Slater–Pauling behavior and half-metallicity in Heusler alloys Mn$_2$CuZ (Z = Ge and Sb)

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**Abstract**

The Slater–Pauling behavior and half-metallic properties of full-Heusler alloys Mn$_2$CuZ (Z = Ge and Sb) have been studied by first-principles calculations. It is found that the total spin moment ($M_t$) and the number of valence electrons ($Z_t$) follow a Slater–Pauling rule of $M_t = Z_t - 28$ rather than $M_t = Z_t - 24$ in normal Heusler alloys. Mn$_2$CuSb is predicted to be a half-metal at equilibrium lattice constant and Mn$_2$CuGe is also half-metallic with a small expansion of the lattice. Mn$_2$CuGe and Mn$_2$CuSb are both ferrimagnets with total spin moment of +0.97μ$_{B}$/f.u. and +2.00μ$_{B}$/f.u., respectively. Considering Mn$_2$CuGe and Mn$_2$CuSb have 29 and 30 valence electrons, the S-P curve of $M_t = Z_t - 28$ works quite well. This different S-P rule is strongly related to the low-lying Cu states and the weak hybridization between the d states of Cu and Mn.

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1. Introduction

In the last decade, the Mn-based Heusler alloys have attracted much attention for their potential applications as half-metallic materials. The so-called half-metallic materials have an energy gap in one spin direction at the Fermi level $E_F$, whereas the other spin band is strongly metallic. As a result, a complete spin-polarization of the conduction electrons can be obtained [1].

The half-metals have a 100% spin-polarized current and can be used as spin injectors for magnetic random access memories and other spin dependent devices [2]. Many Mn-based Heusler alloys have the half-metallic band structure and high Curie temperatures, which make them suitable for technical applications [3–7].

During the investigation for half-metals, besides experimental studies, first-principles calculations also play an important role in exploration for new materials.

In 1999, Weht et al. predicted the half-metallicity in Mn$_2$VAl by theoretical calculations [3]. Then Mn$_2$VZ (Z = Al, In, Si, Ge and Sn) [4], Mn$_2$CrSb [5], Mn$_2$FeZ (Z = Al, Sb) [6] and Mn$_2$CoZ (Z = Al, Ga, Si, Sb) [7] have also been predicted as half-metallic materials by theoretical and experimental studies.

Quite recently, a series of Mn$_2$CuZ (Z = Al, Ge, Sn, Sb) half-metallic Heusler alloys has been reported. Unlike other 3d elements such as Fe, Co, the Cu atom has a 4s subshell, which makes Mn$_2$CuZ have interesting properties compared with other Mn-based Heusler alloys. Li et al. studied the electronic structure of Mn$_2$CuAl and found that with a small contraction of the equilibrium lattice, Mn$_2$CuAl became a half-metallic antiferromagnet [8]. Then Mn$_2$CuAl ribbon was synthesized by Feng et al. and its magnetic properties were studied [9].

Wei et al. predicted Mn$_2$CuGe and Mn$_2$CuSb to be half-metals with total spin moment of $-1\mu_B$/f.u. and $-2\mu_B$/f.u., respectively [11,12]. However, these results are somewhat unusual compared with other half-metallic Heusler alloys. It is known that, generally, the total spin moment for a stoichiometric half-metallic Heusler alloy is an integral value and follows the Slater–Pauling curve $M_t = Z_t - 24$, where $M_t$ is the total magnetic moment per formula unit and $Z_t$ is the total number of valence electrons. According to Refs. [11,12], the $Z_t$ for Mn$_2$CuGe and Mn$_2$CuSb derived from the S-P curve is 23 and 22, respectively. Since Sb has one more valence electron than Ge, it is interesting to find why Mn$_2$CuSb has smaller $Z_t$ compared with that of Mn$_2$CuGe. Further more, usually Cu is known to have 11 valence electrons (3d$^{10}$4s$^1$), accordingly the valence electrons in Mn$_2$CuGe and Mn$_2$CuSb should be 29 and 30, which are different from the value derived from the S-P curve. So it is meaningful to investigate proper S-P rule for Mn$_2$CuZ alloys.

