Tunable multifunctional properties in thin films of Heusler and other intermetallic compounds

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Heusler compounds constitute a remarkable class of materials with tunable and multifunctional properties. Thin films and devices prepared using Heusler compounds are useful for many applications, such as spintronics, skyrmionics, new permanent magnets, and antiferromagnetic materials. Since 2014, we have been attempting to fabricate and study novel materials. Our work focuses on the growth and characterization of thin films and heterostructures of Heusler and other intermetallic compounds, thus facilitating the discovery of new physics and future technological applications. The morphological, structural, magnetic, and magnetotransport properties of thin films can be controlled via epitaxial growth and strain engineering, providing a platform to study novel phenomena of interest in both pure and applied sciences. Measurements in thin films allow continued exploration of topologically driven physical effects, as well as the application of these materials in functional devices. Tetragonal Mn-based Heusler compounds with large perpendicular magnetic anisotropy (PMA) and tunable magnetization are useful for numerus spintronic applications, such as data storage. We can tailor the properties of multifunctional $Mn_{3-x}Ga$ thin films by growing them on appropriate substrates and underlayers or by substitution of Mn with other transitions metals (Pt or Fe). We also found evidence of chiral or helical magnetic structure in Mn_2RhSn thin films through magnetotransport measurements. We demonstrate the growth and characterization of hexagonal noncollinear antiferromagnetic Mn_3Sn films, suitable for the rapidly developing field of antiferromagnetic spintronics.

Heusler compounds constitute a remarkable class of materials with tunable multifunctional properties and various potential applications. The development of simple rules to understand the relationship between structure and function of magnetic Heusler compounds allowed the discovery of many unique properties for different applications.

Our research focuses on the understanding of the physical properties of various Heusler and other intermetallic compounds. We obtained a deeper understanding of the tunability of these properties, providing a platform to study novel phenomena of interest in both pure and applied sciences. For this investigation, we employ various techniques like X-ray diffraction (XRD), magnetization, electrical transport, transmission electron and atomic force microscopies (TEM and AFM, respectively).

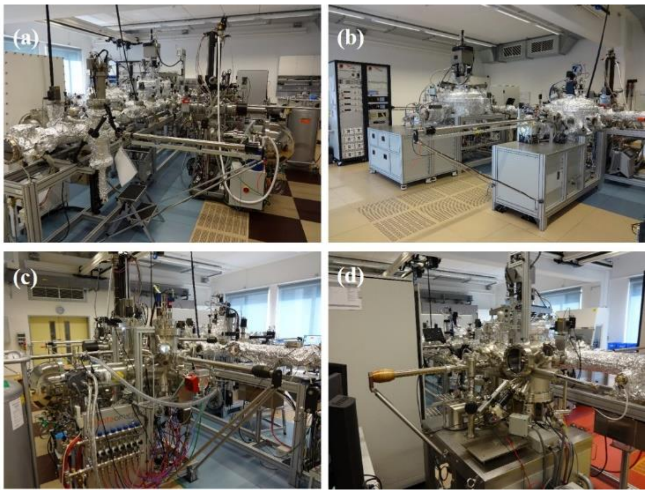
Fig.-1: (a) State-of-the-art UHV cluster tool for the growth and characterization of thin films. (b) Two sputter deposition systems, (c) the MBE and ARPES systems and (d) the UHV scanning probe microscope.

Overview of the thin films laboratory

In 2014, a new thin films laboratory building was constructed to host the most modern facilities for the fabrication and characterization of thin films. The layout of the laboratory is based on cleanroom standards. This laboratory is equipped with a state-of-the-art ultra-high vacuum (UHV) cluster tool [Fig. 1(a)]. It has two sputtering systems with thirteen and eight sources [Fig. 1(b)]. The first sputtering system was installed in 2014, and the second at the end of 2016. Both are equipped with direct current (DC) and radio frequency (RF) sources for the growth of various metallic, semiconducting, and insulating films. The target-to-substrate distance can be varied and the substrate holder can be rotated during the deposition to ascertain homogenous film growth. The maximum reachable substrate temperature is 1000 °C. All the processes are computer-controlled to guarantee reproducible high-quality films.

