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# L<sub>21</sub> and XA Ordering Competition in Hafnium-Based Full-Heusler Alloys Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb)

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**Abstract:** For theoretical designing of full-Heusler based spintronic materials, people have long believed in the so-called Site Preference Rule (SPR). Very recently, according to the SPR, there are several studies on XA-type Hafnium-based Heusler alloys X<sub>2</sub>YZ, i.e., Hf<sub>2</sub>VAl, Hf<sub>2</sub>CoZ (Z = Ga, In) and Hf<sub>2</sub>CrZ (Z = Al, Ga, In). In this work, a series of Hf<sub>2</sub>-based Heusler alloys, Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb), were selected as targets to study the site preferences of their atoms by first-principle calculations. It has been found that all of them are likely to exhibit the L<sub>21</sub>-type structure instead of the XA one. Furthermore, we reveal that the high values of spin-polarization of XA-type Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb) alloys have dropped dramatically when they form the L<sub>21</sub>-type structure. Also, we prove that the electronic, magnetic, and physics nature of these alloys are quite different, depending on the L<sub>21</sub>-type or XA-type structures.

**Keywords:** site preference; Hf-based full-Heusler compounds; first-principles study; band structures; magnetic properties; mechanical properties

## 1. Introduction

Heusler alloys are a noticeable class of intermetallic materials that represent as usual by the formula X<sub>2</sub>YZ (often called full-Heusler) [1–15] or XYZ (usually named as half-Heusler) [16], where X, Y are transition-metal-element atoms and Z is a main group element. The structure of full-Heusler alloys consists of four interpenetrating fcc lattices with four equidistant sites as basis along the diagonal of the unit cell. According to the well-known Site Preference Rule (SPR) [1–15], when the valence of the X is larger than that of Y, the atomic sequence is X<sup>A</sup>-Y<sup>B</sup>-X<sup>C</sup>-Z<sup>D</sup> and the structure is the well-known L<sub>21</sub> one with prototype Cu<sub>2</sub>MnAl. Otherwise, the alloys crystallize in the so-called XA structure, where the sequence of the atoms is then X<sup>A</sup>-X<sup>B</sup>-Y<sup>C</sup>-Z<sup>D</sup> and the prototype is Hg<sub>2</sub>CuTi. The latter alloys are also named as inverse Heusler alloys.

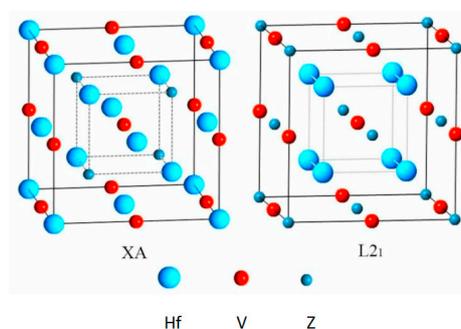
To the best of our knowledge, SPR has been applied extensively in the theoretical design of full-Heusler alloys and in predictions of their electronic, magnetic, and transport behavior. Some XA-type full-Heusler alloys, Mn<sub>2</sub>CoAl [16], Ti<sub>2</sub>MnAl [17], and Ti<sub>2</sub>CoSi [18], were predicted to be novel spin-gapless semiconductors (SGSs) [19,20]. Furthermore, lots of XA-type full-Heusler alloys, Sc<sub>2</sub>-, V<sub>2</sub>-, Cr<sub>2</sub>-, Mn<sub>2</sub>-, Ti<sub>2</sub>-, Zr<sub>2</sub>-, and even Hf<sub>2</sub>-based alloys, were revealed to be excellent half-metallic materials (HMMs) [21]. Surprisingly, one counterexample after another, including X<sub>2</sub>CuAl [22] and Ti<sub>2</sub>FeZ (Z = Al, Ga) alloys [6], has been reported very recently, in which these alloys show the L<sub>21</sub>-type structure and disobey the SPR, so that Y with more electrons enters the B sites.

In this work, a systematic theoretical work has been carried out to examine whether the conventional SPR was suitable for the Hf<sub>2</sub>-based highly-ordered full-Heusler alloys. To this end, the competition between the XA and L2<sub>1</sub> orderings of Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb) full-Heusler alloys has been studied through the first-principles calculations. Our current work shows that not all the full-Heusler alloys obey the SPR, and further, the SPR can not be considered as a concise judgement principle for the structure of highly-ordered full-Heusler alloys. Remarkably, we exhibit that atomic site occupation in these Hf<sub>2</sub>VZ alloys is decisive in determining their electronic, magnetic, and Slater-Pauling properties. For the L2<sub>1</sub>-type Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb) full-Heusler alloys, the phase stability from the aspect of the formation energy and mechanical behaviors has also been examined in term of theory. Details of the results are shown in the following discussion.

## 2. Computational Details

First-principles electronic-structure calculations were performed using density function theory (DFT) implemented in the CASTEP code [23,24] according to the plane-wave pseudo-potential method. The generalized gradient approximation (GGA) [25] was adopted for the exchange-correlation functional. For the XA-type and L2<sub>1</sub>-type Heusler alloys Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb), a Monkhorst-Pack special k-point mesh of  $9 \times 9 \times 9$  was used in the Brillouin zone integrations with a cutoff energy of 400 eV and a self-consistent field tolerance of  $10^{-6}$  eV. The quality of the k-point separation for the band structure calculation is  $0.01 \text{ \AA}^{-1}$ .

As shown in Figure 1, the crystal structures of XA and L2<sub>1</sub> types Hf<sub>2</sub>VZ Heusler alloys have been given. For the former, the two Hf atoms sitting at the two inequivalent sites, and Hf 1, Hf 2, V and Z atoms occupy the Wyckoff coordinates A (0, 0, 0), B (0.25, 0.25, 0.25), C (0.5, 0.5, 0.5) and D (0.75, 0.75, 0.75), respectively; For the latter, the two Hf atoms are essentially equivalent, and they have the same atomic environment. Hf 1, Hf 2, V and Z atoms occupy the Wyckoff coordinates A (0, 0, 0), B (0.5, 0.5, 0.5), C (0.25, 0.25, 0.25) and D (0.75, 0.75, 0.75), respectively.



**Figure 1.** Crystal structures of XA and L2<sub>1</sub> types Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb) alloys. This  $1 \times 1 \times 1$  super-cell system contains 16 atoms, i.e.,  $8 \times \text{Hf}$ ,  $4 \times \text{V}$  and  $4 \times \text{Z}$ .

