Seebeck coefficients of half-metallic ferromagnets

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Abstract

In this report the Co2 based Heusler compounds are discussed as potential materials for spin voltage generation. The compounds were synthesized by arc melting and consequent annealing. Band structure calculations were performed and revealed the compounds to be half-metallic ferromagnets. Magnetometry was performed on the samples and the Curie temperatures and the magnetic moments were determined. The Seebeck coefficients were measured from low to ambient temperatures for all compounds. For selected compounds high temperature measurements up to 900 K were performed.

Key words: Seebeck coefficients, Halfmetallic ferromagnets, Electronic structure, Heusler compounds
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1 Introduction

In the recent years Heusler alloys have attracted a lot of interest as suitable materials for spintronic applications [1]. A huge amount of studies investigating the half-metallic properties theoretically and experimentally and enhancing the performance of the compounds and devices for different type of applications were done. In 2005, Hashemifar et al [2] showed in a density
functional theory study that it is possible to preserve the half-metallicity at the Heusler compound Co$_2$MnSi(001) surface and very recently, Shan et al. [3] demonstrated experimentally the half-metallicity of Co$_2$FeAl$_{0.5}$Si$_{0.5}$ at room temperature. The ability of growing well ordered half-metallic Heusler thin films on semiconductors (e.g. Ge (111)) makes Heusler compounds suitable for spin injection as shown very recently by Hamaya et al. [4].

The recent observation of the spin Seebeck effect allows to pass a pure spin current over a long distance [5] and is directly applicable to the production of spin-voltage generators which are crucial for driving spintronic devices [6,7,8]. For an effective generation of a spin current the spin Seebeck coefficient and the spin voltage namely the difference in the chemical potential of the spin up $\mu_\uparrow$ and spin down $\mu_\downarrow$ should be large [9]. In this report Co$_2$ based Heusler compounds are investigated on their potential as spin voltage generators. The high application potential of the compounds is demonstrated. For a further optimization the electronic and magnetic properties of the compounds can be designed easily.

2 Experimental Details

The samples were produced by arc melting of stoichiometric amounts of the elements and afterwards annealed in evacuated quartz tubes for 21 days. For more details about the sample preparation see Ref. [10]. The magnetic properties of the samples were investigated by a superconducting quantum interference device (SQUID, Quantum Design MPMS-XL-5). The measurements of the Seebeck coefficient were carried out with a Physical Property Measurement System (Model 6000 Quantum Design) on bars of about $(2 \times 2 \times 8)$ mm$^3$ which were cut from the pellets and polished before the measurement. In the temperature range above 350 K the Seebeck coefficient was measured by a steady-state method using the RZ2001i measurement system from Ozawa science, Japan. For more details about the preparation, structural and magnetic properties see References [11,12,13,14].

3 Results and Discussion

3.1 Calculational Results

As a starting point, the electronic structure of the compounds was calculated using the FLAPW method. The detailed description of the calculations for Co$_2$YZ [15] can be found in [13,15]. The investigated compounds are displayed in Table [1] In spin polarized calculations the compounds turn
Fig. 1. Band structure of Co\textsubscript{2}MnSi.
The band structure of Co\textsubscript{2}MnSi is displayed for the majority and the minority channel.

out to be half-metallic ferromagnets as was previously shown by various authors \cite{16,17,18,19,20}. As an example the majority and minority band structure of Co\textsubscript{2}MnSi is displayed in Figure 1.

For selected Heusler compounds the majority band structures are shown in Figure 2. For a better comparison only the energy range ±2.5 eV around the Fermi energy $\varepsilon_F$ is shown. One can clearly see the difference between Co\textsubscript{2}MnSi and Co\textsubscript{2}FeSi (upper panels) and Co\textsubscript{2}TiSi and Co\textsubscript{2}TiAl (lower panels). In the case of Co\textsubscript{2}MnSi and Co\textsubscript{2}FeSi the bands which cross $\varepsilon_F$ are strongly dispersive while the bands are almost flat around $\varepsilon_F$ for Co\textsubscript{2}TiSi and Co\textsubscript{2}TiAl. The minority bands are not shown here because they look almost the same for almost all compounds with a gap around $\varepsilon_F$. Furthermore, the minority electrons don’t contribute to the transport properties for not too high temperatures. This minority gap is characteristic for half-metallic materials. The occurrence of the gap in one spin direction is a fundamental prerequisite for materials used as spin voltage generators.
3.2 Experimental Results

Table 1 summarizes the measured data on the various compounds that will be discussed below in detail. The compounds are grouped by their number of valence electrons.
The Slater-Pauling curve [21,22] is a simple way to study for ferromagnetic alloys the interrelation between the valence electron concentration and the magnetic moments. It is well known that Heusler compounds based on $\text{Co}_2$ follow the Slater-Pauling rule for predicting their total spin magnetic moment [23,19,24] that scales linearly with the number of valence electrons. In the case of four atoms per primitive cell, as in Heusler compounds, one has to subtract 24 (for more details see Ref. [17] from the accumulated number of valence electrons in the primitive cell $N_V$ (s, d electrons for the transition metals and s, p electrons for the main group element) to find the magnetic moment per cell ($m$):

$$m = N_V - 24,$$

(1)

with $N_V$ denoting the accumulated number of valence electrons in the primitive cell. In the case of Heusler compounds, the number 24 arises from the number of completely occupied minority bands that have to be 12 in the half-metallic state. In particular these are one $s$ ($a_{1g}$), three $p$ ($t_{1u}$), and eight $d$ bands [23,25]. The latter consist of two triply degenerate bands with $t_{2g}$ symmetry and one with $e_g$ symmetry (note that the given assignments of the irreducible representations are only valid at the Γ-point and neglecting the spin of the electrons.).

