Spintronic properties of $\text{Li}_{1.5}\text{Mn}_{0.5}\text{Z}$ ($\text{Z}=\text{As}, \text{Sb}$) compounds in the Cu_2Sb structure

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Abstract

We have investigated the spintronic properties of two formula units of $\text{Li}_{1.5}\text{Mn}_{0.5}\text{Z}$ ($\text{Z}=\text{As}, \text{Sb}$), in the Cu_2Sb tetragonal crystal structure based on first-principles density-functional theory calculations, at, and near, their equilibrium (minimum total energy) lattice constants. Two groups of configurations, A and B, are formed for each type of alloy by interchanging Mn with each Li located at four different positions with respect to Li_4Z_2 . Mn has four nearest neighbors in group-A and has one nearest neighbor in group-B. The bonding features of the alloys are compared to the ionic bonding in Li_4Z_2 , and the tetragonal structure of cubic LiMnZ . The magnetic moments of these compounds are reasonably large and range from 3.724 to 4.056 μ_B , where μ_B is the Bohr magneton. Both group-B Li_3MnZ_2 , with $\text{Z}=\text{As}$, exhibit half-metallic properties at their equilibrium lattice constants while only group-A of the $\text{Z}=\text{Sb}$ compounds are half-metals. Both the modified Slater–Pauling–Kübler rule and the ionic model can predict the magnetic moments of the alloys showing half-metallicity. The modified rule can be used for exploring other potential half-metals in this class of material.

Key words: spintronic materials, ferromagnetic, half-metals

I. Introduction

Compounds formed by group-I, and group-V elements and manganese, Mn, I-Mn-V, such as LiMnAs in cubic structures, have recently attracted much interest due to their high antiferromagnetic ordering temperature and large spin–orbit-induced anisotropy^{1–3}. They are therefore promising candidates for spintronic materials. For simple spintronic applications, the preferred materials should show ferromagnetic or ideal half-metallic properties and be stable at their respective equilibrium lattice constants, so that devices made from them can have a long lifetime. Using data collected in Ref. 4, we note that many Heusler alloys and transition metal (TM) compounds with the zincblende (ZB) structure do not exhibit the preferred half-metallic properties at their equilibrium lattice constants. It has been argued by Akinaga *et al.*⁴ that strained materials are tolerable because of the use of thin-film forms in devices. These authors grew thin films of CrAs on GaAs. However, the actual lifetime for such a device has not been measured. Our studies of LiMn-V type compounds, in the three atomic arrangements (α , β , and γ phases) of the half-Heusler (HH) structure at their respective equilibrium lattice constants, show no ferromagnetic half-metallicity⁵ because Li can easily contribute its electron to the conduction band edge in the insulating channel. After exploring a range of lattice constants that exhibit half-metallic properties, the total energy differences are higher than 0.5 eV as compared to the equilibrium ones. Damewood *et al.* calculated the vibrational modes of β - LiMnP (the atomic arrangement of LiMnP with the lowest total energy), a HH structure, and found that the compound was stable at the equilibrium lattice constant and at a strained lattice constant that gives half-metallic properties⁵.

In the cubic structures, such as full-Heusler, HH and ZB alloys with TM elements, the desired magnetic properties, in particular half-metallicity, are a consequence of three competing mechanisms⁶: (a)

The crystal field splits the d-states of TM elements into triply- and doubly-degenerate states. (b) The triply degenerate states and the sp^3 orbitals of the neighboring non-metal element hybridize to form a gap between bonding and anti-bonding states. This is called d-p hybridization, which is responsible for the primary bonding and total energy of the sample. Also, the doubly degenerate states originated from d_{z^2} and $d_{x^2-y^2}$ states form non-bonding states that lie within the bonding/anti-bonding gap. (c) The exchange interaction shifts the electrons occupying minority spin states to majority spin states, or vice versa. When these three mechanisms combine properly, the Fermi energy, E_F , intersects one spin state and falls in the gap of the other spin channel. In cubic materials, a proper combination resulting in half-metallicity happens when the lattice constant is strained away from the equilibrium lattice constant. In the TM Heusler alloys, there is a further complication due to the interaction of the d-states between the two neighboring TM elements⁷⁻⁸. The interaction between the non-bonding and either the bonding or anti-bonding d-p states forms a smaller gap. It does not play a crucial role in determining the total energy of an alloy as compared to the d-p hybridization, but it can affect the occurrence of half-metallicity due to the fact that the d-d interaction is weaker and can close the gap in the insulating channel.