At the beginning of 2017, we expanded our laboratory by including a molecular beam epitaxy (MBE) deposition system, containing six effusion cells, and an angle-resolved photoemission spectroscopy (ARPES) system [Fig. 1(c)]. Our goal is to grow ultra-thin and thin films of topological materials to demonstrate the quantum anomalous Hall effect (QAH) at room temperature. ARPES is a useful tool for studying the electronic structure of surfaces of topological materials.

We have also installed a scanning probe microscope (SPM) for the characterization of the fabricated films at temperatures between 30 and 650 K [Fig. 1(d)]. The UHV-SPM system combines the functionalities of a scanning tunnelling microscope (STM) and an atomic force microscope (AFM) and consists of a flexible two-level preparation chamber.

All the above-described UHV systems are connected via a long transfer line under high vacuum. The samples can be transferred from one deposition system to another or characterized *in situ* using SPM and ARPES without exposure to ambient conditions.

Furthermore, we have installed a four-cycle diffractometer to study the structure, thickness, and epitaxy of our films. Finally, at the beginning of 2018, we installed an AFM system combined with a variable magnetic field module to study the topography and magnetic state of our films at room temperature.

Loss of anisotropy in ultrathin strained Mn-Ga films

Our first project was the study of $L1_0$ Mn-Ga films in collaboration with the IBM Research Center, Almaden, where we investigated the magnetization and loss of anisotropy in ultrathin strained and unstrained Mn-Ga films at room temperature [1]. Mn-Ga films of two different compositions, one of which was doped with Co, were grown on Cr-buffered MgO (001) substrates. Films with thicknesses below 10 nm are highly strained and the tetragonal distortion, in terms of the c/a ratio vs. thickness plot, was studied depending on composition [Fig.-2]. The perpendicular magnetic anisotropy is drastically reduced with decreasing thickness and increasing strain. These findings should be considered for films thicker than 20 nm. The strain can effectively be reduced by introducing an additional Pt buffer, thus maintaining high perpendicular magnetic anisotropy for thicknesses as low as 6 nm. Our results are highly relevant for downscaling Mn-Ga films to be implemented in spintronic devices.

Compensated ferrimagnetic $Mn_{3-x}Pt_xGa$ Films

The first novel Heusler compound fabricated in our laboratory was Mn-Pt-Ga. In this pioneering study, we propose that a fully compensated ferrimagnetic (CFI) Heusler compound can be obtained by tuning the magnetization of the two sublattices in tetragonal Mn_3Ga [Fig. 3(a)], which in turn is achieved by changes in composition. Density functional theory calculations helped us identify the needed compositional variations for Mn-Y-Ga (Y = Pt, Au, Ag), which are experimentally confirmed for Y = Pt. Specifically, we have demonstrated that magnetic anisotropy in the tetragonal $Mn_{3-x}Pt_xGa$ thin films can be successfully tuned to obtain a compensated magnetic state [2]. By partially replacing Mn in the Mn–Mn plane by Pt, the effective moment in this plane can be reduced to match that in the Mn-Ga plane

