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Effect of the Y element on the structural, electronic and magnetic properties of Heusler compounds Co_2YIn (Y = V, Nb, and Ti): An *ab initio* study

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ABSTRACT

We report the effect of varying the Y element on the structural, electronic and magnetic properties of Co_2YIn (Y = V, Nb, Ti) Heusler compounds using Density Functional Theory (DFT). The effect of the lattice parameter and total number of valence electrons on spin polarization and the magnetic properties of these Heusler compounds is compared. Co_2VIn and Co_2NbIn have the same number of valence electrons as Nb and V are from the same group in the periodic table. Co_2VIn has almost the same lattice constant as Co_2TiIn but they differ in the total number of valence electrons by one, as Ti and V are next neighbors in the same period of the periodic table. The optimized lattice parameters for Co_2NbIn and Co_2TiIn are found to be 6.20 Å and 6.05 Å respectively, while that of Co_2VIn has been reported to be 6.00 Å. Co_2NbIn is half metallic with an energy band gap of 0.1 eV in the minority states and has total magnetic moments of 2.02 μ_B/f.u. very close to the 2.00 μ_B/f.u. predicted by the Slater-Pauling rule, while Co_2TiIn is not half metallic but has a highly spin polarized electronic structure having a spin polarization of 89.59% and total magnetic moments of 1.04μ_B/f.u. While reducing the number of the valence electrons by one in Co_2TiIn has a significant effect on the magnetic moments and spin polarization, an increase in the lattice parameter while maintaining the same number of valence electrons in Co_2NbIn does not result in the destruction of the half metallic gap.

INTRODUCTION

The first material to be proposed to be half metallic was half-Heusler NiMnSb.[1–3] It belongs to the XYZ class of Heusler compounds, in which X and Y are mostly transition or rare earth metals and Z a main group element.[4] Since then, there has been increased research activity in a quest to search for more half metallic Heusler compounds due to the great technological impact of half metallicity in spintronics research.[5,6] In particular, Co based Co_2YZ Heusler compounds with an $L2_1$ structure, whose prototype is the first Heusler compound to be discovered, Cu_2MnAl, have attracted increased investigation.[7,8] The efforts have paid off with amongst other technologically relevant properties, the observation of a large tunneling magnetoresistance (TMR) at room temperature in magnetic tunnel junctions made using $Co_2Fe_{0.4}Cr_{0.6}Al$, Co_2MnGe, $Co_2FeAl_{0.5}Si_{0.5}$ and Co_2MnSi.[9] Apart from half metallicity, some Heusler compounds have also been characterized as completely compensated ferrimagnets, non-magnetic semiconductors, superconductors and some have even been classified as topological insulators, making them relevant for future technologies.[6,10]

Properties of the X_2YZ Heusler compounds such as magnetic moments and presence of a half metallic gap are determined by the choice of the X, Y, and Z elements. This is due to the fact that varying the elements composition could have an effect on the number of valence electrons of the constituent atoms as well as the magnitude of the lattice parameter, which has a direct influence on the hybridization between the *d* states of the transition metal elements. It has been found that contraction of the lattice favors hybridization in the system, hence affecting the position of the Fermi level.[11]

The effect of the magnitude of the lattice parameter on the electronic structure of Heusler systems has been investigated in various studies. In a study in which the X element was varied in XMnSb, X = Co, Ni, Rh, Ir, Pd, Pt, a 2% expansion and contraction of the lattice resulted in a rigid shift of the bands, with a small re-arrangement of the peaks to account for charge neutrality, causing the Fermi level to move closer to the valence band and conduction bands respectively, without destroying the gap, just as had been observed for Mn_2VAl. This observation was explained to be as a result of squeezing the delocalized *p* electrons of Sb as the transition metal *d* electrons are localized.[12] In Mn_2VAl, it was observed that upon expansion or compression, the Fermi level moved towards the valence band and in the direction of the conduction band respectively, without destroying the half metallic character.[13] In the calculation of the bulk lattice constant in NiMnSb, compression of the lattice was found to push the majority *p* states to higher energies and also increased the hybridization between the *d* orbitals of the different transition metal atoms. The spin moment of Mn decreased as a result of the increased hybridization.[14]

