Calculated electronic and magnetic properties of the half-metallic, transition metal based Heusler compounds

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Abstract
In this paper, results of ab initio band structure calculations for $A_2BC$ Heusler compounds that have $A$ and $B$ sites occupied by transition metals and $C$ by a main group element are presented. This class of materials includes some interesting half-metallic and ferromagnetic properties. The calculations have been performed in order to understand the properties of the minority band gap, the peculiar transport properties and magnetic behaviour found in these materials. Among the interesting aspects of the electronic structure of the materials are the contributions from both $A$ and $B$ atoms to the total magnetic moment. The magnitude of the total magnetic moment shows a trend consistent with the Slater–Pauling type behaviour in several classes of these compounds. The total magnetic moment also depends on the kind of $C$ atoms although they do not directly contribute to it. In Co$_2$ compounds, a change of the $C$ element changes the contribution of the $t_{2g}$ states to the moment at the Co sites. The localized moment in these magnetic compounds resides at the B site. Other than in the classical Cu$_2$-based Heusler compounds, the $A$ atoms in Co$_2$, Fe$_2$ and Mn$_2$-based compounds may contribute significantly to the total magnetic moment. It is shown that the inclusion of electron–electron correlation in the form of LDA + $U$ calculations helps to understand the magnetic properties of those compounds that already exhibit a minority gap in calculations where it is neglected. Besides the large group of Co$_2$ compounds, half-metallic ferromagnetism was here found only in such compounds that contain Mn.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The Heusler compounds [1] are ternary intermetallics with a 2:1:1 stoichiometry and the chemical formula $A_2BC$. They usually consist of two transition metals ($A$, $B$) and a main group element ($C$). They first attracted the interest of the magnetism community when Heusler et al [2] had shown that the compound Cu$_x$Mn$_y$Al becomes ferromagnetic in the 2:1:1 form ($x = 2$ and $y = 1$), even though none of its constituents is ferromagnetic by itself. However, it took three decades before their structure was explained to be that of an ordered compound with a face centred cubic structure [3, 4].

The general crystal structure of the Heusler compounds is displayed in figure 1.

The main interest during the first decades after their discovery was concentrated on Cu and Mn containing compounds. Co$_2$-based compounds were synthesized and investigated in the 1970s [5]. Kübler et al [6] recognized that the minority spin densities at the Fermi energy ($\epsilon_F$) nearly vanish for Co$_2$MnAl and Co$_2$MnSn. The authors concluded that this should lead to peculiar transport properties in these Heusler compounds because only the majority density contributes to the states at $\epsilon_F$. At the same time, de Groot et al [7] proposed the concept of the so-called half-metallic
ferromagnets (HMF) that are materials predicted to exhibit 100% spin polarization at $\epsilon_F$. This exceptional property would make the HMF ideal candidates for spin injection devices to be used in spin electronics [8].

The calculation of the electronic structure plays an important role in determining the magnetic properties of Heusler compounds and, in particular, for predicting half-metallic ferromagnetism. Therefore, the band structure calculations must be performed very carefully. The first attempt to calculate the band structure of some Co$_2$-based compounds (Co$_2$MnSn, Co$_2$TiSi and Co$_2$TiAl) did not indicate half-metallic ferromagnetism [9]. These calculations displayed a minimum of the minority density of states (DOS) at $\epsilon_F$ but not a gap. At that time, the calculations were based on spherical potentials, and the exchange-correlation potential of the local spin density approximation (LSDA) was used in a rather simple form [10–13]. The first clear indication of half-metallic ferromagnetism in Co$_2$-based Heusler compounds was reported by Ishida et al [14, 15] for Co$_2$MnC and Ru$_2$MnC (C = Al, Si, Sn and Sb). Using full symmetry potentials, Mohn et al [16] found the magnetic ground state of Co$_2$TiC (C = Al and Sn), but not a half-metallic state. Galanakis et al [17] reported half-metallic behaviour in various A$_2$BC compounds, but not for the Co$_2$ compounds with Ti or Fe. The results were compatible with those found for the Mn compounds as calculated by Picozzi et al [18] using the generalized gradient approximation (GGA) instead of the pure LSDA. The GGA, as introduced by Perdew et al [19–22], accounts for gradients of the density that are absent in the pure LSDA parametrization of the exchange-correlation functional [10–13]. Using spherical potentials and the GGA, a half-metallic state could not be verified for Co$_2$FeAl [23, 24]. A half-metallic ferromagnetic ground state was also found for the complete series Co$_2$Cr$_{1-x}$Fe$_x$Al, when the full symmetry potentials were used along with the GGA in the calculations [25]. This clearly indicates that one principally needs both the full symmetry potentials and the GGA to find the correct electronic structure and ground state for the Heusler compounds.

With this information, the properties of the reported transition metal-based Heusler compounds were calculated in the present work using both the GGA and the full symmetry potentials. Even at that state of sophistication, however, for some compounds the magnetic properties could not be explained properly. The reason was found in an underestimation of the electron–electron on-site correlation in the LSDA or GGA calculations [26, 27]. Therefore, the LDA + $U$ method [28, 29] was used for selected compounds to study the effect of on-site correlation at the transition metal sites on the magnetic and half-metallic properties of the Heusler compounds.

A systematic examination of the electronic and the magnetic structure of the Heusler compounds was carried out in this work. The results from the electronic structure calculations are compared to study the effect of the different kinds of atoms and valence electron concentration on the magnetic properties and, in particular, on the band gap in the minority states.

1.1. Spin polarization and half-metallic ferromagnets

For both scientific and technological reasons it is useful to define the electron spin polarization at Fermi energy of a material, although it is difficult to measure [30]. The spin polarization at $\epsilon_F$ is given by

$$P = \frac{\rho_{\uparrow}(\epsilon_F) - \rho_{\downarrow}(\epsilon_F)}{\rho_{\uparrow}(\epsilon_F) + \rho_{\downarrow}(\epsilon_F)},$$

where $\rho_{\uparrow}(\epsilon_F)$ and $\rho_{\downarrow}(\epsilon_F)$ are the spin dependent density of states at the $\epsilon_F$. The arrows $\uparrow$ and $\downarrow$ assign states of opposite spin that are majority and minority states, respectively. $P$ vanishes for paramagnetic or in anti-ferromagnetic materials even below the magnetic transition temperature. However, it has a finite value in ferromagnetic or ferrimagnetic materials below the Curie temperature. The electrons at $\epsilon_F$ are fully spin polarized ($P = 100\%$) when either $\rho_{\uparrow}(\epsilon_F)$ or $\rho_{\downarrow}(\epsilon_F)$ equals zero.

In the present work, the classification scheme for half-metals as proposed by Coey et al is used [8, 31]. The first class is Type I, where only one type of spin polarized electrons (either $\uparrow$ or $\downarrow$) does contribute to the conductivity. This is the situation described by de Groot et al [7], where one has—for one spin direction—a gap in the density of states that includes the Fermi energy. The half-metallic gap appears in the minority density of states in Type Ia half-metals such that only itinerant majority electrons contribute to the conductivity. In Type Ib, the majority density of states vanishes at $\epsilon_F$. The electrons at $\epsilon_F$ are itinerant in Type I half-metals, whereas they are localized in Type II. In Type III half-metals no gap appears at the Fermi energy but one has at $\epsilon_F$ itinerant electrons for one spin direction and localized electrons for the other. In Type IV half-metals, the conductivity is semi-metallic rather than metallic like in Type III. Type IIIa (IVa) and Type IIIb (IVb) distinguish half-metals with the localized (or itinerant) states in opposite spin channels. In Type III or IV half-metals, a gap may appear in one of the spin channels that is located below or above $\epsilon_F$. In Types I and II half-metals the spin polarization $P$ is always 100%, whereas lower values appear in Types III and IV.
It is worthwhile to note that half-metallic conductivity, as explained above, is different from semi-metallic conductivity. Semi-metals, of which graphite is a textbook example, have small and equal numbers of electrons and holes due to a small overlap between valence and conduction bands and they exhibit a pronounced anisotropy in the conductivity.

1.2. The Slater–Pauling rule and Heusler compounds

The Slater–Pauling curve [32, 33] is a simple way to study for ferromagnetic alloys the interrelation between the valence electron concentration and the magnetic moments (see figure 2). It is well known that Heusler compounds based on Co₂ follow the Slater–Pauling rule for predicting their total spin magnetic moment [17, 34, 35] that scales linearly with the number of valence electrons. The Co₂-based compounds are found on the so-called localized part of the Slater–Pauling curve [34, 35] where the magnetic moment increases with an increasing number of valence electrons. In this part of the curve one has in majority materials with bcc or bcc-derived structures. Like for the example of iron, the electronic structure of these alloys exhibits a minimum in the minority density of states and the Fermi energy is pinned in this minimum. The minimum in the minority spin density constrains the number of occupied electrons in the minority bands to be approximately three such that the number of majority electrons increases proportionally to the total number of electrons and so does the magnetic moment as a direct consequence (for more details see for example: [34, 35]).

