Ab initio prediction of half-metallic properties for the ferromagnetic Heusler alloys Co₂M₅Si (M=Ti, V, Cr)

Xing-Qiu Chen, R. Podloucky, and P. Rogl
Institut für Physikalische Chemie, Universität Wien, Sensengasse 8, A 1090, Vienna, Austria

Abstract

By means of density functional calculations the magnetic and electronic properties and phase stabilities of the Heusler compounds Co₂M₅Si (with M=Ti, V, Cr, Mn, Fe, Co, Ni) were investigated. Based on the calculated results we predict the ferromagnetic phases of the compounds Co₂Ti₅Si, Co₂V₅Si and Co₂Cr₅Si to be half-metals. Of particular interest is Co₂Cr₅Si because of its high density of majority spin states at Fermi energy in combination with a reasonably high estimated Curie temperature of 747K. The compounds Co₂Ti₅Si and Co₂V₅Si are thermodynamically stable, whereas Co₂Cr₅Si is a metastable phase which might be stabilized by suitable experimental techniques.

I. INTRODUCTION

In the pioneering work of de Groot et. al., Ni₃MnSb and PtMnSb were predicted to be half-metal ferromagnets, for which the majority-spin states are of metallic character whereas the minority-spin states have a gap at Fermi energy. A larger class of Heusler alloys has such peculiar electronic and magnetic properties, which, in combination with large magnetic moments and high Curie temperatures, makes these materials attractive for the design of single-spin electron sources and spin injectors in the field of magnetoelectronics and related technological applications.

Within the series of Co₂M₅Si compounds (for M=Ti, V, Cr, Mn, Fe, Co, Ni), Co₂Fe₅Si and Co₂Mn₅Si were studied to some extent. For Co₂M₅Si a Curie temperature of Tᵥ = 985 K and a total magnetic moment of about 5 μB were measured. For Co₂Fe₅Si, the measured Curie temperature of Tᵥ = 1100 K is the highest for all known Heusler alloys reflecting the large total magnetic moment of about 6 μB. Recently, thin films of Co₂M₅Si and Co₂M₅Ge were fabricated, for which their magnetic properties are still under debate. Density functional theory (DFT) calculations for Co₂M₅Sn confirmed its half-metal properties and the measured large magnetic moment. A conventional DFT study on Co₂Fe₅Si derived that Fermi energy does not fall any more into the gap of the minority-spin states. Treating the d-like states of Fe as strongly localized states, the half-metal ferromagnetic property could be recaptured, as it is claimed by experiment.

In the present work, by means of a DFT approach we examined the series of Heusler alloys Co₂M₅Si (with M=Ti, V, Cr, Mn, Fe, Co, Ni) assuming they crystallize in the typical L₂₁ structure. For all these compounds we derived magnetic and electronic properties as well as thermodynamical stabilities and elastic properties. In the seven compounds, only for M=Ti, V, Mn, Fe compounds with the L₂₁ structure were synthesized. The experimentally claimed structure of Co₂Co₅Si (or Co₃Si) is of the D0₁₉ type at temperatures of about 1200 °C whereas below 1192 °C the compound could not be stabilized. Concerning Co₂Cr₅Si and Co₂Ni₅Si, no experimental data are available in literature. Nevertheless, for the sake of completeness and comparison, Co₂Cr₅Si, Co₂Co₅Si, and Co₂Ni₅Si with the L₂₁ structure are included in our study.

