A Density Functional Theory Study of Half-Metallic Ferromagnets (HMFs) Behavior in Co$_2$YSb (Y = Sc, Ti)

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Based on the density functional theory (DFT) calculations, the electronic and magnetic properties of Heusler compounds Co$_2$YSb (Y = Sc, Ti) were investigated using the generalized gradient approximation (GGA). Amongst the systems under investigation Co$_2$ScSb gives 100% spin polarization at $E_F$. Co$_2$ScSb is the most stable half-metallic ferromagnets (HMF) with an energy gap of 0.40 eV at the Fermi level in the spin down channel. We have also found that the increase in the total magnetic moments as Y goes from Sc to Ti. The calculated magnetic moments for Co$_2$ScSb and Co$_2$TiSb are 1.9998 $\mu_B$ and 1.5219 $\mu_B$, respectively. Based on the calculated results, we have predicted that the compound Co$_2$ScSb is a half-metal ferromagnetic (HMF) which can be applicable for spintronic devices. We tried to make Co$_2$TiSb a HMF by treating the d-states as strongly correlated states by means of including an extra parameter called Coulomb repulsion (U) in the conventional local spin density approximation (LSDA).

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I. INTRODUCTION

Spintronics or spin electronics, also known as magnetoelectronics, is the newest growing branch of magnetism [1]. The motive behind the development of spintronics is to replace the conventional electronics where the spin of the electron now plays an important role instead of the charge in communicating the information. This will provide for low energy consumption in combination with other interesting properties, like non-volatility for magnetic random access memories (MRAMs), spin valve, giant magneto resistance (GMR), etc. The emergence and rapid growth of research has found that half-metallic ferromagnets (HMFs) are the suitable compounds for spintronics devices [2]. One of the promising characters of the half-metallic ferromagnet compounds is that one spin channel presents a gap at the Fermi level, while the other has a metallic character, leading to 100% carrier spin polarization at $E_F$ [3]. Several new HMFs and their properties have been initially predicted by theoretical ab-initio calculations and later verified by experiments. Some of the X$_2$YZ type full-Heusler compounds show HMF behaviour. Full Heusler alloys are the ternary intermetallic compounds with composition X$_2$YZ, where X and Y are transition elements (Ni, Co, Fe, Mn, Cr, Ti, V, etc.) and Z is a III, IV, or V group element (Al,

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TABLE I: Muffin Tin Radius (RMT).

<table>
<thead>
<tr>
<th>RMT (a.u.)</th>
<th>Co$_2$ScSb</th>
<th>Co$_2$TiSb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>2.43</td>
<td>2.39</td>
</tr>
<tr>
<td>Y</td>
<td>2.43</td>
<td>2.39</td>
</tr>
<tr>
<td>Sb</td>
<td>2.29</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Ga, Ge, As, Sn, In, etc.). The electronic and magnetic properties of Co$_2$MnAl [4] and Co$_2$CrSi [5] using the local spin density approximation (LSDA) shows the half-metallicity at the ground state. Rai and Thapa have also investigated the electronic structure and magnetic properties of X$_2$YZ (X = Co, Y = Mn, Z = Ge, Sn) type Heusler compounds by using a first principle study and reported HMFs [6]. Rai et al. (2012) also studied the electronic and magnetic properties of Co$_2$CrAl and Co$_2$CrGa using both the LSDA and the local spin density approximation plus coulomb repulsion (U) (LSDA+U) and reported an increase in the band gap, hybridization of $d-d$ orbitals, as well as $d-p$ orbitals when treated with the LSDA+U [7]. In this present work we have investigated the half metallic ferromagnetic behaviour of the compounds like Co$_2$ScSb and Co$_2$TiSb using the GGA.

II. COMPUTATION DETAILS

A computational code (WIEN2K) [8] based on the full potential linearized augmented plane wave (FP-LAPW) method was applied for the structure calculations of Co$_2$YSb. The GGA [9] was used for the exchange correlation potential. The multipole expansion of the crystal potential and the electron density within the muffin tin (MT) spheres was cut at $l = 10$. Nonspherical contributions to the charge density and potential within the MT spheres were considered up to $l_{max} = 6$. The cut-off parameter was $R_{MT} \times K_{max} = 7$. In the interstitial region the charge density and the potential were expanded as a Fourier series with wave vectors up to $G_{max} = 12$ (a.u.)$^{-1}$. The number of k-points used in the irreducible part of the Brillouin zone is 286. The Muffin Tin sphere radii (RMT) for each atom are tabulated in Table I.

