International Journal of Advanced Research and Development
ISSN: 2455-4030
Impact Factor: RJIF 5.24
www.advancedjournal.com
Volume 2; Issue 5; September 2017; Page No. 345-349

The evolution of the heusler compounds within the framework of emerging trends in condensed matter physics

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Abstract

Heusler compounds are an extraordinary class of materials having a wide range multi-functional properties including halfmetallic ferromagnets, antiferromagnetism, multi-ferroics, shape memory alloys, and tunable topological insulators, energy technologies, and magneto-caloric applications. Heusler compounds are a huge family of binary, ternary and quaternary compounds. The widespread tunability of the Heusler compounds through chemical substitutions and structural pattern make these compounds especially interesting. Here in this article we take a glimpse of major developments in the field of Heusler compounds in the historical perspective. In the recent period, a variety of properties derived from topology which includes: topological metals with Weyl and Dirac points; a range of non-collinear spin textures including the very recent observation of skyrmions at room temperature; and giant anomalous Hall effects in antiferromagnetic Heusler compounds with triangular magnetic structures were observed. An outline of these major developments are given in case of Heusler materials within the context of recent emerging trends in condensed matter physics.

Keywords: tetragonal heusler alloys, topological insulators, weyl points, skyrmions, non-collinear spin structures

1. Introduction: Discovery of Ferromagnetic materials from Non Magnetic elements

In 1903, Friedrich Heusler announced the discovery of a ferromagnetic material at room temperature, formed from the elements, Cu, Mn, and Al that show no magnetism at room temperature. The structure of the compound that Heusler prepared was also unknown in 1903, although Heusler realized that a chemical compound must have been formed. Heusler compounds form a special class of materials, that are located at the border between compounds and alloys, and which combine features of both, namely, the chemical stability of a covalent lattice from which the Heusler compound is constructed, while single sites within the lattice can be substituted by different species and thereby behave as alloys. In a nutshell, covalency and tunability best describe the uniqueness of these materials. In 1934 Otto Heusler, Heusler's son [1], and Bradley [2], determined the crystal structure of Cu_2MnAl. The Heusler structure can be described as four interpenetrating fcc sublattices, of which two are formed from the same element. After Heuslers discovery, Nowotny and Juza, published outcome on a different group of materials, all main-group element compounds, that are nowadays referred to as Nowotny-Juza Phases. The connection between the Nowotny-Juza phases and the Heusler compounds, was established by L. Castelliz, who first synthesized NiMnSb [3, 4]. The Nowotny-Juza-Phases are now described as half - Heusler compounds in which one of the four fcc sublattices of the full Heusler is empty. By filling this fourth sub-lattice a series of compounds can be formed between half and full Heuslers, which we can describe as XYZ and X_2Y Z, respectively, where X, Y are transition metal elements and Z is a main group element. The full Heusler compounds have several variants including the inverse structure in which one of the X elements is swapped with Y, and quaternary Heuslers in which one of the X is replaced by a fourth distinct element. Thus, it is clear that the Heusler name now refers to a broad family of compounds. Furthemore, all of these variants can be subjected to various structural distortions including a tetragonal elongation or compression along one of the cubic crystal axes, or a distortion along the [111] that leads to an hexagonal structure [5]. The three main prototypical Heusler stoichiometric structural types, namely the half, regular and inverse are shown in Figure 1

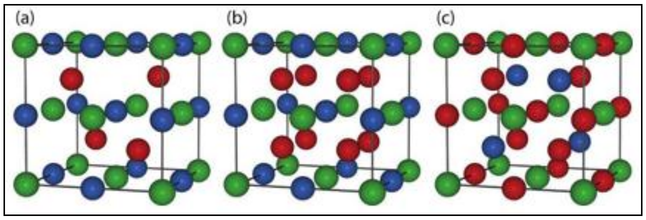

Fig 1: The three prototypical Heusler structures, wherein X atoms are represented by red spheres, Y atoms by blue/light blue and Z atoms by green spheres: (a) half -Heusler, (b) regular Heusler, (c) inverse Heusler structure.