Half-metallic ferromagnets, like the Co₂-based Heusler compounds, are supposed to exhibit not only a minimum but a real gap in the minority density of states and the Fermi energy is pinned inside of that gap. From this point of view, the Slater–Pauling rule is strictly fulfilled with

\[ m_{\text{HMF}} = n_V - 6 \] (2)

for the mean magnetic moment per atom \(m_{\text{HMF}}\). \(n_V\) is the mean number of valence electrons per atom found by averaging over all atoms and 6 is twice the mean number of occupied minority states. The advantage of this equation is that it neither depends on the number of atoms in the compound nor relies on integer site occupancies.

For ordered compounds with different kinds of atoms it might be more convenient to work with all atoms of the unit cell. In the case of four atoms per unit cell, as in Heusler compounds, one has to subtract 24 (6 multiplied by the number of atoms) from the accumulated number of valence electrons in the unit 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 unit cell \(m\):

\[ m = N_V - 24 \] (3)

with \(N_V\) denoting the accumulated number of valence electrons in the unit cell containing four atoms. In the case of Heusler compounds, the number 24 arises from the number of completely occupied minority bands that has to be 12 in the half-metallic state. In particular these are one \(s\) (\(a_{1g}\)), three \(p\) (\(t_{2g}\)), and eight \(d\) bands [34, 36]. 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 valid only at the Γ-point and neglecting the spin of the electrons).

This kind of rule was first noted by Kühler et al [36] for C₁₅ compounds with three atoms per unit cell \(m_{\text{C₁₅}} = N_V - 18\). In both cases the magnetic moment per unit cell becomes strictly integer (in multiples of Bohr magnetons \(\mu_B\)) for Type I or II half-metals, which may be seen as an advantage of the valence electron rule (equation (3)) compared with the original Slater–Pauling approach (equation (2)) even so it suggests the existence of different laws. It is worthwhile to note that equation (3) leads only for ternary 2 : 1 : 1 compounds to integer magnetic moments but not for quarternary derivatives like \(A_2B_{1-x}C'\) or \(A_2BC_{1-x}C'\), as reported in [37] or [38], respectively. In those cases, one observes from (3) non-integer values of the magnetic moment even in the half-metallic case due to the non-integer site occupancy. The present work deals only with 2 : 1 : 1 compounds, therefore, the number of electrons and magnetic moment in the unit cell will be used below for better comparison with previously reported values.

The Slater–Pauling curve is shown in figure 2. Experimental values of the magnetic moments in selected Co₂-based Heusler compounds are compared with 3d transition metals and their alloys. This comparison is possible only if the Slater–Pauling rule in the formulation of (2) is used. The itinerant part of the curve is included for clarity about the behaviour of the Heusler compounds in comparison with other ferromagnetic alloys. For a detailed discussion of that part see [31, 34, 35].

2. Crystal structure and calculational details

The \(A_2BC\) Heusler compounds crystallize in the cubic \(L2₁\) structure (space group no 225: \(F\ 3m\n\)), the prototype is AlCu₂Mn. The structure was first explained by Heusler [3] as well as Bradley and Rodgers [4]. In general, the \(A\) and \(B\) atoms are transition metals and \(C\) is a main group element. In some cases, \(B\) is replaced by a rare earth element. The \(A\) atoms are placed on the Wyckoff position 8c \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\).
The $B$ and $C$ atoms are located on 4a $(0,0,0)$ and 4b $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ positions, respectively. The cubic $L2_1$ structure consists of four interpenetrating fcc sub-lattices, two of which are equally occupied by $A$. The two $A$-site fcc sub-lattices combine to form a simple cubic sub-lattice. The crystal atoms occupy alternatingly the centre of the simple cubic sub-lattice. The $B$ and $C$ atoms occupy alternatingly the centre of the simple cubic sub-lattice resulting in a CsCl-type superstructure. The crystal structure of Heusler compounds is illustrated in figure 1 with the positions shifted by $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with respect to the standard $Fm\bar{3}m$ cell to make the CsCl superstructure better visible. The $\Gamma$ point of the paramagnetic $L2_1$ structure has the symmetry $O_h$. The symmetry of the 4a and 4b positions is $O_h$, whereas the 8c position has $T_d$ symmetry. However, the wave functions at the $\Gamma$ point have to be described by $C_{\text{lm}}$ in the ferromagnetic state to account for the correct transformation of the electron spin.

The cubic $A_2BC$ compounds are only found not with the AlCu$_2$Mn type structure but also with the CuHg$_2$Ti type structure (note that the classification of the cubic $A_2BC$ compounds with those two structures is sometimes not uniquely given in Pearson’s Handbook [39]). The CuHg$_2$Ti type structure exhibits $T_d$ symmetry (space group no 216: $F\bar{4}3m$). In that structure the $A_2$ atoms occupy the non-equivalent 4a, 4c Wyckoff positions at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The $B$ and $C$ are located on 4b $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and 4d $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ positions, respectively. All four positions adopt $T_d$ symmetry and there is no position with $O_h$ symmetry. This structure is similar to the $ABC$ compounds with $C_1$ structure, but with the vacancy filled by an additional A atom. This structure is frequently observed if the nuclear charge of the $B$ element is larger than the one of the $A$ element from the same period, that is $Z(B) > Z(A)$ for two 3$d$ transition metals. The structure may also appear in compounds with transition metals from different periods. However, the two structures may be hardly distinguishable by x-ray diffraction and much care has to be taken in the structural analysis, as both have the general fcc-like symmetry. It is interesting to note that both types of structures result in the $A1$ structure (bcc-like) if the atoms are randomly distributed over the sites of the unit cell, that is for complete alloying. In that case the magnetic moment might still follow the localized part of the Slater–Pauling curve displayed in figure 2 even though the half-metallic character is lost and the gap in the minority bands is closed and only a minimum appears in the minority density of states. In this paper, only calculations for compounds of the AlCu$_2$Mn type are respected to stay within the $O_h$ symmetry.

In the present work, the electronic structure calculations based on density functional theory were performed using the full-potential linear augmented plane wave (FLAPW) code WIEN2k [40]. The exchange-correlation functional was evaluated within the GGA, using the Perdew–Burke–Ernzerhof [21] parametrization. The energy threshold between the core and the valence states was set to $-81.6$ eV. The muffin-tin-radii ($R_{\text{MT}}$) were chosen to ensure nearly touching spheres and minimizing the interstitial space. $R_{\text{MT}} \times k_{\text{max}} = 7$ was used for the number of plane waves and the expansion of the wave functions was set to $l = 10$ inside of the muffin tin spheres. The self-consistent calculations employed a grid of $455$ $k$ points in the irreducible Brillouin zone taken from a $25 \times 25 \times 25$ mesh. It turned out that this number of irreducible $k$ points is a good compromise to balance the quality of the integration and the speed of the calculation. The energy convergence criteria was set to $10^{-5}$ Ry and the charge convergence was monitor simultaneously (note: The calculations were restarted if the charge convergence was after energy convergence still above 0.01 electrons).

It was recently reported that the LSDA and GGA schemes are not sufficient to describe the electronic structure correctly for Co$_2$FeSi [27]. Therefore, the LDA + $U$ method [41] was also used here to account for on-site correlation at the transition metal sites. The LDA + $U$ method accounts for an orbital dependence of the Coulomb and exchange interaction that is absent in the pure LDA or GGA. In particular, the effective Coulomb-exchange interaction ($U_{\text{eff}} = U - J$) was used for the present calculations. The LDA + $U$ self-interaction correction (SIC) scheme is used in WIEN2k to account for double-counting corrections. The use of $U - J$ neglects, however, multipole terms in the expansion of the Coulomb interaction. It should be mentioned that the $+U$ was used on top of GGA rather than LSDA parametrization of the exchange correlation functional. No significant differences were observed using one or the other of the parametrizations.

The $U_{\text{eff}}$ values being used for the calculations are summarized in table 1 for the different 3$d$ elements. The values for Co, Mn and Fe are able to explain the magnetic moment in Co$_2$Mn$_{1-x}$Fe$_x$Si over the whole range of Fe concentration, as was found in previous calculations [37]. All values correspond to about 7.5% of those calculated for 3$d$ ions using Cowan’s program [42] and are close to the values for the Coulomb interaction $U_{\text{dd}}$ for $d$ electrons in the elemental 3$d$ transition metals, as reported in [43]. Comparing the semi-empirical values of table 1 with the values found in constrained LDA calculations (for details see [37]), it was found that the latter are too high to explain the magnetic moments. Additional calculations for the elemental 3$d$ transition metals revealed that all values for $U_{\text{eff}}$ found in constrained LDA calculations are considerably too high to explain those metallic systems correctly. This is despite the fact that such calculations may result in reliable values for Mott insulators [29]. The constrained LDA calculations revealed that the $U_{\text{eff}}$ values at the Co site may vary by about ±10% depending on the atoms on $B$ or $C$ sites. As $U_{\text{eff}}$ was here used as a parameter for LDA+$U$, fixed values have been preferred for better comparison.

