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ARTICLE

Band Structure, Half-Metallicity and Magnetic Properties of Cr_2VZ (Z=P, As) Full-Heusler Alloys

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Abstract: Using first-principles calculations based on density functional theory, the band structures, half-metallicity and magnetic properties of Cr_2VZ (Z=P, As) full-Heusler alloys were investigated. The results reveal that Cr_2VZ (Z=P, As) is stable in the ferrimagnetic configuration. The total magnetic moment of Cr_2VAs is determined as $-2\ \mu_B$ per formula unit in the equilibrium state, obeying the Slater-Pauling rule. Cr_2VP alloy is a common magnet in the stable state. The occurrence of energy gap in the minority spin band was analyzed based on the hybridization among the Cr 3d and the V 3d electrons. The half-metallic properties of Cr_2VP and Cr_2VAs alloys can be obtained when the lattice constants change in the range of 0.5700~0.5900 nm and 0.5704~0.6054 nm. The current investigation can offer basic support for the application of Cr_2VZ (Z=P, As).

Key words: first principles; full-Heusler alloy; half-metallicity; Slater-Pauling rule

Recently, half-metallic materials (HMMs) have attracted much attention due to their potential applications for spintronics devices, such as non-volatility of magnetic random access memory, spin valves, giant magnetoresistance [1-3]. According to reports, the known HMMs include magnetic oxides, transition-metal oxides[4], pnictides and chalcogenides containing transition-metals[5], and $La_{0.7}Sr_{0.3}MnO_3$[6], diluted magnetic semiconductors[7], CrAs in the zinc-blende structure[8], half- and full-Heusler alloys[2], and spin gapless semiconductors[9]. Among the HMMs, Heusler alloys seem to be good candidates for their higher Curie temperatures, structural similarity to GaAs and InP, and ease of fabricate.

Now, the ideal half-metal magnets, such as Co_2-based[10], Mn_2-based[11], Ti_2-based[12], and Fe_2-based[13], and even V_2-based Heusler alloys[14] have been predicted theoretically. Also, Li et al theoretically predicted the Cr_2VX[15] and Cr_2TiX[16] alloys as half-metallic ferrimagnets. Singh et al[17] studied the half-metallicity of $Cr_{2-x}Fe_xCoAl$ and $Cr_{2-x}Fe_xCoSi$. Cr_2ZnSi alloy[18] is also thought to be a spin gapless semiconductor. Roy et al[19] reported the electronic and magnetic properties of X_2PtGa (X=Cr, Mn, Fe, Co) full-Heusler alloys.

In this study, we employed first-principles plane-wave pseudo-potential method for the Cr_2VZ (Z=P, As). Band structures, half-metallicity and magnetic properties of the both Heusler alloys were comprehensive investigated.

1 Computation Details

The present calculation was performed by Cambridge serial total energy package (CASTEP) code[20]. The Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA) was adopted. A Monkhorst-Pack grid (12×12×12) with 56 irreducible k-points was used for Brillouin zone. The plane-wave basis of cut-off energy was set as 700 eV. The self- consistency computational accuracy was as follows: the total energy change $<1\times10^{-6}$ eV/atom, maximum displacement $<5.0\times10^{-5}$ nm, maximum force<0.1 eV/nm, and maximum stress tensor <0.02 GPa.

