



Research articles

Site preference, magnetic and electronic properties of half-metallic Vanadium-based full Heusler alloys



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ABSTRACT

We reported a new atomic site preference occupation for Vanadium-based X_2YZ full Heusler alloys. It tells that alloys with less 24 valence electrons form the $L2_1$ -type structure, while others form the XA -type structure. This fact means that the site preference rule for Vanadium-based alloys depends on the total number of valence electrons instead of the electropositive between X and Y atoms. The magnetic moments of XA -type alloys follow the Slater-Pauling rules, with two forms, $M_t = N_v - 24$ and $M_t = N_v - 18$ corresponding to different origins of the band gaps. XA -type V_2YZ ($Y = \text{Cr, Mn and Fe; } Z = \text{Ga, Ge and As}$), $V_2\text{CoGa}$, $V_2\text{CoGe}$ and $V_2\text{NiGa}$ alloys have half-metallic property. $L2_1$ -type V_2YZ ($Y = \text{Cu and Zn; } Z = \text{Ga, Ge and As}$) alloys show no spin polarization and no half-metallic property due to the structural symmetry and the non-magnetism of copper and zinc atoms.

1. Introduction

Heusler alloys are highly ordered intermetallic compounds with a very simple crystal structure [1]. Some of the most important characteristics of these alloys are highly adjustable electronic structure, and the simple linear relationship between magnetic moment and valence electrons [2–6]. Therefore, the band structure and magnetic properties of these alloys are highly adjustable [7–10]. This is very advantageous for obtaining new spintronic materials. For example, spintronic materials with specific band structure such as half-metallic or spin gapless semiconducting were found in many Heusler alloys [11–15]. By adjusting the number of valence electrons, a zero net magnetic moment can be obtained without changing the half-metallic or spin gapless semiconducting band structure [8,16,17]. These materials have the characteristics of high spin polarization, zero net magnetic moment at the same time [18,19]. Heusler alloys usually have Curie temperature that much higher than room temperature, which makes this kind of materials has a very broad application prospect in the field of spintronics [20–22].

The X_2YZ ($X, Y = \text{transition metals, } Z = \text{main group element}$) full-Heusler alloys have two structural configurations. Fig. 1 gives the crystal structure. When the element X is less electropositive than Y , the alloy crystallizes into the well-known $L2_1$ -type configuration ($Fm\bar{3}m$, space group no. 225) with Cu_2MnAl as prototype [2]. The primitive cell of the $L2_1$ -type configuration contains four atoms that form the base of

the fcc primitive cell. The Wyckoff positions $4a$ (0, 0, 0), $4b$ (0.5, 0.5, 0.5) and $8c$ (0.25, 0.25, 0.25) are occupied by Z , Y , and X , respectively. When the element X is more electropositive than Y , the alloy crystallizes into the XA -type configuration ($F\bar{4}3m$, space group no. 216) with Hg_2CuTi as prototype [23]. This structure is still described by four interpenetrating fcc sublattices, but the X atoms do not form a simple cubic lattice. Instead, they are placed on the Wyckoff positions $4b$ (0.5, 0.5, 0.5) and $4c$ (0.25, 0.25, 0.25), while the Y and Z atoms are located at $4c$ (0.75, 0.75, 0.75) and $4a$ (0, 0, 0), respectively. Such electropositive depended site preference rule have been successful in Cr_2 -based, Mn_2 -based, Fe_2 -based, Co_2 -based, Ni_2 -based and Cu_2 -based full-Heusler alloys [24–28].