II. COMPUTATIONAL DETAILS

Our DFT calculations were performed by application of the plane wave Vienna Ab initio Simulation Package (VASP) in its projector augmented wave formulation for the potentials. The exchange-correlation potential and energy were described within the generalized gradient approximation (GGA) of Perdew and Wang in combination with the parametrization of Vosko et al. for spin polarized densities. The cubic lattice parameters were optimized self-consistently, and care was taken to converge the total energy in terms of basis functions and of k points for the Brillouin zone integration. Ferromagnetic as well as some selected antiferromagnetic orderings were considered. Local properties (such as projected densities of states and local magnetic moments) were determined within suitably chosen spheres centered at the atomic positions. Finally, thermodynamic and elastic stabilities were derived by a procedure reported in Ref. 21. For Co₂Cr₅Si and Co₂Fe₅Si, additional studies were made by treating the d-like states as strongly localized states in terms of a so-called LDA+U approach with only the one effective parameter U-J, similar to the LDA+U approach of Ref. 10. Our LDA+U calculations were done on the basis of the GGA potentials as used for the conventional calculations.

III. RESULTS AND DISCUSSIONS

Fig.1 summarizes trends of the density of states (DOS) and related quantities which were derived from the described VASP calculations applying GGA potentials. For M=Ti, V, Cr, Mn the Fermi energy EF lies in the pronounced gap of the minority-spin states (left side panels), determining the half-metal character of these compounds. According to Fig.1b the width of the band gap has values in the range of 0.6 to 0.7 eV. The Heusler alloy Co₂Fe₅Si, however, is not a half-metal anymore, because EF lies in an uprising peak of the minority-spin states. The -now indirect- band gap is only 0.1 eV wide, being strongly reduced due to a flat tail of the mentioned peak (see corresponding left side panel). For the half-metal compounds, however, this pronounced peak is totally unoccupied. For M=Co, Ni the gap vanishes, because all the d-bands are nearly filled and the separation of the Co-d and M-d band center is now too small for the formation of a gap. The crucial gap for the half-metal compounds, as discussed by
Galanakis et al. for Co₂MnSi₂, is due to a strong hybridization between Co-d and M-d states, combined with large local magnetic moments and a sizeable separation of the d-like band centers. We found that a related strong hybridization feature (a small gap for M=Ti, V or a deep valley for M=Cr, Mn, Fe) occurs already in the non-spin-polarized DOS, for which E_F cuts through a pronounced peak indicating instability. When allowing for ferromagnetic spin polarization the Fermi energy is then pinned in the gap of the minority-spin DOS as long as there are not too many states to be filled and the gap is sufficiently large, which is the case for the compounds with M= Ti, V, Cr, Mn. In these cases, the local magnetic moments $m_{\text{M}}$ of the M-atoms increase linearly, whereas $m_{\text{Co}}$ remains rather constant (see Fig.1b). It should be noted, that the numerical values of the local moments depend on the choice of the localization criterion (e.g. on the choice of radii of atomic spheres in our case), and therefore - in general - they are not integer numbers. However, the total magnetic moments $m_{\text{tot}}$ are exactly integer numbers for the true half-metal compounds, as shown by Table II.

Comparing Co₂MnSi to Co₂FeSi, the local moment $m_{\text{Fe}}$ is now smaller than $m_{\text{Mn}}$, and the linear trend for $m_{\text{M}}$ (for M=Ti, V, Cr, Mn) is now destroyed, as shown by Fig.1c. The reason is that according to a conventional DFT GGA calculation Co₂FeSi is not a half metal. This is consistent with a recent DFT study by Wurmehl et. al, who also found that the Fermi level is not in the band gap of the minority-spin DOS when applying GGA or the local density approximation (LDA) for the exchange-correlation potential. Treating the d-states as strongly localized states by means of an LDA+U approach and choosing suitable parameters for U,J the compound Co₂FeSi became a half-metal with a local moment of 6 $\mu_B$ in agreement to experiment. We reproduced the LDA+U results which can also be obtained from conventional GGA calculations for a volume which is expanded by 5% compared to the calculated equilibrium value. It should also be mentioned that in the case of Co₂MnSi, our results agree well with earlier DFT studies.

