Electronic, magnetic and transport properties of full and half-metallic thin film Heusler alloys

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The electronic and magnetic bulk properties of half-metallic Heusler alloys such as Co₂FeSi, Co₂FeAl, Co₂MnSi and Co₂MnAl are investigated by means of ab initio calculations in combination with Monte Carlo simulations. The electronic structure is analyzed using the plane wave code Quantum Espresso and magnetic exchange interactions are determined using the KKR method. From the magnetic exchange interactions the Curie temperature is obtained via Monte Carlo simulations. In addition, electronic transport properties of the trilayer systems consisting of two semi-infinite platinum leads and a Heusler layer in between are obtained from the fully relativistic KKR method by employing the Kubo-Greenwood formalism. The focus is on thermoelectric properties, namely the Seebeck effect and its spin dependence. It turns out that already thin Heusler layers provide highly polarized currents within the systems. This is attributed to the recovery of half-metallicity with increasing thickness. The absence of electronic states of the spin down electrons around the Fermi level suppresses the contribution of this spin channel to the total conductivity. This strongly influences the thermoelectric properties of such systems and results in polarized thermoelectric currents.

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I. INTRODUCTION

The question how a spin current can be generated and injected into functional devices is of great interest for future technological applications. Recently, spin dependent phenomena in the field of thermoelectrics raised a discussion about the interplay between spin, charge and heat currents. For example, there is the possibility that a strong spin dependence of the Seebeck coefficient can be used to generate spin accumulation by applying a temperature gradient. This spin accumulation could be used to drive spin currents into functional devices. In other words, one is interested in a thermally driven spin current generator.

The ferromagnetic half-metals are promising candidates in this field because they exhibit a 100% spin-polarization of the electronic density of states (DOS) at the Fermi level. This means that there is a gap in one of the spin channels and it should, in principle, be possible to extract a 100% spin-polarized current out of these materials. Unfortunately, the sensitive dependence of half-metallicity on details like interfaces and interface defects have up to now hindered a simple generation of spin currents with high polarization from the half-metals. Therefore, theoretical investigations of possible thermoelectric devices which can inject spin currents of high polarization, is of great importance.

In this work, results of ab initio simulations of Co, Fe and Mn based Heusler alloys are reported. These alloys are half-metallic ferromagnets and have already been considered for spintronics applications (see, e.g., Ref. 3). Structural, electronic and magnetic properties as well as the Curie temperatures of the alloys are determined by combining ab initio methods with Monte Carlo simulations. The Curie temperature is of special interest because it is required to be sufficiently high in order to allow the design of devices which keep the ferromagnetic half-metallicity beyond room temperature. Details of the half-metallic electronic structure are discussed in terms of the symmetry resolved density of states (DOS) within the t²g and e₈g representation.

In addition, ab initio calculations of thermoelectric transport properties of Co₂FeAl, Co₂FeSi, Co₂MnSi and Co₂MnAl with Pt contacts are performed. A strong dependence on layer thickness and composition is found. Furthermore, the contributions of the two spin-channels reveal the possibility that spin-polarized currents can be generated by applying a thermal gradient.

The Heusler system within platinum layers can be considered as an analogue to the copper-cobalt multilayers investigated by Gravier et al. The authors report interesting spin-dependent electronic and thermoelectric properties such as the magneto-resistance and magneto-thermopower. In the present work the role of the non-magnetic copper is taken over by platinum that introduces strong spin orbit coupling and the magnetic Co is replaced by Co based Heusler alloys.

For the determination of transport properties a fully relativistic description of the electronic structure within the screened Korringa-Kohn-Rostoker (SKKR) method in combination with the Kubo-Greenwood formalism is employed. This ensures that the spin-orbit coupling introduced by platinum is taken into account. The relativistic spin-projection operator introduced by Lowitzer et al. is used to evaluate the spin dependent contributions. This operator allows the projection of current con-
Heusler alloys with perfect L2$_1$ by disorder. But it is possible to grow thin layers of such alloys as half-metallic spin in the platinum lattice is comparable to the lattice constants of the Heusler alloys. This ensures that the lattice mismatch between both metals is between 0.06 and 0.11 Å.

The main goal of this work is to evaluate the possibility to drive a highly spin-polarized current by applying a thermal gradient. As it is very difficult to grow large crystals of Heusler alloys with perfect L2$_1$ structure, a direct application of such alloys as half-metallic spin injectors is hindered because half-metallicity is suppressed by disorder. But it is possible to grow thin layers of Heusler alloys with perfect L2$_1$. Therefore, if it turns out that a thin film of half-metallic Heusler between two leads already induces a high spin-polarization of the current, the systems under consideration here are of special interest. It is shown throughout this paper that exactly this is possible.