Recently, Ti_2 - and V_2 -based Heusler alloys have been attracting much attention due to the potential for achieving half-metallic ferromagnets, spin gapless semiconductors or fully compensated ferromagnets for spintronic applications [29–38]. According to the site preference rule, Ti_2 -based alloy should be crystallized to the XA -type structure, and most of the recent predictions were based on this structural type. However, there are some exceptions for the occupation rule. For example, Ti_2CrGa , which should crystallize into XA -type structure since element Ti is more electropositive than Cr , was however more likely to form $L2_1$ -type structure [36]. Wang *et al.* performed a more systematic work and found that most of the Ti_2 -based alloys are likely to form $L2_1$ -type structure instead of XA -type structure [37]. These results indicate that the electropositive depended site preference rule

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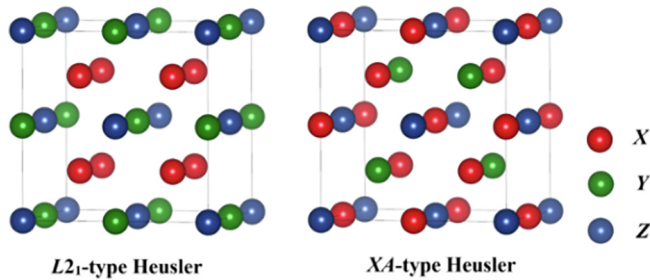


Fig. 1. Crystal structure of the X_2YZ full-Heusler alloys including the L_{21} -type and XA -type configurations.

failed in Ti_2 -based full-Heusler alloys. It is known that the configuration type of structure has significant influence on the magnetic and electronic properties of alloys. Half-metallicity, spin-gapless semi-conducting, and Slater-Pauling behavior that were observed in the XA -type structure would be fully destroyed in L_{21} . For example, half-metallic property of Ti_2CoAl only exists in XA -type structure [36].

Vanadium is also a $3d$ transition metal. Xing *et al.* predicted the half-metallic properties in XA -type V_2YSb ($Y = Cr, Mn, Fe, Co$) Heusler alloys [29]. Zhang *et al.* studied the phase stability, magnetism and Slater-Pauling rule of vanadium-based inverse Heusler alloys [30,33]. It can be seen that all of these predictions for Vanadium-based alloys were based on XA -type configuration. However, no work has yet been done to confirm that whether the electropositive depended site preference rule is suitable for Vanadium-based full-Heusler alloy.

In this work, systematic theoretical work were carried out to examine if the conventional site preference rule is applicable for V_2 -based full Heusler alloys. For this purpose, the competition between the XA - and L_{21} -type structures of V_2YZ ($Y = Ti, Cr, Mn, Fe, Co, Ni, Cu$ and Zn ; $Z = Ga, Ge$ and As) has been studied by first-principles calculations. It is found that the atomic site preference occupation in these alloys is determined by the total number of the valence electrons of the alloys instead of the electropositivity of components X and Y . These results are different from the cases for Ti_2 -based, and other high valence metals such as Cr_2 -, Mn_2 -, Fe_2 -, Co_2 -, Ni_2 -, and Cu_2 -based full-Heusler alloys.

2. Calculations methods

We have employed the *Vienna ab-initio* simulation package (VASP) for the first-principles calculations [39]. It is based on norm-conserving pseudopotential and pseudo-atomic localized basis functions. For all cases, the plane wave basis set cut-off was 500 eV, and a mesh of $15 \times 15 \times 15$ k -points was employed for Brillouin zone integrations. The exchange–correlation functional within a generalized gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof has been used [40]. The convergence tolerance for the calculations was selected as a difference in total energy within 1×10^{-6} eV/atom. These parameters ensure good convergence of the total energy.

3. Results and discussions

In order to determine the theoretical lattice parameters and the competition between the XA and L_{21} structures, we performed structural optimization calculations on V_2YZ ($Y = Ti, Cr, Mn, Fe, Co, Ni, Cu$ and Zn ; $Z = Ga, Ge$ and As) alloys, both for L_{21} and XA configurations. Fig. 2(a) gives the results of the calculations. ΔE represents the energy difference between XA and L_{21} configurations, i.e. $\Delta E = E(XA) - E(L_{21})$. The fact of $\Delta E < 0$ indicates the alloys likely form XA structure, while $\Delta E > 0$ indicates the alloys tend to form L_{21} structure. According to the typical electropositivity depended site preference rule, V_2YZ ($Y = Cr, Mn, Fe, Co, Ni, Cu$ and Zn) should be crystallized to XA structure since elements Cr, Mn, Fe, Co, Ni, Cu and Zn are all less electropositive than V . Element Ti is more electropositive than V , thus

