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Spintronic properties of $Li_{1.5}Mn_{0.5}Z$ (Z=As, Sb) compounds in the Cu_2Sb structure

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ABSTRACT

We have investigated the spintronic properties of two formula units of $Li_{1.5}Mn_{0.5}Z$ (Z=As, 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 Z=As, exhibit half-metallic properties at their equilibrium lattice constants while only group-A of the Z=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.

1. 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-metallicity [5] 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 properties [5].

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 mechanisms [6]: (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_{z2} and d_{x2-y2} 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.

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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 elements [7,8]. 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 structure [8] 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 Wyckoff [9], 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-metals [10,11]. 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, $\boldsymbol{k}=0$, 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 alloys [5], 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 results [13] 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 Wyckoff [8]. 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 rule [14] and the ionic model [15] have successfully been used to predict the magnetic moments of full- and half-Heusler alloys [5–8] as well as other half-metals [13] 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 Cu_2Sb structure alloys can be fruitful?

In this paper, we address the following issues: What are the bonding features in these compounds compared to Li_4As_2 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 Cu_2Sb structure, can the Slater–Pauling–Kübler rule [14] and the ionic model [15] be successfully applied to predict magnetic moments? In Section 2, we discuss the crystal structure of Cu_2Sb 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 3. Results and discussion will be given in Section 4. In Section 5, we shall give a summary.

2. Crystal structure of Cu_2Sb and the alternative structure of $Li_{1.5}Mn_{0.5}V$

Pearson [17] and Wyckoff [9] describe the crystal structure of Cu_2Sb in detail. The tetragonal unit cell has two molecular units, shown in Fig. 1, with the following characteristics: The lattice constants are $a=4.000$ Å 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 notations [9] for the positions of the atoms are adopted. The unit cell has $P4/nmm$ space group symmetry.

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 Li_4V_2. For Li_3MnV_2, 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 1. Due to the alloying, the positions given in Table 1 are not the equilibrium positions.

3. Computational methods

The first-principles pseudopotential code VASP [18–20] is used for this study. The pseudopotentials of the elements are constructed by the projector augmented wave (PAW) method [21] and provided by the code package. The Perdew–Burke–Ernzerhof form of the generalized gradient approximation [22], 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 scheme [23], with (15,15,11) specifying the mesh, was used. For Li_4As_2, 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 $m\mu_B$, respectively. Due to the alloying, atomic positions in each compound are relaxed within the given structural constraints until the components of the