It was found theoretically by Mavropoulos et al [44] that the spin–orbit interaction has only a weak influence on the half-metallic ferromagnetism in Heusler compounds. Later Picozzi et al [18] and Galanakis [45] reported the same for Co$_2$-based Heusler compounds, therefore spin–orbit interaction was neglected in the calculations discussed here. To verify this assumption, test-calculations, including spin–orbit

| Element | $U_{\text{eff}}$ (eV) |
|---------|-------------------|
| Ti      | 1.36              |
| V       | 1.34              |
| Cr      | 1.59              |
| Mn      | 1.69              |
| Fe      | 1.80              |
| Co      | 1.92              |

Table 1. $U_{\text{eff}}$ values used for the different elements in the LDA + $U$ calculations of Heusler compounds.
interaction, were performed for several Co$_2$-based Heusler compounds. These calculations revealed a ratio of the orbital to spin moment ($m_o/m_s$) in the order of only 10$^{-2}$. These values are in agreement with those earlier reported by Ishida et al [46]. Therefore, the present calculations include only the mass velocity and Darwin terms to correct for relativistic effects.

3. Results and discussions

In the half-metallic Heusler compounds discussed here, the gap stays with few exceptions in the minority spin channel, whereas $\epsilon_F$ cuts through bands in the majority spin channel. For the majority spin channel, the position of $\epsilon_F$ is in the region of the $d$ derived bands. These states are shifted to lower energies with respect to the corresponding minority spin states by the exchange splitting. Half-metallic behaviour has already been predicted for a large number of Heusler compounds which are members of the series of ferromagnetic compounds. In general the $B$ atoms and in some cases also the $A$ atoms carry the magnetic moments in these compounds. It is well known that the magnetic properties of these compounds depend sensitively on the valence electron concentration [17, 23, 34]. The magnetic properties depend on whether the $C$ component is a member of the 3$A$ or 4$A$ main group, with the latter group resulting in higher magnetic moments and Curie temperatures. Spin polarized electronic structure calculations indicate that the moments are predominantly of 3$d$ origin. The density of state of the minority states is almost zero at the Fermi energy whereas the majority $d$ density can have a peak or a valley close to $\epsilon_F$. It is filling and emptying of the majority states that is assumed to produce the change in the size of the magnetic moment and the Curie temperature. In order to verify this, and to obtain further evidence for half-metallic behaviour, a series of calculations for $A_2BC$ compounds was performed and is presented in the following.

3.1. Structural optimization for Co$_2$CrSi and Co$_2$ScSi

It might be of interest to first have a look at those compounds which are missing (no report in the literature found) from the series of Co$_2$ BC Heusler compounds. The compound Co$_2$ScSi is not reported in any experiment, and neither is Co$_2$CrSi. Within the FLAPW scheme, a structural optimization was performed for these two compounds to find the lattice parameter resulting in the minimum of the total energy. It was also confirmed that the ferromagnetic configuration is lower in energy than the non-spin polarized case for both compounds. An anti-parallel spin arrangement of the Cr atoms with respect to the Co atoms in the cubic lattice showed to be energetically unfavourable with respect to the ferromagnetic arrangement in the Co$_2$CrSi compound. The results of the structural optimization are shown in figure 3. The detailed values of the optimized lattice parameters are given later in table 3. Details of the values of the calculated total spin magnetic moment and the elemental resolved moments are also included in table 3.

The calculated total magnetic moments are 1 $\mu_B$ and 4 $\mu_B$ for Co$_2$ScSi and Co$_2$CrSi, respectively. This is in good agreement with a Slater–Pauling-like behaviour. The magnetic moment at the Co site is 0.6 $\mu_B$ in Co$_2$ScSi and 1 $\mu_B$ in Co$_2$CrSi, the remainder arises mainly from the $B$ site (see table 3).

Figure 4 shows the calculated DOS and band structures of both hypothetical compounds. These band structures may serve as a common basis for the explanation of many Co$_2$-based Heusler compounds. It is easily seen that the band structures are very similar, the main difference is the position of the majority bands with respect to the Fermi energy or the minority bands. Typical for Heusler compounds is the occurrence of a hybridization gap that splits the low lying $s$ bands (at below about $-8$ eV) from the high lying $p$ and $d$ bands. The size of that gap, appearing in both spin directions, increases with increasing hybridization strength. It should be noted that the strongly dispersing bands seen in the majority states of Co$_2$CrSi starting just above the Fermi energy are of $d$ character.

Both compounds exhibit a clear gap in the minority band structure and thus a half-metallic ferromagnetic behaviour with only majority bands crossing $\epsilon_F$. The band gap in the minority states results in $P = 100\%$ spin polarization for these compounds at $\epsilon_F$.

The majority density of states at $\epsilon_F$ is lower in Co$_2$ScSi (1.36 eV$^{-1}$) as compared with the Co$_2$CrSi compound (2.9 eV$^{-1}$), as expected. The Cr compound exhibits a considerably larger minority gap compared with the Sc compound, as is seen from the density of states as well as the band structure. Both compounds exhibit a different size of the minority band gap that is determined by the top of the valence band at the Gamma point and the bottom of the conduction band at the X-point. The restriction of the upper energy of the gap by the bottom of the conduction band at the X-point is typical for the most Co$_2$-based Heusler compounds. In some cases the gap becomes closed by pulling the conduction band just in the vicinity of the X-point below $\epsilon_F$. Here, the width of the minority band gap is found to be 0.246 eV and 0.878 eV for Co$_2$ScSi and Co$_2$CrSi, respectively.

3.2. Calculated magnetic and electronic structure

In the following sections the electronic structure and magnetic properties of the Heusler compounds are discussed in
more detail. The starting point is the Co$_2$-based Heusler compounds.

### 3.2.1. Magnetic properties calculated in the GGA

Starting with the Co$_2$-based compounds, all the information about the calculated total magnetic moments, atom-resolved moments and hyperfine fields, as well as the experimental lattice parameters and magnetic moments are summarized in Table 2. For each compound, calculations were carried out using the experimental lattice parameters, and most of them exhibit at least nearly a HMF type character (gap in the minority or majority states). This is clear from Figures 6 and 7 where the spin projected density of states of nine selected compounds are shown. (Note, details will be discussed later.)

In most of the cases given in Table 2, the calculated total spin magnetic moment is exactly integer as expected for a half-metallic system. The experimental magnetic moments $m_{\text{exp}}$ are also given in Table 2 for comparison with the calculations. In most cases, the calculated magnetic moments $m_{\text{cal}}$ are in good agreement with the experimental results. Deviations between experimental and calculated values appear particularly for compounds carrying a high magnetic moment like Co$_2$FeSi or Co$_2$FeGe where the calculations result in too low values.

An inspection of the site resolved magnetic moments ($m_{\text{Co}}$ and $m_{\text{B}}$) reveals that the Co and B atoms may both possess high spin magnetic moments in this series of compounds. In the case of small magnetic moment compounds, the Co atoms contribute mostly to the moment, when compared with the compounds with large magnetic moments. While going from the low to the high magnetic moment side, the B atoms contribute an increasing moment.

It should be noted that $m_{\text{cal}}$ is the calculated total spin magnetic moment of the compound found by integration over the entire cell. Therefore, it is not just the combination of the moments at the A (2 times), B and C sites but respects also the moment of the interstitial between the sites. The interstitial is due to the calculational scheme using non-overlapping spheres to define the sites. That is the reason why the site resolved values $m_A$ and $m_B$ alone are not summing up to result in $m_{\text{cal}}$. The missing or excess of the total moment is found at the C sites and to some extent also in the interstitial between the sites where the wave functions are expanded as plane waves. It should also be pointed out that there might be a discrepancy with measurements of the x-ray magnetic circular dichroism (XMCD) in photoabsorption as this method integrates strictly over the extent of the initial state wave functions that are the 2$p$ core level in absorption at the L edges.

In all reported compounds, the C atoms carry a negligible magnetic moment, that does not contribute much to the overall moment. In most of the compounds it is aligned anti-parallel to the A and B moments. It emerges from hybridization with the transition metals and is caused by the overlap of the electron wave functions. Here, the small moments found at the C sites are mainly due to a polarization of these atoms by the surrounding, magnetically active atoms on the A and B sites. This polarization also results in non-vanishing hyperfine fields at the nucleus of the atoms on C sites.