V_2TiZ should crystallize into L_{21} structure. However, our calculations (see Fig. 2(a)) give different results. Although V_2YZ with $Y = Fe, Mn$ and Cr form XA structures agreeing with the site preference rule, it failed in alloys with $Y = Co, Ni, Cu$ and Zn . When $Y = Cu$ and Zn , alloys form L_{21} structure. When $Y = Co$ and Ni , the structure even depends on element Z . For example, V_2CoGa, V_2CoGe and V_2NiGa form XA structure, but V_2CoAs, V_2NiGe and V_2NiAs form L_{21} structure. Therefore, it is impossible to come up with a uniform atomic occupation rule for all V_2 -based full Heusler alloys when only considered the electropositivity of the atoms.

It should be pointed out that the alloys which crystallize into XA structure have less than 24 valence electrons, while L_{21} type alloys have more than 24 valence electrons. To further prove such behavior, we take V_2TiZ ($Z = Ga, Ge$ and As) alloys which have less than 24 valence electrons as examples. According to the electropositivity depended rule, V_2TiZ ($Z = Ga, Ge$ and As) should form L_{21} structures. However, the result of $\Delta E < 0$ illustrates V_2TiZ ($Z = Ga, Ge$ and As) alloys crystallize into XA structure. These results indicate that when we use the total number of valence electrons instead of the constituent atoms to describe the site preference of alloys, we can make the atomic occupancy uniform for all the selected alloys. Noted that it is true only in V_2 -based alloys.

In order to detect the phase stability of V_2YZ full Heusler alloys, the formation energy (E_{Form}) is calculated by the formula:

$$E_{Form} = E_{V_2YZ} - (2E_V + E_Y + E_Z)$$

where E_{V_2YZ} is the total energy of V_2YZ alloys, E_V, E_Y and E_Z represent the energy when V, Y and Z crystallized in pure metal. Results are shown in Fig. 2(b). The calculated formation energy turns out to be negative for all the alloys expect for V_2CuGa and V_2ZnGa indicating high possibility of realization in experiment.

Fig. 3 gives the magnetic moments (M_t) as a function of N_V for V_2 -based Heusler alloys. Both L_{21} and XA structures were included. Depending on N_V , the alloys are divided into two classes. The first part is the area of low valence electron concentrations ($N_V < 24$). In this area, M_t and N_V follow the Slater-Pauling rule but with two different forms. When $N_V \leq 21$, they have the form of $M_t = N_V - 18$. When $21 < N_V < 24$, the corresponding Slater-Pauling rule is then $M_t = N_V - 24$. Due to the loss of half-metallic property, magnetic moments of some alloys that with L_{21} -type configuration does not obey the Slater-Pauling rule. For example, N_V of V_2CoGa is 22, but M_t is 3.59 μ_B . The second part is the area of high valence electron concentrations ($N_V \geq 24$). In this area, M_t of alloys with L_{21} structure is no longer related to N_V but remains zero.

Therefore, not only the atomic occupancy, but also M_t is related to N_V . When $N_V \geq 24$, L_{21} structure is more energetically favorable, and M_t is independent on N_V . When $N_V < 24$, XA type structure is more energetically favorable, and M_t and N_V follow the Slater-Pauling rule with two different forms. In the following analysis, we will further understand the relationship between the magnetic moment and the number of valence electrons through the band structure and density of states (DOS).

According to the schematic representation as shown in Fig. 3(a), we start with a discussion of the possible $d-d$ hybridization between the transition-metal elements for the XA -type V_2YZ Heusler alloys. Based on the work of Galanakis *et al.* [2,23], we first take into account the hybridization between $V(A)$ and Y atoms that within octahedral symmetry. It gives the birth to five bonding and five anti-bonding states. Then these states hybridize with those of $V(B)$ atom and finally determine the distribution of 15 d -orbitals. Including the orbitals of element Z , the final hybridized orbitals from low energy to high energy are $1 \times s, 3 \times p, 2 \times e_g, 3 \times t_{2g}, 3 \times t_{1u}, 2 \times e_u, 2 \times e_g$ and $3 \times t_{2g}$. Then one can trace these hybridized states in the corresponding electronic band structure. It is known that the Slater-Pauling rule of half-metal is $M_t = N_V - 2N$, where N is the number of valence electrons that fully fill in the semiconducting band of half-metals.