The influence of the number of *d* electrons of constituent atoms on hybridization and hence resulting magnetic moments has equally been investigated in various Heusler systems. In half Heusler compounds of type XMnSb, the effect of the X element on the spin magnetic moment of Mn was studied, in which it was found that when X was varied across the 3 *d* series from Fe–Co–Ni–Cu, a significant increase in the Mn magnetic moment was exhibited. This was explained to be due to decreased hybridization between Mn states with those of atoms with more *d* electrons, resulting in increased localization of the spin, tending towards an atom-like behavior.[15] In full Heusler system Co_2MnAl, substitution of Mn with Fe, which has one electron more compared to Mn resulted in an increase in the Co spin moment. Substituting Si in place of Al, which would cause an increase of one in the valence electron count, also resulted in an increase in the Co spin moment. Further, substitution of Co with Rh in Co_2MnAl, which has the same number of valence electrons as Co, but a larger atomic radius, caused the Mn spin moments to increase because hybridization between Mn and Rh *d* states is weaker than between Mn and Co *d* states.[15]

The electronic properties of full Heusler compound Co_2VIn have been reported from the results of first principle studies.[16–18] Replacing V with Nb, which has not yet been reported to the best of our knowledge, would contribute to the understanding of the influence of increasing the lattice parameter, while keeping the total valence count constant, on the formation of the half metallic gap in the Co based full Heusler system. Further, the influence of varying the total electron count by replacing V with Ti, with very little change on the lattice parameter would reveal the effect of changing the total valence electron count and number of *d* electrons of the transition metal elements on the electronic properties of the same Heusler compound.

In the continued search for half metallic materials, we have investigated Heusler compounds Co_2YIn (Y = Nb, Ti), in which we compare the effect of varying the total electron count and increasing the lattice parameter, when Y is Ti and Nb respectively, as compared to Co_2VIn which has already been studied. The results provide useful information in engineering of Heusler compounds for spintronic applications.

COMPUTATIONAL DETAILS

The spin polarized DFT calculations based on the Kohn-Sham formalism were performed using the Vienna *ab initio* Simulation Package (VASP), using the Projector Augmented Wave (PAW) method to represent the atomic cores. The exchange correlation interactions were treated using the Perdew-Burke-Ernzerholf parameterization of the Generalized Gradient Approximation (PBE-GGA). A 1 x 1 x 1 unit cell with 16 ions, in the $L2_1$ structure, space group F-m3m, space group number 225 was modeled for each compound. A Monkhorst-Pack uniform mesh of 21 x 21 x 21 **k** points and a uniform energy cut off of 430eV was chosen for all the calculations. Geometries were optimized by relaxing both the unit cell and the positions of all the atoms within the unit cell using the conjugate-gradient algorithm with a stopping criterion of energy change less than 10^{-6} eV. The linear tetrahedron method with Blöchl corrections was employed to carry out the integration over the irreducible part of the Brillouin zone with an energy convergence criterion of 10^{-7} eV.

RESULTS AND DISCUSSIONS

In this section, the effect of replacing V in Co_2VIn by Ti and Nb, which belong to the same period and group respectively, is reported. The effect of Ti would be to decrease the number of valence electrons by one, while that of Nb would be to increase the lattice constant without an effect on the number of valence electrons.