In summary, the magnetic moment of most of the compounds shown in Table 2 exhibits a linear behaviour with the number of valence electrons and thus follows the Slater–Pauling rule (equation (3)). However, there are some deviations from this trend: for example, Co$_2$FeAl, Co$_2$VGa, Co$_2$TiGa and Co$_2$ScSi. That means, there are some cases where the pure LSDA or GGA does not give the magnetic moments expected for half-metallic ferromagnetism, and $\epsilon_F$ may not fall into the minority gap.
magnetic moments but also the hyperfine fields are too small
can be determined by nuclear magnetic
resonance (NMR) or Mössbauer spectroscopy. In particular,
determined from NMR spin echo measurements or those of Fe
the hyperfine field at Mn or Co can easily be distinguished and
increase with increasing site resolved magnetic moments. This
is worthwhile to note that for Co\textsubscript{2}FeSi not only the calculated
also found for the high moment Fe containing compounds. It
Mn in combination with a group IIIa element. Deviations are
is expected because the increasing partial magnetic moments
in the vicinity of the
values as reported in
The calculated total magnetic moments \( m_{\text{exp}} \) are compared to experimental values \( m_{\text{exp}} \). All magnetic moments are given in \( \mu_\text{B} \). \( N_\text{v} \) is the number of valence electrons per formula unit (within parentheses). Total magnetic moments are given per unit cell. \( m_{\text{exp}} \) and \( m_{\text{g}} \) are the site resolved magnetic moments on Co and B sites, respectively. The calculated hyperfine fields \( H_{hf} \) at Co and B sites are given in M\text{Am}^{-1}. Most of the experimental values of the lattice parameter \( m_{\text{exp}} \) and magnetic moment \( m_{\text{exp}} \) are taken from [39, 47–52], additional references on experimental data are given in the last column of the table.

Besides the total magnetic moment, another easily
accessible experimental quantity is the hyperfine field. Values
for the hyperfine fields can be determined by nuclear magnetic
resonance (NMR) or Mössbauer spectroscopy. In particular,
the hyperfine field at Mn or Co can easily be distinguished and
determined from NMR spin echo measurements or those of Fe
by Mössbauer spectroscopy. Table 2 also lists the calculated
hyperfine fields, that may be compared with experimental values as reported in Landolt–Börnstein (see [51, 52] and references therein) or in the additional references given in table 2. In general, the hyperfine fields show a trend to
increase with increasing site resolved magnetic moments. This
is expected because the increasing partial magnetic moments
increase the polarization of the \( s \) electrons—being mainly
responsible for the hyperfine field—in the vicinity of the
nucleus. This trend is broken for Co in compounds with Cr and
Mn in combination with a group IIIa element. Deviations are
found for high moment Fe containing compounds. It is
worthwhile to note that for Co\textsubscript{2}FeSi not only the calculated
magnetic moments but also the hyperfine fields are too small
in the GGA calculations compared with experimental values
[81, 83].

In all comparison between the experimental and the
calculated quantities, lattice parameter, magnetic moments
or hyperfine fields, one should carefully check whether the
compound under investigation has had the required \( L2_1 \)
structure in the experiments.

The following will be concentrated on selected compounds; these nine compounds are Co\textsubscript{2}BC Heusler compounds with \( B = \text{Ti, V, Cr, Mn, Fe} \) and \( C = \text{Al, Ga and Si} \). They will be used as representatives of the compounds
as listed in table 2. By making such a choice, one covers both
a range of electronically different kinds of \( B \) and \( C \) atoms with
Co atoms at the A site.

### Table 2. Magnetic properties of Co\textsubscript{2}BC Heusler compounds.

| Compound  | \( N_\text{v} \) | \( m_{\text{exp}} \) | \( m_{\text{calc}} \) | \( m_{\text{Co}} \) | \( m_{\text{B}} \) | \( H_{hf}(\text{Co}) \) | \( H_{hf}(\text{B}) \) | References |
|-----------|-----------------|---------------------|--------------------|--------------------|----------------|-----------------------|-----------------------|------------|
| Co\textsubscript{2}TiAl | 25 | 5.847 | 0.74 | 1.00 | 0.67 | -0.18 | 4.23 | 3.89 | [53] |
| Co\textsubscript{2}TiGa | 26 | 5.743 | 1.65 | 2.00 | 1.03 | -0.01 | 5.63 | 5.48 | [37] |
| Co\textsubscript{2}TiGe | 26 | 5.807 | 1.59 | 1.97 | 1.05 | -0.06 | 5.56 | 5.89 | [37] |
| Co\textsubscript{2}TiSn | 26 | 6.077 | 1.96 | 1.96 | 1.08 | -0.07 | 4.82 | 6.12 | [53, 58–60] |
| Co\textsubscript{2}VAi | 26 | 5.722 | 1.95 | 2.00 | 0.94 | 0.22 | 5.31 | 6.92 | [37, 61] |
| Co\textsubscript{2}VGa | 26 | 5.779 | 1.92 | 2.01 | 0.97 | 0.16 | 4.79 | 6.07 | [62, 63] |
| Co\textsubscript{2}VSi | 27 | 5.657 | — | 3.00 | 1.09 | 0.79 | 5.11 | 7.80 | [64] |
| Co\textsubscript{2}VSn | 27 | 5.960 | 1.21 | 3.03 | 1.10 | 0.86 | 3.26 | 8.59 | [57, 65] |
| Co\textsubscript{2}CrAl | 27 | 5.727 | 1.55 | 3.00 | 0.83 | 1.47 | 1.45 | 11.35 | [61, 63] |
| Co\textsubscript{2}CrGa | 27 | 5.805 | 3.01 | 3.05 | 0.76 | 1.63 | 2.46 | 11.08 | [61, 66, 67] |
| Co\textsubscript{2}CrIn | 27 | 6.060 | 1.10 | 3.20 | 0.67 | 1.98 | — | — | [68] |
| Co\textsubscript{2}MnAl | 28 | 5.749 | 4.04 | 4.04 | 0.76 | 2.75 | 13.89 | 16.49 | [61, 69, 70] |
| Co\textsubscript{2}MnGa | 28 | 5.767 | 4.05 | 4.12 | 0.75 | 2.78 | 11.71 | 15.12 | [61, 70] |
| Co\textsubscript{2}MnSi | 29 | 5.645 | 4.90 | 5.00 | 1.00 | 3.00 | 8.02 | 16.19 | [61, 71–74] |
| Co\textsubscript{2}MnGe | 29 | 5.749 | 4.93 | 5.00 | 1.02 | 3.06 | 8.15 | 16.51 | [61, 71] |
| Co\textsubscript{2}MnSn | 29 | 5.984 | 5.08 | 5.03 | 0.97 | 3.23 | 10.72 | 16.63 | [61, 70–72, 75–78] |
| Co\textsubscript{2}FeAl | 29 | 5.730 | 4.96 | 4.98 | 1.23 | 2.80 | 12.82 | 17.41 | [61, 79] |
| Co\textsubscript{2}FeGa | 29 | 5.737 | 5.04 | 5.02 | 1.20 | 2.81 | 12.82 | 18.64 | [61, 66, 67, 80] |
| Co\textsubscript{2}FeSi | 30 | 5.640 | 6.00 | 5.59 | 1.40 | 2.87 | 7.38 | 18.56 | [26, 61, 81–83] |
| Co\textsubscript{2}FeGe | 30 | 5.738 | 5.90 | 5.70 | 1.42 | 2.92 | 7.31 | 19.66 | — | — |

The electronic structure is in most cases independent of the use
of different compounds with different valence electron
concentrations. It cannot be excluded that some of the experimental lattice parameters \( m_{\text{exp}} \) given in table 2
were determined for disordered compounds and not for the
required \( L2_1 \) structure. The use of wrong lattice parameters in
the calculations may lead to the prediction of a wrong ground
state. Therefore, the lattice parameters of the two series of
compounds Co\textsubscript{2}B\textsubscript{2}Al and Co\textsubscript{2}B\textsubscript{2}Si (\( B = \text{Sc, Ti, V, Cr, Mn, Fe} \)) were optimized. The lattice parameter \( a_{\text{exp}} \) minimizing the total energy defines the optimal \( a \) and is tabulated in
table 3. These values were taken as input for further calculations.