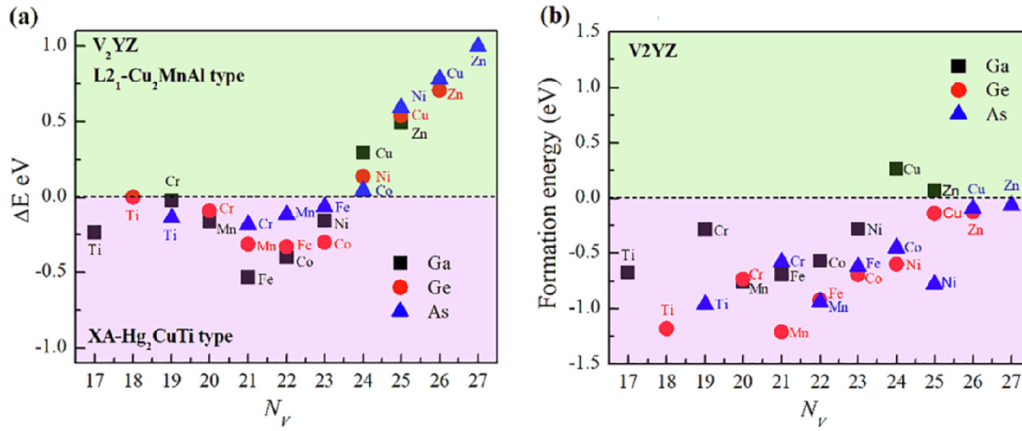


Fig. 2. (a) Energy difference (ΔE) between L2₁ and XA configurations, $\Delta E = E(XA) - E(L2_1)$; (b) formation energy (E_{form}) vs the number of valence electrons for V₂-based alloys.

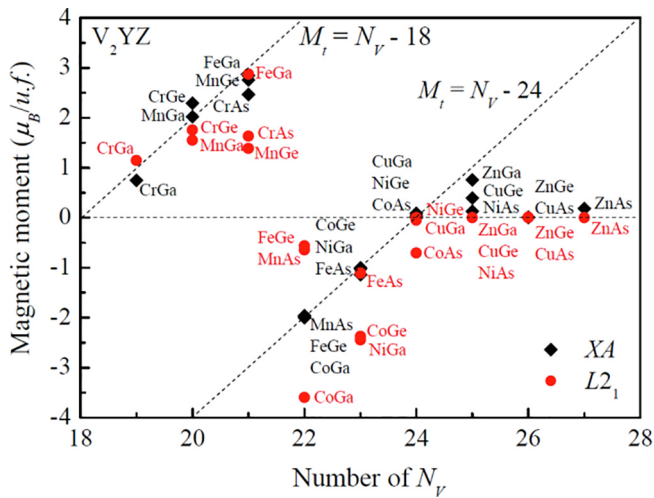


Fig. 3. Total spin magnetic moments (M_t) per unit cell (in μ_B) as a function of the total number of valence electrons (N_V) in the unit cell for V₂-based alloys. The lines represent the two different forms of the Slater-Pauling rule.

Fig. 4(b) shows the spin-polarized band structure of V₂MnGa. The spin-down (red line) channel has a distinct band gap, while the spin-up channel (blue line) exhibits the nature of metal. The band gap is between two states, i.e. t_{2g} and t_{1u} , thus $1 \times s$, $3 \times p$, $2 \times e_g$ and $3 \times t_{2g}$ are filled with 9 valence electrons. In this case, N is 9, and the Slater-Pauling rule is then $M_t = N_V - 18$. This property applies to the alloys with $N_V \leq 21$. Fig. 4(c) shows the spin-polarized band structure of V₂CoGe. The band gap of spin-down channel is however between t_{1u} and e_u . It is filled with 12 valence electrons on $1 \times s$, $3 \times p$, $2 \times e_g$,

$3 \times t_{2g}$ and $3 \times t_{1u}$ orbitals, and no empty orbitals are left below the gap. Then the Slater-Pauling rule comes up to $M_t = N_V - 24$, which applies to alloys with $N_V > 21$. These results indicate that the different origin of the band gap leads to the different form of the Slater-Pauling rule for V₂-based alloys.