Due to the shortcomings in Heusler alloys and CrAs-type materials in meeting the criteria for spintronic materials, we decided to explore I-Mn-V alloys in a structure other than the cubic forms previously studied. A variant of I-Mn-V crystallized in the Cu_2Sb tetragonal crystal structure⁸ provides a simple alternative. Two values are needed to specify the lattice constants a , $b = a$, and c . Assuming the 3d-states in Cu are passive, we expect that the Cu_2Sb structure could be formed by group-I and group-V elements. According to Wyckoff⁹, the unit cell of Cu_2Sb consists of two formula units, such as Li_4Sb_2 . A possible candidate to explore magnetic materials in the Cu_2Sb structure is the $Li_{1.5}Mn_{0.5}V$ compound. The fractional compositions of elements present no problem by considering periodically repeated Li_3MnV_2 . In fact, this type of compound can be constructed by letting Mn replace one of the four Li atoms in Li_4V_2 . Since this unit cell contains one TM element, one expects that these alloys are ferromagnetic and cannot be fully compensated anti-ferromagnetic half-metals¹⁰⁻¹¹. Compared to the cubic case, we expect that the different environment around Mn will modify the mechanisms responsible for half-metallicity. In particular, the Cu_2Sb -type structure splits the d-states differently compared to cubic cases. We hope that these compounds can show desirable magnetic properties at the equilibrium lattice constants. To explore the bonding features in Cu_2Sb structure, we shall compare the features of Li_4As_2 and the alloys of Li_3MnV_2 . We chose to examine Li_3MnAs_2 and Li_3MnSb_2 due to their similar electronegativity: As (2.18) and Sb (2.05)¹². Mn has an electronegativity of 1.55. Questions relevant to the magnetic properties of these materials can be raised: (a) How do the d-states of the Mn split at the Γ point, $\mathbf{k} = 0$, of the Brillouin zone compared to the cubic case? (b) How large can their magnetic moments be? (c) Can these alloys exhibit half-metallicity since, as shown in Li-based HH alloys⁵, the Li atom easily gives its only valence electron to occupy the conduction band edge of the semiconducting insulating spin channel? (d) If these materials are half-metals, can the gap in the insulating channel correlate with the ionic sizes of the group-V elements? (e) If half-metallicity appears at lattice constants that are not the equilibrium values, what is the total-energy difference between equilibrium phase and the half-metallic phase? Our preliminary results¹³ show that the group-B varieties of Li_3MnAs_2 are half-metals at the equilibrium a and the fixed c/a ratio of Cu_2Sb given by Wyckoff⁸. These results encourage further exploration for materials having half-metallic properties at or near the equilibrium lattice constants.

To facilitate further exploration of materials having combinations of other elements in the Cu_2Sb structure, there is a strong desire to have a convenient scheme for predicting the magnetic moment before carrying out first-principles calculations or growth. The Slater–Pauling–Kübler rule¹⁴ and the ionic model¹⁵ have successfully been used to predict the magnetic moments of full- and half-Heusler alloys⁵⁻⁸ as well as other half-metals¹³ if the predicted values are positive. Can the rule and the model predict values of the moment of any Li_3MnV_2 calculated results, so that the future selection of elements that form

Cu₂Sb structure alloys can be fruitful?

In this paper, we address the following issues: What are the bonding features in these compounds compared to Li₄As₂ and cubic LiMnAs? Do the magnetic properties of these compounds depend on the local environment surrounding the Mn atom? What are their magnetic moments? If some of them are half-metals, what are the values of the lattice constants and total energies? Furthermore, is there a correlation between the gap in the insulating channel and the size of the group-V elements? If some configurations are not half-metals, what physical mechanisms are preventing them from being half-metals? Finally, since there can be different combinations of elements to form future spintronic materials with the Cu₂Sb structure, can the Slater–Pauling–Kübler rule¹⁴ and the ionic model¹⁵ be successfully applied to predict magnetic moments? In section II, we discuss the crystal structure of Cu₂Sb and the unit cell having two molecular units of Li_{1.5}Mn_{0.5}V. A description of the methods used in our calculations will be briefly presented in section III. Results and discussion will be given in section IV. In section V, we shall give a summary.