## 3. Results and Discussion

### 3.1. Competition of L2<sub>1</sub> and XA Structure Ordering in Full-Heusler Hf<sub>2</sub>VZ Alloys

First, to confirm the ground state of Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb) full-Heusler alloys, the geometry optimization has been performed by calculating the total energies as functions of the lattice constant (cell volume) [26]. In this work, three possible magnetic states, i.e., paramagnetic (PM), ferrimagnetic (FiM), and antiferromagnetic (AFM) states are taken into account. The PM (or nonmagnetic) state means that the constituent atoms of Hf<sub>2</sub>VZ have no spin polarization. The FiM state implies that the spin magnetic moments of Hf atoms align anti-parallel to those of the V atoms, and the total magnetic moment is not equal to zero, while the AFM state means the spin magnetic moments of Hf atoms align antiparallely to those of the V atoms, and the total magnetic

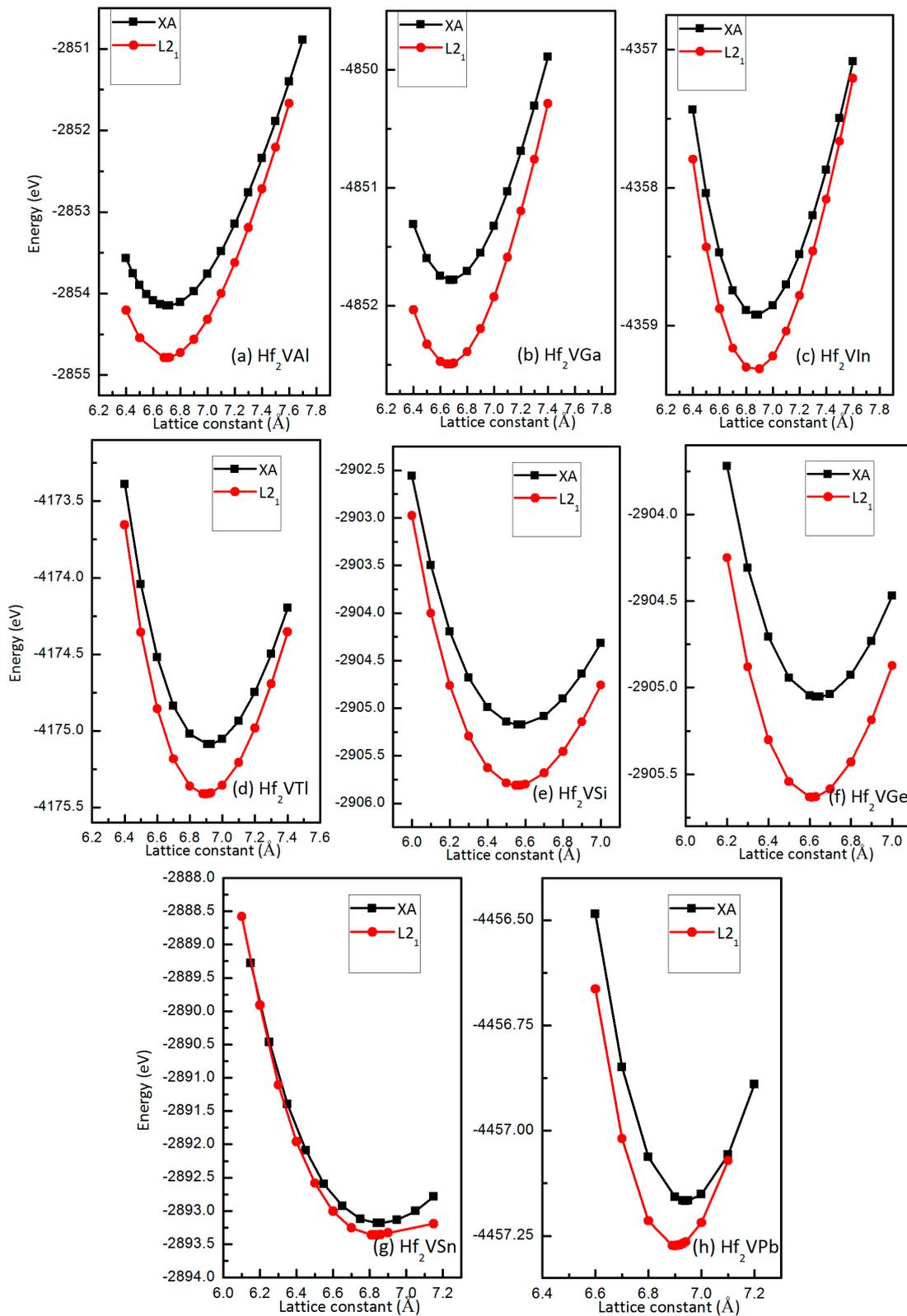
moment is equal to zero. For our Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb) full-Heusler alloys, the FiM state is the most stable among three magnetic states.

As shown in Figure 2, the total energy as functions of lattice constants of full-Heusler Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb) alloys with two atomic occupation orderings, XA and L2<sub>1</sub>, and with their most stable magnetic state, FiM, have been exhibited. Obviously, for all these alloys, the L2<sub>1</sub> state has lower energies than XA state. Therefore, Hf<sub>2</sub>VZ alloys studied in current work prefer to form the L2<sub>1</sub>-type structure as ground state with equilibrium lattice constant of 6.69 Å, 6.66 Å, 6.90 Å, 6.89 Å, 6.56 Å, 6.61 Å, 6.82 Å and 6.90 Å, respectively. The obtained equilibrium lattice constants of these alloys with XA-type and L2<sub>1</sub>-type structures, respectively, and the energy differences between these two structures ( $\Delta E = E_{XA}^{total} - E_{L2_1}^{total}$ ) for Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Ge, Sn, Pb) alloys are also listed in Table 1. A higher value of  $\Delta E$  indicates the L2<sub>1</sub>-type structure is more stable than XA-type. The highest positive value of 0.71 eV/cell appears in Hf<sub>2</sub>VGa alloy, reflecting that the site preference of V for the B position is quite strong. Hence, compared to other Hf<sub>2</sub>-based Heusler alloys, XA-type Hf<sub>2</sub>VGa maybe more difficult to synthesize experimentally due to its largest  $\Delta E$ .

We should point out here that, as we said in the part of Introduction, Hf<sub>2</sub>VZ alloys or even all the Hf-based full Heusler alloys should exhibit XA-type Heusler structure on basis of the SPR. Surprisingly, in current work, our results break the traditional SPR. Also, the data in this work, together with the latest scientific findings in References [6,22,27,28], are sufficient to demonstrate that not all the full-Heusler alloys X<sub>2</sub>YZ obey the well-known SPR, especially X are low-valent transition metals. Since the SPR can not be regarded as the only way to determine the competition of XA and L2<sub>1</sub> structural ordering in Heusler alloys, alloys with L2<sub>1</sub>-type structure should also be taken into account in the previous works [1–3,7–11].

**Table 1.** The calculated energy difference  $\Delta E$ , lattice constant *a*, total and atomic spin magnetic moments for Hf<sub>2</sub>VZ alloys with L2<sub>1</sub> and XA structures, respectively.