Structural properties

The optimized lattice parameters for $L2_1$ crystal structure for Co_2NbIn and Co_2TiIn predicted using the PBE-GGA exchange and correlation approximation are 6.20 Å and 6.05Å respectively as shown in Fig. 1. As expected, the lattice constant for Co_2TiIn is only 0.05Å larger than the 6.00 Å predicted for Co_2VIn[16,17] using the same approximation, while Co_2NbIn is 0.2 Å larger, due to the larger Nb atomic radius. In the $L2_1$ structure, whose prototype is Cu_2MnAl, having spacegroup Fm-3m, space group number 225, the Co atoms occupy the 8c (1/4, 1/4, 1/4) sites, while the Nb (Ti) and In atoms occupy the 4b (1/2, 1/2, 1/2) and 4a (0, 0, 0) positions respectively. Shifting of the Wyckoff positions by (1/2, 1/2, 1/2) results in an equivalent $L2_1$ structure with the X, Y, and Z atoms in the 8c (1/4, 1/4, 1/4), 4a (0, 0, 0), and 4b (1/2, 1/2, 1/2) positions respectively.[19]

Electronic properties

Full Heusler Co_2NbIn displays 100% spin polarization, with a half metallic gap in the minority states as shown in Fig. 2(a), with the Fermi level closer to the conduction band. The narrow energy band gap of 0.1 eV in the minority states is shown in the band structure diagram for the minority states in Fig. 2(b), characteristic of a *d-d* band gap, which is exhibited by full Heusler compounds. The *d-d* band gap has been explained to be as a result of the Fermi level falling

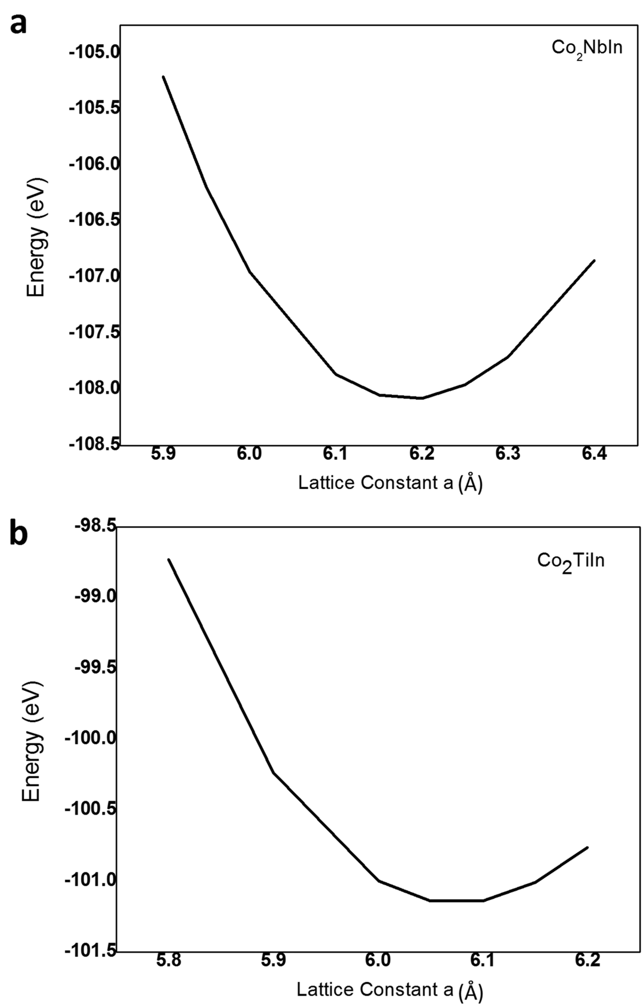

FIG. 1. Volume optimization using PBE-GGA approximation for (a) Co_2NbIn and (b) Co_2TiIn.

