Magnetic behaviour of Co$_2$MnSi full heusler alloy under pressure and uniaxial strain: a relativistic density functional theory study

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Abstract
We have investigated the electronic structure and magnetic properties of the full-Heusler alloy Co$_2$MnSi (CMS) under external pressures and strains. The total and individual spin and orbital magnetic moments were also obtained under pressures and strains. We found a gradual transition from half-metallic to metallic state around 31 GPa in our relativistic study. The spin polarization degree (SPD) was reduced at the Fermi level by including relativistic effect of spin–orbit coupling. The exchange energy describes the trend of decreasing SPD values. The decreasing behavior observed for individual orbital magnetic moments under applied pressures. The metallic behavior was also observed under 8% strain along [001] direction. It was shown that the SPD values decrease in the presence of spin–orbit coupling, whereas the spin magnetism of Co$_2$MnSi under uniaxial strain is marginally affected.

1. Introduction

The Co-based full-Heusler alloys (Co$_2$YZ) are crystallized in the L2$_1$ crystal structure including four interpenetrating face-centered-cubic (FCC) sublattices that were synthesized by Ziebeck and Webster [1]. The transition metal atoms and sp-block elements can be located in Y and Z coordinate positions, respectively [2, 3]. It is well-known that the Co$_2$YZ alloys are half-metallic ferromagnetic (HMF) materials in which they show different metallic and semiconductor behavior for the majority and minority spin states, respectively [4–7]. Their magnetization depends linearly on the number of valence electrons according to the Slater-Pauling rule;

\[ M_s = Z_e \cdot 24 \]

where \( M_s \) and \( Z_e \) are the total spin magnetic moment and the total number of valance electrons, respectively [8–11]. The fully spin polarization degree at the Fermi level in these alloys make them good candidate for spin-electronic devices [12]. The Co-based full-Heusler alloys with the Mn atom in the Y position, Co$_2$MnZ, have attracted considerable attentions due to their high Curie temperature and strong ferromagnetism ordering [13, 14]. The magnetic feature of Mn atom induces ferromagnetic ordering and robust magnetic moment in the Co$_2$MnSi (CMS) alloy [15]. This alloy is expected to be half-metallic with the large energy band gap in its minority spin band (0.81 eV), fully spin polarized degree (SPD) and with a high Curie temperature (\( T_C = 985 \) K) [1, 16, 17]. Therefore, CMS alloy is a promising candidate for spintronic devices [18, 19].

Numerous experimental and theoretical studies have been devoted to the magnetic and electronic properties of CMS alloy. Among these studies, by applying all-electron full-potential linearized augmented plane wave method (FLAPW), Picozzi and co-workers calculated the spin magnetic moment of CMS alloy. They have found that the total spin magnetic moment remained 5 \( \mu_B \) value up to 20 GPa, in while the magnetic moment of individual components relied on the applied pressures [17]. Gökoğlu and Gölsener pressure 95 GPa by employing the spin-polarization generalized gradient approximation (\( \sigma \)-GGA) with Perdew–Burke–Ernzerhof exchange-correlation functional. Moreover, the behavior of band structure is not significantly affected by applied pressure [20]. Akriche and co-workers by means of full-potential (FP-LMTO) approach showed that the spin magnetism of CMS alloy under 40 GPa pressure is followed by Slater–Pauling rule, whereas significant deviation is found for larger pressures [21].
The Co-based full-Heusler alloy, Co$_2$MnSi, is crystallized in the cubic L2$_1$ structure with the presence of spin understood. We explore the behavior of orbital magnetic moment of individual atoms under applied pressure in orbit coupling (SOC). Moreover the effect of strains on the electronic and magnetic properties of CMS alloy were also investigated in the relativistic regime.

The purpose of the present work is to demonstrate both pressure and strain effects on the electronic and orbital magnetism in the CMS alloy using relativistic density functional theory (RDFT). To the best of our knowledge, the effect of high pressures and strains on the orbital magnetism of CMS alloy have not yet been well understood. We explore the behavior of orbital magnetic moment of individual atoms under applied pressure in the presence of spin–orbit coupling (SOC). Moreover the effect of strains on the electronic and magnetic properties of CMS alloy were also investigated in the relativistic regime.

