एक फलन β और (110) शिखर की तीव्रता तापमान बढ़ाने के रूप में तीव्रता को कम करके चुंबकीयकरण व्यवहार की नकल करती है। सूक्ष्म चुंबकीय का स्पिन विन्यास संरचना पूरी तरह से मुआवजा फेरिमैग्नेटिक व्यवहार का सुझाव देती है जहां Cr2 का चुंबकीय क्षण Cr1 और Co चुंबकीय क्षणों के संबंध में विरोधी हैं। इसके अलावा 730±5 K पर जाली मापदंडों में देखी गई विसंगति से पता चलता है कि विरूपण क्रिस्टल संरचना में चुंबकीय चरण संक्रमण में एक महत्वपूर्ण भूमिका निभा सकते हैं।

आम तौर पर, हेसलर मिश्र धातुओं में कुछ प्रकार के विकार पाए जाते हैं; हालांकि, कुछ मिश्र धातु आदेशित संरचना दिखाते हैं। इसलिए, हमने चतुर्धातुक हेसलर मिश्र धातु तैयार की है, और क्रमशः एक्स-रे विवर्तन और चुंबकीय डेटा का उपयोग करके चरण संक्रमण में संरचनात्मक और जटिल चुंबकीय अंतःक्रियाओं का तापमान और चुंबकीय क्षेत्र के एक फलन के रूप में चतुर्धातुक $CoFeV_{0.8}Mn_{0.2}Si$ हेसलर मिश्र धातु का गहन विश्लेषण किया गया है। रिटवेल्ड परिष्कृत

एक्सआरडी पैटर्न से पता चलता है कि नमूना क्रिस्टलीकृत करने के लिए अंतरिक्ष समूह F-43m (संख्या 216) से संबंधित एकल-चरण घन Y- प्रकार की संरचना में पाया जाता है। लौह-चुंबकीय प्रकृति थर्मो-चुंबकीकरण से प्राप्त होती है, जो तापमान सीमा 300-700 K में दर्ज की जाती है जिसमें लौहचुंबकीय संक्रमण तापमान ≈446 K, जो फील्ड-कूल्ड डेटा के व्युत्पन्न से पाया जाता है। 5 K पर संतृप्ति चुंबकीयकरण 2.2 μ_B/f.u. पाया जाता है, जो लगभग स्लेटर-पॉलिंग नियम से मेल खाता है, जो अर्ध-धातु प्रकृति के लिए एक शर्त है। स्पर्शोन्मुख क्रिटिकल घातांक (β, γ, और δ) के मूल्य और T_C को संशोधित अरोट प्लॉट सहित, कौवेल-फिशर (K-F) विधि, और विडोम स्केलिंग संबंध से विस्तृत विश्लेषणात्मक विश्लेषण के माध्यम से निकाला जाता है। दिलचस्प बात यह है कि β = 0.369 और γ = 1.445 के अनुमानित मूल्य 3 डी हाइजेनबर्ग मॉडल के सैद्धांतिक मूल्यों का बारीकी से अनुमान लगाते हैं और T_C में दूसरे क्रम के थर्मोडायनामिक चरण संक्रमण को मान्य करता है। प्राप्त घातांक पुनर्सामान्यीकृत समताप रेखाओं के पतन की ओर ले जाते हैं, चुंबकीयकरण (m) और लागू चुंबकीय क्षेत्र (h) के बीच संबंध द्वारा दर्शाया गया है, T_C के ऊपर और नीचे दो अलग-अलग शाखाओं में, जो विश्लेषण की विश्वसनीयता को मान्य करता है। इसके अलावा, इन प्रतिपादकों का सुझाव है कि स्पिन इंटरैक्शन $J(r) \sim r^{-4.99}$ के क्षय पैटर्न का अनुसरण करता है, जो एक छोटी दूरी के चुंबकीय क्रम के समान भ्रमण-इलेक्ट्रॉन 3 डी हाइजेनबर्ग मॉडल का संकेत देता है।