The optimized lattice parameters were found to be on
average within \(<0.5\%\) of the experimentally obtained lattice
parameters, as is seen from table 3. This implies that the
structure in most cases independent of the use
of the experimental or optimized lattice parameters. A large
deviation is found for Co\textsubscript{2}FeAl that is known to exhibit in
experiments a disordered \( B2 \) structure. The deviation is even
larger for Co\textsubscript{2}MnAl, which may also point to some type
of disorder. Differences in the element specific magnetic
moments are mainly due to the different muffin-tin radii that
were fixed to the lowest needed value during the optimization
procedure while varying only \( a \). In the two cases, Co\textsubscript{2}MnSi and
Co\textsubscript{2}FeSi, the optimized lattice parameter was found to match
the experimental one within the uncertainty of experiment

References
Table 3. Magnetic data for the series Co$_2$BC ($C$ = Al, Si) with optimized lattice parameter.

| Compound   | $a_{\text{opt}}$ | $\Delta(a)$ | $m_{\text{tot}}$ | $m_{C_{\alpha}}$ | $m_B$ |
|------------|------------------|--------------|-------------------|------------------|-------|
| Co$_2$ScAl | 5.960            | —            | 0                 | 0.00             | 0.00  |
| Co$_2$TiAl | 5.828            | —0.3         | 1                 | 0.62             | —0.13 |
| Co$_2$VAl  | 5.754            | +0.6         | 2                 | 0.94             | 0.23  |
| Co$_2$CrAl | 5.708            | —0.3         | 3                 | 0.80             | 1.52  |
| Co$_2$MnAl | 5.695            | —0.9         | 4                 | 0.77             | 2.67  |
| Co$_2$FeAl | 5.692            | —0.7         | 5                 | 1.22             | 2.79  |
| Co$_2$ScSi | 5.865            | —            | 1                 | 0.60             | —0.10 |
| Co$_2$TiSi | 5.760            | +0.3         | 2                 | 1.03             | —0.02 |
| Co$_2$VSi  | 5.688            | +0.5         | 3                 | 1.10             | 0.80  |
| Co$_2$CrSi | 5.647            | —            | 4                 | 1.00             | 2.03  |
| Co$_2$MnSi | 5.643            | 0            | 5                 | 1.06             | 2.99  |
| Co$_2$FeSi | 5.634            | 0            | 5.55              | 1.39             | 2.85  |

Listed are the optimized lattice parameters ($a$ in Å), total magnetic moments ($m_{\text{tot}}$), and atom resolved magnetic moments ($m_{C_{\alpha}}$ and $m_B$). $\Delta(a)$ is the change of the lattice parameter in % with respect to the experimental value. All magnetic moments are given in $\mu_B$.

Figure 5. Element specific magnetic moments of the series Co$_2$BC $(C = \text{Al}, \text{Si})$. Shown is the evaluation of the magnetic moments at the Co and B sites for Fe. Here, the moment at the iron site even decreases compared with Mn. Seemingly this decrease of the moment at Fe cannot be compensated by the Co atoms, resulting in an overall moment being too small to be compatible with the Slater–Pauling rule.

and calculation. However, the magnetic moment of the Fe containing compound is still too low.

In table 3, the total and element specific magnetic moments for Co and the atoms on the B sites are displayed together with the optimized lattice parameters. In the Co$_2$BAI series, the magnetic moment at the Co site first increases and then stays at about 1 $\mu_B$, while the magnetic moment at the B site starts from small negative values and then increases linearly with the valence electron concentration (see also figure 5). In all compounds, the induced magnetic moment at the Al and Si sites is very small and anti-parallel to Co. It seems that the moment of Co is fixed at about 1 $\mu_B$ and compels the B moment to result in the overall magnetic moment according to the valence electron concentration.

In detail, the magnetic moment at the Co site stays at about 1 $\mu_B$ from Ti to Mn and diverges from this value only for Sc and Fe containing compounds. The magnetic moment at the B site increases linearly from Ti to Mn compounds such that the total magnetic moment follows the Slater–Pauling rule but deviates from this trend for Fe. Co$_2$ScAl has 24 valence electrons and the magnetic moment vanishes at all sites. The result is a vanishing total magnetic moment as expected from equation (2). A ferrimagnetic behaviour with compensating moments, as reported for Mn$_2$-based compounds [84], was not observed. The reason is that the single d electron at the Sc site is not able to form a localized moment by filling a majority $e_g$ band completely.

In the Co$_2$BSi series, the trends are the same as in the just discussed Al series. The only difference is the detail of the magnetic moments at Co and B atoms. In particular in Co$_2$ScSi, the Co$_2$ sub-lattice starts to order ferromagnetically whereas the Sc atoms do not contribute to the magnetic moment. The formation of the magnetic Co$_2$ sub-lattice is completely different from the classical Heusler compounds like Cu$_2$MnAl where the magnetic order is mediated only by the strong local moment at the Mn atom. Finally, one observes again the break of the trend of increasing moments at the B site for Fe. Here, the moment at the iron site even decreases compared with Mn. Seemingly this decrease of the moment at Fe cannot be compensated by the Co atoms, resulting in an overall moment being too small to be compatible with the Slater–Pauling rule.

In summary the Co atoms contribute in the Co$_2$BC $(C = \text{Al}, \text{Si})$ compounds about 1 $\mu_B$ to the magnetic moment and drive the properties of the B atoms to have a magnetic moment according to the number of valence electrons of the compounds. The properties of the Co$_2$BC compounds are dominated by the nature of the Co atoms, which force the extent of localization of the electrons and the resulting magnetic moment at the B site. The result is that the total magnetic moment follows the Slater–Pauling rule (compare equations (2) and (3)). The behaviour of the compounds with other elements on the C site is similar, as can be seen from table 2. The increase of the magnetic moments at the Co and B sites is attributed to the rearrangement of the electrons and is discussed briefly in the next section. Obviously, the calculated magnetic moments of the compounds Co$_2$FeSi and Co$_2$FeGe are too small compared with the experimental value. This fact will be discussed later together with on-site correlation.

3.3. Electronic structure and density of states

As seen in the previous section, the Co$_2$BC compounds can be distinguished in two classes, one with small magnetic moments (less than 4 $\mu_B$) and the remainder with high magnetic moments. The class of compounds with small magnetic moments will be called ‘low-$m$’ and the one with high magnetic moments ‘high-$m$’. In the following sections, the density of states and the distribution of the electrons over the various states and atoms are discussed.

3.3.1. Low-$m$ compounds

The DOS for the low-$m$ compounds Co$_2$TiAl, Co$_2$TiSi, Co$_2$VAl and Co$_2$VSi are displayed in figure 6. The upper part of each panel displays the majority spin densities and the lower one the minority spin densities.

The increase of the splitting of the minority states at the Fermi energy is clearly visible. In Co$_2$TiAl the Fermic energy is close to the minority valence states, whereas it is positioned in the upper half of the gap close to the minority conduction band for the remaining compounds. The size of the gap increases if Al is replaced by Si. At the same time the size of
Calculated electronic and magnetic properties

Figure 6. Density of states of selected low-\(m\) \(\text{Co}_2\text{BC}\) compounds. Shown are the spin resolved DOS for compounds with \(B = \text{Ti, V}\) and \(C = \text{Al, Si}\). (Note: upper and lower parts of the panels show for each compound the majority \(\rho^\uparrow\) and minority \(\rho^\downarrow\) DOS, respectively.)

the Heusler-typical gap at below \(-46\) eV increases considerably from some hundred meV to about 2 eV. This points to a much stronger hybridization in the Si containing compounds compared with the Al containing compounds. As typical for low-\(m\) compounds, the majority states exhibit a rather high density in the vicinity of \(\epsilon_F\) that is caused by weakly dispersing, flat bands. The width of the \(d\) bands is almost the same in all four compounds. Indeed, in all four compounds the states at and close to \(\epsilon_F\) are strongly spin polarized and all four systems exhibit a gap in the minority states. The spin polarization is found to be 100%, which characterizes the systems to be half-metallic.

3.3.2. High-\(m\) compounds. In the next step, the six compounds \(\text{Co}_2\text{BC}\) (\(B = \text{Cr, Mn, Fe and C = Al, Ga}\)) with intermediate and high-\(m\) values were chosen. The DOS of these compounds is displayed in figures 7(a)–(f).

The situation of the high-\(m\) compounds with Mn and Fe is somewhat different from the low-\(m\) compounds. All listed compounds exhibit almost the same band width with a gap in the minority states. However, there are distinct differences in the shapes of the densities. Some pronounced changes are observed in the DOS while going from the low-\(m\) compounds to the high-\(m\) compounds. A decrease in the contribution from majority states just at \(\epsilon_F\) is observed. In the Cr compounds, with about 3 \(\mu_B\), one still observes a high majority density of states close to \(\epsilon_F\). In the Mn compounds, with about 4 \(\mu_B\), this high majority density is shifted just below \(\epsilon_F\) and finally one observes only a rather low density in the Fe compounds with 5 \(\mu_B\) that emerges from strongly dispersing bands (compare to the band structure of \(\text{Co}_2\text{CrSi}\) discussed above). This low density of the majority states close to \(\epsilon_F\) is nevertheless arising from \(d\) electrons. The particular shape of the majority DOS of the high-\(m\) compounds is finally the reason for the observed deviation of the magnetic moments in \(\text{Co}_2\text{FeSi}\) or \(\text{Co}_2\text{FeGe}\). The filling of one more electron by replacing Al by Si (or Ga by Ge) will need a much larger energy range to add up 1 \(\mu_B\). It also will shift the states with high density much further away from \(\epsilon_F\), which is obviously not possible if attributing the shift only to an exchange splitting. That might be one reason why LSDA fails to find the correct moments of 6 \(\mu_B\) but needs some additional interaction between the electrons. This interaction can be interpreted in the underestimation of on-site correlation [27]. However, if it plays a role in the high-\(m\) compounds it should do so in the low-\(m\) compounds, too. This fact will be discussed later.

