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I. Galanakis
P. H. Dederichs
(Eds.)

Half-metallic Alloys

Fundamentals and Applications

Springer

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Editors

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Preface

In 1903 Heusler, in his attempt to synthesize new materials for the steel industry, discovered Cu_2MnAl. Thereafter, a whole class of new materials with the same lattice have been successfully grown and they were named after Heusler himself. They attracted considerable attention mainly due to the diversity of the magnetic phenomena which they presented like itinerant and localized magnetism, antiferromagnetism, helimagnetism, Pauli paramagnetism or heavy-fermionic behavior. Recently, the rapid development of the field of magnetoelectronics revived the interest on such materials since some of them where found to possess a newly discovered property, the so-called half-metallicity.

Half-metals are particular ferromagnetic materials, which can be considered as hybrids between metals and semiconductors. The existence of these half-metallic materials was predicted using abinitio calculations by de Groot et al. in 1983. They found that in the Heusler alloy NiMnSb the majority spin band structure shows a metallic behavior, while the minority band structure exhibits a band gap at the Fermi level like in a semiconductor. Due to the gap for one spin direction, electrons at the Fermi level show a 100% spinpolarization.

For a long time such half-metals were considered as exotic materials, interesting, but not important. This completely changed due to the appearance of the new field of magneto or spin electronics. While in conventional electronics the charge of the electrons plays the essential role and the spin is only used for information storage, in the future spin electronics both the charge and the spin will play an equally important role. The development of this field was initiated by the discovery of the giant magnetoresistance effect in 1988 by the groups of Fert in Paris and Grünberg at Jülich. It soon became clear that in such a spin-dependent electronics half-metals can play an important role, since the efficiency of any spin-dependent device will be largest, if the current will be 100% spin polarized. Therefore, half-metals can be considered as the ideal materials for spin electronics.

In the last 10–15 years many materials have been found to be half-metallic. Besides the so-called half-Heusler alloys like NiMnSb a large number of full-Heusler alloys like Co_2MnGe are predicted to be half-metals. Ab-initio calculations also yield half-metallicity for some oxides like CrO_2 and Fe_3O_4

(magnetite), for manganites (e.g. $La_{0.7}Sr_{0.3}MnO_3$), double perovskites (e.g. Sr_2FeReO_6), pyrites (e.g. CoS_2), transition metal chalcogenides (e.g. CrSe) and pnictides (e.g. CrAs) in the zinc-blende or wurtzite structures. Also the much debated diluted magnetic semiconductors belong to this class of materials.

This book is fully devoted to the half-metallic Heusler alloys and the structurally very similar transition metal chalcogenides and pnictides. Heusler alloys are particularly interesting for realistic applications due to their very high Curie temperatures and the similarity between their crystal structure and the zinc-blende structure adopted by the III–V and II–VI compound semiconductors widely used in applications. However, these alloys also offer many problems and challenges for research and applications. Typically, the alloys have a lot of point defects and substitutional disorder. These lead to impurity states in the gap which, due to the high defect concentration, strongly affect the half-metallic properties. Another problem occurs at the interfaces to the semiconductors. Here dangling bond states, i.e. interface states in the minority gap, occur which strongly reduce the spin polarization. Basically, due to these problems it is at present not clear if they can be overcome and if Heusler alloys will be useful materials for spin electronics and also whether they will find applications, e.g. in spin injection, in magnetic tunnel junctions or in GMR sensors.

For these reasons this book summarizes the latest advancements in the understanding and applications of Heusler alloys and related compounds. In Chap. 1 a theoretical study of the electronic and magnetic properties of the Heusler alloys is presented, and in Chap. 2 the effect of defects and interfaces on the properties of these compounds is investigated. Chapter 3 discusses the properties of the spinvalves and Chap. 4 analyzes the magnetic properties of films. Chapters 5 and 6 are devoted on the growth mechanisms of half-Heusler alloys (NiMnSb) and full-Heusler alloys Co_2MnGe. Chapter 7 investigates the phenomena occurring during the creation of surfaces and Chap. 8 the properties of the tunnel junctions with a Heusler alloy as the magnetic electrode. Finally, Chaps. 9 and 10 present a theoretical and experimental investigation of the transition-metal chalcogenides and pnictides which crystallize in a similar structure with the Heusler alloys. We should also note that each chapter is self-contained and can be read independently. The reader is referred to introductions in Chaps. 1 and 3 for a survey of the theoretical and experimental studies on Heusler compounds, while Chap. 9 includes a historical survey of the research on the transition-metal pnictides.

We hope that the book encourages further research on these complex materials leading to successful applications.