पतली फिल्म के रूप में हेसलर मिश्र धातु के थोक गुणों का अध्ययन करने के लिए, हमने स्पंदित लेजर जमाव प्रणाली का उपयोग करके एकल क्रिस्टलीय MgO(001) सब्सट्रेट पर Co_2CrAl हेसलर मिश्र धातु की एक एपिटैक्सियल पतली फिल्म को सफलतापूर्वक विकसित किया है। θ-2θ मोड में एक्स-रे विवर्तन पैटर्न ने (002) और (004) चोटियों की उपस्थिति के साथ एकल चरण B2-प्रकार आदेशित घन संरचना में फिल्म की वृद्धि को दिखाया और फिल्म MgO(001) सब्सट्रेट की दिशा के साथ उन्मुख है। । प्लेन (220) के साथ में ϕ स्कैन चार गुना समरूपता और एपिटैक्सियल ग्रोथ संबंध $Co_2CrAl(001)[100]||MgO(001)[110]$ की पुष्टि करता है। एक्स-रे परावर्तन डेटा के विश्लेषण के माध्यम से लगभग 12 nm की मोटाई निकाली है। समतापीय चुंबकीयकरण (एम-एच) वक्र 5 और 300 K पर महत्वपूर्ण हिस्टैरिसीस वाली पतली फिल्म की फेरोमैग्नेटिक (एफएम) प्रकृति की पुष्टि करते हैं। इन-प्लेन M-H वक्रों से, संतृप्ति चुंबकीयकरण मान क्रमशः 5 K और 300 K पर 1.6 μ_B/f.u और 2.1 μ_B/f.u होने के लिए निर्धारित किए जाते हैं, जो फिल्म में मुलायम FM व्यवहार का सुझाव देता है जिसमें 5 K पर जबरदस्ती क्षेत्र ≈522 Oe है। थर्मो-चुंबकीयकरण (M-T) माप, 500 Oe चुंबकीय क्षेत्र पर फील्ड-कूल्ड और शून्य-क्षेत्र-ठंडा वक्रों के बीच द्विभाजन 100 K के नीचे दिखाते

हैं। सामान्यीकृत क्षेत्र-ठंडा चुंबकीयकरण वक्र T^2 निर्भरता का अनुसरण करता है, और विश्लेषण से क्यूरी तापमान (T_C) लगभग 335±11 K का पता चलता है। इसके अलावा, प्रतिरोधकता में कमी तापमान के साथ अर्धचालक व्यवहार को इंगित करती है, और फिल्म में प्रतिरोधकता का नकारात्मक तापमान गुणांक (5.2×10^{-4} /K) है।

Contents

List of Figures

List of Tables

Organization of Thesis Chapters

The research conducted for this thesis is structured into seven chapters, each exploring different aspects of the topic. A concise overview of all the chapters is provided below, highlighting the key outcomes made in each one.

Chapter 1 of the thesis provides an introduction to Heusler alloys, with a primary focus on their structural properties and an examination of potential structural disorder. It also presents the fundamental properties of these alloys and includes a comprehensive literature survey. The subsequent section of the thesis delves into the critical behavior of Heusler alloys, emphasizing a thorough review of previous studies conducted on cobalt-based and other Heusler alloys. This analysis aims to analyze the magnetic interaction in the proximity of the ferromagnetic transition temperature, particularly in the context of spintronics applications. Furthermore, it highlights the motivation behind investigating different types of Heusler alloys, which exhibit complex magnetic interactions at low temperatures, resulting in various magnetic features such as spin glass and superparamagnetism. Lastly, the chapter provides a concise overview of thin film Heusler alloys deposited on single crystalline substrates, utilizing different systems such as pulsed laser deposition and sputtering techniques. This overview emphasizes the significance of thin film systems in a wide range of applications.