In order to understand the electronic structure of Mn$_2$CuZ (Z = Ge and Sb) further, we studied the electronic structure and...
magnetism of them by first-principles calculations. The half-metallicity and Slater–Pauling behavior of them were discussed.

2. Computational methods

The electronic structure was calculated by means of CASETP code based on pseudopotential method with a plane-wave basis set [13,14]. The interactions between the atomic core and the valence electrons are described by the ultrasoft pseudopotential [15]. The electronic exchange–correlation energy has been treated under the local-density approximation (LDA) [16,17]. For all cases, a plane-wave basis set cut-off of 500 eV was used and a mesh of $15 \times 15 \times 15$ $k$-points was employed for Brillouin zone integrations. These parameters ensured good convergence of the total energy. The convergence tolerance in the calculations was selected as $1 \times 10^{-6}$ eV/atom. The calculations were performed based on the theoretical equilibrium lattice parameters.

It is known that Mn$_2$CuZ Heusler alloys all crystallize in an highly-ordered Hg$_2$CuTi-type structure, in which two Mn atoms occupy the A (0, 0, 0) and the B ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) sites, respectively. Cu atom enters the C ($\frac{1}{2}, \frac{1}{2}, 0$) site and leaves the D ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) site to the main-group atom Z [8,11,12]. The site preference of 3d atoms in Mn$_2$CuZ is determined by the number of their valence electrons. The elements with less d electrons prefer occupying the B sites whereas elements with more electrons prefer the (A, C) sites [18], which is a common rule in Heusler alloys.

3. Results and discussion

Structural optimizations on Mn$_2$CuGe and Mn$_2$CuSb were performed first to determine the equilibrium lattice constants. Paramagnetic, ferromagnetic and ferrimagnetic states were considered in the calculations. It is found that the ferrimagnetic state is lower on energy scale in both Mn$_2$CuGe and Mn$_2$CuSb, suggesting the antiparallel alignment between Mn moments is more stable in these compounds. The equilibrium lattice constant was obtained by minimizing the total energy and listed in Table 1, which is 5.66 Å for Mn$_2$CuGe and 5.93 Å for Mn$_2$CuSb. These lattice parameters are smaller than the 5.7 Å and 5.96 Å in Refs. [11,12].

The calculated total and partial density-of-states (DOS) for Mn$_2$CuGe and Mn$_2$CuSb are presented in Figs. 1 and 2, respectively. Due to the same crystal structure and similar chemical surroundings in these alloys, the total DOS of these alloys have similar structures, which are separated to several parts by energy dips in both spin directions.

The low energy part below $-8$ eV is mainly the s states of Ge or Sb. The s states are relatively small and are separated from the d states by a gap in DOS in both spin directions. We omitted them in the figure to show the details around $E_F$. The d states of Cu locate in $-5$ eV to $-3$ eV and are excluded from the Mn d states by an energy gap in both minority and majority spin states. So the hybridization between Cu and Mn 3d states is rather weak compared with other Heusler alloys like Mn$_2$FeSb or Mn$_2$VAl [4,6]. The d states of Cu are rather symmetric in both spin directions and are equally populated with small contributions to the total moment.

The d states of Mn atoms extend from $-3$ eV to $+2$ eV and hybridize with each other, forming a wide-spread d band. In Figs. 1 and 2 we can see that it is the Mn atoms that determine the magnetic properties of Mn$_2$CuZ. It may be noted that the structures of the PDOS of Mn (A) and Mn (B) are opposite to each other. This configuration suggests that the partial spin moments of Mn (A) and Mn (B) are in antiparallel alignment [19].