The measured values are displayed in Table 1 and almost all the compounds follow the Slater-Pauling behaviour very well which is a precondition for half-metallic ferromagnetism. The magnetic moment of $\text{Co}_2\text{TiAl}$ is lower than the
Fig. 3. Temperature dependent magnetisation of Co$_2$TiAl, Co$_2$TiSi, Co$_2$MnAl, and Co$_2$FeSi. The data are normalized for better comparison. The magnetisation was measured in a low induction field to make the phase transition clearly visible. This causes that the shape of the curves differ from the molecular field-like behaviour. Expected of 1 $\mu_B$, this is explained by partial disorder (for details see Ref. [13]).

Figure 3 shows the measurements of the temperature dependent magnetisation of Co$_2$TiAl, Co$_2$TiSi, Co$_2$MnAl, and Co$_2$FeSi. From this kind of measurements the Curie temperatures were distinguished, the values are summarized in Table I. With the increase of the number of valence electrons and therefore as well the increase of the magnetic moment the Curie temperature increases. One can nicely see the increase of the Curie temperature for the samples with higher numbers of valence electrons. These behaviour is well known for Heusler compounds and was reported already some years ago [24,26]. This measurements show the easy tunability of the magnetic properties of the Heusler compounds. By controlling the number of valence electrons one can design the properties of the materials.

In Figure 4 the measured Seebeck coefficients ($S$) are displayed for temperatures from 2 K to 350 K. The absoule values increase with increasing temperature. The values at 300 K of all the measurements are summarized in Table II. For an increase of the valence electron count the absolute value of the Seebeck coefficient is decreased. This is explained by the increase of the electron concentration in the bands. By increasing the valence electron count additional electrons are added to the d-band at the Fermi energy [27]. This leads to an
increase of the carrier concentration. The increase of the carrier concentration leads to a decrease of the Seebeck coefficient [28]. The interrelationship between carrier concentration and Seebeck coefficient can be seen from relatively simple models of electron transport. For simple metals or degenerate semiconductors with parabolic bands and energy-independent scattering the Seebeck coefficient $S$ is given by

$$S = \frac{8\pi^2 k_B^2}{3\varepsilon h^2} m^* T \left(\frac{\pi}{3n}\right)^{3/2},$$  

where $n$ is the carrier concentration and $m^*$ is the effective mass of the carrier. It can be clearly seen that $S$ dependens on the carrier concentration and on the effective mass $m^*$. The latter depend on the shape of the bands. Although, the Seebeck coefficient is decreasing with increasing carrier concentration it is remarkable that Sn containing compounds yield large absolute values for the Seebeck coefficient. This effect is related to changes in the band structure and consequential changes in the effective mass $m^*$. The Seebeck coefficient of the investigated compounds is negative over the entire temperature range. The found absolute values are quite large compared to elemental metals ($S_{\text{Co}}=-30.8$, $S_{\text{Mn}}=-9.8$, $S_{\text{Ti}}=+9.1$ $S_{\text{Al}}=-1.66$, $S_{\text{Sn}}=-1$, values at $T=300$ K and in $\mu\text{VK}^{-1}$). Especially the Sn containing compounds show high absolute Seebeck coefficients.

For selected compounds high temperature measurements of the Seebeck co-
efficient have been carried out. The results are shown in Figure 5. At the ferromagnetic to paramagnetic transition temperature a significant change in the slope is observed around $T_c$. For the compounds $\text{Co}_2\text{TiSi}$, $\text{Co}_2\text{TiGe}$, and $\text{Co}_2\text{TiSn}$ a nearly constant behaviour of the Seebeck coefficient above $T_c$ is observed [14]. Although not shown here, measurements of the Seebeck coefficient for $\text{Co}_2\text{FeSi}$ have been carried out up to 1300 K. A pronounced peak of the Seebeck coefficient has been observed around $T_c$.

4 Summary

$\text{Co}_2$ based Heusler compounds have been investigated on their potential use as spin voltage generators. The compounds have been synthesized by arc melting and consequent annealing. Magnetometry was performed and the Curie temperatures and the magnetic moments were determined. The Seebeck coefficient was investigated in the low temperature range from 2 K to 350 K and for selected compounds for higher temperatures. The observed Seebeck coefficients were all negative in the whole temperature range. The absolute values are quite large compared to simple metals. Especially the Sn containing compounds show high Seebeck coefficients with high Curie temperatures. This makes them attractive candidates for materials used in spin voltage generators.
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