The remainder of the paper is organized as follows: First, details of the calculations are described. Special attention is paid to the details of the transport calculations and the modeling of the Pt-Heusler-Pt systems. Subsequently, results of calculations of the electronic structure of the bulk Heusler system are presented followed by a discussion of the corresponding magnetic exchange interactions and Curie temperatures. Subsequently, a detailed investigation of transport properties and electronic structure of the Pt-Heusler-Pt systems is carried out. In the final section the results are summarized and the conclusions drawn from the calculations are given.

II. TRANSPORT THEORY FORMALISM

The calculation of the electronic transport properties is carried out within the linear response formalism by employing the Kubo-Greenwood formula

$$\sigma_{\mu\nu}(r, r') = \frac{\hbar}{\pi N \Omega} \text{Tr} \left[ \hat{J}_\mu G^+(r, r', E) \hat{J}_\nu G^-(r, r', E) \right]$$

(1)

where $\sigma_{\mu\nu}$ is the conductivity tensor, $\hat{J}$ is the current operator and the $G^+$ and $G^-$ the advanced and retarded Green’s function which is obtained from the KKR formalism and the trace is taken in the four-component Dirac-space.

The total conductance of a particular devices is expressed as

$$g = \int_{S_R} dS \int_{S_L} dS' \hat{n} \sigma(r, r') \hat{n}'$$

(2)

where the $S$ and $S'$ are surfaces in the asymptotic region of the leads and $\hat{n}, \hat{n}'$ are the corresponding normal vectors. To distinguish between contributions of the two spin channels, the fully relativistic spin-projection operator

$$\hat{P}_z^\pm = \frac{1}{2} \left[ 1 \pm \left( \beta \gamma_5 \hat{p}_z\frac{mc}{\hbar} \right) \right]$$

(3)

is employed to define the spin-projected current operators $\mathcal{J}^\pm = \hat{P}_z^\pm \hat{J}$ and the spin current operator $\mathcal{J} = (\hat{P}_z^+ - \hat{P}_z^-) \hat{J}$. Therewith, a correlation between a current induced in one lead and the spin-polarized response current in the other lead is determined. From here on the two spin channels are denoted by $\uparrow$ and $\downarrow$ instead of $\pm$.

The Seebeck coefficient is evaluated using the approach of Sivan and Imry who defined the moments

$$L_n = -\int g(E) (E - \mu)^n \left[ \frac{\partial}{\partial E} f(E, \mu, T) \right] dE$$

(4)

from which the Seebeck coefficient

$$S = -\frac{1}{eT} \frac{L_1(\mu, T)}{L_0(\mu, T)}$$

(5)

can be calculated. Using this approach two types of spin-dependent thermoelectric quantities can be defined. The first one is obtained by splitting the numerator of Eq. 4 into two additive contributions, which leads to the definition

$$\tilde{S}_\sigma = -\frac{1}{eT} \frac{L_{1,\sigma}(\mu, T)}{L_0(\mu, T)}, \quad \sigma = \uparrow, \downarrow$$

(6)

where the quantities $\tilde{S}$ should not be confused with the Seebeck coefficient of a single spin channel.

The definition in Eq. 6 gives insight into how the two spin channels give additive contributions to the total Seebeck coefficient. It allows to determine which of both channels is responsible for the major contribution.
Employing the spin current operator leads to

\[
\mathbf{\dot{S}}_{\text{spin}} = -\frac{1}{eT} L_{1,\uparrow}(\mu, T) - L_{1,\downarrow}(\mu, T) \quad (7)
\]

which is understood as a measure of the spin accumulation that is driven by the thermal gradient.

III. COMPUTATIONAL DETAILS

The determination of structural parameters of the bulk material is carried out with Quantum Espresso, where a relaxation of the volume is performed and tendencies for tetragonal distortions are examined. The GGA exchange correlation functional of Perdew, Burke and Ernzerhof (PBE) is used because the structural parameters of metals obtained with this functional are in good agreement with experimental data.

Calculations of magnetic exchange parameters are carried out with the SPR-KKR package. Therefore, a scalar relativistic determination of the multiple scattering properties is performed using the PBE functional. The structural parameters obtained from Quantum Espresso serve as input for the KKR calculation. Afterwards, the magnetic exchange parameters are calculated from the scattering properties by employing the Lichtenstein formalism.