Alloy	Structure	$\Delta E$ (eV/cell)	<i>a</i> (Å)	<i>M<sub>t</sub></i> (μ <sub>B</sub> /f.u.)	<i>M<sub>Hf 1</sub></i> (μ <sub>B</sub> )	<i>M<sub>Hf 2</sub></i> (μ <sub>B</sub> )	<i>M<sub>V</sub></i> (μ <sub>B</sub> )	<i>M<sub>Z</sub></i> (μ <sub>B</sub> )	Stable Structure
Hf <sub>2</sub> VAl	XA	0.64	6.71	2	−0.65	0.14	2.62	−0.12	L2 <sub>1</sub>
	L2 <sub>1</sub>		6.69	1.65	−0.21	−0.21	2.19	−0.11	
Hf <sub>2</sub> VGa	XA	0.71	6.68	1.99	−0.59	0.15	2.55	−0.13	L2 <sub>1</sub>
	L2 <sub>1</sub>		6.66	1.68	−0.13	−0.13	2.06	−0.12	
Hf <sub>2</sub> VIn	XA	0.39	6.88	2	−0.75	−0.01	2.88	−0.12	L2 <sub>1</sub>
	L2 <sub>1</sub>		6.90	1.70	−0.24	−0.24	2.31	−0.13	
Hf <sub>2</sub> VTl	XA	0.32	6.92	1.98	−0.79	−0.1	3.0	−0.12	L2 <sub>1</sub>
	L2 <sub>1</sub>		6.89	1.61	−0.17	−0.17	2.06	−0.11	
Hf <sub>2</sub> VSi	XA	0.63	6.57	1.02	−0.74	−0.25	2.08	−0.06	L2 <sub>1</sub>
	L2 <sub>1</sub>		6.56	0.24	−0.03	−0.03	0.31	−0.01	
Hf <sub>2</sub> VGe	XA	0.58	6.64	1.03	−0.83	−0.34	2.26	−0.06	L2 <sub>1</sub>
	L2 <sub>1</sub>		6.61	0.2	−0.02	−0.02	0.26	−0.01	
Hf <sub>2</sub> VSn	XA	0.18	6.85	1	−1.07	−0.51	2.64	−0.05	L2 <sub>1</sub>
	L2 <sub>1</sub>		6.82	0.49	−0.06	−0.06	0.63	−0.03	
Hf <sub>2</sub> VPb	XA	0.11	6.94	1	−1.17	−0.63	2.87	−0.04	L2 <sub>1</sub>
	L2 <sub>1</sub>		6.90	0.32	−0.03	−0.03	0.41	−0.02	



**Figure 2.** Calculated total energies of XA and L2<sub>1</sub> types Hf<sub>2</sub>VAl (a); Hf<sub>2</sub>VGa (b); Hf<sub>2</sub>VIn (c); Hf<sub>2</sub>VTI (d); Hf<sub>2</sub>VSi (e); Hf<sub>2</sub>VGe (f); Hf<sub>2</sub>VSn (g); Hf<sub>2</sub>VPb (h) alloys with respect to the lattice constant.

### 3.2. Structural and Mechanical Properties of Heusler-Based Hf<sub>2</sub>VZ with L2<sub>1</sub>-Type Ordering

Further, we aim to check the structural stability of the L2<sub>1</sub>-type full-Heusler Hf<sub>2</sub>VZ according to their calculated formation energies and mechanical properties. Similar methods [29,30] have been applied extensively to analyze the stability for Heusler alloys in term of theory. The formation energies of these alloys can be obtained from the following equation:

$$E_f = E_{\text{Hf}_2\text{VZ}}^{\text{total}} - (E_{\text{Hf}1}^{\text{bulk}} + E_{\text{Hf}2}^{\text{bulk}} + E_{\text{V}}^{\text{bulk}} + E_{\text{Z}}^{\text{bulk}}) \quad (1)$$

where  $E_{\text{Hf}_2\text{VZ}}^{\text{total}}$  is the total energy of Hf<sub>2</sub>VZ per formula unit, and  $E_{\text{Hf}1}^{\text{bulk}}$ ,  $E_{\text{Hf}2}^{\text{bulk}}$ ,  $E_{\text{V}}^{\text{bulk}}$ , and  $E_{\text{Z}}^{\text{bulk}}$  are the total energies per atom of each element in the bulk form for the Hf 1, Hf 2, V, and Z, respectively. The results have been given in Table 2, we can see that all these alloys have negative formation energies. Furthermore, the total energy of L2<sub>1</sub>-type Hf<sub>2</sub>VZ is lower than XA-type Hf<sub>2</sub>VZ (see Figure 1), and thus, the  $E_f$  of L2<sub>1</sub>-type Hf<sub>2</sub>VZ should be lower than XA-type Hf<sub>2</sub>VZ. This implies that L2<sub>1</sub>-type Hf<sub>2</sub>VZ should be more stable than the XA-type Hf<sub>2</sub>VZ alloys.

Next, we come to the mechanical properties of these alloys and examine their stability based on achieved elastic constants  $C_{ij}$ . For these alloys with cubic structure, only three independent elastic constants ( $C_{11}$ ,  $C_{12}$  and  $C_{44}$ ) are needed to be taken into consideration, and the  $C_{ij}$  can be shown as below [31]:

$$\begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \quad (2)$$

For a small strain on a cubic system, the change of elastic energy  $\Delta E$  can be shown as below [32]:

$$\Delta E = \frac{V}{2} \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} e_i e_j \quad (3)$$

where  $V$  stands for the volume of the unit cell. The strain tensors are always symmetric, and they can therefore be expressed more compactly as 6-component vectors, using the so-called Voigt notation. We select three strain tensors  $(0, 0, 0, \delta, \delta, \delta)$ ,  $(\delta, \delta, 0, 0, 0, 0)$  and  $(\delta, \delta, \delta, 0, 0, 0)$  to obtain the elastic constants:

$$\frac{\Delta E_1}{V} = \frac{3}{2} C_{44} \delta^2 \quad (4)$$

$$\frac{\Delta E_2}{V} = (C_{11} + C_{12}) \delta^2 \quad (5)$$

$$\frac{\Delta E_3}{V} = \frac{3}{2} (C_{11} + C_{12}) \delta^2 \quad (6)$$

where  $\Delta E_1, \Delta E_2, \Delta E_3$  are the change of elastic energy for small strain tensors  $(0, 0, 0, \delta, \delta, \delta)$ ,  $(\delta, \delta, 0, 0, 0, 0)$  and  $(\delta, \delta, \delta, 0, 0, 0)$ , respectively.