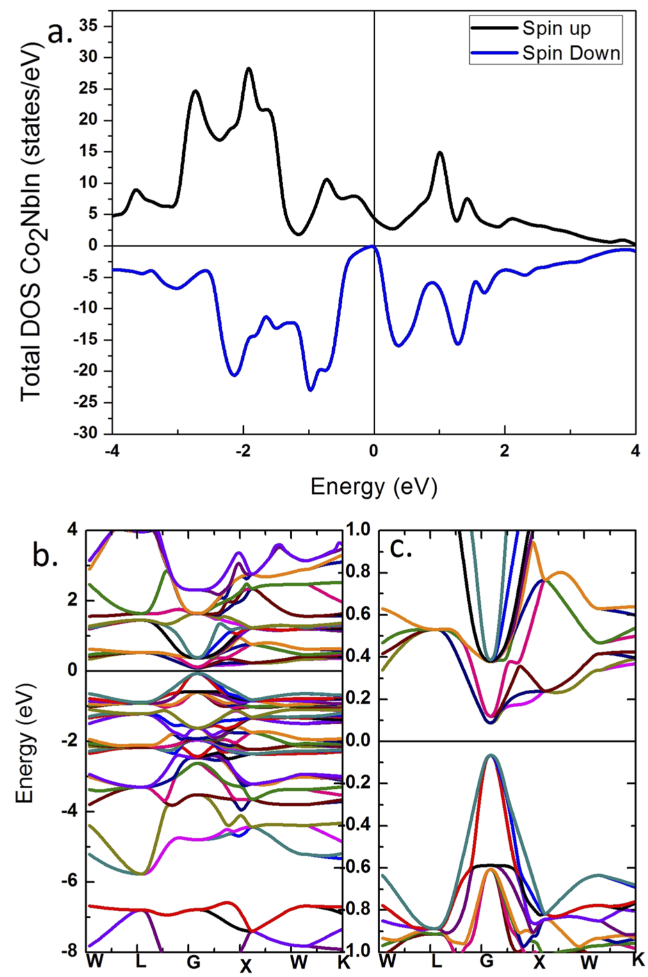

FIG. 2. (a): Total density of states (TDOS) for Co_2NbIn (b) band structure of minority states of Co_2NbIn and (c) band structure of minority states of Co_2NbIn near Fermi level using PBE-GGA approximation.

between the double degenerate and triple degenerate antibonding hybrids transforming with the e_u and t_{1u} representations respectively, in one of the spin directions, after hybridization between the *d* orbitals of the X element.[20]

The width of the energy band gap is very small as it depends on the strength of the crystal field splitting between the t_{2g} and e_g states, which is determined by the symmetry and coordination of the atoms.[21] The total density of states (TDOS) and projected density of states (PDOS) in Fig. 3 show the dominance of the Co states around the Fermi level, suggesting a gap in the crystal field split bands of Co, resulting in a *d-d* band gap. As is the case with V in Co_2VIn, the Nb minority states in Co_2NbIn are far below the Fermi level, resulting in a gap with a Co like character while the In states are found well below the Fermi level.[16]

Full Heusler Co_2TiIn displays a gap in the minority spin channel with a spin polarization of 89.59%, determined as a percentage of the ratio between the difference of the densities of the majority and minority states and the sum of the densities in both spin directions at the Fermi level, E_F, i.e.

$$P = \frac{\rho\uparrow(E_F) - \rho\downarrow(E_F)}{\rho\uparrow(E_F) + \rho\downarrow(E_F)} \tag{1}$$

Where, $\rho\uparrow(E_F)$ and $\rho\downarrow(E_F)$ are the spin dependent densities of states at E_F for the majority and minority-spin cases, respectively. Even though the Fermi level is more centrally placed between the valence and conduction bands as compared to Co_2NbIn, it is still closer to the conduction band and a few states are found in the minority channel at the Fermi level, reducing the spin polarization as shown in the TDOS and PDOS in Fig. 4. The slight shift in the position of the Fermi level results in reduction in the spin polarization, as it falls in a region where some minority states are found. As compared to Nb, Ti states are found at higher energies as seen in the PDOS in Fig. 4 and the gap between the peaks adjacent to the Fermi level in the minority spin channel is wider as compared to the one in Co_2NbIn.