Fig. 5 gives the total and atom-resolved DOS for L2₁-type V₂CoAs, V₂CuGe and V₂ZnGe. For V₂CoAs (Fig. 5(a)), Co and V contribute the main part of DOS that near the Fermi level. Whereas, the equivalence of chemical environment between atom V (A) and atom V(C) leads to symmetric distributions of DOS for V (A) and V (C) but with a opposite direction of spin. The DOS of As localized at region that very low in energy and has negligible contribution for the total DOS at Fermi level. In magnetism, the splitting of DOS corresponds to a large localized magnetic moment. The magnetic moment of V (A) would equal to that of V(C), and they are antiparallel and completely compensated to each other. For the existence of Co, it makes the symmetry of magnetic moment broken, and leads to a nonzero magnetic moment. For V₂CuAs (see Fig. 5(b)), V(A) and V(C) still contribute symmetric DOS with opposite direction. Element Cu contribute DOS that mainly ranged from -3 eV to -2 eV, where there is very little DOS of V, indicating that d electrons of Cu hardly hybridize with those of V. Meanwhile, the DOS of atom Cu barely split so that Cu does not carry any spin moment. As a result, the total DOS of V₂CuAs alloy keeps symmetry for spin down and up directions, and the net spin moment of the alloy would be zero. The situation of V₂ZnGe is similar to the electronic structure of V₂CuAs as shown in Fig. 5(c).

Table 1 lists the corresponding M_t for V₂-based Heusler alloys. They are $0.7 \mu_B$, $0 \mu_B$ and $0 \mu_B$ for V₂CoAs, V₂CuGe and V₂ZnGe, respectively. When $Y = Co$, the magnetic moments of atom V (A) and atom V (C) cancel each other, but Co provides a net magnetic moment, element Z carries no magnetic moment. Therefore, V₂CoAs carries a net

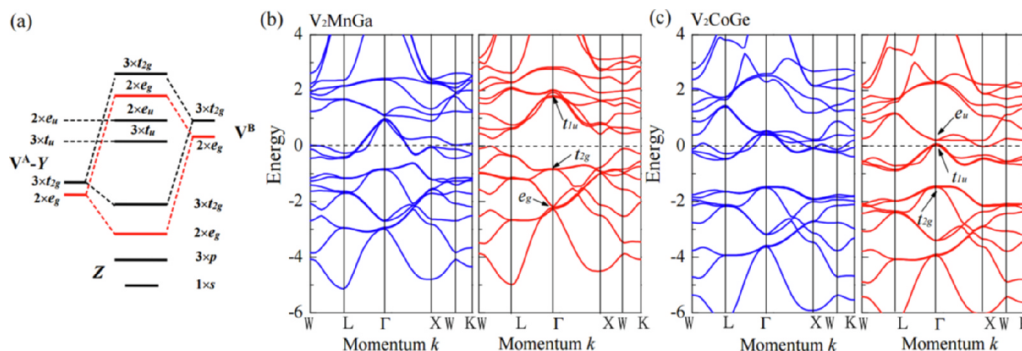


Fig. 4. (a) The sketch of possible d - d hybridizations between the transition-metal elements in the V₂YZ inverse Heusler compounds. Spin-polarized band structures for V₂MnGa (b) and V₂CoGe (c), respectively.