The exchange parameters are subsequently used in Monte Carlo (MC) simulations of the classical Heisenberg model to determine the Curie temperature. The exchange interactions are cut off after three lattice constants. This is sufficient because exchange parameters of larger distance are too small to be relevant for the theoretical estimation of the Curie temperature. The simulation box used within the MC simulations includes \(10 \times 10 \times 10\) Heusler unit cells.

Calculations of transport properties are carried out using the fully relativistic screened KKR formalism. The linear response formalism in the formulation of Baranger and Stone is first implemented by Mavropoulos et al. is used. In order to ensure an accurate determination of the transport properties, more than 90,000 \(k\)-points within the irreducible wedge of the two-dimensional Brillouin zone are used. The imaginary part is set to 0.0001 Ry. The energy grid for the calculation of the Seebeck coefficient is 0.001 Ry.

IV. DETAILS OF THE TRANSPORT GEOMETRY

Details of the geometry used in the transport calculations are shown in Fig. 1. The layer distance at the interface between platinum and the Heusler system is the averaged value of the layer distance in platinum and that in the Heusler. No lattice relaxations are included.

Within the S-KKR method the system is assumed to be translational invariant in the \(x\)- and \(y\)-direction and in the \(z\)-direction the system is terminated on both sides by two semi-infinite leads. Due to the two dimensional translational invariance a two-dimensional lattice constant \(a_{2d}\) has to be defined by

\[
a_{2d} = \sqrt{2}a_{bcc} \quad (8)
\]

where \(a_{bcc}\) is the three-dimensional lattice constant of the underlying bcc lattice of the Heusler part of the system. Hence, the distance between two subsequent monolayers is given by

\[
d = \frac{a_{3d}}{2} = \frac{\sqrt{2}}{4}a_{2d} \quad (9)
\]

The atomic positions are defined for the following basis vectors using a frame of reference that is rotated by 45° with respect to that of Fig. 1:

\[
a_1 = a_{2d}(1, 0, 0) \quad (10)
\]

\[
a_2 = a_{2d}(0, 1, 0) \quad (10)
\]

\[
a_3 = a_{2d}(0, 0, 1) \quad (10)
\]

The platinum and the Heusler lattices are rotated by 45° with respect to each other. This ensures the smallest possible lattice mismatch between the two structures. For example, the lattice constant of the Heusler cell of Co2FeSi is 2.81 Å (which is half of the lattice constant of the 16 atoms cell) and the lattice constant of Pt is 3.92 Å. This is of the same order as the diagonal of the Heusler structure which is 3.97 Å and therefore close to the Pt lattice constant. The lattice mismatch is between 0.06 to 0.11 Å depending on the particular Heusler system.

For the calculations it is assumed that the lattice constant of Pt is the same as that of the two-dimensional lattice constant of the Heusler system:

\[
a_{3d,Pt} = a_{2d,Heusler} \quad (11)
\]

The atomic volume of the Heusler is \(a_{bcc}^3/2 = a_{2d}^3/4\sqrt{2}\), hence, the (average) Wigner-Seitz radius is calculated by

\[
\frac{4\pi}{3} R_{ws}^3 = \frac{a_{2d}^3}{4\sqrt{2}} \Rightarrow R_{ws}^{Pt} = \frac{1}{4\sqrt{32}} \left( \frac{3}{4\pi} \right)^{1/3} a_{2d}
\]

\[
\simeq 0.138 a_{2d}. \quad (12)
\]

In the fcc Pt lattice the atomic volume is \(a_{fcc}^3/4 = a_{2d}^3/4 + 2a_{bcc}^3 = a_{2d}^3/\sqrt{2}\), thus,

\[
\frac{4\pi}{3} R_{ws}^3 = \frac{a_{2d}^3}{4} \Rightarrow R_{ws}^{Pt} = \frac{1}{\sqrt{4}} \left( \frac{3}{4\pi} \right)^{1/3} a_{2d}
\]

\[
\simeq 0.391 a_{2d} \quad (13)
\]

Four layers of Pt are considered in each interface region to join smoothly to the two semi-infinite bulk regions. The Heusler layer is always terminated by a Co monolayer on both sides. Therefore, the interface between Pt and the Heusler system is always metallic. The distance between
Pt and Co monolayer in the interface is taken to be the average of the Pt and the Heusler interlayer distances, i.e. \((1/2 + \sqrt{2}/4)/2 = (2 + \sqrt{2})/8\). In this way, the atomic radii for all Pt atoms can be taken as \(R_1\), the average of the Pt and the Heusler interlayer distances, i.e. Pt and Co monolayer in the interface is taken to be the expected integer values under consideration. The magnetic moments are close to magnetic moments and Curie temperatures of all systems is presented. Table I summarizes structural properties, other half-metallic Heusler systems. This problem has to be kept in mind for the interpretation of the LDA+U method. The DOS in Fig. 3 shows that in particular the description of the \(e_g\) states of iron is deficient because some of the states that should belong to the conduction band leak into the half-metallic gap. The total magnetic moment of 5.57 \(\mu_B\) is by more than 0.4 \(\mu_B\) smaller than the expected integer value of 6.0 \(\mu_B\). This problem has to be kept in mind for the interpretation of the later results.