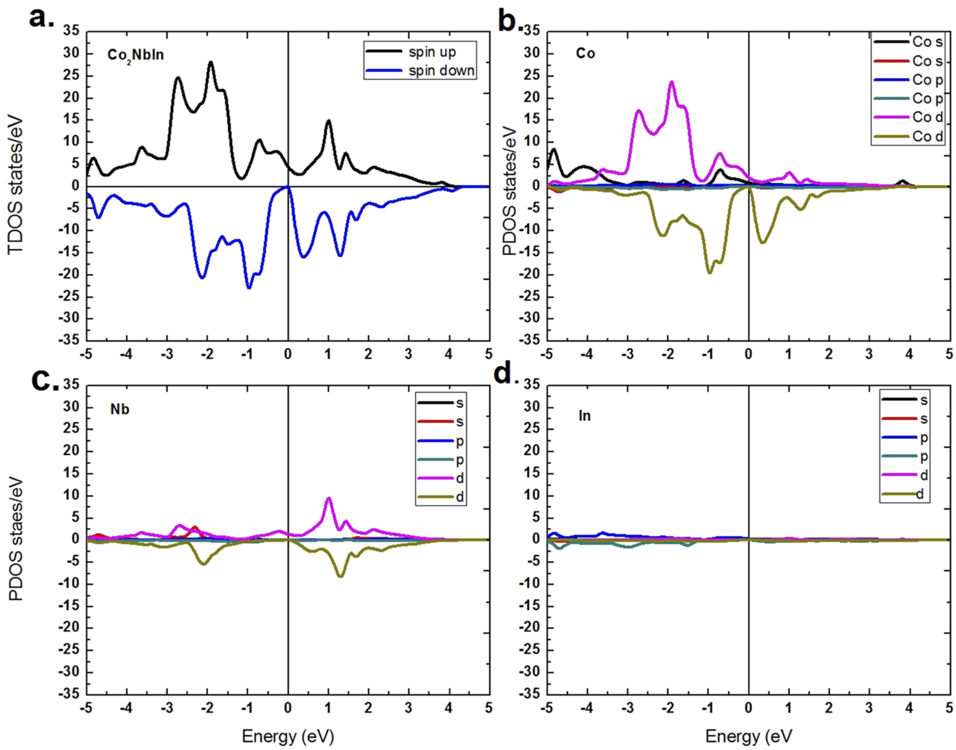

FIG. 3. (a): TDOS, (b) Co PDOS, (c) Nb PDOS and (d) In PDOS for Co_2NbIn using PBE-GGA approximation.

