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Electronic and magnetic properties of Li$_{1.5}$Mn$_{0.5}$As alloys in the Cu$_2$Sb structure

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Abstract

We investigated two formula-units of Li$_{1.5}$Mn$_{0.5}$As alloys, such as Li$_3$MnAs$_2$, in the Cu$_2$Sb crystal using an ab-initio algorithm. By interchanging Mn with each Li located at different positions of Li$_4$As$_2$ in the unit cell, four separate alloys are formed. At the optimized lattice constant, two of these alloys are predicted to be ferromagnetic metals and the other two are half metals. The half metallicity of the first two is also explored. Both the modified Slater-Pauling-Kübler rule and the ionic model can characterize the magnetic moments of the half metals.

Key words: ferromagnetic, half metals, bonding properties.

I. Introduction

Compounds formed by group I, group V elements and manganese, Mn, I-Mn-V, such as LiMnAs in cubic structures have recently attracted much interest$^{1-3}$ for their high antiferromagnetic ordering temperature and large spin-orbit induced anisotropy. They are promising candidates for spintronic materials. There is another class of materials which is a variance of I-Mn-V and is in alloy form, I$_x$Mn$_{1-x}$V, such as Li$_{1.5}$Mn$_{0.5}$As. They crystallize in the form of Cu$_2$Sb, a tetragonal crystal structure, instead of cubic structures. Since it contains Mn and As, one expects that these alloys can be ferromagnetic half metals, such as zinc-blende MnAs$^4$. However, our studies of LiMnAs, in the half Heusler structure$^5$ at the optimized lattice constant, shows no half metallicity. This half Heusler compound is not a half metal because Li gives up its electron causing the conduction band edge in the semiconducting channel to be occupied. It will be interesting to ask: since there is more than one Li atom in Li$_{1.5}$Mn$_{0.5}$As, do the Li atoms give up their electrons and destroy the half metallicity if it exists? To answer these questions, we first consider an alternative structure having an integer number of atoms/formula-unit: Li$_3$MnAs$_2$. In this paper, we restrict ourselves to one Mn in the unit-cell. Thus, the issue of antiferromagnetism is not addressed. We make use of the idea of alloying to decide where to place the Mn in the unit-cell— a Mn atom can substitute any Li atoms in the unit-cell. The following issues are addressed: A. do the properties of these alloys depend on where the Mn is located? If so, more issues are to be addressed: B. can they exhibit ferromagnetic or ferromagnetic half metallic properties? C. if some of them are half metals, what are the values of the lattice constants, total energies, and magnetic moments? Finally, D. for the half metals, can their moments be accounted for by either the modified Slater-Pauling-Kübler rule or the ionic model$^6$? The ionic model can suggest whether Li gives up its electron.

In section II, the crystal structure of Cu$_2$Sb, for an alternate structure of Li$_{1.5}$Mn$_{0.5}$As with integer number of atoms/formula-unit, will be discussed. Method of calculations will be 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 Cu$_2$Sb and the alternative structure of Li$_{1.5}$Mn$_{0.5}$As

Crystal structure of Cu$_2$Sb has been analyzed in detail by Pearson$^7$. Wyckoff$^8$ gives the tetragonal unit-cell having two molecular units. The experimental lattice constants are $a = 3.992$ Å in the x-y plane and $c = 1.5258$ a along the z-direction. In the unit-cell, two Cu (1) atoms are at (2a) with coordinates (0, 0, 0) and (0.5, 0.5, 0), two Cu (2), are at (2c) with (0, 0.5, $v$) and (0.5, 0, $-v$), where the first two numbers are in fraction of $a$, while the last number is the fraction of $c$. Two Sb atoms are at (2c) with coordinates (0, 0.5, $u'$) and (0.5, 0, $-u'$), where $u' = -0.265$. The unit-cell has the P4/nmm symmetry. Fig. 1 shows the atomic arrangements in the tetragonal cell.

![Fig. 1 Two-formula units of Cu2Sb in the tetragonal unit-cell. Cu atoms are shown in light brown and Sb atoms are shown in purple.](image)

We apply the structure shown in Fig. 1 to Li$_3$MnAs$_2$, not Li$_{1.5}$Mn$_{0.5}$As. In terms of this alternative structure, Li atoms replace the four Cu atoms and Sb atoms are replaced by the As atoms. For Li$_3$MnAs$_2$, we consider four configurations—Mn replacing each of the four Li atoms, respectively. We label the four cases by Li$_j$, where $j = 0, 1, 2, 3$. The positions of the Mn at the four sites are summarized in Table I.