In Fig. 3 the symmetry resolved electronic DOS of Co and Mn in Co\(_2\)MnAl is shown. There is an obvious gap in the minority spin channel. The Fermi energy is not located within the gap.

FIG. 2: Symmetry resolved electronic density of states of cobalt and iron in Co\(_2\)FeAl. This result shows that there is a gap in the density in the minority spin channel. The Fermi energy lies at the upper edge of this gap.

FIG. 3: Symmetry resolved electronic density of states of cobalt and iron in Co\(_2\)FeSi. However, this calculation does not reproduce the expected half-metallic behavior. Although, there is a gap in the DOS of the minority spin channel, the Fermi energy is not located within the gap.

### V. RESULTS

At first a discussion of electronic and magnetic properties of bulk Co\(_2\)FeAl, Co\(_2\)FeSi, Co\(_2\)MnAl and Co\(_2\)MnSi is presented. Table I summarizes structural properties, magnetic moments and Curie temperatures of all systems under consideration. The magnetic moments are close to the expected integer values except for Co\(_2\)FeSi where a significant deviation from the expected 5\(\mu_B\) is found. This shows that the ab initio description of this particular system is deficient compared to the description of the other half-metallic Heusler systems. This problem has been discussed extensively in literature (see Refs. 17–20).

In the following a discussion of the electronic structure and the magnetic properties of the bulk systems is given. Afterwards the transport properties and in particular the Seebeck coefficient of the trilayer systems are presented. The main features found in the calculation of the Seebeck coefficient are subsequently discussion on the basis of the layer resolved DOS of the trilayers.

#### A. Electronic structure

Figure 2 shows the symmetry resolved electronic density of states of cobalt and iron of bulk Co\(_2\)FeAl. The DOS shows that Co\(_2\)FeAl is half-metallic because there is a pronounced gap in the minority spin channel and the Fermi energy is located exactly at the upper edge of this gap. The total magnetic moment of 4.99\(\mu_B\) shows that the calculations nicely reproduce the expected integer value, revealing only a very small deviation.

Figure 3 shows the symmetry resolved electronic DOS of cobalt and iron in Co\(_2\)FeSi. There is also a gap in the minority spin channel but the Fermi energy is not located within this gap. This may be attributed to some kind of a breakdown of standard GGA for the description of the electron structure of half-metallic Co\(_2\)FeSi. This has been discussed in more detail in literature (see e.g. Refs. 21). It is argued that strong correlations of the \(d\)-electrons are responsible for this breakdown and in addition it is demonstrated that this lack can be cured by employing the LDA+U method. The DOS in Fig. 3 shows that in particular the description of the \(e_g\) states of iron is deficient because some of the states that should belong to the conduction band leak into the half-metallic gap. The total magnetic moment of 5.57 \(\mu_B\) is by more than 0.4 \(\mu_B\) smaller than the expected integer value of 6.0 \(\mu_B\). This problem has to be kept in mind for the interpretation of the later results.
| Composition     | Magnetic order | $a$ (Å) | $c/a$ | $\mu_{tot}$ ($\mu_B$) | $T_C$ (K) | $T_{C, exp}$ (K) |
|-----------------|----------------|---------|-------|------------------------|-----------|------------------|
| $\text{Co}_2\text{FeAl}$ | FM             | 5.70    | 1     | 4.99                   | 1050      | -                |
| $\text{Co}_2\text{FeSi}$  | FM             | 5.63    | 1     | 5.57                   | 750       | 1100             |
| $\text{Co}_2\text{MnAl}$  | FM             | 5.70    | 1     | 4.03                   | 480       | 697              |
| $\text{Co}_2\text{MnSi}$  | FM             | 5.63    | 1     | 5.00                   | 755       | 985              |

TABLE I: Lattice parameters and magnetic order obtained from Quantum Espresso (GGA) calculations. In addition, the critical temperatures obtained with MC simulations are listed. The experimental value of the critical temperature of $\text{Co}_2\text{FeAl}$ is not known because it is located close to a structural transition.

is located at the lower edge of the gap in contrast to the case of $\text{Co}_2\text{FeAl}$ where the Fermi energy is located at the upper edge. In addition, the magnetic moments is close to the expected integer value.