III. CRYSTAL STRUCTURE

We consider Heusler alloy [10] with the chemical formula Co$_2$YSb (Y = Sc, Ti). The full Heusler structure consists of four penetrating fcc sublattices with atoms at the X1(1/4,1/4,1/4), X2(3/4,3/4,3/4), Y(1/2,1/2,1/2), and Z(0,0,0) positions which results in a L$_{21}$ crystal structure having space group Fm-3-m, as shown in Fig. 1.
IV. RESULTS AND DISCUSSIONS

IV-1. Structural optimization

Systematic calculations of the electronic and magnetic properties of the Heusler compounds Co$_2$YSb were carried out in this work. The results of the electronic properties calculations are compared to study the effect of the different kinds of atoms and the valence electron concentration on the magnetic properties and in particular the band gap in the minority states. The structural and electronic properties were calculated using the GGA. The optimized lattice constant, the isothermal bulk modulus, and its pressure derivative are calculated by fitting the total energy to the Murnaghan equation of state [11]. The optimized lattice parameters were slightly higher than the experimental lattice parameters, the change in lattice parameters are given by $\Delta(a_o)$. It is confirmed that the ferromagnetic configuration is lower in energy than the non-spin polarized case for the systems Co$_2$YSb [Table II]. In Co$_2$ScSb the lattice parameter and bulk modulus are 6.210 Å and 145.541 GPa, respectively, as reported by Kervan et al. [12]. Similarly, Lee et al. reported the respective values of lattice constant and bulk modulus to be 6.071 Å and 164 GPa in Co$_2$TiSb [13]. The results of the structural optimization are shown in Fig. 2. The detailed values of the optimized Lattice parameters and bulk modulus are given in Table II.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Lattice Constants $a_o$ (Å)</th>
<th>Bulk Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Previous</td>
<td>Calculated</td>
</tr>
<tr>
<td>Co$_2$ScSb</td>
<td>6.205</td>
<td>6.244</td>
</tr>
<tr>
<td>Co$_2$TiSb</td>
<td>6.071</td>
<td>6.105</td>
</tr>
</tbody>
</table>
IV-2. Spin Polarization and half-metallic ferromagnets

The electron spin polarization (P) at the Fermi energy (E\(_F\)) of a material is defined by Equation (1) [15],

\[
P = \frac{\rho \uparrow (E_F) - \rho \downarrow (E_F)}{\rho \uparrow (E_F) + \rho \downarrow (E_F)},
\]

where \(\rho \uparrow (E_F)\) and \(\rho \downarrow (E_F)\) are the spin dependent density of states at the \(E_F\). The \(\uparrow\) and \(\downarrow\) assigns the majority and the minority states, respectively. P vanishes for paramagnetic or anti-ferromagnetic materials even below the magnetic transition temperature. It has a finite value in ferromagnetic materials below the Curie temperature [16]. The electrons at \(E_F\) are fully spin polarized (P = 100%) when \(\rho \uparrow (E_F)\) or \(\rho \downarrow (E_F)\) equals zero. In the present work, we have studied the systems like Co\(_2\)YSb (Y = Sc, Ti), among them only Co\(_2\)ScSb shows 100% spin polarization at \(E_F\) [Table III]. According to our results, the compound containing Sc and Co atoms shows a DOS at the Fermi energy \(E_F\), \(\rho \uparrow (E_F) = 0.10\) states/eV [Table III]. The reason for this value of the DOS is that \(E_F\) cuts through strongly localized states of Sc-\(d\) as well as Co-\(d\) atoms, as illustrated in Fig. 3(a). On the other hand \(\rho \downarrow (E_F)\) equals zero, as a result Co\(_2\)ScSb does not give 100% spin polarization.