2. Co-based Half-metallic Ferromagnets

The Co_2-based Heusler compounds were found to be half-metallic ferromagnetic (HMF). Half-metallic ferromagnets, exhibit metallic behavior in one spin channel and an insulating behavior in the other, and thus are of great interest because they intrinsically should have fully spin polarized electronic states at the Fermi energy [6]. Such materials are also of great interest for spintronic applications, for example, as magnetic electrodes in magnetic tunnel junctions. In 1983, Kubler studied the formation and coupling of the magnetic moments in Co_2MnSn and similar Co based alloys, and remarked how their spin magnetic moments follow a linear behavior with the number of valence electrons. These findings were soon put into context, and chemical trends were established of which the backbone is the Slater-Pauling (SP) rule. The Slater-Pauling rule is a simple yet powerful tool for the prediction of half-metallic ferromagnets. The theory of Heusler alloys showed how the SP-rule could be described using molecular orbital coupling schemes and symmetry analysis. The use of half-metallic ferromagnets in spin-valve structures lead to large magneto resistance, from which the field of spintronics came into limelight. In 2014, spin-polarized photoemission experiments conducted by Jourdan *et al.*, supported by theoretical calculations, provided proof of half-metallic ferromagnetism in Co_2-based Heusler alloys [7].

3. Mn-based Half-metallic Ferrimagnets

The discovery of the tetragonally distorted Mn-based Heusler compounds attracted a lot of attention. The most prominent member was Mn_3Ga [8], whose potential for spintronic applications was recognized in the late 2000s. Mn-based materials received attention in the late 2000s, when ferrimagnetic Heusler compounds were proposed as free-magnetic layers for spin-valve structures, such as, for example, magnetic tunnel junctions, in which a spin-polarized current is used to trigger the switching of the free-layer. In theory Mn_3Ga crystallizes in the centrosymmetric space group 225 (prototype BiF_3) showing compensated ferrimagnetism [9]. It is found in various studies, that systems incorporating early transition metals as Y elements prefer the regular order, while choosing late transition metals the inverse order is preferred [10], where the early and late transition metals are separated by Mn. This study is known as Burch's rule [10]. In experimental studies, it was found that bulk Mn_3Ga stabilize in a tetragonal lattice. In Half Metallic Ferromagnets (HMFs) we can obtain 100% spin polarization, but along with it HMFs typically produce large magnetic dipole fields that can hinder the performance of spintronic devices that contain them. Therefore, materials that display 100% spin polarization but with very low or, even zero net magnetic moment are of special interest, both technologically as well as scientifically. According to the Slater-Pauling [11] rule Heusler compounds with 24 valence electrons should exhibit a zero net magnetic moment. The search for compensated ferrimagnetic Heusler compounds with 24 valence electrons has been focussed on the Mn-based Heusler compounds since the Mn atoms sit in an octahedral environment that results in a strongly localized magnetic moment. An example of a 24 valence electron based Heusler compound is Mn_3Ga, which is predicted to display half-metallicity in the cubic $L2_1$ structure.

4. Spin-gapless Semiconductors

Spin Gapless Semiconductors (SGSs) were originally proposed by Wang in 2008[12] and are formed when a gapless semi-conductor is doped with magnetic ions. The fcc-type band structure, that is an inherent feature of Heusler compounds, allows for this peculiar electronic feature. A simplified molecular orbital diagram shows how a sequence of doubly and triply degenerate states are successively filled for 18, 21, 24 and 26 valence electrons also the fermi energy touches the edges of the conduction and valence bands[13]. Synthesized and characterized by Ouardi *et al.*, Mn_2CoAl show a peculiar electronic structure, that was termed a spin-gapless semiconducting state [14], which depicts the band-gap in the minority spin-channel, accompanied by an indirect zero-band-gap in the majority spin-channel. SGSs are expected to find applications in spintronic devices, especially semiconductor spintronics as the electronic excitations in the gapless state do not require a threshold energy, but the carriers, whether holes or electrons, remain completely spin-polarized. These materials thus may serve, for example, as spin-injectors.

Table 1: Some examplary spin-gapless semiconductors, exclusively crystallizing in space group 216.

NV	Materials				
21	FeVTiSi	CoVScSi	FeCrScSi	FeMnScAl	
26	Mn_2CoAl	CoFeCrAl	CoMnCrSi	CoFeVSi	FeMnCrSb
28	CoFeMnSi				

5. Spin-Transfer Torque Applications and Tetragonal Structure

Tetragonal Heusler compounds were described by Suits in the 1970s, but major research began only in the 1990s when research focused on reversible structural phase transitions from cubic to tetragonal lattices, i.e. from austenite to martensite phase. Shape memory materials rely on this transition. The latest advances in tetragonal Heusler compounds research began with the realization of the large magneto crystalline anisotropy of Mn_3Ga [8] by Balke *et al.*, in spintronic applications. The tetragonal distortion induces a preferred orientation of the magnetization towards the in-plane or out of plane directions (Figure 2).