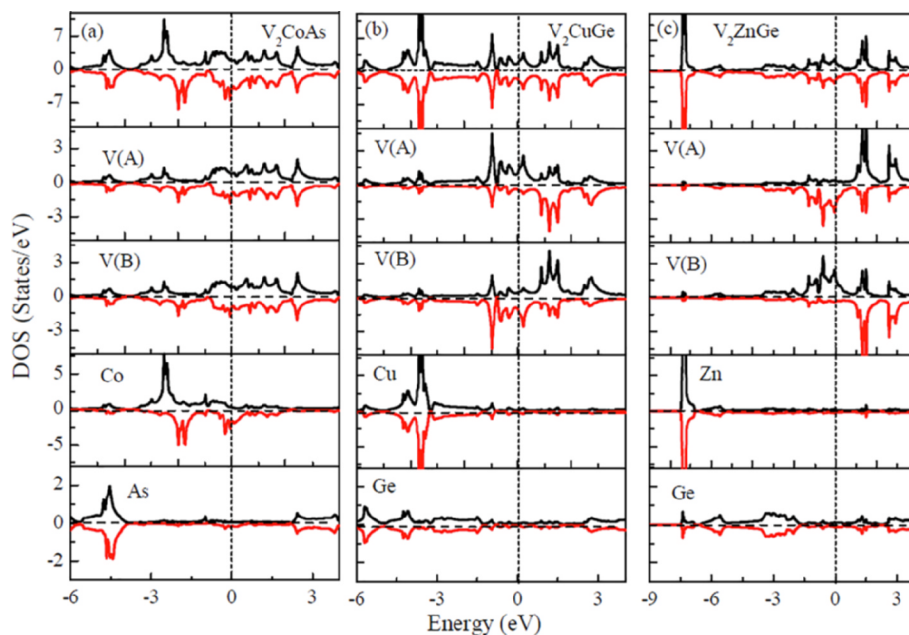


Fig. 5. The total and atoms resolved DOS for L_{21} type (a) V_2CoAs , (b) V_2CuGe , and (c) V_2ZnGe .

Table 1

Number of valence electron (N_V) per unit cell, structure, equilibrium lattice constants, atom-resolved and total spin moments in μ_B of V_2 -based full Heusler alloys. V_1 and V_2 represent V(A) and V(B) for XA structure, V(A) and V(C) for L_{21} structure.

Alloys	N_V	Structure	$a/\text{\AA}$	$M(V_1)$	$M(V_2)$	$M(Y)$	$M(Z)$	M_t
V_2TiGa	17	XA	6.18	1.96	-0.82	-0.59	-0.03	0.52
V_2TiGe	18	XA	6.15	1.79	-0.81	-0.87	0.01	0.10
V_2CrGa	19	XA	6.02	1.73	0.88	-3.24	0.06	0.56
V_2TiAs	19	XA	6.07	0.16	-0.08	-0.15	0.00	0.07
V_2MnGa	20	XA	5.94	1.7	-0.7	1.13	-0.11	2.02
V_2CrGe	20	XA	5.97	1.34	-1.12	2.25	-0.17	2.29
V_2FeGa	21	XA	5.91	2.33	-0.47	1.14	-0.15	2.85
V_2MnGe	21	XA	5.93	2.08	-0.89	1.67	-0.10	2.76
V_2CrAs	21	XA	5.93	1.65	-1.2	2.17	-0.14	2.47
V_2CoGa	22	XA	5.92	2.02	-0.45	0.54	-0.11	2.00
V_2FeGe	22	XA	5.86	1.83	-0.73	0.96	-0.08	1.98
V_2MnAs	22	XA	5.88	1.58	-0.99	1.43	-0.06	1.96
V_2NiGa	23	XA	5.97	1.64	-0.55	0.12	-0.07	1.14
V_2CoGe	23	XA	5.88	1.17	-0.53	0.42	-0.04	1.02
V_2FeAs	23	XA	5.82	0.86	-0.54	0.71	-0.02	1.00
V_2CuGa	24	L_{21}	6.06	2.02	-2.02	0.00	0.00	0.00
V_2NiGe	24	L_{21}	5.97	1.14	-1.14	0.00	0.00	0.00
V_2CoAs	24	L_{21}	5.91	0.21	-0.21	-1.04	-0.09	0.71
V_2ZnGa	25	L_{21}	6.15	2.44	-2.44	0.00	0.00	0.00
V_2CuGe	25	L_{21}	6.02	1.88	-1.88	0.00	0.00	0.00
V_2NiAs	25	L_{21}	5.91	0.00	0.00	0.00	0.00	0.00
V_2ZnGe	26	L_{21}	6.13	2.59	-2.59	0.00	0.00	0.00
V_2CuAs	26	L_{21}	6.02	1.97	-1.97	0.00	0.00	0.00
V_2ZnAs	27	L_{21}	6.15	2.68	-2.68	0.00	0.00	0.00