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

<table>
<thead>
<tr>
<th>$j$</th>
<th>Mn Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (2a)</td>
<td>(0.00, 0.00, 0.00)</td>
</tr>
<tr>
<td>1 (2a)</td>
<td>(0.50, 0.50, 0.00)</td>
</tr>
<tr>
<td>2 (2c)</td>
<td>(0.00, 0.50, 0.33)</td>
</tr>
<tr>
<td>3 (2c)</td>
<td>(0.50, 0.00, 0.67)</td>
</tr>
</tbody>
</table>

III. Method of calculation

The first-principles code, VASP$^9$-$^{11}$, is used for this study. The pseudopotentials of the elements are constructed by the projector augmented wave (PAW) method$^{12}$ provided by the code. The Perdew-Burke-Ernzerhof form of the generalized gradient approximation$^{13}$, GGA, is used at this point to avoid any empirical parameters to treat the exchange-correlation between electrons. The spin-orbit interaction is not considered. The basis functions are plane waves with a cutoff energy of 700 eV. The Monkhorst-Pack special k-point scheme$^{14}$, with (15,15,11) specifying the mesh, was used. The total energy and the magnetic moment of each alloy converge better than 1.0 meV and 1.0 $\mu_B$, where $\mu_B$ is the Bohr magneton. Due to the alloying, atomic positions in each alloy are relaxed until the components of the forces acting on atoms are less than 0.6 meV/Å.
IV. Results and discussion

A. Do the properties of these alloys depend on where the Mn is located?

To address this issue, we determine the optimized lattice constant, \( a \), for the lowest total energy for each alloy. The optimized lattice constant, the associated total energy, the magnetic moment and whether it is a semiconductor, a metal and a half metal are given in Table I. In all cases, the lattice constant in the \( z \)-direction, \( c \), is kept the value for \( \text{Cu}_2\text{Sb} \) given in Sec. II.

Among the four cases, \( \text{Li}_0 \) and \( \text{Li}_1 \), the (2a) sites, have a lower energy. But they are not half metals. \( \text{Li}_2 \) and \( \text{Li}_3 \) occupying two different (2c) sites have higher total energies. They are, however, half metals. The difference can be attributed to the neighboring configuration of the Mn—in the (2a) cases, Mn is close to only one As, while in cases of (2c) the two As atoms are the neighbors of the Mn atom. Fig. 2 shows \( \text{Li}_1 \) and \( \text{Li}_2 \) atomic arrangements after respective relaxations. From the values of the optimized lattice constants and the energetic points of view, the properties of the alloys depend on the location of the Mn atom.

Table II. The optimized lattice constant, total energy, and magnetic moment of the four alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Lattice constant (Å)</th>
<th>Total energy (eV)</th>
<th>Magnetic moment (( \mu_B/\text{unit-cell} ))</th>
<th>Semiconductor, metal, or half-metal?</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}_0 ) (2a)</td>
<td>4.050</td>
<td>-26.976</td>
<td>3.756</td>
<td>Metal</td>
</tr>
<tr>
<td>( \text{Li}_1 ) (2a)</td>
<td>4.045</td>
<td>-26.974</td>
<td>3.724</td>
<td>Metal</td>
</tr>
<tr>
<td>( \text{Li}_2 ) (2c)</td>
<td>3.982</td>
<td>-26.291</td>
<td>4.000</td>
<td>Half-metal</td>
</tr>
<tr>
<td>( \text{Li}_3 ) (2c)</td>
<td>3.980</td>
<td>-26.291</td>
<td>4.000</td>
<td>Half-metal</td>
</tr>
</tbody>
</table>

Fig. 2 Atomic arrangements of (a) \( \text{Li}_1 \) and (b) \( \text{Li}_2 \). Li in yellow, Mn in blue and As in red.

