International Journal of Enhanced Research in Science, Technology & Engineering
ISSN: 2319-7463, Vol. 5 Issue 11, November-2016

Structural & Magnetic Charateristics of Heusler Compounds and Alloys

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ABSTRACT

This paper focuses on the structural and physical properties of Heusler compounds and alloys for spintronic and thermoelectric applications. Heusler compounds are a significant class of intermetallic materials with 1:1:1 or 2:1:1 composition comprising more than 1500 members. They are still a field of active research after more than a century of their discovery. New properties and potential fields of applications emerge constantly; the prediction of topological insulators is the most recent example. The properties of many Heusler compounds can easily be predicted by the valence electron count. Their flexible electronic structure offers a toolbox which allows the realization of demanded functionalities within one ternary compound. Devices based on multifunctional properties, i.e. the combination of two or more functions such as superconductivity and topological edge states will revolutionize technological applications. Thus, great interest has been attracted in the fields of thermoelectrics and spintronics research. The wide range of their multifunctional properties is also reflected in extraordinary magneto-optical, magnetoelectronic, and magnetocaloric properties. Here, we give a comprehensive overview and a prospective on the magnetic properties of Heusler materials.

Keywords: heusler, compound, alloys, magnetic, characteristics, structural.

INTRODUCTION

The discovery of Heusler alloys dates back to 1903 when Heusler reported that the addition of sp elements (Al, In, Sn, Sb or Bi) turn Cu-Mn alloy into a ferromagnetic material even though the alloy contains none of the ferromagnetic elements. The basic understanding of crystal structure and composition of these alloys remained unknown for a long time. In 1929 X-ray measurements of Potter on Cu-Mn-Al alloy revealed that all constituents of this system was ordered on an fcc super lattice. Bradley and Rodgers investigated Cu-Mn-Al system in detail using X-ray and anomalous scattering. The authors established a relationship between composition, chemical order and magnetic properties.

Heusler compounds are an interesting class of compounds with wide-ranging and tunable properties. They are intermetallic compounds with the general composition X2YZ, where X and Y are transition or rare-earth metals and Z is a main-group element. Heusler compounds include half-metallic ferri- and ferromagnetic materials, shape memory alloys, topological insulators, high potential magnetocalorics, and materials for spintronic applications.

The addition of the spin degree of freedom to the conventional electronic devices based on semiconductors has several advantages like non-volatility, increased data processing speed, decreased electric power consumption and increased integration densities. In the half-metallic materials the two spin bands show a completely different behavior. The majority spin band shows the typical metallic behavior, and the minority spin band exhibits a semiconducting behavior with a gap at the Fermi level. The existence of the gap leads to 100% spin-polarization at the Fermi level and thus a fully spinpolarised current should be feasible in these compounds maximizing the efficiency of magnetoelectronic devices.

The family of Heusler compounds, named after von Heusler, incorporates a huge number of magnetic members exhibiting diverse magnetic phenomena like itinerant and localized magnetism, antiferromagnetism, helimagnetism, Pauli paramagnetism or heavy-fermionic behavior. The first Heusler alloys studied were crystallizing in the L21 structure which consists of 4 fcc sublattices. Afterwards, it was discovered that it is possible to leave one of the four sublattices unoccupied (C1b structure). The latter compounds are often called half- or semiHeusler compounds or simply Heuslers, while the L21 compounds are known as full-Heusler compounds. The most-well known semi-Heusler compound is NiMnSb.

With the discovery of half-metallic ferromagnetism in NiMnSb and the observation of shape memory effect in Ni2MnGa compound, Heusler alloys received tremendous experimental and theoretical interest. In this chapter we will briefly present the previous experimental and theoretical studies on structural and magnetic properties of Heusler alloys. Also, an overview of the experimental and theoretical studies on exchange coupling will be given.