The paper is organized as follows: section 2 contains details about the computational methods and crystal structure. Section 3 presents the results and discussion (calculated spin and orbital magnetism, density of states (DOS) of CMS under different pressures and uniaxial strains). Finally, the paper is summarized in section 4.

2. Computational method and crystal structure

The Co-based full-Heusler alloy, Co$_2$MnSi, is crystallized in the cubic L2$_1$ structure with $Fm\bar{3}m$ space group (No. 225 in the International tables [22]). The Co atoms occupy two FCC sublattices with origin at (1/4 1/4 1/4), (3/4 3/4 3/4). Mn and Si atoms are located at two other FCC sublattices originated at (0 0 0), (1/2 1/2 1/2), respectively (see figure 1) [23]. The CMS unit cell has sixteen atoms that consists of eight Co atoms, four Mn atoms and four Si atoms. The eight Co atoms are surrounded by Mn and Si atoms (see figure 1).

The magnetic and electronic calculations of CMS were carried out in the framework of density functional theory (DFT) [24] using the relativistic version [25] of the full-potential local-orbital scheme, FPLO-14 package [26]. In this scheme, the four-component Kohn–Sham–Dirac (KSD) equation has been implemented self-consistently. The Darwin terms and mass-velocity in the KSD equation have been taken into account in our scalar relativistic (SR) calculations, besides spherical average of the SOC has been implemented in the SR scheme. The full relativistic (FR) calculations were implemented in the kinetic term of KSD equation and implicitly contains the exact form of the SOC. Our calculations were carried out using the generalized gradient approximation (GGA) for the exchange-correlation (XC) functional [27]. The site-centered potentials and densities were expanded in spherical harmonic contributions up to $l_{\text{max}} = 12$. In the FPLO package as all-electron, full-potential scheme, localized atomic-like orbitals have been used as basis sets. These basis sets are divided into the valence and core-states. However by using exact transformation the problem of $H\Psi = e\Psi$ is reduced to the solution of the valence state problem while all electrons are presented in our calculations under this transformation [26]. In our calculations, the following states were included in the valence basis set: the (3s3p; 4s4p; 3d) states of Co, Mn atoms and the (2s2p; 3s3p;3d) states of Si atom, respectively. The 3d orbital states of Si atom was utilized to improve the completeness of the basis set. The total energy converged within $10^{-6}$ eV. The Brillouin zone (BZ) was sampled with sufficient $20 \times 20 \times 20 = 8000$ k-points. According to the symmetry of CMS compound, our pressure calculations were done by decreasing the lattice parameter, while the strain calculations were performed using $P_1$ symmetry, without any constraints.
3. Results and discussion

3.1. Pressure

As a starting point of discussion, we have calculated volume changes under the applied pressures with respect to the total energy. All energies have been calculated in the magnetic SR regime. The optimized lattice constant of cubic CMS structure were depicted in figure 2 with respect to the energy minimization. This alloy exhibits the most stable structure at the volume of 179.884 Å³ per unit cell. Therefore, the optimized cubic lattice constant of 5.645 Å was found. This lattice constant optimization is in good agreement to experimental lattice constant [4, 28]. Kandpal and co-workers by using the FLAPW scheme within the GGA approximation have shown that the optimized lattice constant of CMS alloy is 5.651 Å [29]. Candan and co-workers have also shown that the volume optimization gives an optimum lattice constant of 5.633 Å by means of self-consistent pseudopotential plane wave method [30].