Figs. 3, 4 summarize the results of the DOS which were calculated using the GGA. For the compounds like Co\(_2\)ScSb, \(E_F\) is exactly located at the middle of the gap in the minority states, whereas for Co\(_2\)TiSb the gap is prominent but the \(E_F\) is not located at the middle of the gap. The \(E_F\) has shifted towards the high energy side, as shown in Fig. 4(a). The Sc-\(d\) and Ti-\(d\) states do not show any exchange splitting, only Co-\(d_{eg}\) states gives the exchange splitting, as a result the magnetic moments in both the compounds are low. It is observed that the majority contribution in the conduction region is due to the Sc-\(d\) and Ti-\(d\) states of Co\(_2\)ScSb and Co\(_2\)TiSb, respectively [Figs. (3,4)]. The contribution
TABLE III: Energy gap and spin polarization.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Energy gap $E_g$ (eV)</th>
<th>Spin Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{max}}(\Gamma)$</td>
<td>$E_{\text{min}}(X)$</td>
</tr>
<tr>
<td>Co$_2$ScSb</td>
<td>$-0.20$</td>
<td>0.20</td>
</tr>
<tr>
<td>Co$_2$TiSb</td>
<td>$-0.60$</td>
<td>$-0.20$</td>
</tr>
</tbody>
</table>

FIG. 3: Partial DOS of Co, Sc, and Sb.

in the valence region is due to the Co-\(d\) states, as shown in Figs. (3,4) in both the cases. It has been observed that the Co-\(d\) states of Co$_2$ScSb show high peaks in the valence region, as compared with the Co-\(d\) states of Co$_2$TiSb, so one can expect a higher value of the magnetic moment in the Co sites of Co$_2$ScSb as well as the total magnetic moment. The total magnetic moment of Co$_2$TiSb is less, as there occurs a hybridization between the Co-\(d\) and Sb-\(p\) states at $-4$ eV to $-4.5$ eV in both the channels; as a results the moments will cancel each other as shown in Fig. 4(b), as well as the Ti-\(d\) states have a lower energy than the Sc-\(d\) states. In this situation the Co-\(d\) are repulsed to lower energy, which results in the minority spin states being occupied by more electrons. Whereas in case of Co$_2$ScSb there is
a small hybridization of the Co-$d$ and Sb-$p$ states at $-3.8$ eV to $-4.2$ eV only in the spin up channel. For Co$_2$ScSb the Fermi energy ($E_F$) lies in the middle of the gap of the minority-spin states, determining the half-metal character [Fig. 5]. The minority channel exhibits a clear band gap, the width of which is given by the energies of the highest occupied band along the $\Gamma$ symmetry and the lowest unoccupied band along the $X$ symmetry. According to Figs. 5, 6, the indirect band gaps along the $\Gamma$-$X$ symmetry for Co$_2$ScSb and Co$_2$TiSb are 0.4 eV and 0.4 eV, respectively. However the Heusler alloy Co$_2$TiSb is not a half-metal, even though there is a gap, because $E_F$ falls into an uprising peak (Co-$d_{eg}$) of the minority states [Figs. 4 (a, b)]. The compound Co$_2$TiSb can be made a HMF by treating the $d$-states as strongly correlated states by means of including an extra parameter called Coulomb repulsion ($U$) in the conventional GGA or LSDA. The formation of a gap for the half-metal compounds was discussed by Galanakis et al. [17] for Co$_2$MnSi; it is due to the strong hybridization between Co-$d$ and Y-$d$ states, combined with large local magnetic moments and a sizeable separation of the $d$–like band centers. For HMF the $E_F$ is located in the gap of the minority-spin DOS, as long as there are not many states to be filled, and the gap is considerable in the case of compounds like Co$_2$YSb ($Y = $ Sc and Ti).
FIG. 5: Total DOS and Band structure of Co$_2$TiSb (GGA).

FIG. 6: Total DOS and Band structure of Co$_2$ScSb (GGA).

IV-3. LSDA+U

By using the GGA we obtained a gap in Co$_2$TiSb, but the Fermi energy ($E_F$) is not located at the middle of the gap; our aim was to bring $E_F$ exactly at the gap in the spin down channel. In other words we can say that to obtain the HMF in Co$_2$TiSb, the LSDA+U was used. We have calculated the on-site coulomb repulsion ($U$) using Equation (1) for Co and Ti atoms [18, 19]. The calculated values of $U$ for Co and Ti are 0.29 Ry and 0.053
Ry, respectively. For the calculation of the parameter $U$ we used the method introduced by Gunnarsson et al. [20]. We have used a 8-unit supercell and set the hopping integrals to the $d$ shell of the central transition-metal ion equal to zero. The $d$ occupancies of the other 3$d$ ions were kept fixed at integral values by removing the hopping. The values of $U$ barely depend on how one constrains the other 3$d$ shells, as long as the systems are rather localized. The occupancies of the $d$ shell of the central atom are at two values ($n_{d\uparrow} = n/2 + 1/2$, $n_{d\downarrow} = n/2$) and ($n_{d\uparrow} = n/2 + 1/2$, $n_{d\downarrow} = n/2 - 1$), and for these configurations the fully self-consistent potentials were determined, allowing all electrons to contribute to the screening. According to Slater’s transition rule [21] one obtains

$$U = \varepsilon_{3d\uparrow} (n_{d\uparrow} = n/2 + 1/2, n_{d\downarrow} = n/2) - \varepsilon_{3d\downarrow} (n_{d\uparrow} = n/2 + 1/2, n_{d\downarrow} = n/2 - 1),$$