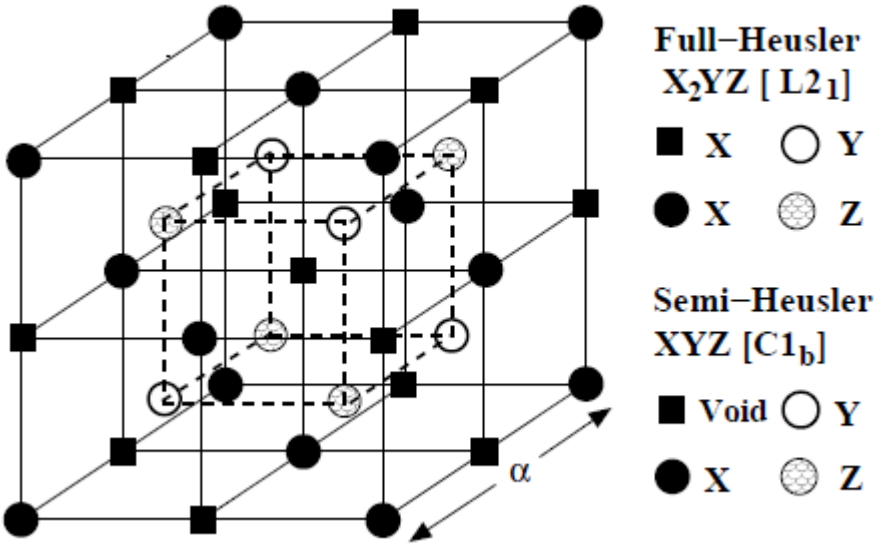

Figure 1: C1b and L21 structures adapted by the half- and full-Heusler alloys. The lattice is consisted of 4 interpenetrating f.c.c. lattices. In the case of the half-Heusler alloys (XYZ) one of the four sublattices is vacant.

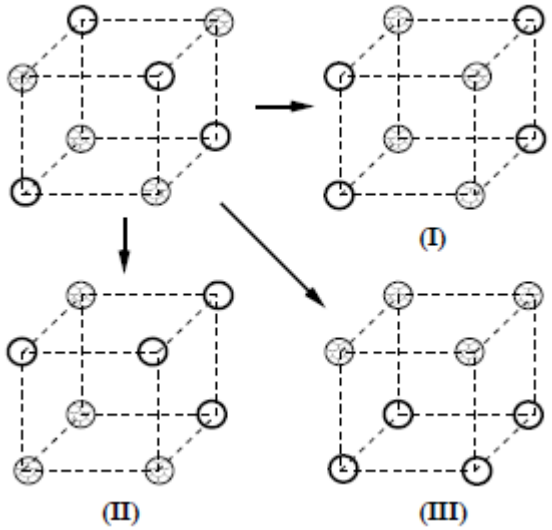

Figure 2: Three possible configuration of the occupation of Y and Z sublattices in B2-type disordered structure

RELATED WORK

In literature they are named either half-metallic fully-compensated ferrimagnets (HM-FCF) [207] or half-metallic antiferromagnets (HMAs) which was the initial term used by van Leuken and de Groot when studying the semi-Heusler compound CrMnSb in 1995

In 1983 de Groot and his collaborators showed using first-principles electronic structure calculations that this compound is in reality half-metallic, i.e. the minority band is semiconducting with a gap at the Fermi level EF, leading to 100% spin polarization at EF.

Bowen et al. have observed such a current in trilayers made up of half-metallic La0.7Sr0.3MnO3 as electrodes and SrO3 as a barrier.

Picozzi et al. and Galanakis et al. have shown that the interfaces of such structures are not half-metallic. Although, the cubic structure and ferromagnetism in these compounds is particular stable, it has been shown that defects and vacancies

can lead to loss of the halfmetallic character, although a small degree of disorder may lead to halfmetallic ferrimagnetism instead of ferromagnetism.

Li et al. have shown that also Mn3Al which has 24 valence electrons is a HF-FCF and when Cr was substituted for Mn, Cr3Al was found to have a total spin-magnetic moment of −3μB in accordance to the Slater-Pauling rule for half-metallic Heusler compounds. Doping of Mn3Al with vanadium leads to the loss of half-metallicity.

Spintronics emerged from discoveries in the 1980s concerning spin-dependent electron transport phenomena in solid-state devices. This includes the observation of spin-polarized electron injection from a ferromagnetic metal to a normal metal by Johnson and Silsbee and the discovery of giant magnetoresistance independently by Albert Fert et al. and Peter Grünberg et al.

The origins of spintronics can be traced to the ferromagnet/superconductor tunneling experiments pioneered by Meservey and Tedrow and initial experiments on magnetic tunnel junctions by Julliere in the 1970s. The use of semiconductors for spintronics began with the theoretical proposal of a spin field-effect-transistor by Datta and Das in 1990 and of the electric dipole spin resonance by Rashba in 1960.

Although gapless-semiconductors are well known in literature, it was not until 2008, that Wang proposed that the doping of PbPdO2, a gapless semiconductor, with transition metal atoms would lead to a spin gapless semiconductor. Experimental confirmation was offered in 2014 by Kim and collaborators who studied pollycrystalline films of Mn and Co doped PbPdO2.