II. Crystal structure of Cu₂Sb and the alternative structure of Li_{1.5}Mn_{0.5}V

Pearson¹⁷ and Wyckoff⁹ describe the crystal structure of Cu₂Sb in detail. The tetragonal unit cell has two molecular units, shown in Fig. 1, with the following characteristics: The lattice constants are $a = 4.000 \text{ \AA}$ in the x-y plane and $c = 1.525a$ along the z-direction. In the unit cell, two Cu atoms are at (2a) with coordinates (0, 0, 0) and (0.5a, 0.5a, 0), and two Cu are at (2c) with (0, 0.5a, u) and (0.5a, 0, -u), where $u = 0.27c$. Two Sb atoms are at (2c) with coordinates (0, 0.5a, u') and (0.5a, 0, -u'), where $u' = 0.70c$. The Wyckoff notations⁹ for the positions of the atoms are adopted. The unit cell has $P4/nmm$ space group symmetry.

Fig. 1. (Color online) Two formula units of Cu₂Sb in the tetragonal unit cell.

We use the structure shown in Fig. 1 to construct two molecular units of Li_{1.5}Mn_{0.5}V. First, bypass the assumed passive Cu d-state by letting Li atoms replace the four Cu atoms and denote the V element as either As or Sb. The chemical formula per unit cell is Li₄V₂. For Li₃MnV₂, we consider four configurations where Mn replaces each one of the four Li atoms, respectively, as periodic compounds. We may group the 4 compounds in two sets: group-A has Mn at $z = 0$ and the group-B has Mn at finite z . We label the four cases by Li_j, where $j = 0, 1$,

(group-A) 2, 3 (group-B). The initial positions of the Mn at the four sites in fraction of the lattice constants a and c are summarized in Table I. Due to the alloying, the positions given in Table I are not the equilibrium positions.

Table I. Positions of the Mn atom for each of the four cases. The position is in terms of the fraction of the lattice constants (a, a, c) and are indicated in the form of (x, y, z).

Group	Alloy	Mn Position
A	Li ₀ (2a)	(0, 0, 0)
	Li ₁ (2a)	(1/2, 1/2, 0)
B	Li ₂ (2c)	(0, 1/2, 1/3)
	Li ₃ (2c)	(1/2, 0, 2/3)

III. Computational Methods

The first-principles pseudopotential code VASP¹⁸⁻²⁰ is used for this study. The pseudopotentials of the elements are constructed by the projector augmented wave (PAW) method²¹ and provided by the code package. The Perdew–Burke–Ernzerhof form of the generalized gradient approximation²², GGA, is used to treat the exchange-correlation between electrons. The basis functions used are plane waves with a cutoff energy of 1000 eV. The Monkhorst–Pack special k -point scheme²³, with (15,15,11) specifying the mesh, was used. For Li₄As₂, the total energy is converged to the order of 1 meV. For the magnetic materials, the total energy and the magnetic moment of each compound are converged to better than 1.0 meV and 1.0 μ_B , respectively. Due to the alloying, atomic positions in each compound are relaxed within the given structural constraints until the components of the forces acting on atoms are less than 0.6 meV/Å. The spin–orbit interaction is considered separately and its effect will be discussed.

We also performed preliminary calculations using the more accurate Green function many-body (GW) theory²⁴ and the hybrid functional HSE06²⁵. These tests and our previous experience with the GW method²⁶ suggest that these time-consuming calculations produce two effects in semiconductors and half-metals: (1) The widening of the fundamental gap and (2) the broadening of valence bandwidths. Neither of these effects results in a loss of half-metallicity in materials that are found to be half-metals using the GGA for the exchange-correlation. We anticipate that highly converged GW or HSE06 calculations will not predict substantially different behavior for the Cu₂Sb half-metals.