(2)

where $\varepsilon_{3d\uparrow}$ and $\varepsilon_{3d\downarrow}$ are the 3$d$ eigenvalues at the central atom calculated at the fixed occupancies.

The impact of onsite Coulomb repulsion ($U$) on the electronic states is to increase the splitting between the bands of different symmetry. This causes a shift of the Fermi energy with respect to the gap in the minority states as well as increases the gap. The spin resolved DOS and band structure of Co$_2$TiSb are calculated using LSDA+U. The partial DOS of Co$_2$TiSb is shown in Fig. 7. It is found that there is a strong hybridization between Co-$d_{t_2g}$ and Sb$-p$ at $-5.0$ eV in the spin down channel. We have also found hybridization between the Co-$d_{t_2g}$ and Sb$-p$ in spin up channel at a range of 0.00 to 2.0 eV. Due to the localization of electrons below $E_F$ in the spin down channel, and above $E_F$ in spin up channel there exist an exchange splitting. The exchange splitting among the Ti-$d_{t_2g}$ states are responsible for the creation of the energy band gap [22]. For Co$_2$TiSb the exchange splitting is due to the Ti-$d_{t_2g}$ states at the sharp peaks at $-2.5$ eV and 0.8 eV, as shown in Fig. 7 (a, b), as a result Ti-$d$ gives a bigger gap. The Fermi energy is located at the middle of the gap in the minority-spin, as shown in Fig. 5 in the case of Co$_2$ScSb, but Co$_2$TiSb treated with GGA does not give a bigger gap in the minority-spin, as well the Fermi energy is not exactly located at the middle of the gap. On the other hand the system Co$_2$TiSb treated with the LSDA+U version, which roughly shifts the unoccupied orbital energies upward by $U/2$ and occupied energies downward by $U/2$ independent of the shell (even for filled and empty shells) thus gives a larger exchange splitting [23] as well as the energy gap. For Co$_2$TiSb, the width of the gap is given by the energies of the highest occupied band at the L-point and the lowest unoccupied band at the X-point. The energy gap was measured between L and X, thus it is an indirect band gap. The conclusion drawn from the displayed electronic structure is that the states around the Fermi energy are strongly polarized in the case of the LSDA+U. As shown in Fig. 8, the DOS at the $E_F$, $\rho \uparrow (E_F)=1.20$ states/eV and $\rho \downarrow (E_F) = 0.03$ states/eV due to $E_F$ cuts through the Ti-$d_{t_2g}$ states; as a result the spin polarization is 95%, which is a much better improvement over the GGA.
FIG. 7: Partial DOS of Co ($d_{eg}, d_{t_{2g}}$), Ti($d_{eg}, d_{t_{2g}}$), and Sb ($s, p$) using the LSDA+U.

FIG. 8: Total DOS and Band Structure of Co$_2$TiSb using the LSDA+U.
V. MAGNETIC PROPERTIES