Based on obtained  $C_{ij}$ , the mechanical properties, including bulk modulus  $B$ , shear modulus  $G$ , Voigt's shear modulus  $G_V$ , Reuss's shear modulus  $G_R$ , Young's modulus  $E$ , Pugh's ratio  $B/G$ , anisotropy factor  $A$ , of Hf<sub>2</sub>VZ can be calculated by using the following equations [29]:

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (7)$$

$$G = \frac{G_R + G_V}{2} \quad (8)$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (9)$$

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad (10)$$

$$E = \frac{9GB}{3B + G} \quad (11)$$

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (12)$$

As shown in Table 2, we can see that all these alloys with L2<sub>1</sub>-type structure are mechanical stable due to their calculated elastic constants follow the generalized elastic stability criteria [33]:

$$C_{44} > 0 \quad (13)$$

$$\frac{(C_{11} - C_{12})}{2} > 0 \quad (14)$$

$$B > 0 \quad (15)$$

$$C_{12} < B < C_{11} \quad (16)$$

Moreover, some special mechanical properties of these alloys can also be observed from Table 2. We addressed some as follows: (1) the values of  $B/G$  of these alloys are all larger than 1.75, reflecting they are ductile according to Pugh's criteria; (2) the values of  $A$  for all these alloys are not equal to 1, meaning the fact that they are anisotropic; (3) as is known, the higher the value of  $E$ , the stiffer is the materials, and therefore, the relative stiffer order of these Hf<sub>2</sub>VZ materials is Hf<sub>2</sub>VAl > Hf<sub>2</sub>VSi > Hf<sub>2</sub>VGa > Hf<sub>2</sub>VGe > Hf<sub>2</sub>VIn > Hf<sub>2</sub>VSn > Hf<sub>2</sub>VTi > Hf<sub>2</sub>VPb.

**Table 2.** Calculated elastic constants  $C_{ij}$ , bulk modulus  $B$ , shear modulus  $G$ , Young's modulus  $E$  (GPa), Pugh's ratio  $B/G$ , anisotropy factor  $A$ , and formation energy (eV) for Hf<sub>2</sub>VZ alloys with L2<sub>1</sub> structure.

Alloy	$C_{11}$	$C_{12}$	$C_{44}$	$B$	$G$	$E$	$B/G$	Formation Energy	Anisotropy Factor
Hf <sub>2</sub> VAl	164.4	117.6	73.0	133.2	46.8	124.6	2.8	−0.54	3.10
Hf <sub>2</sub> VGa	143	104.3	72.9	117.9	43.0	115.10	2.7	−1.19	3.76
Hf <sub>2</sub> VIn	179.8	154.3	49.7	162.8	28.9	82.0	5.6	−0.05	3.89
Hf <sub>2</sub> VTi	110.4	100.1	46.8	103.5	20.5	57.9	5.0	−0.85	9.08
Hf <sub>2</sub> VSi	191	146.9	63.7	161.6	41.6	115.12	3.8	−0.66	2.88
Hf <sub>2</sub> VGe	158.2	123.1	54.1	134.8	34.5	95.4	3.9	−0.41	3.08
Hf <sub>2</sub> VSn	187.5	155.6	42.2	166.2	28.5	81.1	5.8	−0.07	2.64
Hf <sub>2</sub> VPb	109.1	97.9	18.2	101.6	11.4	32.9	8.9	−0.91	3.25

### 3.3. Calculated Electronic Behaviors of L2<sub>1</sub> and XA Types Hf<sub>2</sub>VZ

Electronic-structure calculation theory has clearly indicated [20,34,35] that the spintronic properties of materials among Heusler family has an unusual sensibility to the atomic occupation in crystal cell. Hence, in this section, a discussion about the spintronic property differences, including the magnetic, electronic, half-metallic, and the spin polarization ratio ( $p$ ), between the XA and L2<sub>1</sub> Hf<sub>2</sub>VZ ( $Z = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb}$ ) full-Heusler alloys should be performed. Figures 3–5 show the calculated band structures for XA and L2<sub>1</sub> types Hf<sub>2</sub>VZ ( $Z = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb}$ ) at their equilibrium lattice constants.

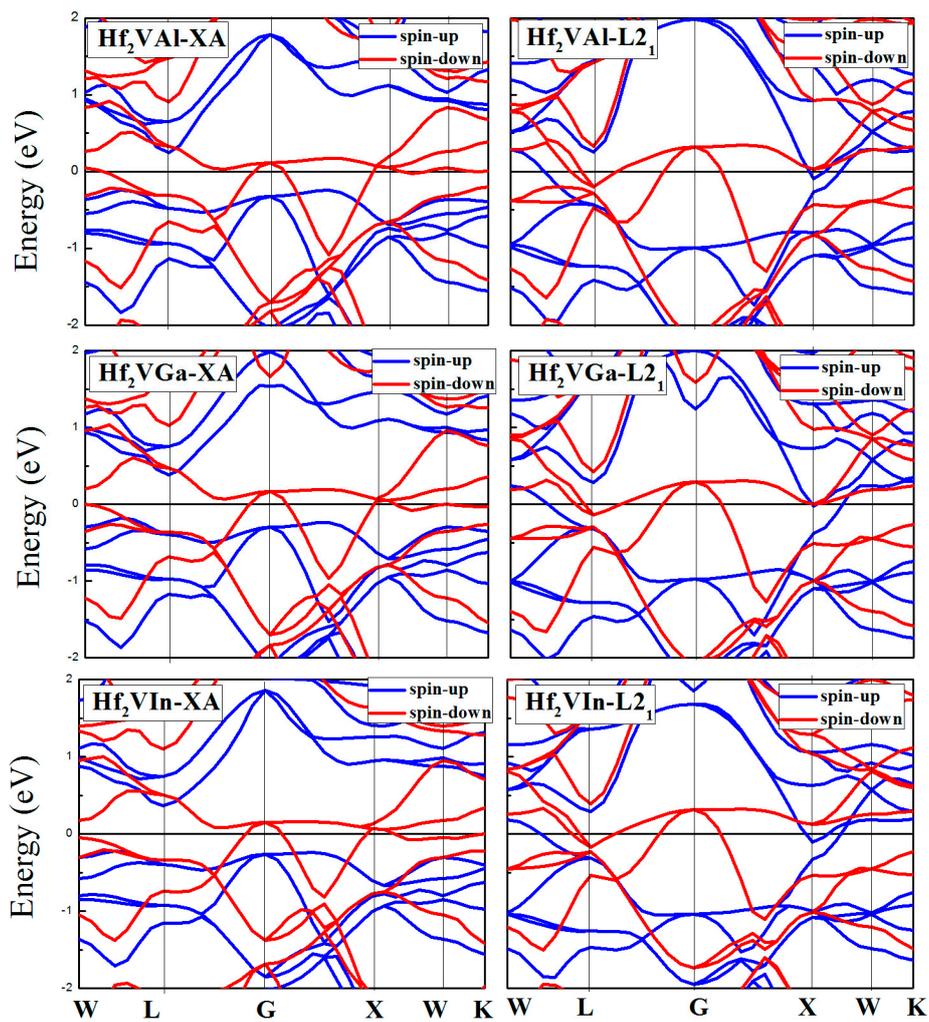


Figure 3. Calculated band structures of XA and L2<sub>1</sub> types Hf<sub>2</sub>VZ (Z = Al, Ga, In) alloys.