Results and discussion

In the following, we first compare the bonding features of Li₄As₂ and the alloys. Then, we present results associated with the alloys with Mn at different positions and at their respective equilibrium lattice constants. We compare the lattice constants and total energies for the compounds exhibiting half-metallic properties with lattice constants away from the equilibrium values. We also comment on the effect of the spin–orbit interaction. Finally, we discuss the applicability of the Slater–Pauling–Kübler rule and the ionic model.

A. The bonding features of Li_4As_2 and Li_3MnAs_2

Figure 2 shows the bonding features of the As-based compounds in plots of the charge density contours. In Fig. 2(a), the charge distributions of Li_4As_2 are shown in the region containing the two As atoms. Yellow circles indicate the position of the Li atoms. The first thing we notice is that there is essentially no charge around the Li atoms. It is intuitively clear that Li atoms contribute their electrons to the As atoms. Also, the contours between the As atoms show no strong bond formed between the two As atoms. The bonding picture in Li_4As_2 can simply be described by: (1) Each As takes electrons from the Li atoms; (2) The charges centered around the two As atoms simply overlap. In Fig. 2(b), the charge density contours of Li_3MnAs_2 with the Mn at $(0.0, 0.0, 0.0)a$, Li₀ in group-A, are plotted. The region is the same as shown in Fig. 2(a) except that the Mn replaces the center Li. For group-A compounds, four nearest neighbor As surround each Mn. The nearest neighbor interaction plays a crucial role in determining the bonding. This bond has a covalent quality due to the presence of the d-states of the Mn. The large electronegativity of As causes the bond charge to be located close to the As atom, denoted by the arrow (i) in the figure. The feature of the bonding for the alloy differs greatly from the one in Li_4As_2 . Fig. 2 (c) shows the charge density in a section containing the As, Li and Mn with the Mn at one of sites of group-B. The difference between Figs. 2(b) and (c) is the number of the nearest neighbors of the Mn. For group-B configuration, there is only one nearest neighbor As located above the Mn as shown in Fig. 2(c). The covalent feature is clearly exhibited by the large closed contour at (ii) between the Mn and the As atoms. In Fig. 2(d), we plot the charge distribution of the HH alloy, LiMnAs . This distribution is very similar to the one shown in Fig. 2(b) because the Mn also has four nearest neighbor As.

The effects of different crystal structures can be seen from the degeneracies of bands at the Γ point. Despite having similar charge densities, group-A compounds and the HH compounds have different degeneracies. Group-A compounds form doubly degenerate states from the p_x and p_y -type states of As and the d_{xz} and d_{yz} states of Mn. The HH structure forms triply degenerate states between the p-type states of As and the so-called t_{2g} states (d_{xy} , d_{yz} , d_{xz} states) of Mn.

B. Effect of Mn–As bonding on the magnetic properties

Comparing the charge density plots in Figs. 2(b) and 2(c), the properties of these compounds depend greatly on the location of the Mn atom. Figure 3 demonstrates the geometric difference between the two groups. The difference in the magnetic properties has been established by our earlier calculations¹³.

Fig. 2. (Color online) Total charge density of (a) Li_4As_2 , (b) Li_3MnAs_2 with Mn at the Li_0 site, (c) Li_3 site, and (d) HH LiMnAs . Arrows (i) and (ii) point to bound charges near the As atoms.

In Ref. 13, we reported preliminary results of Li_3MnAs_2 with the lattice constants c/a fixed at the value of 1.5258 for Cu_2Sb (Fig. 1) as given by Wyckoff⁹. In Table II, we reproduce our earlier results. We found that Li_0 and Li_1 , at the (2a) sites (group-A) have lower energy, but they are not half-metals. Their magnetic moments are above $3.7 \mu_B$. Li_2 and Li_3 at two different (2c) sites (group-B) have higher total energies and they are half-metals. The difference can be attributed to the neighboring configuration of the Mn. For group-A, Mn is close to four As atoms, while in group-B only one As is the nearest neighbor. For the (2a), group-A cases, the d - p hybridization is weaker than the one in the cubic case because the bond length of the compounds is longer ($2.87 \text{ \AA}$) as compared to the one in typical cubic case ($2.5 \sim 2.6 \text{ \AA}$), as shown in Fig. 2(d). Therefore, there is no gap between the bonding and the antibonding states formed by the hybridization. For the (2c) (group-B) sites, there is a bonding and antibonding gap ($\sim 0.17 \text{ eV}$) formed by the d_{z^2} state of Mn and p_z state of the As atom with the bond length of $2.1 \text{ \AA}$. These qualitative features of the two groups of compounds are maintained when the c/a ratio is changed to further reduce the total energy.