There is an energy gap around $E_F$ in the minority DOS of Mn$_2$CuGe and Mn$_2$CuSb, while in the majority spin there is a DOS peak, which results in a high spin polarization ratio in these alloys. There are still some minority states in the gap of Mn$_2$CuGe and the spin polarization of it is not complete yet. The minority DOS in the gap mainly come from the antibonding states of Mn and the spin polarization of it is not complete yet. The minority gap in Mn$_2$CuSb is a real gap and a 100% spin polarization is achieved. In Mn$_2$CuSb, the minority DOS of Mn$_2$CuSb move to higher energy compared with Mn$_2$CuGe, which helps to open the half-metallic gap.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$a$ (Å)</th>
<th>NOS</th>
<th>$M_t$ (μB/f.u.)</th>
<th>$M_{Mn}$ (A) (μB)</th>
<th>$M_{Mn}$ (B) (μB)</th>
<th>$M_{Cu}$ (μB)</th>
<th>$M_{Z}$ (μB)</th>
<th>$M_t$ (PPLD result) (μB/f.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_2$CuGe</td>
<td>5.66</td>
<td>15</td>
<td>up</td>
<td>$-0.97$</td>
<td>$-1.44$</td>
<td>2.44</td>
<td>$-0.06$</td>
<td>0.00</td>
</tr>
<tr>
<td>Mn$_2$CuSb</td>
<td>5.93</td>
<td>16</td>
<td>up</td>
<td>$+2.00$</td>
<td>$-1.16$</td>
<td>3.17</td>
<td>$-0.04$</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 1: The calculated equilibrium lattice constants $a$, number of states (NOS), total and partial spin moments of Mn$_2$CuZ (Z = Ge and Sb). The last column gives the total spin moment $M_t$ obtained from PPLD method (taken from Refs. [11,12]).
In the studies of Wei et al., the half-metallic gap is in the spin-up DOS of Mn$_2$CuGe and Mn$_2$CuSb, which implies the calculated total spin moment will be negative for the two compounds [20]. However, in Figs. 1 and 2, the half-metallic gap is in the spin-down direction, so positive total moments $M_t$ are obtained, which are $+0.97\mu_B$/f.u. for Mn$_2$CuGe and $+2\mu_B$/f.u. for Mn$_2$CuSb. The increase of the total spin moments from Mn$_2$CuGe to Mn$_2$CuSb reflects the increase of the valence electrons from Ge to Sb. The partial moments for Mn (A) and Mn (B) are $1.44\mu_B$, 2.44$\mu_B$ in Mn$_2$CuGe and $-1.16\mu_B$, 3.14$\mu_B$ in Mn$_2$CuSb. So a ferrimagnetic structure is confirmed in both Mn$_2$CuGe and Mn$_2$CuSb.

Computing the integrated DOS (number of states NOS) we find that the minority spin band of Mn$_2$CuGe and Mn$_2$CuSb contains 14 valence electrons, which is different from the 12 electrons in normal half-metallic Heusler alloys. The results are presented in Fig. 3. It is interesting to find that there is a platform of about 0.6 eV around $E_F$ in the minority spin channel, which is the result of the half-metallic gap, while in the majority channel, no such platform around $E_F$ is observed. Within the range of this platform, the number of electrons is a constant. In the NOS of Mn$_2$CuGe and Mn$_2$CuSb, there are another platforms in both spin channels at $-3$ to $-2$ eV, which corresponding to the energy gap between Mn and Cu states. For comparison, we also present the NOS of Mn$_2$CoSb in Fig. 3, which has a similar composition with Mn$_2$CuSb and is known as a half-metal follows the S-P rule of $M_t = Z_t - 28$ [7]. In Fig. 3, it is clear that there is also a platform around $E_F$ in the minority spin channel. However, there are 12 and not 14 valence electrons in the minority spin band. So we can expect that the S-P curve in Mn$_2$CuZ may be $M_t = Z_t - 28$ rather than $M_t = Z_t - 24$. Considering the $M_t$ presented above, the $Z_t$ for Mn$_2$CuGe and Mn$_2$CuSb are 29 and 30, respectively. These results answer the question in the introduction section well.