The SPD can be calculated by using the spin dependent DOS at the Fermi level in both the SR and the FR approaches as follows:

\[
SPD(E) = \frac{N \uparrow (E_F) - N \downarrow (E_F)}{N \uparrow (E_F) + N \downarrow (E_F)},
\]

where \(N \uparrow (E_F)\) and \(N \downarrow (E_F)\) correspond to majority and minority spin DOS at the Fermi level [17, 21, 23]. In the SR approach, the CMS alloy shows half-metallic behavior up to 19GPa as a result of fully spin polarization. The value of SPD in the FR approach is not exactly 100% at the ambient pressure and this value is reduced by 1.34% in the presence of SOC. Sargolzaei and co-workers by employing full-potential local-orbital scheme in the LSDA approximation have shown that the SPD value in the presence of the SOC reduces by 3% at the ambient pressure [23]. The difference could be related to different used exchange-correlation functional that used in this work.

The behavior of SPD values under applied pressures in both SR and FR approaches are shown in figure 3 (a). The trend of the SPD values is sharply decreased after the presence of 31 GPa. The transition of the CMS alloy under applied pressure from the half-metallic to the metallic behavior can be shown on the basis of reducing the SPD values. The calculated SPD values at 64 GPa for both SR and FR approaches are 46% and 38.46%, respectively. As it can be seen in figure 3, the spin magnetic moments of Mn and Si atoms show decreasing and increasing behavior under applied pressures, respectively. The spin magnetic moment of Mn atom was decreased from 3.191 \(\mu_B\) to 2.720 \(\mu_B\), in while the negative spin magnetization of Si atom has been increased from...
−0.140μB to −0.041μB. Nonetheless, different behavior can be seen for the spin magnetic moments of Co atom by increasing pressure from ambient pressure up to 64 GPa. It indicates increasing trend up to 38 GPa (maximum value of 1.031μB) then decreases sharply to 0.960μB at 64 GPa. According to our results (see figure 4), the Mn atom has the largest value of spin magnetic moment in the range of applied pressures compared to individual Co and Si atoms. In the SR regime, the calculated integer values of the total spin magnetic moment remain constant (5μB) up to 25 GPa. After this pressure, the total spin magnetic moment does not have exact integer value and decreases to 4.612μB at the 64 GPa. The FR approach has marginally impact on the spin magnetic moments.

In order to better understand the effect of pressures on the spin magnetic moments, we have studied the electronic partial density of states at the studied pressures. The density of 3d-spin states for the Co and Mn atoms at the Fermi level is shown in figure 5. It is clearly determined in figure 5 that increasing applied pressures caused to new states appear in the minority spin at the Fermi level for both Mn and Co atoms after 25 GPa. As it can be seen from figure 5, for nearly fixed number of majority spin states, increasing of minority spin states after 25 GPa can explain decreasing behavior of the individual spin magnetic moment of Mn atom (figure 4). The trend of increasing minority spin states for Co atom is sharper than the Mn atom. Hence, the minority spin states of Co atom which are increased at the pressure of 25 GPa reduce its spin magnetic moment.
Sargolzaei and co-workers have shown that the Co and Mn atoms have the spin magnetic moments of $1.022 \mu_B$ and $3.028 \mu_B$ in the LSDA approximation and at ambient pressure, respectively [23]. Akriche and co-workers have reported the spin magnetic moments of $1.075 \mu_B$ and $2.966 \mu_B$ for Co and Mn atoms without any applied pressure by the FP-LMTO program [21]. Within the FLAPW method, Picozzi and co-workers have observed increasing trend of magnetization for Co atom from $1.04 \mu_B$ to $1.08 \mu_B$ value and decreasing behaviour for the spin magnetic moment of Mn atom from $2.98 \mu_B$ to $2.85 \mu_B$ under applied pressure [17]. Our findings are in a good agreement with Picozzi’s results.

We have studied the magnetic DOS in all studied pressures. Figure 6 elucidates the transition from half-metallic to metallic behavior in the CMS alloy under pressures. In the presence of applied pressure, the majority and minority spin states shift backward below the Fermi level. The higher pressures more than 31 GPa caused to decrease fully SPD and reveal the metallic behavior in CMS alloy. As it can be seen in figure 6, the minority spin states move downward below the Fermi level.