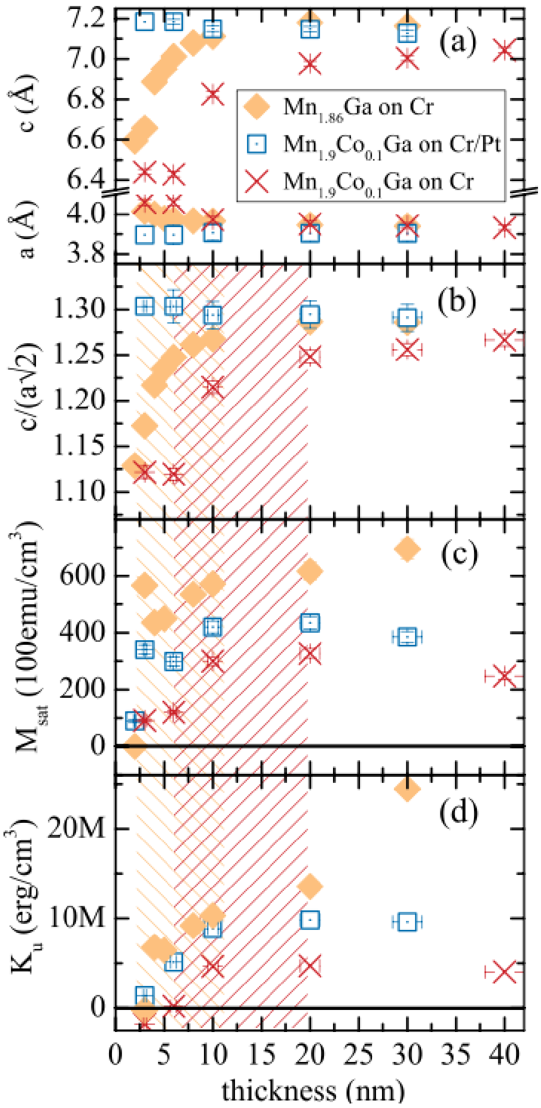

Fig.-2: (a) Lattice constants, (b) tetragonality, (c) saturation magnetization, and (d) effective anisotropy of the different Mn-Ga films.

[Fig. 3(b)], giving rise to a fully compensated magnetic state. With increasing Pt concentration, the magnetization decreases and becomes nearly zero at x = 0.65 [Fig. 3(c)]. This fully compensated film with composition $Mn_{2.35}Pt_{0.65}Ga$ has a magnetization close to zero over the entire temperature range studied. The change in the sign of the anomalous Hall effect above the compensation point is further proof of the compensation state obtained via Pt substitution.

Furthermore, the bilayer formed from compensated/ uncompensated $Mn_{3-x}Pt_xGa$ layers is used to accomplish exchange bias (EB) at temperatures up to room temperature. The exchange bias field (H_{EB}) increases with decreasing temperature and reaches 0.22 T at 5 K and a nonzero value of $\mu_0 H_{EB} \approx 1.5$ mT is obtained at 300 K.

These findings suggest that a single layer of the compensated tetragonal thin film could replace the synthetic antiferromagnet, which is widely used in field-sensing spintronic devices and which has been recently shown to produce highly efficient current-driven motion of domain walls in the racetrack memory device. The achievement of EB up to room temperature in the

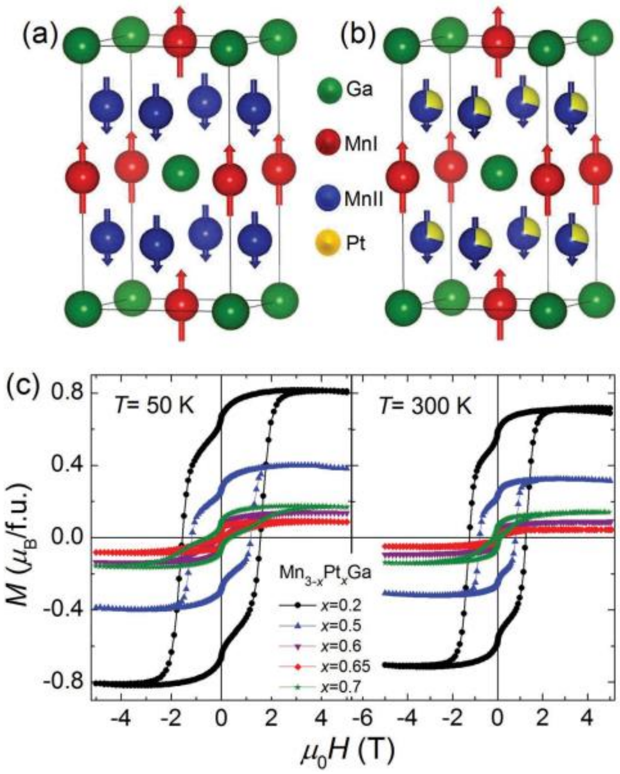

Fig.-3: (a) Crystal and magnetic structure of Mn_3Ga. (b) Crystal and magnetic structure of $Mn_{2.4}Pt_{0.6}Ga$. (c) Out-of-plane magnetization hysteresis curves of $Mn_{3-x}Pt_xGa$ thin films measured at 50 K and 300 K.