At that point, it should be noted that the magnetic moment does not depend on the density of states at the Fermi energy. Neither does it depend much on the particular shape of the DOS or band structure as it is an integrated quantity, namely the difference between the number of occupied majority and minority electrons. From that point of view the magnetic moment may help to find half-metallic ferromagnets; however, it is not suited to prove the existence of band gaps in the minority states.

3.3.3. Distribution of the electrons and influence of the main group element \(C\). On careful examination of the magnetic moments on the Co sites in both series (\(\text{Co}_2\text{BC}\) with \(C = \text{Al and Si}\)), one finds that the Co site is carrying an average of

Figure 7. Density of states for low to high-\(m\) \(\text{Co}_2\text{BC}\) compounds. Shown are the spin resolved DOS for compounds with \(B = \text{Cr, Mn, Fe and C = Al, Ga}\). (Note: upper and lower parts of the panels show for each compound the majority \(\rho^\uparrow\) and minority \(\rho^\downarrow\) DOS, respectively.)
0.8 $\mu_B$ (Al series) and 1.0 $\mu_B$ (Si series). At this point it is not quite clear why the magnetic moment of Co is changing with the exchange of Al by Si. Thus the question arises how C affects the overall magnetic moment without directly contributing to it? To check this, it is necessary to inspect the electron distribution of the system.

The total magnetic moment in the series is defined by the number of occupied $d$ electrons in the majority and minority states because the number of occupied $s$ and $p$ states is rather independent of the spin (note that the total number of valence electrons $N_V$ appears in (3) only because $N_V = N_1 - N_1$, such that $m = N_1 - N_1$ can be rewritten to be $m = N_V - 2N_f$). The total number of $d$ electrons at the Co site is about 7.5 including majority and minority electrons (see figures 8(a) and (b)). The Co $d$ states for majority and minority spin are almost constant and contain about 4 and 3 electrons, respectively. Their values are nearly constant and do not change much if going from Ti to Mn. This is one reason why the magnetic moment of Co is fixed at about 1 $\mu_B$.

The distribution of the $d$ electrons in the majority and minority states for the B element is shown in figures 8(c) and (d). It is clear that filling of both the majority and the minority $d$ electrons increases in parallel up to V and thereafter the electrons start to fill more majority $d$ states as compared with minority $d$ states. Al and Si contribute very less to the $d$ states and in fact they do not contribute directly to the overall magnetic moment. In general, it is found that the trends are the same in the Co$_2$BSi and Co$_2$BAl compounds. Therefore, it is not enough to study only the general behaviour of the $d$ states.

In order to have a deeper insight, the distribution of electrons in states with different symmetry has been studied in the series of Co$_2$BAl and Co$_2$BSi. As determined earlier by Kübler [36], to maximize the number of unpaired electrons, the minority states should be filled by 8 $d$ electrons and the rest of the electrons fill the majority states. In the Co$_2$BAl series, overall (average) 7.85 $d$ electrons are in the minority states. There should be 8 $d$ electrons to fill the $d$ states completely and to have a gap. The missing part of the electrons is found in the interstitial. That is, they are completely de-localized and cannot be attributed to a particular atom. When inspecting the Co$_2$BSi series, the number of total minority $d$ electrons is on average 7.5. The remaining are found in the interstitial and overlap with the Si $s$ and $p$ states. To probe this situation in detail, LMTO-ASA [85] calculations were performed to obtain the crystal orbital Hamiltonian population (COHP) of Co–Al and Co–Si. It was found that the bonding interaction between Co and Si is much stronger than between Co and Al. This is expected from the higher electro-negativity of Si compared with Al. Due to the stronger bonding interaction between Co and Si in Co$_2$BSi, some more electrons are in between the atoms and missing from the expected total count of 8. At the same time, the electrons in the majority states are redistributed with the result of a higher magnetic moment.

Replacement of Al by Si or exchange between other members of the 3A and 4A groups plays an important role for the distribution of electrons in the various symmetry distinguished states ($t_{2g}$ and $e_g$) at Co as well as at B sites, as summarized in figure 9. In fact, the overall number of $d$ electrons remains the same. Addition of an extra electron by replacing Al by Si affects mostly all symmetry distinguished states except the $e_g$ states at the Co site. The latter $e_g$ states form the bonds between the Co sites in the (1 0 0)-like planes.

The number of symmetry resolved $e_g$ and $t_{2g}$ states at B increases linearly. In particular, the $e_g$ states at B are not affected by other states. The reason is that there is no possible direct overlap to other states of the same symmetry at nearest neighbours, whereas the $t_{2g}$ states form the bonds with the atoms at the Co sites. The $e_g$ states at the B site are mainly responsible for the localized magnetic moment at this site. In the Al compounds a moment attributed to the Co $t_{2g}$ states is

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**Figure 8.** Valence $d$ electrons in Co$_2$BC compounds. Shown are the total (tot) and spin resolved ($\uparrow$ = majority, $\downarrow$ = minority) numbers of $d$ electrons in Co$_2$BAl (a), (c) and Co$_2$BSi (b), (d) with $B =$ Sc, Ti, V, Cr, Mn and Fe. (a), (b) are for Co and (c), (d) for atoms at the $B$ site.
however, that the B over the Co and the same at the X-band.\(\Delta 1\) states distinguished for \(\uparrow \) and \(\downarrow \) display the distribution of the majority \(\uparrow\) and minority \(\downarrow\) states in Co\(_2\)Al\((a), (c) and (e)\) and Co\(_2\)BSi\((b), (d)\) and \((f)\).\((a), (b)\) display the distribution of the majority \(\uparrow\) and minority \(\downarrow\) states distinguished for \(e_g\) and \(t_{2g}\) symmetry at Co, and \(c), (d)\) the same at the B sites. The total distribution of the \(e_g\) and \(t_{2g}\) states over the Co and B sites is shown in \((e), (f)\).

only for B = Fe worth mentioning. The interesting point is, however, that the \(t_{2g}\) states at the Co site contribute much more to the magnetic moment in the Si compounds as compared with the Al compounds. This observation, finally, links the indirect connection between the site specific magnetic moment at Co and the hybridization arising from the interaction between the electrons at the C sites with the neighbouring electrons in the Co \(t_{2g}\) states.

3.4. The properties of the minority band gap

The half-metallic ferromagnetism manifests itself in a band gap in one of the spin densities. However, the Fermi energy may fall inside or outside of that gap. The band structure of all calculated compounds was carefully examined to find the top of the valence band \((E_{\text{max}})\) and the bottom of the conduction band \((E_{\text{min}})\) enclosing the gap. Tables 4 and 5 summarize the results calculated for the minority band gap of the Co\(_2\)BC compounds. All of the listed compounds show a gap along \(\Delta = \Gamma - X\) that is in the \(\Delta\)-direction of the paramagnetic state. The \(\Delta\)-direction is perpendicular to the Co\(_2\)\((1 0 0)\)-planes. As was shown earlier [25], just the \(\Delta\)-direction plays an important role in understanding the HMF character and magnetic properties of Heusler compounds. This fact was also pointed out by Öğüt and Rabe [86].

Table 4 is devoted to the properties of Type I half-metals where \(\epsilon_F\) is located inside the gap of the minority band structure. As a direct consequence, the minority density \(\rho_\downarrow(\epsilon_F)\) at the Fermi energy vanishes and the spin polarization \((\epsilon(1))\) is 100%. The listed compounds \(\epsilon\) the except the four shown at the bottom of the table) exhibit a clear gap at \(\epsilon_F\) and behave like half-metallic ferromagnets, at least within GGA.

The minority gaps of the clear Type I half-metals have, with the exception of Co\(_2\)VGa, a width of \(\Delta E \approx 0.5–0.8\,\text{eV}\). The gap is considerably smaller in those compounds being close to Type III-like behaviour (see also figure 10).

Only few compounds containing Cr or V have a remarkably high majority DOS at \(\epsilon_F\) whereas the remainder exhibit lower values of about \(1\,\text{eV}^{-1}\). As one approaches high magnetic moment compounds containing Fe, there is a reduction in the density of states of the majority spin states at \(\epsilon_F\). Instead of a high majority DOS they exhibit only a small DOS. Already the GGA calculations reveal this small DOS at \(\epsilon_F\).