Chapter 2 presents the experimental details for the synthesis of bulk and thin film of Heusler alloys. For describing nicely this section, we divided the experimental part into two main sections. Firstly, we described the process of preparing bulk Heusler alloys using an arc melting under the protective environment of an argon gas. Secondly, we focused on the growth of an epitaxial thin film of Heusler alloy. We utilized the cutting-edge pulsed laser deposition (PLD) system to describe the deposition process of the thin film. The PLD system is equipped with an ultra-high vacuum-compatible chamber connected to a load lock, enabling precise control over the deposition process. Furthermore, we provide a detailed explanation of the characterization techniques employed to analyze structural, magnetic, transport, and topographic properties of our samples. These techniques include the following: high-resolution x-ray diffraction, scanning electron microscopy, energy dispersive x-ray spectroscopy, powder neutron diffraction, atomic force microscopy, superconducting quantum interference device (SQUID), and physical property measurement system (PPMS).

Chapter 3 provides the detailed study of the structural and magnetic properties of the $Ni_2Cr_{1-x}Mn_xAl$ (x = 0, 0.25, and 0.5) Heusler alloys. Our analysis comprised dc and ac susceptibility measurements (χ-T), isothermal magnetization measurements at low temperatures and high magnetic fields, and x-ray diffraction. The Rietveld refinement of the x-ray diffraction patterns at room temperature unveiled the coexistence of cubic ($L2_1$) and tetragonal ($L1_0$) structures in the alloys. Notably, the χ-T curves of the sample with $x = 0$ exhibited

an irreversible behavior, showing an anomaly around 4 K. In contrast, the samples with $x = 0.25$ and 0.5 displayed a broad bifurcation between the zero-field-cooled and field-cooled curves, along with non-saturating behavior in isothermal magnetization measurements. These observations indicated the coexistence of ferromagnetic (FM) and antiferromagnetic (AFM) magnetic interactions. We employed the Curie-Weiss (CW) law to fit the inverse χ curves and determined the effective magnetic moment (μ_{eff}) for each sample. The μ_{eff} values were found to be approximately 1.6, 2.3, and 3.3 μ_{B}/f.u. for the samples with $x = 0$, 0.25, and 0.5, respectively. The increase in the effective moment and the shift from negative to positive CW temperature indicated an enhancement of FM ordering with Mn substitution, possibly due to the exchange interaction between Mn-Mn atoms. Further analysis of the magnetic isotherms using the modified Langevin model confirmed the presence of an interacting super-paramagnetic (SPM) matrix at low temperatures. At higher temperatures, the model revealed SPM clusters embedded in the paramagnetic (PM) matrix. Notably, the suppression of bifurcation and its shift towards lower temperatures under an applied magnetic field suggested the presence of spin glass behavior. This was supported by the analysis of ac-χ data and the determination of the spin relaxation time using the Vogel-Fulcher law and a critical-scaling approach, which confirmed a cluster glass-like behavior in both the samples with $x = 0.25$ and 0.5. Moreover, the low-temperature specific heat capacity exhibited anomalous behavior, increasing the Sommerfeld coefficient (γ) observed with Mn substitution. This behavior indicated the presence of cluster spin glass behavior.

Chapter 4 presents a detailed analysis of the temperature-dependent neutron diffraction patterns of $Cr_2Co_{1-x}Cr_xAl$ ($x = 0$, 0.2) inverse Heusler alloy. Our investigation aims to uncover the microscopic magnetic structure of the alloy and explore its fully compensated ferrimagnetic nature up to the phase transition temperature. The Rietveld refinement of the diffraction patterns confirms the presence of an inverse tetragonal structure by using the $I\bar{4}m2$ space group across a wide temperature range of all the samples. The refinement of the magnetic phase with a wave vector k = (0, 0, 0) reveals the ferrimagnetic nature of the samples. These transition temperatures are determined by empirically fitting the variation in the ordered net magnetic moment and the intensity of the (110) peak as functions of temperature. The spin configuration of the microscopic magnetic structure indicates a nearly fully compensated ferrimagnetic behavior, where the magnetic moments of Cr2 are antiparallel to those of Cr1 and Co. Additionally, we observe an anomaly in the thermal expansion and lattice parameters at 730$\pm$5 K, suggesting that the distortion in the crystal structure may play a significant role in the magnetic phase transition.