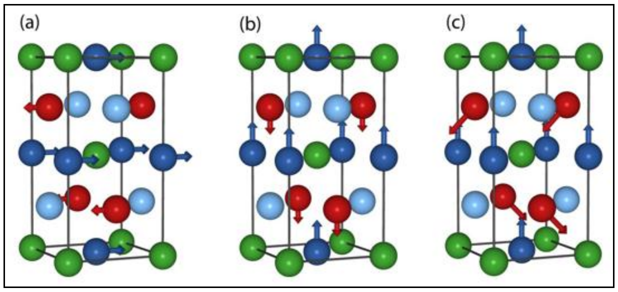

Fig 2: A set of generalized tetragonal Heusler structures (spacegroup 119) are shown depicting the four Wyckoff -positions, that are to be occupied according to Mn (red, blue), Y (light blue), Ga (green, Z) to achieve the inverse-type order; (a) In-plane ($K_U < 0$) and (b) out-of-plane ($K_U > 0$) orientation of the magnetization. (c) Exemplary non-collinear order for competing in-plane and out-of-plane anisotropy contribution.

The Perpendicular magnetic anisotropy, with the magnetization pointing perpendicular to the film surface, is desired for high density memory and storage devices to guarantee thermal stability. Magnetic memory bits can be switched by either magnetic field or via spin-polarized currents through the concept of spin-transfer-torque. Spin-transfer-torque (STT) refers to a torque that is exerted perpendicular to the magnetization, leading to a precessing magnetic moment, that finally switches to the opposite direction. The Slonczewski-Berger equation [15] describes the dependence of the switching current density on materials properties such as magnetic moment M, anisotropy constant K_U and Gilbert damping parameter. As the STT technology requires materials with small switching currents while guaranteeing data retention/thermal stability, the Mn-based Heusler compounds have been explored in searches for new tetragonal phases.

6. Non-collinear spin structures

In recent years interest has been shown in those magnetic materials which exhibit non-collinear spin structures. One of the most exciting uses of non-collinear spin structure is the motion of chiral domain walls using spin polarized currents that generate a large chiral spin-orbit torques to Drive the domain walls[16]. This current driven back and forth motion of the domain walls inside a magnetic nano-wire forms a novel high density, high performance, solid-state storage memory device - Racetrack Memory - that was first proposed by Parkin *et al.* in 2002 and which has the potential to even replace conventional magnetic data storage[17]. The domain wall can be replaced by other non-collinear spin textures such as skyrmions [18]. In this regard, Heusler materials are perfect candidates to modify the magnetic state via competing exchange interactions between different sub-lattices [19]. In addition, most of the Mn-based Heusler materials exhibit a non-centrosymmetric crystal structure, which is necessary for the realization of the Dzyaloshinskii-Moriya (DM) inter-action that leads to the formation of skyrmions [20]. Theoretical calculations also show that the present class of materials with accentric crystal structures should give rise to the formation of skyrmions under appropriate conditions. However, the experimental finding of skyrmions in bulk materials is still awaited. Recently, it has been shown that the thin films of Mn_2RhSn exhibit a considerable topological Hall Effect (THE) as shown in fig.3.

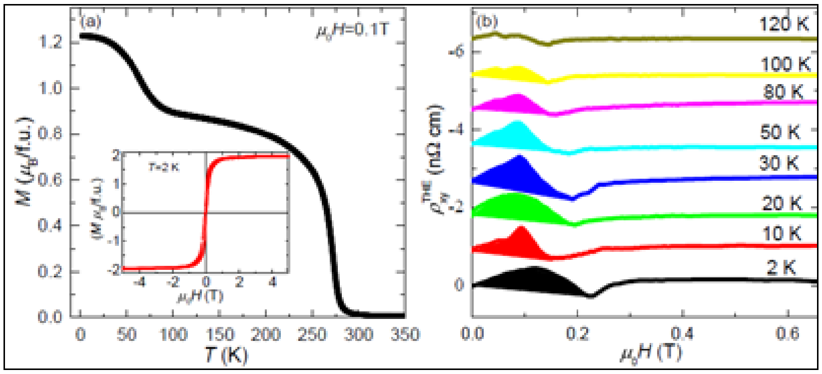

Fig 3: (a) M (T) curve measured in a field of 0:1 T for the Heusler tetragonal compound Mn_2RhSn. The inset shows M (H) loop measured at 2 K. (b) Topological Hall effect (ρ^T_{XY}) at different temperatures for the Mn_2RhSn thin film.