The important conclusion one can draw at this point is that the LSDA-GGA does not estimate the gap and magnetic
is not a necessary condition for the formation of half-metallic ferromagnets. Shown is the size of the gap (ΔE) as a function of the lattice parameter (a). The width of the gap was determined from the band structure calculated with GGA. Type I half-metals are displayed as filled and other materials by open symbols. The line is drawn to guide the eye.

moment (compare table 2) of these compounds correctly and results in a Type III half-metal.

The data for the minority band gaps of the remaining Co2BC compounds, which are Type III in the GGA calculations, are shown in table 5. The minority DOS ρ↓(εF) at εF is listed in addition. In all minority one has from the GGA calculations ρ↓(εF) > ρ↑(εF) resulting in a positive spin polarization. The interesting point to note is—in some cases of Type III Heusler half-metals—that the gap remains at the Γ-point but is closed at the X-point. This means they are metals for one spin direction (majority) and semi-metals for the other (minority).

Summarizing the discussion of the minority gap, figure 10 displays the size of the minority gap as a function of the lattice parameter. From the GGA calculations in figure 10, there is a tendency seen that larger lattice parameters of the compounds lead to smaller band gaps for Type I half-metals. It is obvious that those materials deviate strongly from this trend when the Fermi energy is found to be located outside of the gap. This trend cannot be used quantitatively but is useful as a starting guess to search for good candidates for HMF materials with a reasonable size of the gap. It is interesting to note that the Ti and V compounds exhibit a gap even in the case where they do not form a localized magnetic moment. This gives a clear advice that a localized magnetic moment at the B sites is not a necessary condition for the formation of half-metallic ferromagnetism in the Co2-based Heusler compounds.

3.5. Correlation and the electronic structure within LDA + U

In this section, the influence of correlation on the electronic structure of various compounds is discussed. LDA + U calculations were performed for Co2BC compounds with B = Ti, V, Cr, Mn and Fe and C = Al and Si. The semi-empirical values corresponding to 7.5% of the atomic values of the Coulomb-exchange parameter U_eff have been used for all compounds (see table 1).

| Compound     | N_eff | m_Coeff | m_B | E_max | E_min | ΔE   |
|--------------|-------|---------|-----|-------|-------|------|
| Co2TiAl      | 25    | 1.00    | 0.84| −0.39 | −0.206| 0.914| 1.12|
| Co2TiSi      | 26    | 2.00    | 1.16| −0.18 | −0.583| 0.632| 1.22|
| Co2VAI       | 26    | 2.00    | 1.15| −0.09 | −0.414| 0.072| 0.49|
| Co2VSi       | 27    | 3.00    | 1.20| 0.69  | −0.905| 1.138| 1.04|
| Co2CrAl      | 27    | 3.01    | 0.79| 1.70  | 0.071 | 1.39 | 1.32|
| Co2MnAl      | 28    | 4.28    | 0.73| 3.17  | 0.424 | 1.505| 1.08|
| Co2MnSi      | 29    | 5.00    | 0.98| 3.29  | 0.007 | 1.307| 1.30|
| Co2FeAl      | 29    | 5.00    | 1.22| 2.97  | 0.022 | 0.811| 0.79|
| Co2FeSi      | 30    | 6.00    | 1.50| 3.14  | −0.81 | −0.028| 0.78|

Magnetic moments (m) are given in μB and energies (E) are in eV. For lattice parameters see table 2.

The results of the LDA + U calculations are summarized in table 6. The total magnetic moment is in agreement with the Slater–Pauling rule. A strong deviation is found for Co2MnAl, where the Fermi energy is found far below the gap in the minority states. This deviation also appears if the optimized lattice parameter is used instead of the experimental one. In general, the width of the band gap increases with the inclusion of U in the LDA scheme. However, the gap was already existing in all compounds when using GGA for the calculations. That means U is not creating the half-metallic ferromagnetism but confirms the half-metallic property of those compounds and helps to explain the magnetic properties correctly. The second impact of the on-site correlation on the electronic states is an increase of the splitting between bands of different symmetry. This causes a shift of the Fermi energy with respect to the gap in the minority states, or vice versa depending on the point of view. The effect is that the half-metallic character is changed in some cases from Type III to Type I, indeed, the opposite may appear too as seen from a comparison of the data given in tables 4–6.

Major differences between experimental and calculated moments were found for the high-m compounds containing Fe. Out of these, the electronic structure of the two compounds Co2FeAl and Co2FeGa will be discussed in more detail to explain the effect of the on-site correlation. The spin-resolved density of states for Co2FeAl and Co2FeGa that are calculated using the LSDA and LDA + U approximations are shown in figure 11. There is no major difference between the LSDA and the GGA calculations (compare figures 6(c) and (f)). Both compounds exhibit a very small minority band gap at εF in pure LSDA calculations. This becomes considerably larger when LDA + U is used in the calculations. In both cases, the Fermi energy stays close to the top of the minority valence band. The low lying majority ε↑ states, being responsible for the localized moment at the Fe site, are shifted from about −3.5 eV by about 0.5 eV to lower binding energies. At the same time the unoccupied minority d states are shifted from about 0.6 eV above the Fermi energy to 1.3 eV. The splitting of this band complex is also enlarged from about 0.3 to 0.45 eV. On average, the splitting between occupied majority bands and unoccupied minority bands is increased by about 1.2 eV.

Finally, it should be noted that just the high-m compounds are a sensitive test for the use of electron–electron correlation in the form of LDA + U. In some cases, it is required to explain their electronic and magnetic properties correctly. More
details of the change in the electronic structure are discussed elsewhere for Co$_2$MnSi [37] and Co$_2$FeSi [26, 27, 37].

3.6. Further Co$_2$-based half-metallic ferromagnets

Half-metallic ferromagnetism may appear not only in those Co$_2$BC compounds where B is a 3d element but also if B is a 4d (here Zr or Nb) or 5d (here Hf) transition metal. Indeed, various Co$_2$-based Heusler compounds of this type are reported where B is not a 3d transition metal but one from a higher period. It was found in the present calculations that most of them can be expected to exhibit half-metallic ferromagnetism.

The magnetic properties of several, reported Co$_2$-based Heusler compounds with B being not a 3d transition metal are summarized in table 7. There is obviously a large discrepancy between observed and calculated magnetic moments. However, it is not clear whether the experimentally reported samples exhibited the $L_2_1$ structure (assumed in the calculations), the CuHg$_2$Ti structure or any other type of disorder. For Co$_2$NbSn, neither the measured nor the calculated magnetic moments come close to the value expected for a half-metallic state. It should be noted that this compound is reported to crystallize in the ordered $Fm\bar{3}m$ structure at room temperature and undergoes a structural transition at 235 K from cubic to orthorhombic with $Pmna$ symmetry [95, 96]. Spin-orbit interaction, which was not accounted for in the present calculations, may also play already a role for the Hf containing compounds.

The most interesting point is, however, that in all those compounds only the Co atoms are responsible for the magnetic moment. That means, in none of these compounds a localized magnetic moment at the B atoms is present. This points to the important fact that the existence of a localized moment at the B atoms is not a necessary condition for the occurrence of half-metallic ferromagnetism in Co$_2$-based Heusler compounds, as also mentioned in the previous section.

3.7. Other Heusler compounds exhibiting half-metallic ferromagnetism

So far, only the properties of Heusler compounds based on Co$_2$ were considered. However, there also exist half-metallic ferromagnets in the remaining large group of Heusler compounds. For example, Galanakis et al [17] have proposed half-metallic ferromagnetism in Rh$_2$-based compounds. However, only the compounds Rh$_2$Ge, Ge, Sn or Pb (with $N_V = 29$) crystallize in the required $L_2_1$ structure [97, 98]. In the calculations, these compounds turned out to exhibit a magnetic moment of about 4.7 $\mu_B$ in good agreement with the experiment but incompatible with half-metallic ferromagnetism and a band gap did not appear in either of the spin densities.

From the remaining group of known Heusler compounds, half-metallic ferromagnetism was found only in Mn containing compounds (see table 8). Mn$_2$VAl is one of the few Heusler compounds exhibiting a gap in the majority density of states, unlike the other Heusler compounds. The reason is that Mn$_2$VAl has only 22 valence electrons, that is less than 24; therefore, the completely filled bands appear in the majority states. Indeed, fixing the number of occupied states in the spin channel has to have less electrons occupied. This is expressed in the Slater–Pauling rule where $m$ becomes virtually negative if $N_V < 24$. It should be noted that Mn$_3$Si exhibits in experiments a complicated magnetic behaviour close to antiferromagnetism [99], and this might destroy the band gap.