The calculated individual orbital magnetic moments show decreasing trend under pressures. The contributions of transition metal atoms have a key role to form orbital magnetic moment in the CMS alloy. As it can be seen in figure 7, the orbital magnetic moment of Co atom is larger than the orbital moments of Mn atom in presence of the applied pressures. Picozzi and co-workers have found orbital magnetic moment values of $0.02 \mu_B$ for Co and $0.008 \mu_B$ for Mn atoms in CMS alloy at ambient pressure [17] in qualitative agreement with our findings.

### 3.2. Strain

We also studied the effect of strain on CMS alloy for up to 9% by increasing the lattice constant $c$ along the [001] direction while the other lattice constants were decreased where the volume of the alloy remains constant. The CMS total energy versus the uniaxial [001] positive strain at the SR regime are shown in figure 8.
Figure 7. The calculated orbital magnetic moments of Co and Mn atoms in CMS alloy at the FR regimes.

Figure 8. The CMS total energy as a function of the uniaxial [001] strain.

Figure 9. The SPD values at various positive strains (tensile). The red circle and blue diamond denote our calculations in the SR and FR approaches, respectively.
The behavior of SPD under various strains is shown in figure 9 in both SR and FR approaches. In the SR approach, the CMS alloy has fully spin polarization up to the strain of 8% and shows half-metallic behavior. We predict the CMS alloy has not the half-metallic behavior with SPD ratio of 80% at 9% strain. The calculated SPD values in the presence of SOC (FR approach) are smaller than the SPD values at the SR approach, in while the increasing strain up to around 9% caused to decreasing the SPD values from 99.55% to 63.93%.

The calculated spin magnetic moments of CMS alloy and its components under positive strains at the SR approach are shown in figure 10. The total spin magnetic moment of CMS remains constant (5 μB) up to the 7% strain and decreases to 4.92 μB at about 8% strain. The spin magnetic moments of individual atoms reach to their lowest values at 9% strain, M_s = 0.949 μB (3.172 μB) for Co (Mn) atoms, respectively.

The spin magnetization of Mn and Si atoms almost have decreasing trend, however, the spin magnetic moment of Co atom shows increasing and decreasing behavior before and after the strain of 8%, respectively. Hence, the Co atoms dominate the magnetic behavior of CMS alloy under applied strain. The presence of SOC does not affect on the spin magnetism of the CMS alloy.

The behavior of CMS alloy can be explored based on the majority and minority spin states under the presence of strains. Figure 11 shows the calculated DOS for CMS alloy in the SR approach under strain. The applied positive strains marginally affected the majority spin states, as can be seen in figure 11. However, the minority spin states under strains significantly moved below the Fermi level. On the other hand, the applied strains caused to the new minority states appear at the Fermi level. The presence of the minority and majority spin states can be explored the metallic behavior at about 8% strain.

The calculated orbital magnetic moment of transition metal atoms are shown in figure 12 within the FR approach. According to figure 12, the orbital moment of Co atom remains almost constant under various strains. However, the increasing strain influences the orbital magnetic moment of Mn atom gradually from 0.012 μB to 0.015 μB.

4. Summary and conclusions

In summary, we have studied the magnetic and electronic properties of Co-based full-Heusler alloys, Co2MnSi, under pressure (volume reduction) and uniaxial [001] strain by using relativistic density functional theory. The spin and orbital magnetic moments of individual components were calculated in the CMS alloy in full relativistic regime.

We found metallic behavior for CMS alloy after the pressure of 31 GPa as a consequence of reducing the SPD values. Under applied pressure, the calculated total spin magnetic moment has constant integer value of 5 μB up to 38 GPa. According to our results, the individual spin magnetic moment of Mn atom has the largest value in comparison with the Co and Si atom under pressure. In the presence of external pressure, the calculated orbital...
moments exhibit decreasing behavior. Moreover, the calculated orbital magnetic moment of Co atom is larger than the orbital magnetic moment of Mn atom. We obtained half-metallic behavior for CMS alloy up to strain of 8% in the SR regime. According to our positive strain results, the consideration of SOC reduces the SPD values in comparison with SR results. Our findings confirm the effect of strain on the calculated orbital moments. Further experiments to check our prediction on spin and orbital magnetism of CMS alloys under applied pressures and strain are desirable.