bilayer films studied here is an important step toward practical applications. The flexible nature of Heusler compounds, which helps achieve tunable magnetizations and anisotropies within closely matched materials, provides a new direction to the growing field of antiferromagnetic spintronics. Our goal is to obtain electrical switching between two stable configurations combined with an electrical read-out in fully compensated Mn-Pt-Ga thin film devices.

Tunable magnetic properties in $Mn_{2.7-x}Fe_xGa_{1.3}$ films with perpendicular magnetic anisotropy

The replacement of rare earth elements in permanent magnets (PMs) is desirable, due to the volatility of their prices and the strategic issues associated with them. New magnets with mid-range performance are required, where novel hard magnetic materials can bridge the gap between low-cost hard ferrites and expensive rare-earth-based magnets. Mn-based Heusler compounds with tetragonal distortion are promising hard magnetic materials due to their large magnetocrystalline anisotropy, large coercivity, and high Curie temperature.

We have studied the structural and magnetic properties of $Mn_{2.7-x}Fe_xGa_{1.3}$ films (x = 0 – 1.2) heteroepitaxially grown on MgO (100) substrates [3]. The films were crystallized in the tetragonal $D0_{22}$ structure with the preferred orientation being (001). Upon increasing the Fe content x, both lattice parameters *c* and *a* decrease, while the tetragonality (c/a ratio) increases slightly, which implies that tetragonal distortion is not influenced significantly by Fe content. The high quality of our films was also confirmed by in-plane XRD and TEM analyses. TEM analysis revealed that the films are continuous and chemically homogeneous, and confirmed their heteroepitaxial growth.

The films show remarkably tunable magnetic properties depending on the Fe content, with M_s varying from 290 to 570 kA/m and $\mu_0 H_c$ varying from 0.95 to 0.3 T [Fig. 4(a)]. At the same time, large effective anisotropy (K_u > 1.6 kJ/m^3) can be achieved. Fe substitution leads to significant enhancement in the energy product $(BH)_{max}$ [Fig. 4(b)], which is a key figure of merit for permanent magnets. The $(BH)_{max}$ obtained with the optimized Fe content (37 kJ/m^3) is larger than other tetragonal Mn-based alloys, such as Mn_xGa films (21 or 27 kJ/m^3), MnAl films (35 kJ/m^3) and melt-spun $HfCo_7$ (34 kJ/m^3). The combination of large $K_u \geq 1.4$ MJ/m^3 and high $(BH)_{max}$ up to 37 kJ/m^3 makes these films candidate materials for designing mid-range permanent magnets.

Another short-term goal is to integrate these Mn-Fe-Ga films with tunable magnetic properties to spintronic devices. These novel characteristics will enable us to build a full Heusler giant magnetoresistance (GMR) or tunnelling magnetoresistance (TMR) stack with advantages of matching lattice parameters and matching bands at the Fermi level, due to the flexibility within the tetragonal Heusler structure. For example, a reference layer, comprising a hard magnetic Fe-depleted Mn-Fe-Ga Heusler, could be combined with a free layer of a Fe-rich composition, where both layers show PMA.