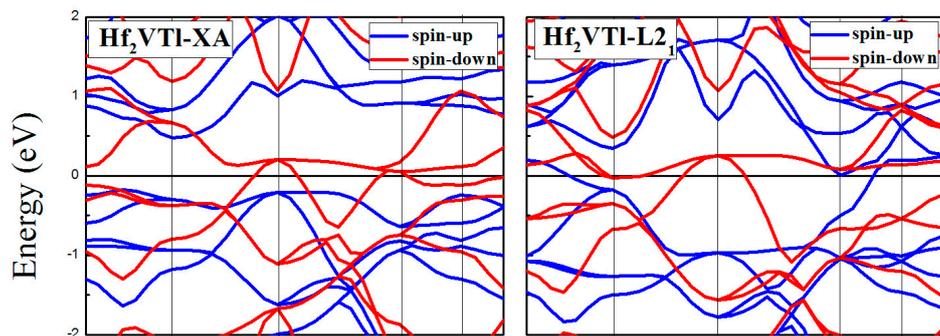


Figure 4. Cont.

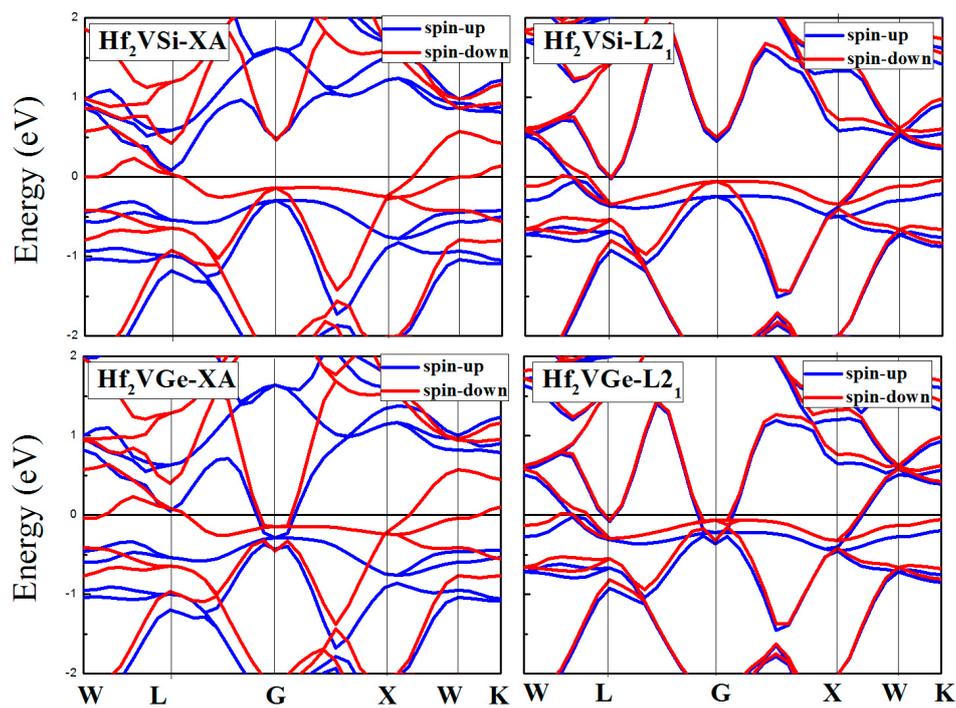


Figure 4. Calculated band structures of XA and L2<sub>1</sub> types Hf<sub>2</sub>VZ (Z = Ti, Si, Ge) alloys.

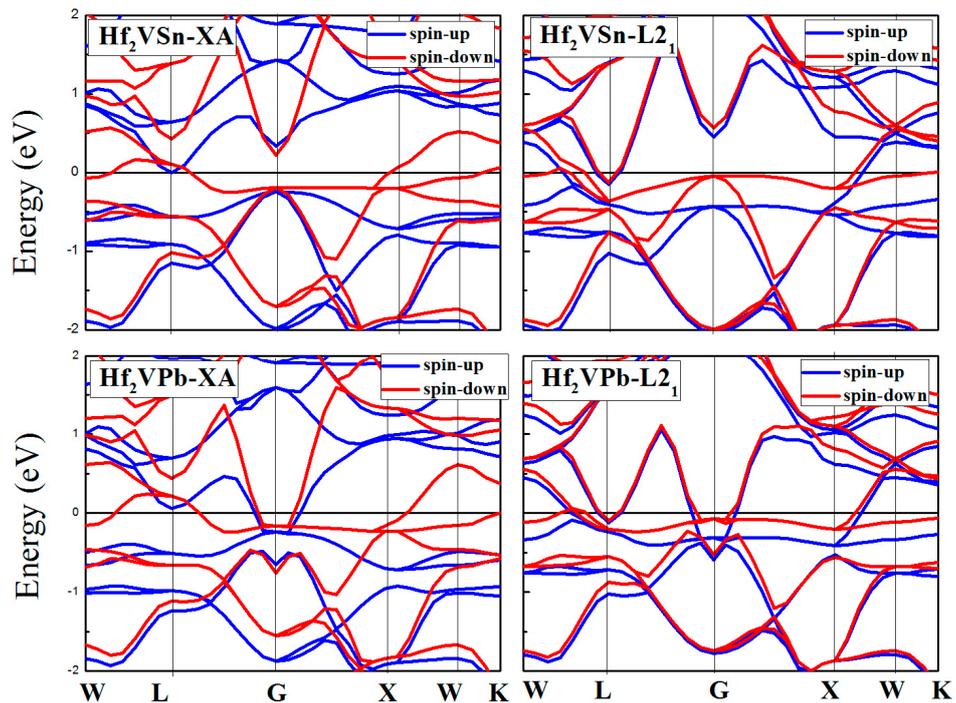


Figure 5. Calculated band structures of XA and L2<sub>1</sub> types Hf<sub>2</sub>VZ (Z = Sn and Pb) alloys.