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References

[1] Webster P J and Ziebeck K R A 1988 Alloys and Compounds of $d$-Elements with Main Group Elements (Part 2) ed H R J Wijn and L.Börnstein 19 New Series, Group III (Berlin: Springer-Verlag) pp. 87–95
[2] Törancel Ş, Şাşоğlu E and Galanakis I 2013 J. Appl. Phys. 113 043912
[3] Kulikov S E, Eremin S V, Kakeshita T, Kulikov S S and Rudenski G E 2006 Mater. Trans. 47 599
[4] Raphael M P, Ravel B, Huang Q, Willard M A, Cheng S F, Das B N, Stroud R M, Bussmann K M, Claassen J H and Harris V G 2002 Phys. Rev. B 66 104429
[5] Galanakis I and Mavropoulos P 2007 J. Phys.: Condens. Matter 19 315213
[6] Hasnip P J, Loach C H, Smith J H, Probert M I, Gilks D, Sizeland J, Lari L, Sagar J, Yoshida K and Oogane M 2014 J. Mater. Res. Express 7 056101
[7] Park J H, Vescovo E, Kim H J, Kwon C, Ramesh R and Venkatesan T 1998 Nature London 392 794
[8] Slater J C 1936 Phys. Rev. 49 931
[9] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864
[10] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[11] Ritchie L, Xiao G, Y I, Chen T Y, Chien C L, Zhang M, Chen J, Liu Z, Wu G and Zhang X X 2003 Phys. Rev. B 68 104330
[12] Kandpal H C, Fecher G H, Felser C and Schönhense G 2006 Phys. Rev. B 73 094422
[13] Sargolzaei M, Richter M, Koepernik K, Opahle I, Eschrig H and chlygin I 2006 Phys. Rev. B 74 224410
[14] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864
[15] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[16] Ritchie L, Xiao G, Y I, Chen T Y, Chien C L, Zhang M, Chen J, Liu Z, Wu G and Zhang X X 2003 Phys. Rev. B 68 104330
[17] Kandpal H C, Fecher G H, Felser C and Schönhense G 2006 Phys. Rev. B 73 094422
[18] FPLO-14 improved version of the original FPLO code by Koepernik K and Eschrig H 1999 Phys. Rev. B 59 1743
[19] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[20] Ritchie L, Xiao G, Y I, Chen T Y, Chien C L, Zhang M, Chen J, Liu Z, Wu G and Zhang X X 2003 Phys. Rev. B 68 104330
[21] Kandpal H C, Fecher G H, Felser C and Schönhense G 2006 Phys. Rev. B 73 094422
[22] FPLO-14 improved version of the original FPLO code by Koepernik K and Eschrig H 1999 Phys. Rev. B 59 1743
[23] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[24] Ritchie L, Xiao G, Y I, Chen T Y, Chien C L, Zhang M, Chen J, Liu Z, Wu G and Zhang X X 2003 Phys. Rev. B 68 104330
[25] Kandpal H C, Fecher G H, Felser C and Schönhense G 2006 Phys. Rev. B 73 094422
[26] FPLO-14 improved version of the original FPLO code by Koepernik K and Eschrig H 1999 Phys. Rev. B 59 1743
[27] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[28] Ritchie L, Xiao G, Y I, Chen T Y, Chien C L, Zhang M, Chen J, Liu Z, Wu G and Zhang X X 2003 Phys. Rev. B 68 104330
[29] Kandpal H C, Fecher G H, Felser C and Schönhense G 2006 Phys. Rev. B 73 094422
[30] Candan A, Uğur G, Charifi Z, Baaziz H and Ellialtıklolu M R 2013 J. Alloy-COMPD 560 215–22