Fig. 3. (Color online) Atomic arrangements of (a) Li_1 and (b) Li_3 . Li is yellow, Mn is blue and As is orange.

Table II. The lattice constants, total energies, and magnetic moments of the four Li_3MnAs_2 compounds. The ratio $c/a = 1.5258$ is kept consistent with the value for Cu_2Sb given by Wyckoff⁹.

Group	Compound	Lattice constant [Å]	Total energy [eV]	Magnetic moment [μ_B /unit cell]	Metal or half-metal?
A	Li_0	4.050	-26.976	3.756	Metal
	Li_1	4.045	-26.974	3.724	Metal
B	Li_2	3.982	-26.291	4.000	Half-metal
	Li_3	3.980	-26.291	4.000	Half-metal

C. Magnetic properties of Li_3MnAs_2 and Li_3MnSb_2 compounds

In the following sections, we present results of Li_3MnAs_2 and Li_3MnSb_2 with adjustments to both the lattice constants a and c .

1. Li_3MnAs_2

The lattice constants given in Table II for group-A are the equilibrium values for the undoped compounds (without Mn). By adjusting the lattice constants from these values we are able to obtain half-metallic properties for the two group-A configurations. The equilibrium lattice constants and c/a ratio of the group-B configurations lower the total energies without destroying the half-metallicity. Results are summarized in Table III.

In Table III, we summarize the half-metallic results of four Li_3MnAs_2 compounds. The configurations within each group result in the same properties at equilibrium since the symmetry and bond lengths are identical. For group-A compounds, the lattice constants and total energies of the half-metallic materials differ from the corresponding equilibrium values given in Table II by less than 1.0 and 4.5%, respectively. The band structures for the As-based configurations are shown in Fig. 4 and the total and partial density of states are in Fig. 5. The Fermi energy, E_F , is right at the bottom of the conduction band as seen in Fig. 5(a). We expect any temperature effect will destroy the half-metallicity. For group-B configurations, on the other hand, the compounds are half-metals at their respective equilibrium lattice constants with E_F right above the valence states. In addition, the total energies for group-B compounds are higher than the ones in group-A by around 0.5 eV, therefore they are less stable than group-A compounds

and cannot be easily grown. Preliminary calculations in the Li_0 configuration of Li_3MnAs_2 using the HSE06 functional suggest that the fundamental gap increases by about 50%. The magnetic moment for this half-metal retains its value of $4.000 \mu_B$ per unit cell. The bond lengths between Mn—As and Li—As are given in Table IV.

Table III. The lattice constants, total energies, magnetic moments, and half-metallic properties of four Li_3MnAs_2 compounds with the constraint on c/a removed. Group-A compounds have lattice constants a and c adjusted to give half-metallic properties. Group-B compounds are half-metals at the equilibrium lattice constants.

Group	Alloy	Lattice constant a [Å]	c/a ratio	Total energy [eV]	Magnetic moment [μ_B /unit cell]	Half-metallic gap [eV]
A	Li_0	4.130	1.5978	-26.950	4.000	0.925
	Li_1	4.130	1.5978	-26.950	4.000	0.925
B	Li_2	3.971	1.5858	-26.466	4.000	0.257
	Li_3	3.971	1.5958	-26.466	4.000	0.257

Fig. 4. The equilibrium band structure of Li_3MnAs_2 in the (left) Li_0 configuration and (right) the Li_3 configuration. Solid lines represent the spin-down channel while dashed lines show the spin-up channel.

Table IV. The average bond lengths (BL) at the equilibrium configuration between nearest Mn—As pair and nearest Li—As pair for the two alloy groups.