Starting with the compounds under investigation, all the information regarding the partial, total, and the previously calculated magnetic moments are summarized in Table IV. In Table IV it is shown that the calculated total magnetic moment is exactly an integer value in the case of Co$_2$ScSb, as expected for the half-metallic systems. The previously calculated total magnetic moment is 2 $\mu_B$, while the atomic magnetic moments are 1.110 $\mu_B$ for Co, $-0.097$ $\mu_B$ for Sc, and 0.028 $\mu_B$ for Sb [12]. In our calculation the calculated magnetic moments are in good agreement with the previous results. In the case of Co$_2$ScSb the Co atoms contribute mostly to the moment, when compared with Co$_2$TiSb [Table IV]. The total magnetic moments are to be exactly an integer number for the true half-metal compounds [14]. As shown in Table IV the Sb atoms carry a negligible magnetic moment, which does not contribute much to the overall moment. We have also noticed that the partial moment of the Sc atoms aligned anti-parallel to the Co moment [Table IV]. The partial magnetic moments of the Sb atoms for the HMF compounds Co$_2$ScSb and Co$_2$TiSb are 0.036 $\mu_B$ and 0.0112 $\mu_B$, respectively. It emerges from hybridization with the transition metals and is caused by the overlap of the electron wave functions, as reported by Kandpal et al. [16]. The total magnetic moment of Co$_2$TiSb is 1.73 $\mu_B$, the partial magnetic moments are 0.850 $\mu_B$ for Co, 0.047 $\mu_B$ for Ti, and 0.022 $\mu_B$ for Sb, as obtained from the GGA calculation [13]. Similarly, in our results Co$_2$TiSb does not give an integer magnetic moment when treated with the GGA, to improve its magnetic moment LSDA+U was applied. The partial magnetic moment of Co has been increased from 0.726 $\mu_B$ to 1.572 $\mu_B$, the partial magnetic moment of Ti gives a negative value, but the moment of Sb is almost constant, as shown in Table IV. As reported by Kandpal et al., in the local density approximation (LDA) method the magnetic moment was found to be less by 12% approximately. In addition, half-metallic ferromagnetism and a magnetic moment equal to the experimental value of 6 $\mu_B$ are found only after increasing the lattice parameter by more than 6%. To overcome these discrepancies, the local density approximation plus coulomb repulsion (U) (LDA+U) scheme was used to respect the on-site electron correlation in the calculations [24]. The system Co$_2$TiSb gives much better result under LSDA+U, the total magnetic moment is found to be 2.988 $\mu_B$, which is almost an integer value. The calculated magnetic moments of Co$_2$ScSb using the GGA and Co$_2$TiSb by using LSDA+U thus obey the Slater-Pauling rule [17].

VI. CONCLUSIONS

We have performed the total-energy calculations to find the stable magnetic configuration and the optimized lattice constant. The DOS, magnetic moments, and band structures of Co$_2$YSb ($Y =$ Sc, Ti) were calculated using the FP-LAPW method within the GGA. The calculated results were in good agreement with the previously calculated results. For the low magnetic moment compound Co$_2$ScSb, the lighter the transition element Sc, the smaller is the number of valence electrons, the wider is the gap and the half-metallicity
TABLE IV: Total and partial magnetic moments.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Magnetic Moment $\mu_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Previous</td>
</tr>
<tr>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>$\text{Co}_2\text{ScSb (GGA)}$</td>
<td>2.01 [14]</td>
</tr>
<tr>
<td>$\text{Co}_2\text{TiSb (GGA)}$</td>
<td>1.51 [14]</td>
</tr>
<tr>
<td>$\text{Co}_2\text{TiSb (LSDA+U)}$</td>
<td>—</td>
</tr>
</tbody>
</table>

is stable. The spin magnetic moment of $\text{Co}_2\text{ScSb}$ is an exact integer value 1.9998 $\mu_B$, which is in qualitative agreement with the previously reported result [14]. In the case of $\text{Co}_2\text{TiSb}$, the magnetic moment is 1.5219 $\mu_B$ which seems to deviate from an exact integer value. Amongst these two compounds $\text{Co}_2\text{ScSb}$ shows half-metallic ferromagnetism with 100% spin polarization at $E_F$. The existence of energy gap in the minority spin (DOS and band structure) is an indication of being a potential HMF. The compound $\text{Co}_2\text{TiSb}$ shows almost a HMF behaviour when treated with the LSDA+U. The calculated values of $U$ are 0.29 Ry and 0.053 Ry for Co and Ti, respectively, were added to conventional the LSDA then $\text{Co}_2\text{TiSb}$ was studied within the LSDA+U. The spin polarization at $E_F$ was found to be 95%, the total magnetic moment has been improved to 2.988 $\mu_B$, not only that the energy gap has increased from 0.40 eV to 0.80 eV. Due to these characteristics, like integer value of magnetic moment, 100% spin polarization at $E_F$, and the energy gap at the Fermi level in spin down channel makes application of half-metallic ferromagnets very important.

The Co-based Heusler alloys $\text{Co}_2\text{YZ}$ (Y is transition elements and Z is the sp elements) are the most prospective candidates for the application in spintronics. This is due to a high Curie temperature beyond room temperature and the simple fabrication process, such as dc-magnetron sputtering in $\text{Co}_2\text{YZ}$.

VII. ACKNOWLEDGMENTS

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References