In 2008 Liu and collaborators synthesized Mn2CoAl using an arc-melting technique and found that it adopted the lattice structure of inverse full-Heuslers with a lattice constant of 5.8388 Å and a total spin magnetic moment of 1.95 μB per formula unit.

The spin-gapless semiconducting character of Ti2MnAl was also confirmed by Jia et al. Wollman et al. confirmed the conclusion of Meinert et al. that direct exchange interactions are responsible for the magnetic order in Mn2CoAl studying a wide range of Mn2-based Heusler compounds and predicted a Curie temperature of 740 K using the spherical approximation. Skaftouros et al. discussed in detail the behavior of the total magnetic moment in inverse Heusler compounds including the spin-gapless materials. Galanakis and collaborators have shown that defects keep the half-metallic character of Mn2CoAl but destroy the spin-gapless semiconducting character. Finally, recent studies on the effect of doping of Mn2CoAl with Co, Cu, V and Ti, as well as the anomalous Hall Effect have appeared in literature.

STRUCTURAL CHARATERISTICS OF HEUSLER COMPOUNDS AND ALLOYS

Heusler alloys are defined as the ternary intermetallic compounds. At the stoichiometric composition, full Heusler alloys (X2YZ) and semi Heusler alloys (XYZ) crystallize in L21 and C1b structures respectively. The elements normally associated with the X, Y and Z are indicated in table1. The unit cell consists of four interpenetrating fcc sublattices with the positions (000) and (1 2 , 1 2 , 1 2) for X, (1 4 , 1 4 , 1 4) for Y and (3 4 , 3 4 , 3 4) for Z atom. The site (1 2 , 1 2 , 1 2) is vacant in semi Heusler compounds. The two structures are closely related with vacant cite. C1b structure can be obtained from L21 one by replacing the half of the X sites in an ordered manner. Consequently, the structure no longer centro-symmetric. In majority of the Heusler alloys Mn element enters as the Y element. The compounds where Mn assumes the X positions are very rare. Up to now, only two systems of this type were studied experimentally: Mn2VAl and Mn2VGa. At the stoichiometric composition, disorder can exist in the form of partial interchange of atoms in different sublattices.

Johnston and Hall proposed a single disordering parameter α to describe the effects of certain types of preferential disorder on the structure amplitudes of alloys of the type X2YZ. For alloys ordered in L21 structure α is defined as the fraction of either Y or Z atoms being not on their correct sites. Partial occupation of Y and Z atoms on each others sublattices leads to L21-B2 type disorder. B2-type structure can be obtained by allowing half of the Y and Z atoms interchange their positions. The ratio of the L21/B2 depends on the heat treatments. Due to smaller interatomic distances in B2-type structure, an antiferromagnetic ordering becomes energetically favorable. At low temperatures several Heusler alloys, e.g. Ni2MnGa, Co2NbSn etc., undergo a martensitic transition from a highly symmetric cubic austenitic to a low symmetry martensitic phase. Unlike atomic order-disorder transitions a martensitic transition is caused by non-diffusional cooperative movement of the atoms in the crystal. It has been suggested that these transitions were driven by a band Jahn Teller mechanism and there has not been any experimental evidence to confirm this conjecture for a long time. Recently the suggested model was confirmed by polarized neutron scattering experiments, where the transfer of magnetic moment from Mn to Ni was found in the martensitic phase of Ni2MnGa.

In the case when the Heusler alloys are magnetic in the martensitic phase, they can exhibit the magnetic shape memory effect (MSM). This occurs especially when the Y constituent is Mn, but other transition elements are also possible. In these alloys, an external magnetic field can induce large strains when applied in the martensitic state.