Z	Configuration	Mn—Z BL [Å]	Li—Z BL [Å]
As	Li_0	2.562	2.562
	Li_3	2.416	2.477
Sb	Li_0	2.746	2.746
	Li_3	2.654	2.703

Fig. 5. Total density of states (states per eV-unit cell) of half-metallic Li_3MnAs_2 in the (a) Li_0 and (e) Li_3 configurations. Partial density of states of half-metallic Li_3MnAs_2 in the (b-d) Li_0 configuration and (f-h) Li_3 configuration showing the p and d components to the density of states around the As and Mn atoms.

2. Li_3MnSb_2

When the Mn occupies the sites of group-A, Li_3MnSb_2 demonstrates half-metallic properties at its equilibrium lattice constant. In group-B, the alloy shows integer magnetic moments at lattice constants away from their respective equilibrium values. The corresponding total energy is more than 0.5 eV as compared to the ones in group-A. The results are summarized in Table V. The spin-polarized band structures are shown in Fig. 6 and the partial density of states are shown in Fig. 7. While it is possible to obtain integer magnetic moment for the group-B alloys, they are not half-metals at equilibrium. The group-B configurations behave differently because only one Sb is a nearest neighbor of the Mn and the separation between them is larger than the separation in Li_3MnAs_2 . The charge transfer from the Mn is not as complete in the group-B compounds as compared to group-A. The spread of the charge distribution can affect the exchange interaction and broaden the bands and diminishes the gap in the semiconducting channel.

Similar to Li_3MnAs_2 , the total energies of the group-B configurations are higher by 0.5eV than the group-A configurations. For group-A, Li_3MnSb_2 compounds can be stable half-metals. Their insulating gaps are larger than 0.5 eV.

Table V. The equilibrium lattice constants, total energies, magnetic moments, and half-metallic properties of four Li_3MnSb_2 compounds. Arrows indicate the spin channel.

Group	Configuration	Lattice constant [$\text{\AA}$]	c/a ratio	Total energy [eV]	Magnetic moment [$\mu_B/\text{unit-cell}$]	Half-metallic gap [eV]
A	Li_0	4.326	1.5758	-25.172	4.000	0.547 $\downarrow$
B	Li_2	4.230	1.5858	-24.697	4.055	Metal

Fig. 6. The equilibrium band structure of Li_3MnSb_2 in the (left) Li_0 configuration and (right) the Li_3 configuration. Solid lines represent the spin-down channel while dashed lines show the spin-up channel.

The Sb-based alloys have larger lattice constants compared to the As-based ones due to atomic size difference (As: 1.21 $\text{\AA}$ and Sb: 1.41 $\text{\AA}$). The Li_3MnSb_2 configurations in group-A seem to have the potential of being half-metallic materials. However, the spin-flip process could destroy half-metallicity, so we carried out spin-orbit calculations on the Li_0 -type Li_3MnSb_2 alloy. Under the spin-orbit interaction, the two spin states are no longer eigenstates of the Hamiltonian so it becomes difficult to demonstrate half-metallicity. The calculated spin moment of group-A Li_3MnSb_2 is 4.0002 μ_B , so it may still be half-metallic. Similar results were also found in Li_3MnAs_2 but the calculated moment of 4.0032 μ_B is larger. We expected Li_3MnSb_2 to have larger deviation than the As-based compound due to the atomic size of Sb. The Sb-based compounds have larger lattice constants and weaker electronegativity so we anticipate that the spin-flip process is reduced. The bond length between the Mn and As atoms in the Li_0 alloy is 2.562 $\text{\AA}$ while it is 2.746 $\text{\AA}$ between the Mn and Sb atoms in the same configuration. The smaller bond length between the Mn and As atoms may account for the larger spin-orbit interaction in the As alloys. The values of the bond lengths of Li_3MnSb_2 were given in Table IV.

Fig. 7. Total density of states (states per eV-unit cell) of half-metallic Li_3MnAs_2 in the (a) Li_0 and (e) Li_3 configurations. Partial density of states of half-metallic Li_3MnAs_2 in the (b-d) Li_0 configuration and (f-h) Li_3 configuration showing the p and d components to the density of states around the As and Mn atoms.