The same DOS is shown in Fig. 4 for the case of $\text{Co}_2\text{MnSi}$. There is a gap in the minority channel and the Fermi energy is located in the middle of this gap. Therefore, the half-metallicity of $\text{Co}_2\text{MnSi}$ is very robust against interfering effects such as increasing temperature.

In summary, the electronic structure of all Heusler alloys except $\text{Co}_2\text{FeSi}$ is in nice agreement with the expected half-metallic structure. Only in $\text{Co}_2\text{MnSi}$, the Fermi energy is located in the middle of the half-metallic gap. This implies that the conductance of the Pt-$\text{Co}_2\text{MnSi}$-Pt system in an energy interval around the Fermi level ($E_F$) is mainly given by spin up electrons. Some contributions from the spin down channel may remain because of tunnel effect transmission through the area where no spin down states are present. Therefore, the Seebeck coefficient which is calculated from the conductance around $E_F$ must show a pronounced contribution from the spin up and a minor one from the spin down channel.

B. Magnetic properties

In this subsection the magnetic exchange parameters and critical temperatures of the Heusler bulk systems are discussed in order to compare between theoretical pre-
predictions of $T_C$ and experimentally observed values. By investigating the calculated magnetic exchange interactions it becomes obvious that the magnetic structure is dominated mainly by the interaction between cobalt and iron or between cobalt and manganese.

In Fig. 7 the exchange interactions of Co$_2$FeAl are shown. Obviously, the most relevant interaction is the one between nearest neighbor cobalt and iron atoms. All other interactions are much smaller and almost negligible. Unfortunately, the predicted critical temperature, which is about 1050 K cannot be compared to experimental values because a structural transition from the ordered L2$_1$ to a disordered B2 structure interferes with the temperature region where the magnetic transition is located. This prevents the identification of the exact temperature of the magnetic transition. Nevertheless, the theoretical prediction meets the expected range of the Curie temperature.

Figure 7 shows the magnetic exchange interactions and the Curie temperature of Co$_2$FeSi. The exchange interactions are qualitatively and quantitatively comparable to those of Co$_2$FeAl. The most obvious difference is that the cobalt-cobalt interactions are stronger in the latter case. The Curie temperature is much smaller than the experimental one. This can be attributed to the incorrect description of the electronic structure within the GGA. As discussed in subsection V A an explicit inclusion of correlation effects would improve the description of the electronic structure. Therefore, it is expected that correlations will also improve the description of the exchange parameters and the theoretical prediction of the Curie temperature.

In the following the cobalt-manganese based Heuslers are discussed. Although, manganese is known to introduce strong antiferromagnetic interactions in the system Co$_2$MnAl and Co$_2$MnSi are clearly ferromagnets. This can be understood by considering that the antiferromagnetism between Mn pairs has a complicated distance dependence and therefore only pair which are separated by certain distances interact antiferromagnetically.

In Fig. 8 the exchange interactions and the Curie temperature of Co$_2$MnAl is shown. Obviously, the interaction between cobalt and manganese is now the strongest contribution, although it is by more than a factor of two smaller compared to the Co-Fe interaction in cobalt-iron based Heusler systems. The strong Co-Mn interaction is somewhat surprising because in binary CoMn the exchange interaction between nearest neighbor pairs is usually small, negative and therefore induces antiferromagnetic coupling.

Although, the half-metallic nature of the DOS is nicely reproduced, the critical temperature deviates significantly from experiment. This is due to the use of LDA in the calculation of the exchange parameters. There is a general trend that LDA tends to underestimate magnetic exchange parameters and therefore leads to smaller critical temperatures in the MC simulations.

Figure 9 shows exchange parameters and critical temperature of Co$_2$MnSi. Qualitatively, the interactions are again very similar to those of Co$_2$MnAl. Here the interactions are stronger and therefore the critical tempera-
ture is higher compared to Co$_2$MnAl. As the deviation of the critical temperature from the experimental value is of the same order as for Co$_2$MnAl, one may conclude that the general trend of the critical temperature is nicely reproduced and the deviation are indeed only due to the systematic errors introduced by the LDA.