Y	X	Z	Magnetic order	Crystal structure
V	Mn	Al, Ga	FM*	$L2_1$
	Fe	Al, Ga	FM	$L2_1$
	Fe	Si	PM	$L2_1$
	Co	Al, Ga, Sn	FM	$L2_1$
Cr	Co	Al, Ga	FM	$L2_1$
	Fe	Al, Ga	FM	$L2_1$
Mn	Cu	Al, In, Sn	FM	$L2_1$
	Cu	Sb	AFM	$C1_b$
	Ni	Al	AFM	B2
	Ni	Sb	FM	$C1_b$
	Ni	Al, Ga, In, Sn, Sb	FM	$L2_1$
	Co	Al, Si, Ga, Ge, Sn	FM	$L2_1$
	Co	Sb	FM*	$C1_b$
	Fe	Al, Si	FM	$L2_1$
	Pd	Al	AFM	B2
	Pd	In	AFM	$L2_1$-B2
	Pd	Ge, Sn, Sb	FM	$L2_1$
	Pd	Sb	FM	$C1_b$
	Pd	Te	AFM	$C1_b$
	Rh	Al, Ga, In	FM	B2
	Rh	Ge, Sn, Pb	FM	$L2_1$
	Rh	Sb	FM	$C1_b$
	Ru	Ga	FM	$C1_b$
	Au	Zn, Cu	AFM	B2
	Au	Al, Ga, In	AFM	$L2_1$
	Au	Sb	FM	$C1_b$
	Pt	Al, Ga	AFM	$L2_1$
	Pt	Ga	FM	$C1_b$
	Ir	Al	AFM	$L2_1$
	Ir	Ga	AFM	$C1_b$
Fe	Fe	Al, Si	FM	$D0_3$
	Co	Al, Si, Ga	FM	$L2_1$
Co	Fe	Ga	FM	$L2_1$
Ni	Fe	Al, Ga	PM	$L2_1$

FM*- Ferrimagnetic

Table 1: Composition, magnetic order and crystal structure of Heusler alloys.

MAGNETIC CHARATERISTICS OF HEUSLER COMPOUNDS AND ALLOYS

Heusler alloys possess very interesting magnetic properties. One can study in the same family of alloys a series of interesting diverse magnetic phenomena like itinerant and localized magnetism, antiferromagnetism, helimagnetism, Pauli paramagnetism or heavy-fermionic behavior [50, 51, 52, 53].

Ferromagnets

The majority of the Heusler alloys order ferromagnetically and saturate in weak applied magnetic fields. If the magnetic moment is carried by Mn atoms, as it often is in the alloys X2MnZ, a value close to 4μB is usually observed. Although they are metals, these compounds have localized magnetic properties and are ideal model systems for studying the effects of both atomic disorder and changes in the electron concentration on magnetic properties. In order to reveal the role of the 3d (X) and sp (Z) atoms on magnetic properties of Heusler alloys extensive magnetic and other measurements have been performed on quaternary Heusler alloys [50]. It has been shown that sp electron concentration is primarily important in establishing magnetic properties, influencing both the magnetic moment formation and the type of the

magnetic order. In table 4.1 we present magnetic Heusler alloys containing 3d transition metals (V, Cr, Mn, Fe, Co, Ni) as the Y site and 3d, 4d and 5d elements as the X site.

Antiferromagnets and ferrimagnets

Although the majority of Heusler alloys are ferromagnetic some of them order antiferromagnetically, in particular those compounds containing 3d element in which the magnetic moment is only carried by Mn atoms at Y site. Experimentally antiferromagnetic order is measured both in semi Heusler(in C1b structure) and in full Heusler alloys (in L21 and B2 structure). Antiferromagnetism is more favorable in full Heusler alloys which has B2-type crystal structure due to smaller interatomic Mn-Mn distances. Indeed, antiferromagnetic behavior in several B2-type disordered X2MnZ (X=Ni, Pd; Z=Al, In) Heusler alloys has been reported [50]. The situation is different in semi Heusler alloys. Due to large Mn-Mn distances in C1b structure the antiferromagnetic interaction between Mn atoms is assumed to be mediated intermediate atoms (X or Z). Ferrimagnetic ordering (antiferromagnetic coupling of X and Y atoms) is very rare in Heusler alloys compared to ferromagnetic or antiferromagnetic one. Ferrimagnetism has been detected [50] only in CoMnSb, Mn2VAl and Mn2VGa compounds. Mn2VAl received much experimental attention. The neutron diffraction experiment gave the ferrimagnetic state of compound with Mn magnetic moment of $1.5 \pm 0.3\mu B$ and V moment $-0.9\mu B$ [40].

CONCLUSION

In this paper, the author has discussed over the Structural & Magnetic Characteristics of Heusler Compounds and Alloys. In view of the large separation of the Mn atoms (> 4 ˚A) and available inelastic neutron scattering experiments in Heusler alloys, the electrons of the unfilled Mn 3d shell can presumably be treated as very well localized, so that the 3d electrons belonging to different Mn atoms do not overlap considerably. The ferromagnetism in these systems is thought to arise from an indirect interaction, by way of conduction electrons, between the Mn moments.

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