B. Can the alloys exhibit ferromagnetic or ferromagnetic half metallic properties?

Even though two of the alloys at their respective optimized lattice constants are not half metals, we can still search the lattice constants for which the alloys show half metallic properties. There is ample evidence that the lattice constant of a half metal needs not to be the same as the optimized lattice constant\(^4,15\). In practice, one grows these alloys on substrates, which may not have a perfect match to the optimized lattice constants of the alloys. For each alloy, we found a range of lattice constants at which each alloy exhibits half metallic properties. Since the four alloys can exhibit half metallic properties, we address the issue in the following section.
C. What are the values of the alloys lattice constants and magnetic moments?
In Table III, we list the typical lattice constants, total energies, magnetic moments, and the gaps of the semiconducting channel. The lattice constant z=c/a is kept the same as the experimental value.

The density of states of Li$_0$ is shown in Fig. 3. In the figure, we identify mainly the states at the top of the valence bands (VB) and the bottom of the conduction bands (CB) in the down spin channel. The top of the VB states originates from the $p_y + p_x$ states of the As with a contribution of 0.257 and Mn $d_{xy} + d_{xz}$ states contributing a fraction of 0.188. The peaks near the bottom of the CB are dominated by Mn $d_{xz}$ and $d_{z^2}$ states with a fraction of 0.851 and 0.716, respectively. With the Fermi energy located in the gap of the semiconducting channel and an integer of magnetic moment, the alloy is a half metal.

Table III. Alloys, lattice constant, magnetic moment, the gap of the semiconducting channel.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Lattice constant (Å)</th>
<th>Total energy (eV)</th>
<th>Magnetic moment (µB/unit-cell)</th>
<th>Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_0$ (2a)</td>
<td>4.210</td>
<td>-26.833</td>
<td>4.000</td>
<td>0.915 ↓</td>
</tr>
<tr>
<td>Li$_1$ (2a)</td>
<td>4.215</td>
<td>-26.823</td>
<td>4.000</td>
<td>0.938 ↓</td>
</tr>
<tr>
<td>Li$_2$ (2c)</td>
<td>3.982</td>
<td>-26.291</td>
<td>4.000</td>
<td>0.177 ↓</td>
</tr>
<tr>
<td>Li$_3$ (2c)</td>
<td>3.980</td>
<td>-26.291</td>
<td>4.000</td>
<td>0.161 ↓</td>
</tr>
</tbody>
</table>

Fig. 3 A representative density of states, DOS, of Li$_0$. Peaks near $E_F$ are labeled with the fraction of atomic contributions to those states.

We notice that the lattice constants of Li$_0$ and Li$_1$ exhibiting half metallic properties are not far (~0.2 Å) from the corresponding optimized values. This is encouraging that the half metallic alloys can be stable. The stability will be reported elsewhere.$^5$

D. Can both the modified Slater-Pauling-Kübler rule and the ionic model account for the calculated magnetic moments?
The integer magnetic moments can be accounted for by both the modified Slater-Pauling rule by Kübler$^{16}$ or explained by the ionic model$^{6,17}$. For example, the number of occupied bands in semiconducting channel of alloy Li$_0$ is 8. The total number electrons/unit-cell is 20. From the rule, its moment should be 4 μB/unit-cell. The calculated result is also 4 μB/unit-cell. The ionic model works well
for the transition metal under the tetrahedral environment\textsuperscript{6}. As seen in Fig. 2, Mn is not under that environment. We propose the following simple picture for ionic model: Each As requires three electrons to fill its n=4 shell. All three Li atoms easily give up their electrons; the Mn atom will supply the other three. The remaining four electrons at the Mn contribute to the moment/unit-cell.

V. Summary

In summary, we investigated a new class of ferromagnetic materials, in alloy form, involving group I, group V and the Mn atom, Li\textsubscript{1-x}Mn\textsubscript{x}As but not in a cubic structure. The alloys Li\textsubscript{3}MnAs\textsubscript{2} are in the modified Cu\textsubscript{2}Sb structure. Two of them are ferromagnetic metals at their respective optimized lattice constants with the Mn occupying the (2a) site having lower energy. They are half metals if the lattice constants differing from the optimized values. The other two with Mn at (2c) site are half metals at their optimized lattice constants and have high total energies with respect to the other two. Both the modified Slater-Pauling-Kübler rule and the ionic model can account for the integer moments.

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