Topological Hall effect in Mn_2RhSn films

Recently, noncollinear magnetic structures have attracted much attention due to their novel transport properties. Mn-based Heusler compounds with multiple magnetic sublattices are excellent candidates to provide suitable platform for the design of anisotropic and acentric room-temperature magnets, and therefore, the formation of chiral spin structures. These Heusler compounds with noncollinear spin structures might be promising candidates for skyrmions. In a collaboration with MPI Halle, we have studied Mn_2RhSn thin films [4]. High-quality epitaxial Mn_2RhSn thin films have been prepared by high-temperature growth on MgO (001) substrates in our laboratory. The films are tetragonally distorted with easy magnetization along the *c* axis. Moreover, the magnitude of the anomalous Hall effect increases strongly below the Curie point near room temperature. Theoretical calculations of the anomalous Hall conductivity were performed by deriving the Berry curvature from the electronic structure of perfectly ordered Mn_2RhSn. Consistent with these calculations, the sign of the anomalous Hall conductivity is negative, although the measured value is considerably smaller than the calculated value. We attribute this difference to small deviations in stoichiometry and chemical ordering. We have also found evidence for a topological Hall resistivity of ~ 50 nΩ cm, which is ~5% of the anomalous Hall effect, at temperatures below 100 K [Fig. 5]. The topological Hall effect signifies the presence of a chiral magnetic structure that evolves from the noncollinear magnetic structure of Mn_2RhSn.

We intend to expand our study on more tetragonal Heusler compounds, like $Mn_{2-x}PtSn$, which are theoretically predicted to show noncollinear spin structure. The first encouraging results were obtained for bulk materials of similar compounds, which show the presence of antiskyrmions. A long-term goal is the realization of a new class of skyrmions, called antiferromagnetic skyrmions, which are tiny magnetic objects with no net magnetic moment. Skyrmions in high-moment magnetic materials are generally too large for spintronics applications. On the other hand,

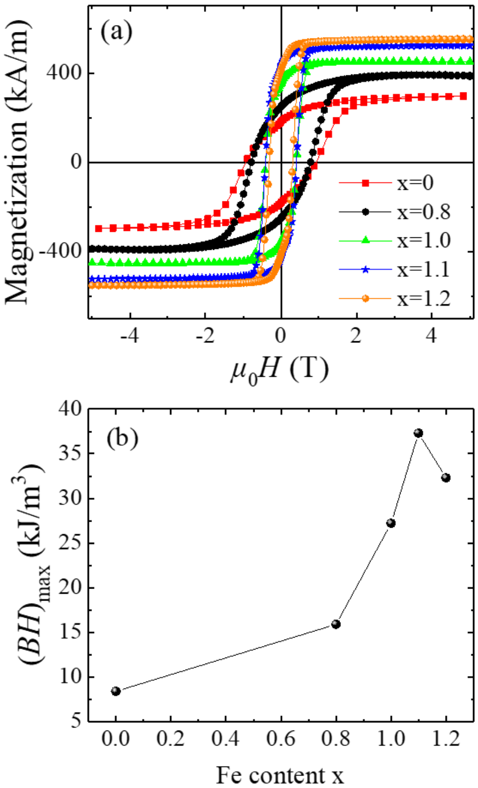

Fig.-4: (a) Typical out-of-plane magnetization curves and (b) $(BH)_{max}$ values of $Mn_{2.7-x}Fe_xGa_{1.3}$ films with different Fe contents x.

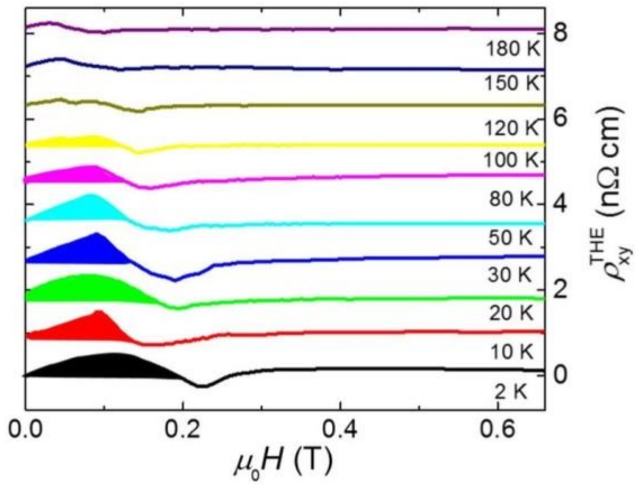

Fig.-5: ρ^{THE} at a few selected temperatures in the range 2–290 K. ρ^{THE} is zero for all temperatures above 100 K. Upon cooling, ρ^{THE} appears at 100 K and increases until the lowest measured temperature is obtained 2 K.

antiferromagnetic skyrmions are more difficult to observe, but have unprecedented small diameters and unique properties that make them interesting for various future applications.