The cause of different S-P curves can be understood as follows: In classic half-metallic Heusler alloys like Co$_2$MnSi, the half-metallic gap mainly comes from the hybridization between the d states of the next near transition metal atoms at (A, C) sites and is a $t_{2g}$-$e_u$ gap, below which there are 12 valence electrons in the minority spin band. But in Mn$_2$CuGe or Mn$_2$CuSb, as can be observed in Figs. 1 and 2, the half-metallic gap is mainly constructed by the minority d states of nearest Mn (A) and Mn (B) atoms. The
Comparison of the spin-projected total DOS for Mn$_2$CuGe calculated at equilibrium lattice constant (5.66 Å) and 5.8 Å, respectively.

Fig. 5. Comparison of the spin-projected total DOS for Mn$_2$CuGe calculated at equilibrium lattice constant (5.66 Å) and 5.8 Å, respectively.

PDOS of Cu at the C site is far below the Fermi level and only has weak hybridization with Mn d states. So the Cu states are low around $E_F$ and contribute little to the formation of the energy gap. We can expect that in Mn$_2$CuZ the origin of the half-metallic gap can be different from normal Heusler alloys and more valence electrons than 12 can enter the minority spin band, which lead to the S-P curve of $M_t = Z_t - 28$. All these are strongly related to the low-lying Cu states and needed further investigation.

As has been discussed above, Mn$_2$CuGe is not a half-metal at equilibrium lattice constant. In order to investigate this further, the energy bands of Mn$_2$CuGe along high-symmetry directions in the Brillouin zone are presented in Fig. 4. It is clear that in the minority spin, the bottom of the conduction band overlap with the Fermi level at the X point, destroying the half-metallicity. Besides this energy gap around $E_F$, there is another energy gap around $-2\,\text{eV}$ to $-3\,\text{eV}$ in both majority and minority spin band, which separates the d bands of Cu from the d bands of Mn and weakens the hybridization between them.

It has been found that the half-metallic properties can be stabilized with a small change of the lattice constants [21]. For comparison we presented the total DOS of Mn$_2$CuGe at equilibrium lattice constant and 5.8 Å in Fig. 5, respectively. With a 2.5% expansion of the lattice, the minority antibonding peak is slightly shifted to higher energy and a real gap is opened around $E_F$, which makes Mn$_2$CuGe a "true" half-metal with a gap width of 0.32 eV. The partial spin moments for Mn (A) and Mn (B) at 5.8 Å are $-2.04\mu_B$ and $3.06\mu_B$, respectively. The Cu and Ge only have small moment of $-0.04\mu_B$ and $0.04\mu_B$. All these result in an integer total moment of $+1.00\mu_B$/f.u.

4. Conclusion

The half-metallicity and Slater–Pauling rule of Mn-based Heusler alloys Mn$_2$CuGe and Mn$_2$CuSb have been studied by first-principles calculations. A new Slater–Pauling rule of $M_t = Z_t - 28$ rather than $M_t = Z_t - 24$ in normal Heusler alloys is reported, which will help to understand the S-P rule in Heusler alloys deeper. Mn$_2$CuSb is predicted to be a half-metal at equilibrium lattice constant and Mn$_2$CuGe is also half-metallic with a small expansion of the lattice. Mn$_2$CuGe and Mn$_2$CuSb are both ferrimagnets with total spin moment of $+0.97\mu_B$/f.u. and $+2.00\mu_B$/f.u., respectively. Considering Mn$_2$CuGe and Mn$_2$CuSb have 29 and 30 valence electrons, respectively, the S-P curve of $M_t = Z_t - 28$ works quite well. This different S-P rule indicates the half-metallic gap in Mn$_2$CuZ may have a different origin compared with other Heusler alloys and is strongly related to the low-lying Cu states and the weak hybridization between the d states of Cu and Mn.

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References