C. Transport properties

In this subsection transport properties, in particular the Seebeck coefficient and its spin dependence of Pt-Heusler-Pt system are discussed. For every type of Heusler, systems containing five monolayers are compared to systems containing nine monolayers of Heusler. The number of monolayers is chosen in a way that the Pt-Heusler interface is purely metallic in the sense that the first Heusler monolayer on both sides contains only cobalt.

Figure 10 shows the calculated temperature dependence of the Seebeck coefficient of Pt-Co$_2$FeAl-Pt with five Heusler monolayers. The Seebeck coefficient increases linearly with temperature. The contribution of the spin up channel is almost by a factor of two larger than the one of the spin down channel. In Fig. 11 the energy dependence of the conductivity is shown. Around the Fermi energy the energy dependence is linear which leads to the linear increase of the Seebeck coefficient with increasing temperature. For energies farther away from the Fermi level, the energy dependence of the conductance becomes more structured. But as these structures are close the the borders of the energy integration and are less weighted by the derivative of the Fermi function, their resulting contribution is only very small. Therefore the temperature dependence of the Seebeck coefficient is still linear.

As shown in Fig. 12, the Seebeck coefficients of a system containing nine monolayers of Co$_2$FeAl is smaller compared to the system with five monolayers. In addition, there is a much larger difference between the contributions of the two spin channels to the total Seebeck coefficient. This can again be explained by regarding the energy dependence of the conductivity where the spin down channel has a slope comparable to that of the total conductivity and the energy dependence of the spin up channel is almost flat. A flat energy dependence leads to small Seebeck coefficients because the slope of this dependence determines the size of the Seebeck coefficient.

The first conclusion that can be drawn from the results for Pt-Co$_2$FeAl-Pt is that the Seebeck coefficient of the layered system depends strongly on the thickness of the
layer. This basically stems from the different shape of the energy dependence of the conductivity. The fact that conductivities are very sensitive to the thickness of layers is well known and described e.g. in Ref. 15.

Now, the Pt-Co$_2$FeSi-Pt systems are discussed. This gives insight into how far compositional changes affect the Seebeck coefficient. In particular, the replacement of Al by Si introduced one more valence electron. It should also be kept in mind Al is a metal whereas Si is a semiconductor.

Regarding Fig. 14 which shows the temperature dependence of the Seebeck coefficient of a system containing five monolayers of Co$_2$FeSi, it is immediately noticed that the Seebeck coefficient is by more than a factor of three smaller compared to the Pt-Co$_2$FeAl-Pt system with five monolayers. In addition, small deviations from the linear behavior of the Seebeck coefficient are found in this system.

The energy dependence of the conductance shown in Fig. 15 is almost linear around $E_F$ but reveals a distinct structure above the Fermi energy and is still quite flat below. There is a pronounced peak above $E_F$ which is connected to numerical inaccuracies that can occur if strong changes of the electronic structure appear during the energy sampling. In such cases the $k$-point mesh used within the calculation can be commensurate with important features in the two dimensional Brillouin zone at a certain energy but can miss some features at another energy. As such structures do not affect the calculation of the Seebeck coefficient the enormous numerical effort which is required to cure this lack is not useful.

Turning to the Pt-Co$_2$FeSi-Pt system with nine monolayers, a strong change occurs in comparison to the system with five monolayers. The Seebeck coefficient of this system is negative and the evolution with temperature is
also not linear as for the systems with five monolayers. In addition, the two additive contributions to the total Seebeck coefficient have opposite signs. The contribution of the spin down channel which gives the strongest contribution, is negative whereas the contribution of the spin up channel is small and positive. Therefore, the resulting total Seebeck coefficient is very small. This can be understood by considering the energy dependence of the conductivity around the Fermi level which is almost flat and therefore gives only small contributions to the Seebeck coefficient. This behavior changes around 0.1 eV away from the Fermi energy when more structure comes into play. Due to this the negative slope of the Seebeck coefficient increases for temperatures above 300K.

In a next step the Y-component of the Heusler compound is changed from iron to manganese. This results in the occurrence of a larger Seebeck coefficient for systems containing five layers of Co$_2$MnAl. Here, the additive contributions of the spin channels to the total Seebeck coefficient are almost of the same size and exhibit a comparable structure. This energy dependence of the conductivity of this system is shown in Fig. 19. It shows a strong slope in the total conductivity and both spin dependent contributions. The strong structure around 0.3 eV below the Fermi energy has no influence on the temperature dependence of the Seebeck coefficient because it is at too high energies to give a significant contribution to the temperature region considered here. Interestingly, the shape of the energy dependence of the conductance of the Pt-Co$_2$FeAl-Pt system with five monolayers is comparable to that of the Pt-Co$_2$MnAl-Pt with the same number of layers.