Jülich,
May 2005

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Half-Metallicity and Slater-Pauling Behavior in the Ferromagnetic Heusler Alloys

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Abstract. A significant number of the intermetallic Heusler alloys have been predicted to be half-metals. In this contribution we present a study of the basic electronic and magnetic properties of both Heusler families; the so-called half-Heusler alloys like NiMnSb and the the full-Heusler alloys like Co_2MnGe. Based on *ab-initio* results we discuss the origin of the gap which is fundamental for the understanding of their electronic and magnetic properties. We show that the total spin magnetic moment M_t scales linearly with the number of the valence electrons Z_t, such that $M_t = Z_t - 24$ for the full Heuslers and $M_t = Z_t - 18$ for the half Heuslers, thus opening the way to engineer new half-metallic alloys with the desired magnetic properties. Although at the surfaces and interfaces the half-metallic character is in general lost, we show that for compounds with Cr as the metallic element the large enhancement of the Cr surface moment can lead to a high polarization at the surface. Moreover we discuss the role of the spin-orbit coupling, which in principle destroys the half-metallic gap, but in practice only slightly reduces the 100% spin polarization at E_F.

1 Introduction

Half-metallic ferromagnets represent a class of materials which attracted a lot of attention due to their possible applications in spintronics (also known as magnetoelectronics) [1]. Adding the spin degree of freedom to the conventional electronic devices has several advantages like non-volatility, increased data processing speed, decreased electric power consumption and increased integration densities [2]. The current advances in new materials and especially in the half-metals are promising for engineering new spintronic devices in the near future [2]. In these materials the two spin bands show a completely different behavior. While the majority spin band (referred also as spin-up band) shows the typical metallic behavior, the minority spin band (spin-down band) exhibits a semiconducting behavior with a gap at the Fermi level. Therefore such half-metals are ferromagnets and can be considered as hybrids between metals and semiconductors. A schematic representation of the density of states of a half-metal as compared to a normal metal and a normal semiconductor is shown in Fig. 1. The spinpolarization at the Fermi level is 100% and therefore these compounds should have a fully spinpolarised

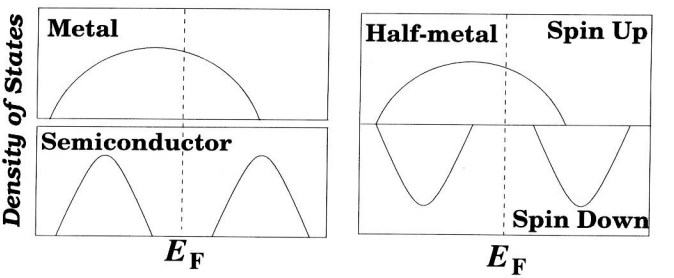

Fig. 1. Schematic representation of the density of states for a half-metal with respect to normal metals and semiconductors

current and might be able to yield a 100% spininjection and thus to maximize the efficiency of magnetoelectronic devices [3].

Heusler alloys [4] have attracted during the last century a great interest due to the possibility to 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 [5–8]. The first Heusler alloys studied were crystallizing in the $L2_1$ structure which consists of 4 fcc sublattices. Afterwards, it was discovered that it is possible to leave one of the four sublattices unoccupied ($C1_b$ structure). The latter compounds are often called half- or semi-Heusler alloys, while the $L2_1$ compounds are referred to as full-Heusler alloys. NiMnSb belongs to the half-Heusler alloys [9]. In 1983 de Groot and his collaborators [10] showed by 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 E_F, leading to 100% spin polarization at E_F as shown in Fig. 1. Other known half-metallic materials except the half- and full-Heusler alloys [11–14] are some oxides (e.g. CrO_2 and Fe_3O_4) [15], the manganites (e.g. $La_{0.7}Sr_{0.3}MnO_3$) [15], the double perovskites (e.g. Sr_2FeReO_6) [16], the pyrites (e.g. CoS_2) [17], the transition metal chalcogenides (e.g. CrSe) and pnictides (e.g. CrAs) in the zinc-blende or wurtzite structures [18–21], the europium chalcogenides (e.g. EuS) [22] and the diluted magnetic semiconductors (e.g. Mn impurities in Si or GaAs) [23, 24]. Although thin films of CrO_2 and $La_{0.7}Sr_{0.3}MnO_3$ have been verified to present practically 100% spin-polarization at the Fermi level at low temperatures [15,25], the Heusler alloys remain attractive for technical applications like spin-injection devices [26], spin-filters [27], tunnel junctions [28], or GMR devices [29] due to their relatively high Curie temperature compared to these compounds [5].

The half-metallic character of NiMnSb in single crystals seems to have been well-established experimentally. Infrared absorption [30] and spin-polarized positron-annihilation [31] gave a spin-polarization of $\sim$100% at the Fermi level. Recently it has also become possible to grow high quality

films of Heusler alloys, and it is mainly NiMnSb that has attracted the attention [32–34]. Unfortunately these films were found not to be half-metallic [15,35–38]; a maximum value of 58% for the spin-polarization of NiMnSb was obtained by Soulen et al. [15]. These polarization values are consistent with a small perpendicular magnetoresistance measured for NiMnSb in a spin-valve structure [39], a superconducting tunnel junction [28] and a tunnel magnetoresistive junction [40]. Ristoiu et al. showed that during the growth of the NiMnSb thin films, Sb and then Mn atoms segregate to the surface, which is far from being perfect, thus decreasing the obtained spin-polarization [41]. But when they removed the excess of Sb by flash annealing, they managed to get a nearly stoichiometric ordered alloy surface being terminated by a MnSb layer, which presented a spin-polarization of about $67 \pm 9\%$ at room temperature [41].