D. Can either the modified Slater–Pauling–Kübler rule or the ionic model account for the calculated magnetic moments?

The half-metallic compounds satisfy Kübler’s modified Slater–Pauling (SP) rule¹⁴. The number of occupied bands in the insulating channel, determined by a prototype calculation of Li_0 , is 8 and the total number electrons/unit cell is 20. From the modified rule,

$$M = (N_t - 2N_v) \quad (1)$$

where N_t is the total number of electrons/unit cell, N_v is the number of occupied bands in insulating channel of the spin states, the moment should be $4 \mu_B/\text{unit cell}$. The calculated result for the half-metallic compounds is also $4 \mu_B/\text{unit cell}$.

The ionic model¹⁵ works well for the TM in the tetrahedral environment²⁷⁻²⁸, however, as seen in Fig. 2, Mn is not in that environment. Our results suggest the following simple picture for ionic model: Each As requires three electrons to fill its $n = 4$ shell and all three Li atoms can easily contribute their electrons while the Mn atom will supply the other three. As a result, the remaining four electrons associated with the Mn contribute to the moment/unit cell.

For group-B Li_3MnSb_2 , the alloys are metals so the modified SP rule should not be used since there is no insulating channel. One can say that for half-metals the rule predicts the moments reasonably well; however, it lacks the predictive power whether the material is a half-metal or not. The reason is that the modified SP rule does not take into account the effects of strength of the exchange interaction due to the change of the lattice constant. One could also argue that the spin-orbit interaction can destroy half-metallicity, so why would we consider the modified SP rule and the ionic model? The answer is that the modified SP rule and ionic models can serve as guides for the initial selection of elements to form compounds possibly exhibiting half-metallic properties and worth exploring by calculations and growth. Also, we suggest avoiding issues with the spin-orbit interaction by selecting low-Z elements to form the alloys.

IV. Summary

We investigated a new class of ferromagnetic materials involving group-I elements, group-V elements, and the Mn atom, in the alloy form of $\text{Li}_{2-x}\text{Mn}_x\text{V}$, formed in a tetragonal structure, for the purpose of exploring ferromagnetic alloys, or even half-metals, at their equilibrium lattice constants. We treat Li_3MnV_2 as compounds of Mn with two molecular units of Li_2V in the Cu_2Sb structure and compare their bonding properties. For both Li_3MnAs_2 and Li_3MnSb_2 , the alloys with Mn occupying either of the two (2a) sites, group-A, have lower total energies than the cases for Mn at either (2c) sites, group-B. The reason is that for group-A, the Mn has four neighboring group-V elements. The lack of triply degenerate states in Li_3MnV_2 at the Γ point illustrates the symmetry reduction of these compounds compared to cubic LiMnAs . All of these alloys show magnetic moments larger than $3.7 \mu_B/\text{unit cell}$. The predicted moments are comparable to Fe, and are the largest possible even with the spin-orbit interaction involved. The Cu_2Sb structure does not drastically reduce the moments as compared to the cubic case. With a fixed c/a ratio (1.525), group-A Li_3MnAs_2 are half-metallic at the lattice constants differing from their respective equilibrium values by less than 1.0%. The group-B compounds, with Mn at the (2c) site, are half-metals at their equilibrium lattice constants but their total energies are 0.5eV/cell higher than group-A compounds. Group-A Li_3MnSb_2 compounds are predicted to be half-metals at their equilibrium lattice constants. There is no half-metallic phase for the group-B Li_3MnSb_2 compounds. This is primarily due to the large size of Sb and only having one Sb as the nearest neighbor of Mn. Both the predictions for the magnetic moments, using either the modified Slater-Pauling-Kübler rule or the ionic model, agree with the calculations showing half-metallic properties.

Our results suggest that it will be worthwhile to explore growth of Li_3MnV_2 for half-metallic properties at or near their equilibrium lattice constants. Our calculations indicate that the Mn for these favored compounds will occupy (2a) site in the Cu_2Sb crystal structure. It will be interesting to replace two Li atoms in the unit cell with Mn so that it will be possible to explore anti-ferromagnetic phases. Other choices of elements guided by the modified Slater-Pauling-Kübler rule and the ionic model for half-metals should expand the search domains for spintronic materials and realizing spintronic devices. Due to the effect of spin-orbit interaction, we suggest the selection of low-Z atoms.

Acknowledgments

Work at UC Davis was supported in part by the National Science Foundation Grant No. ECCS-1232275. Work at Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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