magnetic moment in total. When $Y = Cu, Zn$, the magnetic moment of V (A) equals to that of V (C) with opposite direction, Y and Z does not carry any magnetic moment, so that M_t of the alloy is zero. In such case, M_t is independent with N_V , and the Slater-Pauling rule is failed.

Fig. 6 gives the DOS of the studied alloys. Since alloys with $N_V > 24$ and L_{21} structure have no spin polarization and are not suitable for half-metallic materials, only the DOS of V_2YZ ($Y = Cr, Mn$ and Fe ; $Z = Ga, Ge$ and As), V_2CoGa , V_2CoGe and V_2NiGa are included. The magnetic moments of the alloys are listed in Table 1. The character of half-metal is that the majority-spin electrons are metallic, whereas the minority-spin electrons are semiconducting. Therefore, V_2MnGa , V_2MnGe , V_2MnAs , V_2FeGa , V_2FeGe , V_2FeAs , V_2CoGa , V_2CoGe and

V_2NiGa are potential half-metallic materials and have high spin-polarizability.

For V_2CrZ ($Z = Ga, Ge$ and As) alloys, there is also an energy gap in one of the spin channel, but the Fermi level is not located in the band gap, so their ground states are not half-metallic. Uniform strain simulated by changing the lattice constant was performed to adjust the location of the Fermi level. Fig. 7 shows the adjusted DOS for V_2CrZ ($Z = Ga, Ge$ and As). It can be seen that the DOS for V_2CrZ ($Z = Ga, Ge$ and As) shows half-metallic properties with expansion by -3.81% , -2.68% and 3.71% , respectively, compared to the equilibrium lattice constant.

4. Conclusion

We performed systematic work on crystal structure, site preference, phase stability, magnetic and electronic properties of half-metallic V_2 -based Heusler alloys via first principles calculations. We found that the atomic occupancy for V_2 -based Heusler alloys depends on N_V of the alloys. Alloys with $N_V < 24$ form XA structure, while the others with $N_V \geq 24$ form L_{21} structure. The relationship between M_t and N_V of XA-type alloys follows Slater-Pauling rule with two different forms, which depends on the origin of the band gap. It is $M_t = N_V - 24$ when the energy gap originates from the forbidden zone between orbit t_{1u} and e_u . Energy gap between orbitals t_{2g} and t_{1u} leads to $M_t = N_V - 18$. The Slater-Pauling rule failed for alloys with L_{21} structure and $N_V > 24$ because of the magnetic symmetry. XA-type V_2YZ ($Y = Cr, Mn$ and Fe ; $Z = Ga, Ge$ and As), V_2CoGa , V_2CoGe and V_2NiGa alloys have half-metallic properties. The formation of L_{21} -type V_2YZ ($Y = Cu$ and Zn ; $Z = Ga, Ge$ and As) alloys is due to the fact that the two V atoms occupy equivalently, and electrons of Y atoms do not participate in the hybridization with d -electrons of V. The distribution of the total DOS is symmetrical and no exchange splitting is produced, thus L_{21} -type alloys have no half-metallic properties. Furthermore, the band structure does not show spin polarization and these alloys have no half-metallic property. Therefore, only the V_2 -based Heusler alloys with $N_V < 24$ and XA structure follow the Slater-Pauling rules, and have half-metallic properties.