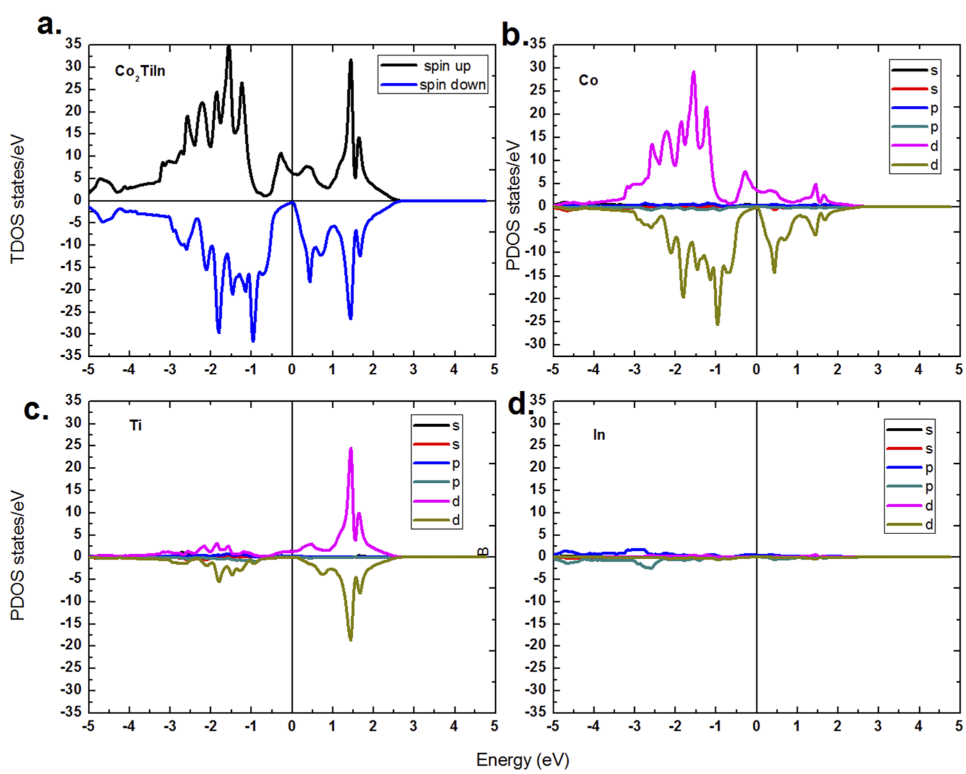

FIG. 4. (a): TDOS, (b) Co PDOS, (c) Ti PDOS and (d) In PDOS for Co_2TiIn using PBE-GGA approximation.

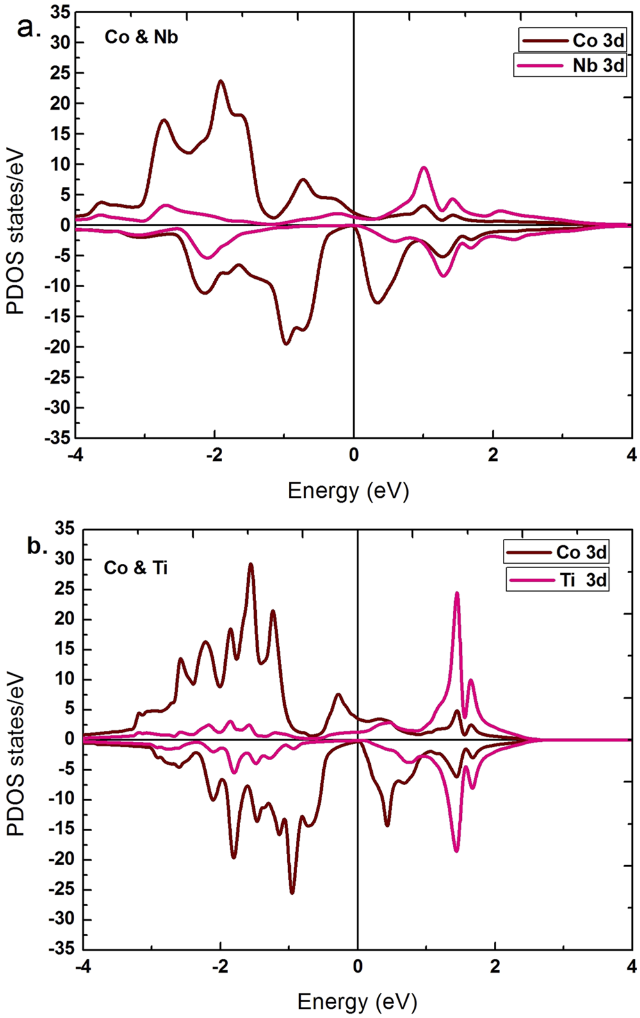

FIG. 5. (a): Co and Nb PDOS for Co_2NbIn and (b) Co and Ti PDOS for Co_2TiIn.

The dominance of the Co states around the Fermi level just as in the case of Co_2NbIn is observed. Ti contributes one less electron as compared to Nb and V per formula unit, causing a change in occupation of states at the Fermi level, resulting in a reduction in the spin polarization. As is evident in Fig. 5(a) and (b), the overlap between the *d* states of Co and Ti is much better in terms of symmetry and energy as compared to that in Co and Nb states, resulting in stronger hybridization and hence a wider gap between the antibonding hybrids adjacent to the Fermi level. However, the occupation of the states is such that a small density of states is observed at the Fermi level in the case of Ti, but in the case of Nb, the Fermi level falls within a very narrow unoccupied region, hence the half metallic gap. Co_2VIn is reported to have a spin polarization of 99.40%, using the same approximation.[16] Increasing the lattice parameter by 0.2Å in Co_2NbIn, as compared to Co_2VIn, while keeping the valence electron count constant, shifts the Fermi level within the *d*-*d* band gap, resulting in the 100% spin polarization. However, a reduction of the valence electron count by one in Co_2TiIn, as compared to Co_2VIn, with a negligible reduction in the lattice parameter of 0.05Å, significantly reduces the spin polarization to 89.90%.