For XA atomic ordering, Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Sn) alloys are excellent half-metallic materials since there is a semiconducting-type band gap in the spin-up direction and the Fermi level locates between the opened gap. However, in the spin-down direction, the semiconducting-type band gap disappeared: although an opened gap can be observed near the Fermi level, the Fermi level has overlapped with the spin-down bands in varying degrees. In the spin-up channel, the significant factors, including the

calculated valence band maximum (VBM), conduction band minimum (CBM), semiconducting band gap, and spin-flip/half-metallic gap, have been given in Table 3, the semiconducting band gap [36] is the sum of the absolute values of CBM and VBM, and the spin-flip/half-metallic gap [36] is defined as the minimum value of the two absolute values of CBM and VBM. The semiconducting band gap values of these alloys are 0.46 eV for Hf<sub>2</sub>VAl, 0.59 eV for Hf<sub>2</sub>VGa, 0.59 eV for Hf<sub>2</sub>VIn, 0.64 eV for Hf<sub>2</sub>VTI, 0.35 eV for Hf<sub>2</sub>VSi, 0.30 eV for Hf<sub>2</sub>VSn, respectively. The spin-flip/half-metallic gap values of these alloys are 0.23 eV for Hf<sub>2</sub>VAl, 0.23 eV for Hf<sub>2</sub>VGa, 0.22 eV for Hf<sub>2</sub>VIn, 0.17 eV for Hf<sub>2</sub>VTI, 0.07 eV for Hf<sub>2</sub>VSi, 0.04 eV for Hf<sub>2</sub>VSn, respectively. For XA atom ordering Hf<sub>2</sub>VGe and Hf<sub>2</sub>VPb alloys, semiconducting band gaps in the both directions disappeared and both alloys exhibit common metallic properties.

**Table 3.** Calculated valence band maximum (VBM), conduction band minimum (CBM), semiconducting band gaps, spin-flip gap/half-metallic gaps and spin polarization ratio (*p*) of Hf<sub>2</sub>VZ alloys with L2<sub>1</sub> and XA structures, respectively.

Alloy	Structure	CBM	VBM	Band Gap	Half-Metallic Gap	<i>p</i> (%)
Hf <sub>2</sub> VAl	XA	0.23	−0.23	0.46	0.23	100
	L2 <sub>1</sub>	-	-	-	-	48
Hf <sub>2</sub> VGa	XA	0.36	−0.23	0.59	0.23	100
	L2 <sub>1</sub>	-	-	-	-	52
Hf <sub>2</sub> VIn	XA	0.37	−0.22	0.59	0.22	100
	L2 <sub>1</sub>	-	-	-	-	36
Hf <sub>2</sub> VTI	XA	0.47	−0.17	0.64	0.17	100
	L2 <sub>1</sub>	-	-	-	-	40
Hf <sub>2</sub> VSi	XA	0.07	−0.28	0.35	0.07	100
	L2 <sub>1</sub>	-	-	-	-	39
Hf <sub>2</sub> VGe	XA	-	-	-	-	88
	L2 <sub>1</sub>	-	-	-	-	33
Hf <sub>2</sub> VSn	XA	0.04	−0.26	0.30	0.04	100
	L2 <sub>1</sub>	-	-	-	-	56
Hf <sub>2</sub> VPb	XA	-	-	-	-	94
	L2 <sub>1</sub>	-	-	-	-	36

For Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Sn) alloys with the XA structure, the V and Hf atoms occupy sites with same symmetry in XA-type Heusler structure, and the hybridization of their d orbitals creates 5 bonding bands ( $3t_{2g}$  and  $2e_g$ ) and 5 non-bonding bands ( $2e_u$  and  $3t_{1u}$ ). Then, the 5 V-Hf bonding d hybrids hybridize in turn with d orbitals of Hf, again forming bonding and anti-bonding bands, while the 5 non-bonding bands ( $2e_u$  and  $3t_{1u}$ ) still exist with no hybridizing. Finally, the distribution of the 15 d orbitals in the minority-spin direction can be determined, i.e.,  $3t_{2g}$ ,  $2e_g$ ,  $2e_u$ ,  $3t_{1u}$ ,  $3t_{2g}$ , and  $2e_g$ , from the high-energy level to the low-energy level. Also, we cannot ignore that Z creates 1s and 3p bands which are totally occupied in Hf<sub>2</sub>VZ and are also below the above-mentioned 15 d orbitals. Therefore, their semiconducting-type band gaps are created by the separated  $\Gamma_{15}$  and  $\Gamma_{25}$  states, coming from the bonding  $t_{2g}$  and antibonding  $t_{1u}$  states.

The calculated total and partial density of states (TDOS and PDOS) for the six Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Sn) alloys with XA and L2<sub>1</sub> atomic orderings and for equilibrium lattice constants have also been calculated in this work to deepen the understanding of their electronic properties. As an example, the results of Hf<sub>2</sub>VAl and Hf<sub>2</sub>VSi alloys are given in Figure 6. Clearly, from the figure, a semiconducting band gap can be found in spin-up direction for XA-type Hf<sub>2</sub>VZ (Z = Al, Ga, In, Tl, Si, Sn) alloys, which is in a good agreement with above-mentioned band structures.

The DOS can be widely used to analyze the bonding/anti-bonding states and the gap formation and similar analytical approach can be observed in References [19,29]. In the spin-up channel, the main peaks of Hf 2 and V atoms occurred at around −0.5 eV. In the spin-down channel, in the similar

energy region (around  $-0.5$  eV), for V and Hf 2 atoms, such hybridized peaks appeared at the same time. Therefore, the hybridization between the V and Hf 2 atoms that formed strong bonding states at around  $-0.5$  eV. Above the Fermi level, in the spin-up channel, the anti-bonding peak can be found at around 1 eV mainly arise from the Hf 1-d electrons, and in the spin-down channel, no opposite energy states are observed. Moreover, in the spin-up channel, the corresponding bonding-antibonding states led to the formation of an opened band gap, and the Fermi level, exactly, locates between the gap.

For  $L2_1$  type atomic ordering, the band structures and the DOS have a big difference with XA type atomic ordering. Namely, all the  $Hf_2VZ$  alloys investigated in this work show conventional metallic behaviors without semiconducting-type band gaps at Fermi level in both spin channels. As shown in Figures 3–6, both spin-up and spin-down bands are crossed by the Fermi level.

Moreover, from the obtained total DOS, we calculated the spin polarization ( $p$ ) at Fermi energy of XA and  $L2_1$  types  $Hf_2VZ$ . The spin polarization  $p$  (%) that can be defined as the ratio of the difference to sum of the DOS values of spin up and spin down version at the Fermi-level [13,16], represented by mathematical formulation as a percent;

$$p = \frac{n \uparrow (E_f) - n \downarrow (E_f)}{n \uparrow (E_f) + n \downarrow (E_f)} \times 100\% \quad (17)$$

where the  $n \uparrow (E_f)$  and  $n \downarrow (E_f)$  stand for the spin-dependent DOS around the Fermi level. The results have been given in Table 3, we can see that the  $p$  of XA-type  $Hf_2VZ$  are quite high ( $>88\%$ ), even some alloys (such as  $Hf_2VAI$ ) have completely spin polarization (100%). High-spin-polarization materials are very useful in spintronic application. However, the  $L2_1$ -type  $Hf_2VZ$  exhibit pretty low spin polarization ( $<56\%$ ). This also implies that the novel spintronic properties (such as half-metallic properties) in XA type structure are disappeared as these alloys form  $L2_1$  type structure.