7. Quantum Spin Hall (QSH) state and Weyl semimetal (WSM)

The prediction of the Quantum Spin Hall (QSH) state [21] triggered remarkable interest in the condensed matter community. It not only lay the basis for a completely new field of research, but the use and application of topological concepts in a wide range of condensed matter research gained much notice. The QSH state was then realized in a HgTe/CdTe quantum well structure [22] materials that crystallize in the same space group (F 43m) as the XZ binary semiconductors (HgTe, CdTe, ZnS) include diamond and the Half-Heusler compounds. Half-Heusler semiconductors with 8 or 18 VEs exist with a wide range of band-gaps [23], and the possibility to find half -Heuslers with a topologically nontrivial state was quickly realized [24]. Chadov *et al.* could show that zero-gap semiconductors within the half -Heusler family exhibit similar features, and an odd number of band inversions is observed in some systems. The zero-gap state, that is a prerequisite for topological insulators, is also a useful feature for thermoelectric materials. Consequently, a connection between topological insulators, the zero gap-state, and thermoelectric performance is deep [25]. Weyl semimetals (WSM) are a class of topological semimetals, beyond topological insulators, where the conduction and valence bands cross in the vicinity of the Fermi level [26]. The crossing points are called Weyl points that are separated in momentum space. These Weyl points, which act as magnetic monopoles in momentum space, always appear in pairs and are connected by an unusual surface state termed the Fermi arc [27].

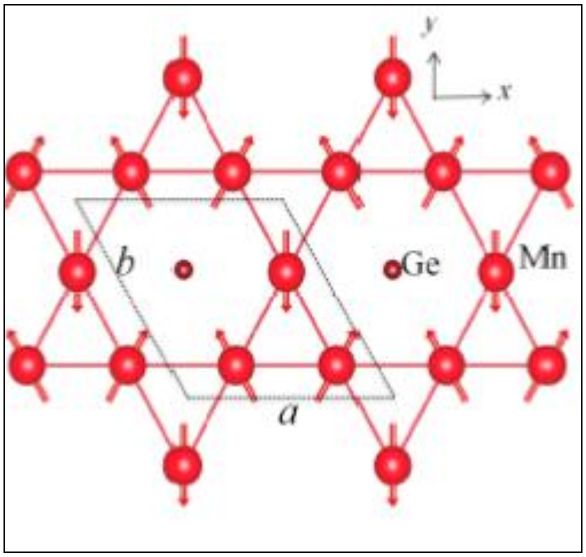

Fig 4: Triangular non-collinear antiferromagnetic configuration for hexagonal Mn_3Ge.

Many of these Mn-based Heusler materials also exhibit a stable hexagonal crystal structure [28]. By varying the preparation conditions cubic, tetragonal and hexagonal phase can be stabilized in one system [29]. It turns out that most of the hexagonal materials display an antiferromagnetic ordering. Neutron diffraction studies of the hexagonal Mn_3Sn and Mn_3Ge compounds reveal the presence of a non-collinear antiferromagnetic ordering [30] as shown in fig.4. Recent theoretical works have demonstrated that materials with non-collinear antiferromagnetic structures and with some special symmetries should exhibit a large anomalous Hall effect (AHE) [31]. Thus, the result of such a large AHE in the antiferromagnetic Mn_3Ge and Mn_3Sn can be explored further for their possible use in antiferromagnetic spintronics.

8. Summary

The Heusler compounds were discovered more than a century ago and yet fascinating new properties continue to emerge even today. The discovery of combinations of essentially non-magnetic elements that form ferromagnetic compounds well above room temperature was a remarkable finding. The theoretical prediction and experimental finding of half-metallicity in certain classes of Heusler materials was another major discovery that lead several decades later to the finding of giant value of tunneling magneto resistance. More complex magnetic structures in which the magnetic moments are aligned non-collinearly have been discovered in a range of Heusler compounds. An entirely new world of Heusler compounds was opened by the application of newly developed ideas of topology that led to the prediction and later experimental proof of topological insulators and, more recently, Weyl semi-metallic Heuslers. So we can say that the prospects of Heusler compounds are very bright.

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