According to our results, amongst the three predicted half metals Co₂MsSi (M= Ti, V, Cr) the Cr compound is the most interesting one, because of its large density of states of the majority spins at Fermi energy of N(↑,E_F) = 0.80 states eV$^{-1}$ spin$^{-1}$ atom$^{-1}$. This is the largest value for all known ferromagnetic half-metals. The reason for this large value is that the Fermi energy cuts through strongly localized states of mostly Cr-d like character, as illustrated by the band structure and d-like DOS in Fig.2. The contribution of Co d-states to N(↑,E_F) is very small, because E_F falls into a deep

### Table I: Results of VASP calculations with GGA potentials:
| Co₂MSi                  | Co₂VSi                  | Co₂CrSi                  | Co₂MnSi                  | Co₂FeSi                  |
|-------------------------|-------------------------|--------------------------|--------------------------|--------------------------|
| m₃Co                    | 1.01                    | 1.03                     | 0.98                     | 1.02                     | 1.34                     |
| m₃M                     | -0.05                   | 0.82                     | 2.08                     | 2.99                     | 2.79                     |
| m₃tot                   | 2                       | 3                        | 4                        | 5                        | 5.48                     |
| N(↑,E_F)                | 0.24                    | 0.35                     | 0.80                     | 0.31                     | 0.18                     |
| N(↓,E_F)                | 0                       | 0                        | 0                        | 0                        | 0.85                     |
| E_g (eV)                | 0.62                    | 0.68                     | 0.72                     | 0.66                     | 0.10                     |
| T_c (K)                 | 385                     | 566                      | 747                      | 928                      | 1109                     |

### Table II: Calculated bulk moduli and elastic constants (c₁₁, c₁₂, c₄₄ in GPa) for the Co₂MSi (M= Ti, V, Cr, Mn, Fe).

| M  | Ti | V  | Cr | Mn | Fe  |
|----|----|----|----|----|-----|
| c₁₁| 215| 216| 227| 221| 204 |
| c₁₂| 303| 255| 297| 316| 247 |
| c₄₄| 172| 197| 193| 174| 182 |
| c ′| 126| 130| 145| 143| 133 |
|    | 65 | 29 | 52 | 71 | 33  |
TABLE III: Calculated lattice parameter (a in Å) and enthalpies of formation (\(\Delta H\), kJ (mol of atoms)\(^{-1}\)) compared to available experimental data for Co\(_2\)MSi (M= Ti, V, Cr, Mn, Fe). NM: non magnetic calculations, FM: ferromagnetic calculations.

| M  | Ti  | V  | Cr | Mn | Fe |
|----|-----|----|----|----|----|
| a  |     |    |    |    |    |
| a  | 5.7205 | 5.6393 | 5.5897 | 5.5582 | 5.5410 |
| FM | 5.7609 | 5.6621 | 5.6295 | 5.6457 | 5.6231 |
| exp. | 5.770 \(^a\) | 5.659 \(^b\) | 5.654 \(^c\) | 5.640 \(^d\) |
| \(\Delta H\) |     |    |    |    |    |
| NM | -61.5 | -32.2 | -11.7 | -9.42 | -4.7 |
| FM | -64.4 | -40.7 | -29.7 | -44.9 | -33.9 |

\(^a\)Ref.15 \(^b\)Ref.14,16 \(^c\)Ref.7 \(^d\)Ref.10

The Curie temperatures \(T_c\) for Co\(_2\)MSi (M=Ti, V, Cr) were estimated similar to a model presented in Ref.10 by applying the relation \(T_c = 23 + 181m_{tot}\), which is linear in the total magnetic moment \(m_{tot}\) per unit cell. The results are 385, 566, and 747 K for Co\(_2\)TiSi, Co\(_2\)VSi, and Co\(_2\)CrSi, respectively. Again, the Cr compound is of special interest, now because of its rather large \(T_c\), making it interesting for technological applications.