In the system containing nine monolayers of Co$_2$MnAl between the platinum leads, the total Seebeck coefficient increases. This is contrary to the Co$_2$FeZ systems where...
the Seebeck coefficient is smaller in the nine layer case. But here there is a sizable slope at low temperatures and seems to saturate for larger temperatures. This saturation stems from the flat regions of the energy dependence of the conductance at more than 1.5 eV away from the Fermi energy. Although there is a pronounced structure below the Fermi energy the average slope in this region is small and therefore this region gives almost no contribution to the Seebeck coefficient. This system is a perfect example of a system with small conductivity (speaking in terms of ballistic conductivity at the Fermi level) but with a large Seebeck coefficient. This shows again that the Seebeck coefficient depends almost exclusively on the slope of the conductivity and much less on its absolute value.

To finish the discussion of the transport properties the Seebeck coefficient of Pt-Co$_2$MnSi-Pt systems has to be discussed. Figure 22 shows its temperature dependence for the system containing five monolayers Heusler. The absolute value is decreased compared to the Pt-Co$_2$MnAl-Pt system. This is analogous to the decrease found in the Co-Fe based system where the exchange of Al by Si reduces the Seebeck coefficient strongly. The evolution of the additive contributions from the spin channels to the total Seebeck coefficient with temperature for Pt-Co$_2$MnSi-Pt is qualitatively comparable with the one of Pt-Co$_2$MnAl-Pt because they are almost of the same size. The energy dependence of the conductance shown in Fig. 23 is linear with almost no structure.

The last system that has to be discussed is the system which contain nine monolayers of Co$_2$MnSi and its Seebeck coefficient is shown in Fig. 24. Obviously this system exhibit a very interesting behavior because the Seebeck coefficient is negative for temperatures below 25K, becomes positive up to temperature below 175K and is again negative for higher temperatures.

The energy dependence of the conductance shows a bump above the energy and a flat behavior below. This asymmetry leads to the unusual temperature dependence of the Seebeck coefficient.

Table II summarizes the sign of the Seebeck coefficient of all systems studied here. It show a systematic difference between systems containing Al and those containing Si. All systems containing Al considered here exhibit a positive Seebeck coefficient for both layer thicknesses in
combination with Fe and also with Mn. The systems that contain Si show a positive Seebeck coefficient for 5 monolayers of Heusler for the case of Fe and Mn and a negative Seebeck coefficient for 9 monolayers in both combinations with Fe and Mn.

D. Electronic structure of the transport systems

In order to gain a deeper insight into how the thermoelectric properties depend on the layer thickness and the composition, the electronic structure of the systems discussed here have to be understood in more detail. Therefore, this subsection is devoted to the discussion of the electronic DOS of Heusler layers between platinum leads. The main question is if there are signatures of half-metallicity in the small Heusler layers and how do they influence the Seebeck coefficient and its spin dependence.

In Fig. 26 and 27 the electronic DOS of the two Pt-Co$_2$FeAl-Pt systems are shown. The DOS of only the first three and five Heusler layers is presented because the subsequent layers reveal the same DOS because of the reflection symmetry of the system. One easily observes that in the systems which contains only five monolayers of Heusler the half-metallic gap is absent even in the Co layer in the middle. But the DOS becomes obviously more similar to that of bulk Co$_2$FeAl in the middle of the Heusler layer compared to the DOS in the monolayer which is directly connected to the Pt lead.

If the DOS of the system that contains nine monolayers of Co$_2$FeAl is examined one observes that the half-metallic gap is recovered in the middle of the system. This means that the influence of the Pt interface is almost completely decayed after four layers. The occurrence of this gap is responsible for certain differences of the Seebeck coefficient between the system with five and
nine monolayers.

The shape of the energy dependence of the conductance around the Fermi level can be related to features of the DOS. Comparing the energy dependent conductances in Fig. 11 and 13 to the DOS in Fig. 26 and 26 it is obvious why the total conductance becomes smaller from five to nine layers and why the contribution of the two spin channel are different. For five layers both spin channel give almost the same contribution to the conductance whereas for nine layers the contribution of the spin up channel is almost twice as large. This can be attributed to the occurrence of the half-metallic gap in the spin down DOS of the system with nine Heusler layers. The absence of states in the spin down channel in the middle of the system reduces the transmission probability of spin down electrons significantly. The remaining transmission can be explained by the occurrence of electrons that flipped their spin on the way through the system and by the occurrence of spin down electron the can tunnel through the small region where there is no spin state.