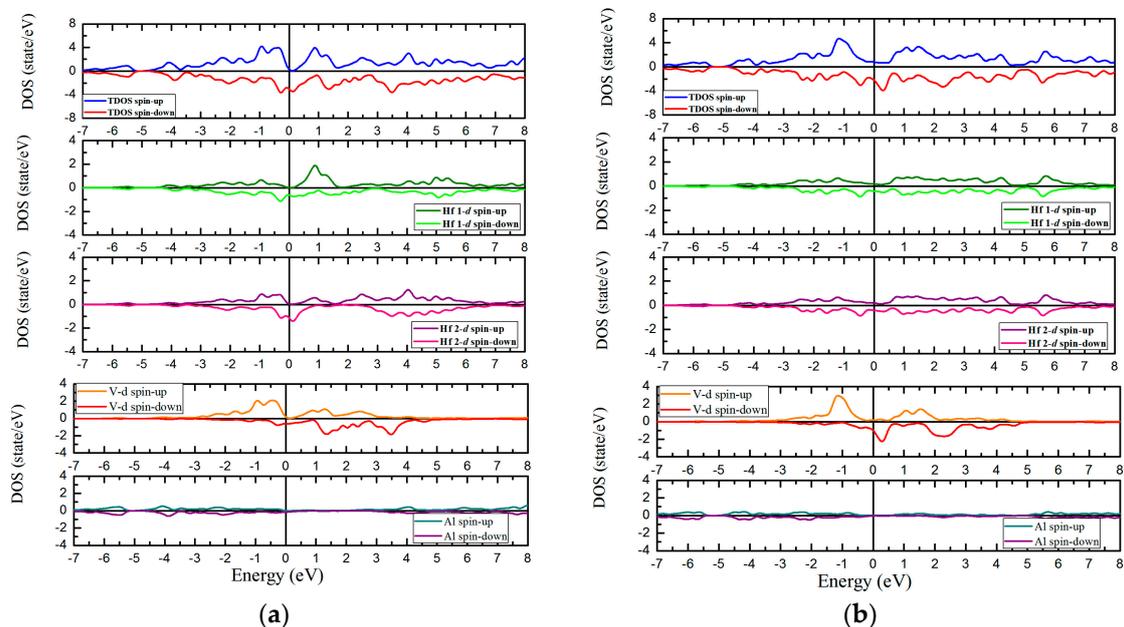
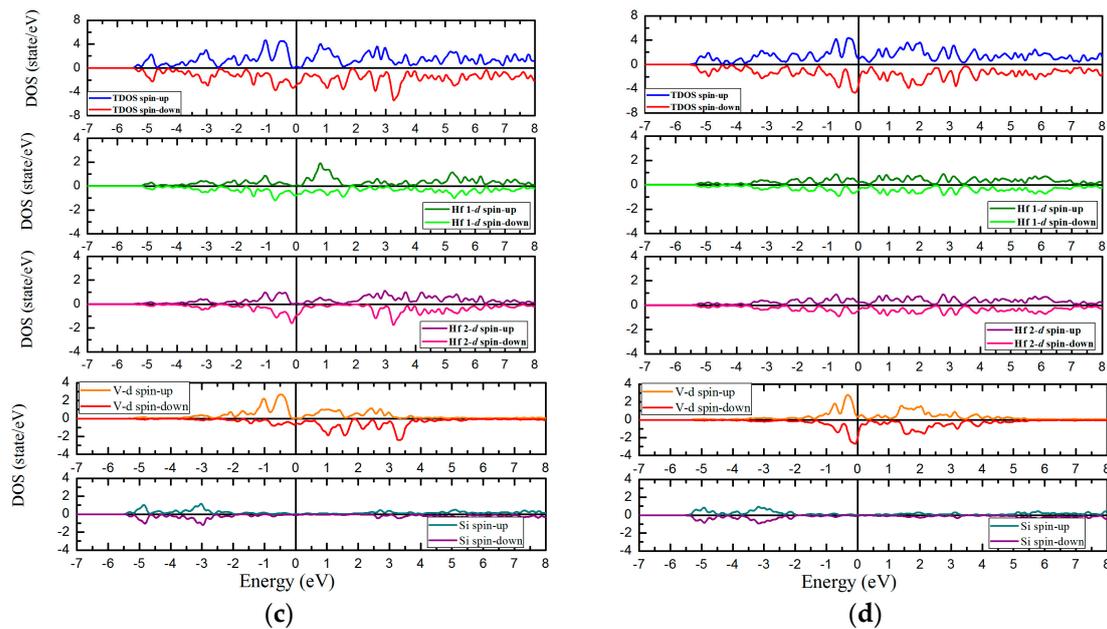


Figure 6. Cont.



**Figure 6.** Calculated band structures of XA type  $\text{Hf}_2\text{VAI}$  (a);  $\text{L}_{21}$  type  $\text{Hf}_2\text{VAI}$  (b); XA type  $\text{Hf}_2\text{VSi}$  (c);  $\text{L}_{21}$  type  $\text{Hf}_2\text{VSi}$  (d); respectively.