The $DO_3$ type structure is the binary derivative of the $L_2_1$ Heusler structure. Mn$_3$Al and Mn$_3$Ga are, besides Mn$_3$Si and many others, two of the binary compounds reported to order in

![Figure 11](image)

Figure 11. Spin-resolved density of states for Co$_2$FeC, C = Al, Ga and Co$_2$FeGa. Shown are the spin resolved density of states for Co$_2$FeAl (a), (c) and Co$_2$FeGa (b), (d) calculated by LSDA in the upper part (a), (b) and LDA + $U$ in the lower part (c), (d). The upper and lower parts of each plot display the majority and minority densities, respectively. (See text for the particular values of $U$ at the different sites.)
a complicated magnetic behaviour (see references in table 8). The 23 valence electron compound Fe$_2$TiAl is an interesting transport properties [100]. Bands overlap by only 10 meV, which might lead to peculiar to be only 300 meV above the highest valence band at the lowest majority conduction band at the case of an ferrimagnet with a near gap-like behaviour. The symmetry. This phenomenon is discussed in detail in [84].

They are not anti-ferromagnets due to a completely different compensated ferrimagnets. It should be firmly emphasized that total magnetic moments and thus are half-metallic completely the same space group as Heusler compounds. Both have zero

electrons, like CoTiSb [101], are usually semi-conductors

magnetic moment, in agreement with the Slater–Pauling rule. The electronically similar $C_1p$ compounds with 18 valence electrons, like CoTiSb [101], are usually semi-conductors [102, 103]. However, a clear indication for a semi-conducting ground state was not indicated in the calculations for the Heusler compounds with 24 valence electrons. Here, only some behaviour close to semi-metallic was found (see figure 12). Despite the fact of a different symmetry in $L_2_3$ and $C_1p$ compounds, this might also point to an underestimation of electron–electron correlation by GGA for $L_2_2$ compounds. Some Fe$_2$-based compounds exhibit at least bands without direct overlap in the Brillouin zone, whereas the iso-electronic compounds Co$_2$ScC ($C = \text{Al, Ga}$) exhibit touching bands at the $\Gamma$ and $X$-points. The remaining two Fe$_2$-based compounds exhibit a gap in the minority band structure. The calculations predict Fe$_2$MnAl to be a half-metallic ferrimagnet with an anti-parallel orientation of the spins at the Fe and Mn sites. Fe$_2$MnSi is a Type I half-metallic ferrimagnet.

A further family of Heusler compounds studied here is based on Ru$_2$. They all have a gap in the majority states being located above $\epsilon_f$. Therefore, they are Type III half-metals, at best. Note that the $A$ atoms—here Ru—carry negligible spin moments in the compounds with $N_v = 27$. In all cases, the Mn moment is large and mainly responsible for the total magnetic moment. On the other hand, some of the Ru$_2$ compounds were recently reported to exhibit anti-ferromagnetism [104]. In that case the half-metallicity will be lost. The reason for the anti-ferromagnetic ground state may be found in on-site correlation at the Mn atoms, that was not respected here.

Ir$_2$MnAl is another $5d$-based Heusler compounds exhibiting half-metallic behaviour in the GGA calculations. The Fermi energy of this material is just at the top of the valence band. In the present study, there was no compound found from other Ni$_2$, Cu$_2$ or Pd$_2$-based Heusler compounds that exhibits half-metallic ferromagnetism. Most of those are paramagnetic or regular ferromagnets without any gap and independent of the valence electron concentration.

It is interesting to note that all Heusler compounds predicted to be half-metallic ferromagnets contain Mn when Co$_2$ is replaced by other elements. The Mn atoms may replace either the Co atoms on $A$ positions or the second transition metal on the $B$ position. In the latter case, the Mn atoms

| Compound          | $N_v$ | $\alpha_{exp}$ | $m_{exp}$ | $m_{calc}$ | $m_A$ | $m_B$ | $\Delta E$ | Type    | References |
|-------------------|-------|----------------|-----------|------------|-------|-------|------------|---------|------------|
| Mn$_2$VAl         | 22    | 5.897          | 1.82      | -1.99      | -1.52 | 0.95  | 0.32       | HF      | [70, 105]  |
| Mn$_2$MnAl        | 24    | 5.804          | 0.00      | -1.42      | 2.84  | 0.55  |            | CF      |            |
| Mn$_2$MnGa        | 24    | 5.823          | -0.01     | -1.54      | 3.03  | 0.17  |            | CF      |            |
| Mn$_2$MnSi        | 25    | 5.722          | 1.00      | -0.88      | 2.69  | 0.62  |            | HF      | [99]       |
| Fe$_2$TiAl        | 23    | 5.879          | -0.95     | -0.67      | 0.28  | -0.01 |            |         |            |
| Fe$_2$VAl         | 24    | 5.761          | 0         | -0.04      | 0.04  | -0.04 |            | SM      | [107–109] |
| Fe$_2$VGa         | 24    | 5.782          | 0         | 0.55       | -0.17 | -0.20 |            | SM      | [108, 109]|
| Fe$_2$VSi         | 25    | 5.675          | 0.81      | 0.55       | -0.17 |        |            |        |            |
| Fe$_2$MnAl        | 26    | 5.816          | 2.00      | -0.31      | 2.62  | 0.39  |            | HF      | [70]       |
| Fe$_2$MnSi        | 27    | 5.671          | 2.33      | 3.00       | 0.20  | 2.63  | 0.63       | HF      | [70, 110] |
| Ir$_2$MnAl        | 28    | 6.025          | 4.00      | 0.28       | 3.42  | 0.37  |            | HF      |            |
| Ru$_2$MnGe        | 27    | 5.985          | 3.8       | 3.03       | -0.01 | 3.00  | 0.13       |        | [104, 113]|
| Ru$_2$MnSi        | 27    | 5.887          | 3.00      | 0.02       | 2.92  | 0.10  |            |        | [104]      |
| Ru$_2$MnSn        | 27    | 6.217          | 3.08      | -0.06      | 3.21  | 0.14  |            |        | [104]      |
| Ru$_2$MnSb        | 28    | 6.200          | 4.4       | 4.02       | 0.22  | 3.55  | 0.28       |        | [104, 113]|
carry a magnetic moment of about $3 \mu_B$. The same is true for the Co$_2$MnC compounds where the Mn atoms also carry a magnetic moment of about $3 \mu_B$. A very interesting case is Mn$_2$CoSb, which was not mentioned above because it adopts the CuHg$_2$Ti structure and not the Heusler AlCu$_2$Mn structure. Actually, this seems to be the only Heusler-like 2:1:1 compound that exhibits half-metallic ferromagnetism in the $F$ 43m symmetry [114]. Summarizing all these observations, there exist two classes of half-metallic Heusler compounds. First, the Co$_2$-based compounds with the magnetic moment located dominantly in the (1 0 0)-like planes and second the Mn compounds with a strongly localized moment at the $B$ site.

4. Summary and conclusions

Ab initio calculations have been used to examine the electronic structure of $A_2BC$ Heusler compounds that exhibit half-metallic ferromagnetism. The examination revealed two classes of half-metallic Heusler compounds. First, the Co$_2$-based compounds with the formation of dominant bonds and magnetic moments located in the (1 0 0)-like planes containing the Co atoms and second, the Mn compounds with a strong localized moment at the $B$ site. This suggests the occurrence of two concurring mechanisms being responsible for the half-metallic ferromagnetism in Heusler compounds.

It has been found that the half-metallic properties in Co$_2$BC Heusler compounds are dominated by the presence of C atoms. According to the results described here, nearly all Co$_2$BC compounds will be half-metallic ferromagnets even if no localized magnetic moment is formed. The magnetic moment carried by the Co and B atoms is restricted by the C atoms even though they do not directly contribute to the magnetic properties. The influence of the valence electron concentration on the total and partial magnetic moments was investigated in detail. It is found that the Co$_2$BC compounds fulfill the Slater–Pauling rule, whereas other compounds may exhibit pronounced deviations from a Slater–Pauling type behaviour. The findings were supported by an analysis of the site resolved occupancy of the $d$ states and their symmetry. Further, it was found that the minority band gap shows a trend to decrease with increasing lattice parameter. It increases with stronger hybridization, as found from an analysis of the Al and Si containing compounds.

The inclusion of electron correlation in the form of LDA + $U$ on top of the LSDA and GGAs, does not destroy or produce a half-metallic gap. Its effect is to enlarge the gap if it is already present and to shift the minority bands with respect to the majority bands or the Fermi energy. The use of effective Coulomb parameters in the order of distinctly below 2 eV is able to explain the magnetic moments of all compounds if compared with experiments. The remaining question, however, namely whether $\epsilon_F$ is located in reality inside of the gap of the minority states or outside, has to be answered by suitable experiments.

In summary, it was shown that state-of-the-art ab initio calculations are a suitable method to explain the electronic and magnetic structure of Heusler compounds and to predict new half-metallic ferromagnets in this class of compounds.

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