The same arguments are also valid for the Pt-Co$_2$FeSi-Pt systems. Their DOS is shown in Fig. 28 and 28. Again the occurrence of the gap in the spin down channel in the nine layer system leads to a contribution of this channel which is 50% smaller than that of the spin up channel. The sudden increase of the conductance above the Fermi energy in the nine monolayer system can be related to the peak in the DOS above the Fermi energy. The sudden occurrence of states in the middle of the system leads to the occurrence of many new transmission channels.

The energy dependence of the five layer Pt-Co$_2$MnAl-Pt is also easily described by features of the DOS which is shown in Fig. 30. The DOS of both spin channels is relatively large at the Fermi energy which should lead to the occurrence of many transmission channels and therefore to a quiet large conductance. In the nine layer system the total conductance is again reduced and also the spin down conductance is again almost a factor of two smaller. This is again attributed to the occurrence of the half-metallic gap (see Fig. 31).

Concerning the DOS of the Pt-Co$_2$MnSi-Pt systems the results are similar to those of the other systems. The half-metallic gap is fully recovered in the nine monolayer system. Therefore, the small conductance contribution of the spin down channel in this system can be attributed to this feature. Although the Fermi level of this system is almost exactly in the middle of the gap the conductance is only small but not zero. This shows that there must be enough tunneling channels through which electrons can travel from one side to the other.

The systematic difference between of the sign of the Seebeck coefficient as summarized in Table II can be related to the features of the electronic DOS. The DOS of the Pt-Co$_2$FeAl-Pt and Pt-Co$_2$MnAl-Pt systems shows that the Fermi energy has the tendency to be located
FIG. 31: DOS of the Pt-Co$_2$MnAl-Pt system with nine monolayers of Heusler between the platinum leads.

FIG. 32: DOS of the Pt-Co$_2$MnSi-Pt system with five monolayers of Heusler between the platinum leads.

FIG. 33: DOS of the Pt-Co$_2$MnSi-Pt system with nine monolayers of Heusler between the platinum leads.

closer to the valence edge of the spin down channel. This is different in Pt-Co$_2$FeSi-Pt and Pt-Co$_2$MnSi-Pt where the Fermi energy shows a tendency for the conduction edge of the spin down channel.

VI. CONCLUSIONS

Theoretical predictions of electronic, magnetic and thermoelectric properties of half-metallic Heusler alloys have been reported. The half-metallic shape of the DOS of the bulk material is reproduced very nicely except for the case of Co$_2$FeSi.

The calculation of magnetic exchange parameters leads to an accurate reproduction of the experimental trends of the Curie temperatures of Co-based Heuslers. The Heisenberg description of the finite temperature magnetism of the Co-based Heusler alloys is a good choice because the expected thermal fluctuations of the important magnetic moments of Co, Mn and Fe are basically transversal and therefore captured by the MC simulation of the Heisenberg model.

The transport calculations presented here are carried out for the ballistic regime. Therefore, no inelastic scattering of electrons is considered. The temperature dependence enters the calculation only the derivative of the Fermi function. Therewith, the additional activation of transport channels with increasing temperature is taken into account. Effects of phonons and magnetic excitations are neglected.

The transport calculations show that the Seebeck coefficient strongly depends on the details of the system. Therefore small changes of the layer thickness and of the composition can result in strong changes of the behavior of the Seebeck coefficient.

It can be stated that the Seebeck coefficient does only depend on coarse properties of the energy dependence of the conductance. The main contribution is given by the averaged slope of this property.

If the calculated Seebeck coefficients of the composite Pt-Heusler-Pt systems are compared to the experimental measurements of bulk Seebeck coefficients of Co-based Heusler alloys (see Ref. 23) fundamental differences are observed. The most obvious point is that all except the nine layer Co$_2$FeSi and Co$_2$MnSi system show positive Seebeck coefficients over the whole temperature range. The experimental observation of Seebeck coefficients of the corresponding bulk materials reveal negative values for all systems. It is even more surprising that the composite systems exhibit positive Seebeck coefficients because Pt shows also a negative Seebeck coefficient above 200K.

It clearly turns out that thin films of half-metallic Heusler alloy between platinum leads give rise to strong spin-polarized currents and in addition to possible spin-
polarized thermoelectric currents. They only need to consist of nine monolayers because from nine monolayers on half-metallicity is recovered within the Heusler film.

The only drawback of this interpretation is that fact that the half-metallicity of Co-based Heusler alloys is strongly temperature dependent. Therefore, the spin-polarization in such Heusler alloy is strongly reduced at higher temperatures.

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