Chapter 5 explores the critical phenomena displayed by a quaternary $CoFeV_{0.8}Mn_{0.2}Si$ Heusler alloy through measurements of dc susceptibility $\chi(T)$ and isothermal magnetization (MH) across paramagnetic to ferromagnetic transition temperature. The x-ray diffraction analysis conducted at room temperature reveals that the sample possesses a single-phase cubic Y-type

structure, belonging to the F$\bar{4}$3m (no. 216) space group. The magnetic properties, characterized by the dc susceptibility $\chi(T)$ and isothermal magnetization measurements, exhibit a ferromagnetic behavior with a second-order thermodynamic phase transition from paramagnetic to ferromagnetic at approximately 446 K. The saturation magnetization at 5 K is determined to be 2.2 μ_B/f.u., as obtained from the isothermal magnetization. This value closely adheres to the Slater-Pauling rule, indicating a half-metallic nature of the alloy. To investigate the critical behavior in more detail, we calculate precise values of the asymptotic critical exponents (β, γ, and δ) and the Curie temperature (T_C) using various analytical methods such as the modified Arrott plot, the Kouvel-Fisher (KF) method, and critical isotherm analysis. These values play a crucial role in identifying the second-order thermodynamic phase transition and magnetic interactions in the vicinity of T_C. Furthermore, we employ the KF approach and the Widom scaling relation to deepen our understanding of the system. The estimated values of $\beta = 0.369$ and $\gamma = 1.445$ closely align with the theoretical values of the 3D Heisenberg model. The renormalized isotherms, plotting magnetization (m) against the applied magnetic field (h), collapse into two distinct branches above and below T_C, further confirming the reliability and precision of the obtained exponents and our analysis. Moreover, these exponents indicate that the spin interaction decays as $J(r)\sim r^{(-4.99)}$, suggesting a short-range ordering behavior characteristic of the weak itinerant-electron 3D Heisenberg model.

Chapter 6 provides an investigation of the structural, magnetic, and transport properties of an epitaxial thin film of Co_2CrAl Heusler alloy. Using the pulsed laser deposition technique, the film is grown on a single crystalline MgO(001) substrate. Analysis of the x-ray diffraction pattern in θ-2θ mode reveals that the film exhibits a single phase with a B2-type ordered cubic structure. The presence of (002) and (004) peaks indicates the film's orientation along the MgO(001) direction. Further confirmation of the epitaxial growth relation is obtained through a ϕ-scan along the (220) plane, which exhibits four-fold symmetry. The epitaxial relationship is identified as $Co_2CrAl(001)[100]||MgO(001)[110]$. The film thickness is determined to be approximately 12 nm based on the analysis of the x-ray reflectivity data. The isothermal magnetization (M-H) curves demonstrate the ferromagnetic (FM) nature of the thin film, showing significant hysteresis at both 5 K and 300 K. The saturation magnetization values obtained from the in-plane $M - H$ curves are found to be 2.1 μ_B/f.u. at 5 K and 1.6 μ_B/f.u. at 300 K, indicating a soft ferromagnetic behavior. The coercive field is approximately 522 Oe at 5 K. Thermo-magnetization measurements conducted at a magnetic field of 500 Oe reveal a bifurcation between the field-cooled and zero-field-cooled curves below approximately 100 K. The normalized field-cooled magnetization curve follows a T^2 dependency. Analysis of the data yields a Curie temperature of approximately 335$\pm$11 K. Additionally, the low-temperature resistivity measurements exhibit semiconducting behavior with temperature. Notably, a negative

temperature coefficient of resistivity (5.2×10^{-4}/K) is observed in the film. Our findings provide valuable insights into the structural, magnetic, and transport properties of an epitaxial thin film of Co_2CrAl Heusler alloy grown on a MgO(001) substrate using pulsed laser deposition.

Chapter 7 serves as a comprehensive conclusion to our research endeavors to understand the detailed structural and magnetic properties of Heusler alloys. Using various characterization techniques, as discussed in the preceding chapters, we examined these alloys in bulk and thin film forms. By synthesizing, we have done the investigations to understand the properties of Heusler alloys. Our comprehensive analysis has shed light on our potential studies and provided valuable insights for future research directions with the limitations and constraint encountered during the research.