Several groups have verified the half-metallic character of bulk NiMnSb using first-principles calculations [42, 43]. Larson et al. have shown that the actual structure of NiMnSb is the most stable with respect to an interchange of the atoms [44] and Orgassa et al. showed that a few percent of disorder induce states within the gap but do not destroy the half-metallicity [45]. Recently, Galanakis has shown by first-principle calculations that NiMnSb surfaces do not present 100% spin-polarization [46] but Wijs and de Groot proposed that at some interfaces it is possible to restore the half-metallic character of NiMnSb [47]. These results were also confirmed by Debernardi et al. who studied the interface between NiMnSb and GaAs [48]. Jenkins and King studied by a pseudopotential technique the MnSb terminated (001) surface of NiMnSb and showed that there are two surface states at the Fermi level, which are well localized at the surface layer [49] and they persist even when the MnSb surface is covered by a Sb overlayer [50]. Finally Kübler calculated the Curie temperature of NiMnSb [51] which was in excellent agreement with the experimental value of 770 K [5]. A similar technique has been also employed to study the Curie temperature of some full-Heusler alloys which are not half-metallic [52].

Webster and Ziebeck [53] and Suits [54] were the first to synthesize full-Heusler alloys containing Co and Rh, respectively. Kübler et al. studied the mechanisms stabilizing the ferro- or the antiferromagnetism in these compounds [55]. Ishida and collaborators have proposed that the compounds of the type Co_2MnZ, where Z stands for Si and Ge, are half-metals [56, 57]. Also the Heusler alloys of the type Fe_2MnZ have been proposed to show half-metallicity [58]. But Brown et al. [59] using polarized neutron diffraction measurements have shown that there is a finite very small spin-down density of states (DOS) at the Fermi level instead of an absolute gap in agreement with the *ab-initio* calculations of Kübler et al. for the Co_2MnAl and Co_2MnSn compounds [55]. Recently, several groups managed to grow Co_2MnGe and Co_2MnSi thin films on various substrates [60–62], and there also exist first-principles calculations for the (001) surface of such an alloy [63]. Geiersbach

and collaborators have grown (110) thin films of Co_2MnSi, Co_2MnGe and Co_2MnSn using a metallic seed on top of a MgO(001) substrate [64] and studied also the transport properties of multilayers of these compounds with normal metals [65]. But as Picozzi et al. have shown the interfaces of such structures are not half-metallic [66]. Finally, Kämmerer and collaborators managed to built magnetic tunnel junctions based on Co_2MnSi and found a tunneling magnetoresistance effect much larger than when the $Ni_{0.8}Fe_{0.2}$ or $Co_{0.3}Fe_{0.7}$ are used as magnetic electrodes [67]. Similar experiments have been undertaken by Inomata and collaborators using $Co_2Cr_{0.6}Fe_{0.4}Al$ as the magnetic electrode [68].

In this contribution, we present a study of the basic electronic and magnetic properties of the half-metallic Heusler alloys. Analyzing the *ab-initio* results using the group-theory and simple models we explain the origin of the gap in both the half- and full-Heusler alloys, which is fundamental for understanding their electronic and magnetic properties. For both families of compounds the total spin magnetic moment scales with the number of valence electron, thus opening the way to engineer new half-metallic Heusler alloys with the desired magnetic properties. Although in general the surfaces loose the half-metallic character and show only a small degree of spin-polarization, we show that in the case of compounds containing Cr, the very large Cr moments at the surface reduce the importance of the surface states and the spin-polarization of such surfaces is very high, e.g. 84% for the CrAl-terminated $Co_2CrAl(001)$ surface. Finally we discuss the role of defects and spin-orbit coupling on the half-metallic band gap.

In Sects. 2 and 3 we present the electronic and magnetic properties of the XMnSb (X=Ni,Co,Rh,Pd,Ir or Pt) and Co_2MnZ (Z=Al,Si,Ga,Ge or Sn) compounds, respectively. In Sect. 4 we investigate the effect of compressing or expanding the lattice and in Sect. 5 the properties of the quaternary Heusler alloys. In Sects. 6 and 7 we review the role of defects and of the spin-orbit coupling, respectively and finally in Sect. 8 we review the surface properties of these alloys.

2 Electronic Structure and Magnetism of Half-Heusler Alloys

2.1 Band Structure of Half-Heusler Alloys

In the following we present results for the densities of states of some typical half-Heusler alloys of $C1_b$ structure (see Fig. 2), sometimes also referred to as semi-Heusler alloys. To perform the calculations, we used the Vosko, Wilk and Nusair parameterization [69] for the local density approximation (LDA) to the exchange-correlation potential [70] to solve the Kohn-Sham equations within the full-potential screened Korringa-Kohn-Rostoker (FSKKR) method [71,72]. The prototype example is NiMnSb, the half-metal discovered in 1983