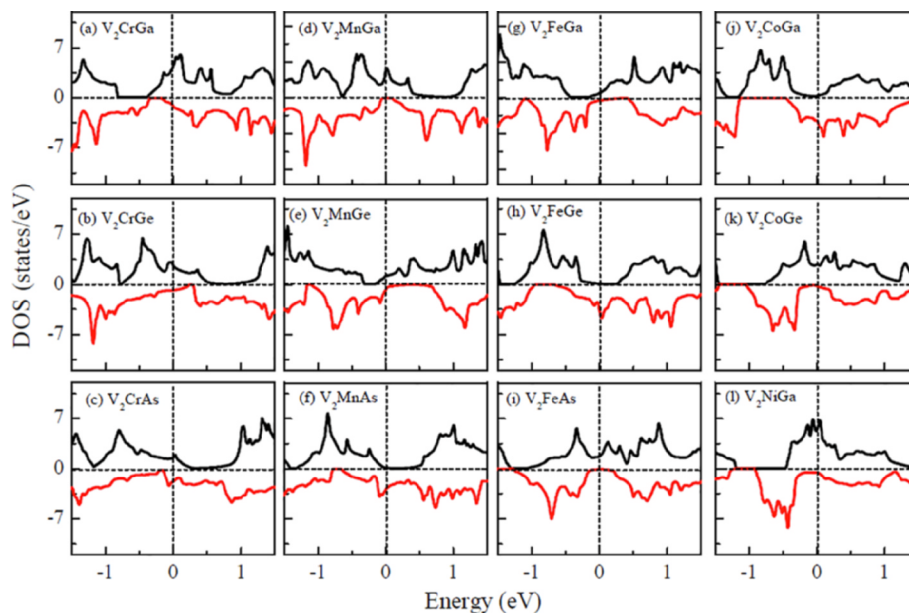


Fig. 6. Spin-polarized DOS of V_2YZ ($Y = \text{Cr, Mn and Fe}$; $Z = \text{Ga, Ge and As}$), $V_2\text{CoGa}$, $V_2\text{CoGe}$ and $V_2\text{NiGa}$ alloys.

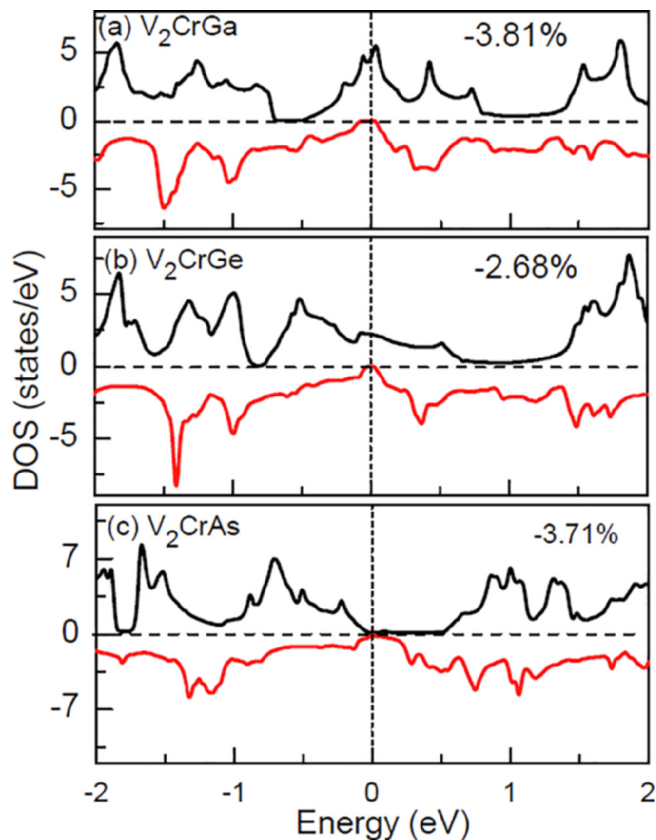


Fig. 7. The adjusted total DOS for $V_2\text{CrZ}$ ($Z = \text{Ga, Ge and As}$) alloys with expansion by -3.81% , -2.68% and 3.71% , respectively, compared to the equilibrium lattice constant. Negative sign means compression.

CRedit authorship contribution statement

Xingzhe Du: Writing - original draft. **Yajiu Zhang:** Methodology, Conceptualization, Writing - review & editing. **Zhuohong Liu:** Writing - review & editing. **Zhigang Wu:** Writing - review & editing. **Shifeng Xu:** Supervision. **Xingqiao Ma:** Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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