Noncollinear antiferromgnetic Mn_3Sn films

Antiferromagnetic (AF) materials have attracted new-found research interest due to their potential applications in spintronic devices operated without net magnetization. Noncollinear AFs are especially promising, with the topological character of their chiral spin texture yielding novel electrotransport, thermoelectric, and magneto-optical phenomena. Such materials with hexagonal structures, e.g. Mn_3Sn, are particularly interesting because they show very large anomalous Hall effect (AHE), although their net magnetization is almost zero, driven by the non-vanishing Berry curvature arising from their chiral spin structure. Until now, the only reports on these materials have focused on bulk polycrystalline or single crystal samples.

This paper describes an original work in which we demonstrate, for the first time, the growth of Mn_3Sn thin films [5]. Mn_3Sn films with different thicknesses were heteroepitaxially grown on ZrO_2 substrates with Ru underlayer. We find that the films crystallize in the hexagonal $D0_{19}$ structure with the preferred orientation being (0001) and the *c* axis being normal to the film plane. TEM analysis confirms the crystal structure of the films and reveals a nearly perfect heteroepitaxy of the epilayers [Fig. 6 (a)]. The Mn_3Sn films exhibit small net magnetization with in-plane anisotropy. The weak ferromagnetism in this class of materials is useful, because it allows control of their transport properties by switching the moment orientation of the chiral spin structure using a small electric field. We have also studied the exchange bias effect in a Mn_3Sn/Py bilayer, in which exchange bias fields up to $\mu_0 H_{EB}$ = 13 mT were achieved [Fig. 6 (b)]. The exchange bias not only confirms the antiferromagnetic nature of the Mn_3Sn films, but can also be used to investigate spin transfer phenomena applicable to the developing field of antiferromagnetic spintronics.

Such films are anticipated to have a major impact in the community and measurements in thin-film samples will allow continued exploration of new antiferromagnetic structures. Lithographically patterned devices could be used to study, for example, the anomalous Hall and spin Hall effects caused by Berry curvature, spin orbit torques (SOT) in exchange-biased Mn_3Sn/ferromagnet heterostructures, or thermoelectric and magneto-optical phenomena like the Nernst and Kerr effects.

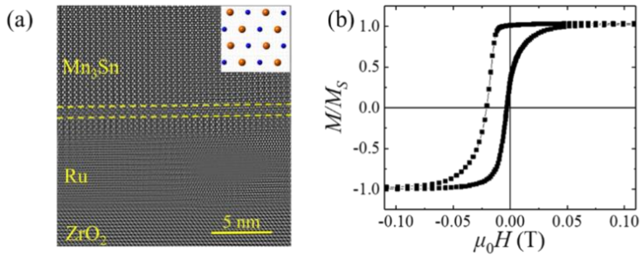

Fig.-6: (a) Cross-section HRTEM image of Mn_3Sn film and (b) in-plane magnetization hysteresis loops of the Mn_3Sn(40 nm)/Py(5 nm) bilayer at 5 K after 1-T field cooling.

Conclusions

Mn-Y-Ga films with tailored magnetic properties can be fabricated by growing them on appropriate substrate and underlayer or by substitution of Mn with other transitions metals (Pt or Fe). These tetragonal Heusler compounds range from compensated ferrimagnets for spintronic applications to high-magnetization materials for permanent magnet applications. Furthermore, we found evidence of THE in Mn_2RhSn, which signifies the presence of a chiral magnetic structure. We demonstrate, for the first time, the epitaxial growth of hexagonal noncollinear antiferromagnetic Mn_3Sn thin films. Our future plans involve integration of the above-mentioned materials into functional devices. We also intend to expand our work in the field of topological and antiferromagnetic materials, and understand the underlying physics.

External Cooperation Partners

S. S. P. Parkin (MPI of Microstructure Physics, Halle, Germany), J. M. Taylor (MPI of Microstructure Physics, Halle, Germany)

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