Because the Cr d-states at \(E_F\) are strongly localized one might argue that these states have to be treated in a more suitable way e.g. in terms of the LDA+U approach as described previously for the study of Co\(_2\)FeSi. In our case, we applied the approach of Dudarev et al. which needs only the difference \(\Delta = U - J\) of the on-site Coulomb and exchange parameters. Similar to the study Wurmehl et al. we chose \(\Delta = 4.8\) eV for Co, whereas for Cr \(\Delta\) was varied between 0 and 3 eV. (The choice of \(\Delta = 0\) corresponds to the conventional GGA calculation.) For \(\Delta = 2\) eV, Co\(_2\)CrSi is still a half-metal with a strongly increased gap for the minority spin states of 1.9 eV however, for \(\Delta = 3\) eV the Fermi energy cuts through minority spin states, and the half-metal character is destroyed. The main effects of the localization enforced by the LDA+U treatment are an increased gap width and the occupation of more majority spin states than for the conventional GGA or LDA approaches which lowers the Fermi energy. This lowering effect could be so strong (i.e. for larger \(\Delta\)), that finally \(E_F\) cuts through minority spin states below the gap. The applied LDA+U approach has the advantage, that only one unknown parameter needs to be introduced, namely the difference of \(U\) minus \(J\). Most of the other LDA+U approaches (e.g. Ref.22) rely on the two independent parameters \(U\) and \(J\). A suitable choice of these parameters is however at present not possible, because no experimental information is yet available. For Co\(_2\)CrSi being a half-metal or not, more elaborate calculations might be necessary to determine either the unknown parameters, or to go beyond the limitations of the LDA+U approaches.

Measurements of the magnetic and electronic properties of Co\(_2\)CrSi would give the answer. However, the preparation of suitable samples is not straightforward, because Co\(_2\)CrSi is thermodynamically metastable. (In contrast to Co\(_2\)TiSi and Co\(_2\)VSi, which are even known to exist thermodynamically.) According to our \(ab initio\) calculations of the enthalpy of formation, the compound Co\(_2\)CrSi is unstable against a thermodynamical separation into the phases Co\(_2\)Si, Cr and Si by 3 kJ (mol of atoms\(^{-1}\)). On the other hand, Co\(_2\)CrSi is stable against decompositions into Co\(_3\)Si, Cr and Si (by 23 kJ (mol of atoms\(^{-1}\)), Co\(_3\)Si, Cr and Si (by 6kJ), and Co, Cr, Si (by 29.7 kJ). Obviously, Co\(_2\)CrSi might be stabilized by advanced experimental techniques for synthesizing metastable states. Elastically, however, the Cr compound is very stable as demonstrated by the calculated elastic constants of \(c_{11}=297\) GPa, \(c_{12}=193\) GPa, and \(c_{44}=145\) GPa, and the bulk modulus of \(B=227\) GPa (see Table IV).
The calculated lattice parameters listed in Table III for the known Ti-, V-, Mn-, and Fe-based half-metals are -as expected- in good agreement to experiment. In this table, enthalpies of formations are also given. In particular, non spinpolarized (NM) calculations are compared to ferromagnetic (FM) calculations, which result in significant energy gains, in particular for the Cr-, Fe-, and Mn-based alloys. The calculated elastic constants are given by Table II, which show no anomalous behaviour. In particular, the Co\textsubscript{2}CrSi alloy fits in the trend of the other compounds, and is certainly elastically stable. (For Co\textsubscript{2}CoSi and Co\textsubscript{2}NiSi with their assumed artificial structures the derived shear moduli $c'$ are negative, indicating elastic instability).

IV. CONCLUSION

Summarizing, based on density functional calculations we predict three ferromagnetic half-metals, namely Co\textsubscript{2}TiSi, Co\textsubscript{2}VSi, and Co\textsubscript{2}CrSi. The Cr compound is of particular interest because of its high density of states of 100% polarized states at Fermi energy together with a strong selectivity of Cr-d states and an elevated Curie temperature. We hope that our work stimulates experiments on Co\textsubscript{2}CrSi once this metastable phase could be synthesized.

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