### 3.4. Magnetic and Slater-Pauling Properties of $\text{L}_{21}$ and XA Types $\text{Hf}_2\text{VZ}$

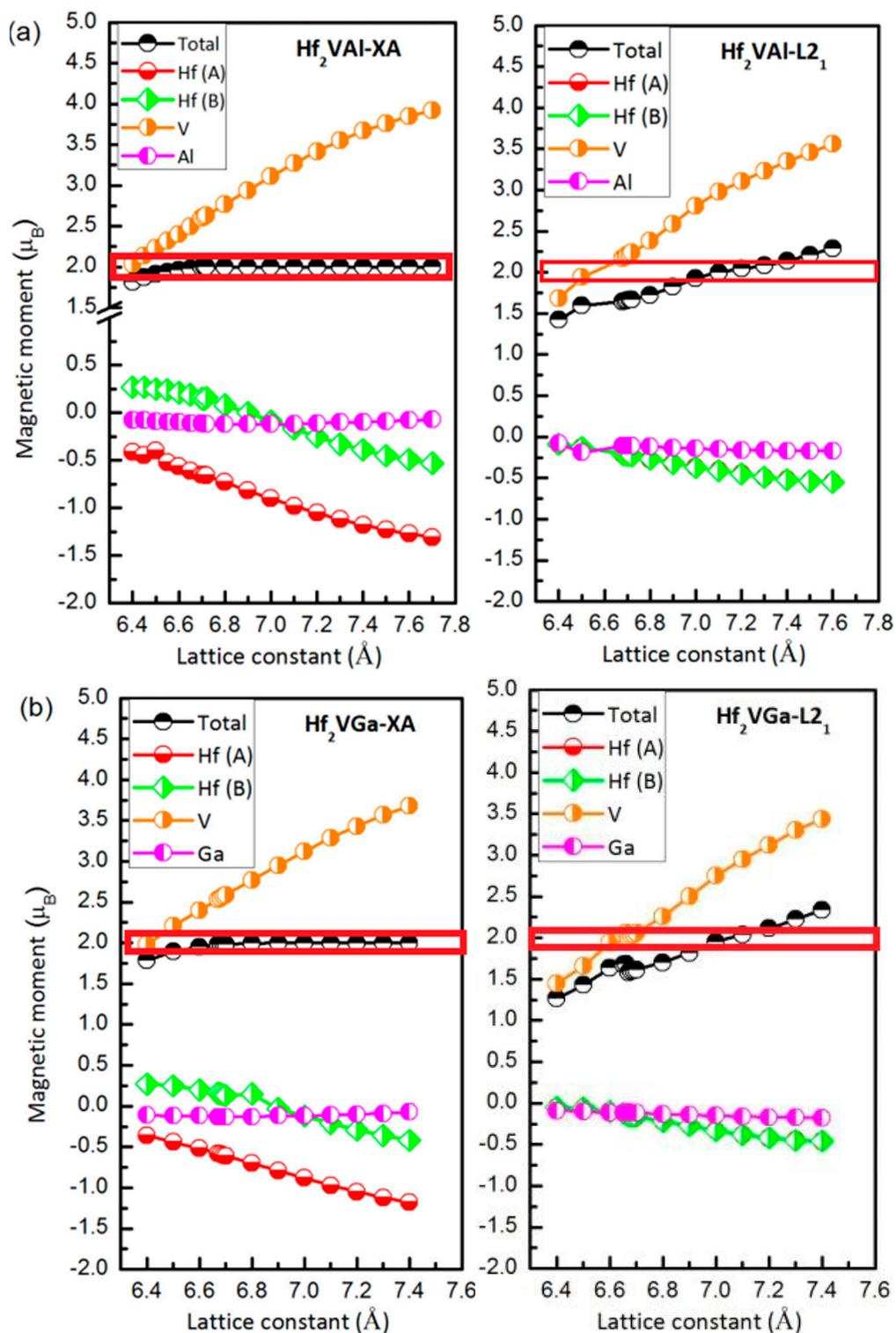
Finally, in this section, we come to discuss the magnetism and Slater-Pauling rule of  $\text{L}_{21}$  and XA types  $\text{Hf}_2\text{VZ}$  ( $Z = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb}$ ) alloys. The total and atomic magnetic moments of these alloy with XA and  $\text{L}_{21}$  atomic ordering are shown in Table 1. Obviously, all these alloys, with either XA or  $\text{L}_{21}$  type structures, exhibit FiM properties with the atomic magnetic moments of Hf antiparallel aligned with that of V atoms. Based on Table 1, V carries the largest moment and therefore, V atom makes the most contribution to the total magnetic moment.

For XA-type  $\text{Hf}_2\text{VZ}$  full-Heusler materials, their total magnetic moments are almost integer values ( $2 \mu_B/\text{f.u.}$  or  $1 \mu_B/\text{f.u.}$ ), reflecting their high spin polarization properties. Furthermore, from Table 1, we can see that their total magnetic moments follow the well-known Slater-Pauling rule [37]:

$$M_t = Z_t - 18 \quad (18)$$

where the  $M_t$  stands for the total magnetic moment of these materials and the  $Z_t$  means the number of total of valence electrons in  $\text{Hf}_2\text{VZ}$  alloys. For  $\text{L}_{21}$  type  $\text{Hf}_2\text{VZ}$  full-Heusler materials, their total magnetic moments are all largely deviated from integer values, indicating the half-metallic properties have been totally destroyed when these alloys are in  $\text{L}_{21}$  type structure. For  $\text{Hf}_2\text{VSi}$  and  $\text{Hf}_2\text{VGe}$ , both alloys have a very weak moment of  $0.24 \mu_B/\text{f.u.}$  and  $0.20 \mu_B/\text{f.u.}$ , respectively. Therefore, the  $\text{L}_{21}$  type  $\text{Hf}_2\text{VZ}$  full-Heusler alloys do not obey the above-mentioned Slater-Pauling rule.

The magnetism for XA and  $\text{L}_{21}$  types full-Heusler alloys  $\text{Hf}_2\text{VZ}$  ( $Z = \text{Al, Ga, In, Tl, Si, Sn}$ ) alloys at their strained lattice constants has also been examined. As an example, the results of  $\text{Hf}_2\text{VAI}$  and  $\text{Hf}_2\text{VGa}$  have been given in Figure 7. According to the Slater-Pauling and generalized electron-filling rules [11,13], the integer values of total magnetic moments which follow the Slater-Pauling rule indicate the half-metallic properties of materials and thus stand for their high spin polarization. From Figure 7, we can see that the high spin polarization properties of XA type  $\text{Hf}_2\text{VZ}$  ( $Z = \text{Al, Ga, In, Tl, Si, Sn}$ ) alloys are very robust, however, the region with high spin polarization (integer values of total magnetic moments) of  $\text{L}_{21}$ -type  $\text{Hf}_2\text{VZ}$  alloys is extraordinarily narrow. For the atomic magnetic moments of XA and  $\text{L}_{21}$  types  $\text{Hf}_2\text{VZ}$ , the values of Hf decreases, whereas the V atom, it increases.



**Figure 7.** (a,b) Calculated total and atomic spin magnetic moments of  $\text{Hf}_2\text{VZ}$  ( $Z = \text{Al, Ga}$ ) alloys as functions of the lattice constant. The red boxes show the high-spin polarization regions.

#### 4. Conclusions

To sum up, the atomic occupation of a series of  $\text{Hf}_2$ -based full-Heusler alloys was investigated by theoretical first-principle calculations. We observed that all  $\text{Hf}_2\text{V}$ -based alloys studied in current work are likely to form the  $\text{L}2_1$  structure instead of XA structure. Our results also indicate that the spintronic

properties (half-metallic or high spin-polarization properties), and Slater-Pauling behaviors that exist in XA for Hf<sub>2</sub>VZ are fully destroyed in L2<sub>1</sub>. With our study, it is clear that not all full-Heusler alloys X<sub>2</sub>YZ obey the SPR, especially when X are low valence metal elements.

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