The lattice parameter, minority band gap energy, magnetic moments and spin polarizations for Co_2YIn (Y = V, Nb, Ti) determined from this work and from literature are recorded in Table I.

Magnetic properties

The coupling of the Co and Nb (Ti) moments is ferrimagnetic while in the case of V, it is ferromagnetic,[16,17] as shown in Table I, except for a slightly expanded lattice of Co_2VIn, where a ferrimagnetic coupling is found.[18] The expanded lattice would have the effect of weakening the hybridization between the *d* states, hence increasing the Co moment, while decreasing the V moment. This trend is consistent in all the cases for Co_2VIn. The Co moment in Co_2NbIn is larger at 1.060 μ_B than it is in Co_2VIn at 0.968 $\mu_B$and 0.992μ_B as determined from our previous work[16] and that of Kenchoul *et al.*, 2016, respectively for the same approximation, while it is less in Co_2TiIn, at 0.66 μ_B and 0.700 μ_B as reported in literature.[17] This is in line with expected behavior for an expanded lattice

TABLE I. Optimized lattice parameter, minority band gap energies, spin polarization, atomic magnetic moments and total magnetic moments (M_T) of Co_2NbIn and Co_2TiIn determined using PBE-GGA approximation from this and previous works.

Compound	Opt. [a](Å)	Minority band gap energy (ev)	Spin polarization (%)	X (μ_B)	Y (μ_B)	Z (μ_B)	M_T (μ_B/f.u.)
Co_2NbIn	6.200	0.10	100.00	1.060	−0.080	−0.020	2.02
Co_2TiIn	6.050	0.00	89.59	0.660	−0.240	−0.040	1.04
Co_2TiIn[b]	6.080	0.00	...	0.700	−0.191	−0.015	1.19
Co_2VIn[a]	6.001	0.09	99.40	0.968	0.131	−0.056	2.01
Co_2VIn[b]	6.009	...	...	0.992	0.128	−0.019	2.09
Co_2VIn[c]	6.010	...	...	1.187	−0.152	−0.019	2.20

[a]Reference 16.
[b]Reference 17.
[c]Reference 18.

with the same number of valence electrons in Co_2NbIn, due to the effect of reduced hybridization, causing the magnetic moments to become more atom-like. However, the lattice constant is not too big to inhibit hybridization. The Co moment is also expected to be less in Co_2TiIn due to the reduced number of *d* electrons in Ti as compared to V, increasing the hybridization and hence causing a decrease in the magnetic moment. The Slater-Pauling rule predicts the total magnetic moments of a half metallic Heusler system from the relation, $M_T = N_v - 24$, where M_T is the total magnetic moments of the system per formula unit, Nv is the total number of valence electrons and 24 is double the total number of states that the minority states are fixed at in a half metallic full Heusler system.[20] Co_2NbIn has a total number of 26 valence electrons just like Co_2VIn and is therefore expected to have total magnetic moments of 2 μ_B per formula unit from the Slater-Pauling rule if half metallic. It is found to be 2.02 μ_B, hence resulting in the half metallic gap. In the case of Co_2TiIn, with a total number of 25 valence electrons, the expected moment is 1 μ_B per formula unit. It is found to be 1.04 μ_B, hence the highly spin polarized electronic structure.

CONCLUSION

The importance of the number of valence electrons in a Heusler compound in maintaining the half metallic gap has been displayed in this work. In particular, the number of *d* electrons plays a major role in determining the extent of hybridization, hence determines whether a Heusler compound is half metallic or not. An increase in the lattice parameter to an extent where the *d* orbitals of the transition elements still overlap, does not destroy the half metallic gap. The consideration of these factors while engineering materials for spintronic devices is likely to lead to more favorable outcomes in spintronic device performance.

AUTHORS' CONTRIBUTIONS

All authors contributed equally to this work.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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