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2 Results and Discussion

According to the report[18], the Cr_2VZ full-Heusler alloys will prefer to the Cu_2MnAl-type structure. That is to say, A (0, 0, 0), called as Cr(A), and C (0.5, 0.5, 0.5), called as Cr(C), sites are occupied by Cr atoms, while V and *Z* atoms occupy B (0.25, 0.25, 0.25) and D (0.75, 0.75, 0.75) sites in Wyckoff coordinates, respectively. The stability of 3 magnetic states, i.e. the paramagnetic (PM), ferromagnetic (FM), and ferrimagnetic (FI) configurations, was studied. Fig.1 represents the calculated total energy as a function of lattice constant in the PM, FM and FI configurations. It should be noted that the FI configuration has the lowest total energy. Besides, the equilibrium lattice constant is determined as 0.570 and 0.585 nm for *Z*=P, As, respectively. The equilibrium lattice constants of the Cr_2VSb[21], Cr_2MnP, and Cr_2MnAs[21] alloys are determined as 0.6073, 0.5590 and 0.5778 nm, respectively (Table 1). Considering that atomic radius (0.137/0.141 nm) of V/Sb atoms is larger than that of Mn/P & As ones (0.132 /0.111 and 0.121 nm), we thought that the lattice constants of Cr_2VZ (*Z*=P, As) are reasonably reliable.

In Fig.2 and Fig.3, we give the energy bands for majority spin and minority spin electrons in the Cr_2VP and Cr_2VAs full-Heusler alloys. From Fig.2a, at the equilibrium lattice constants of 0.570 nm for Cu_2MnAl-type Cr_2VP alloy, the valence bands overlap with conduction ones in majority spin

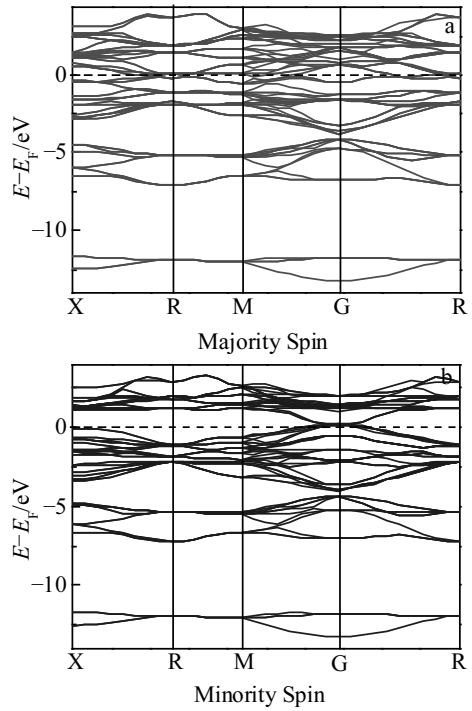

Fig.2 Calculated majority spin (a) and minority spin (b) band structures for Cr_2VP at its equilibrium lattice constants (horizontal dashed line in zero energy represents the Fermi level)

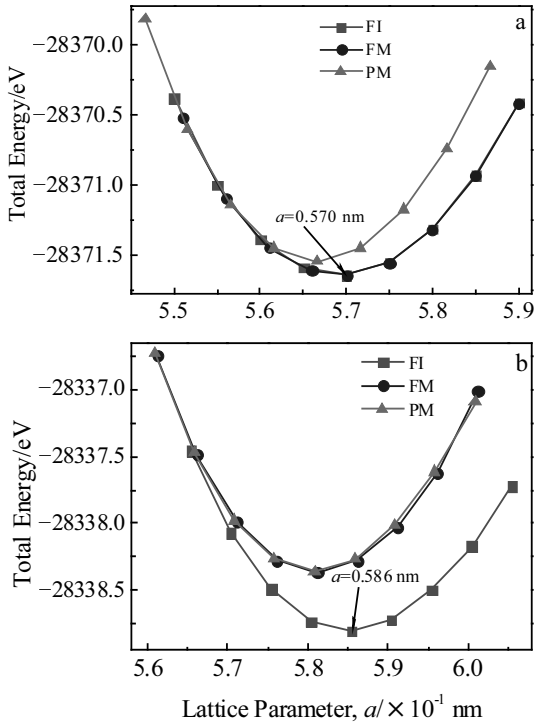

Fig.1 Calculated total energy as a function of lattice constant in the ferrimagnetic (FI), ferromagnetic (FM) and paramagnetic (PM) configurations for Cr_2VP (a) and Cr_2VAs (b)

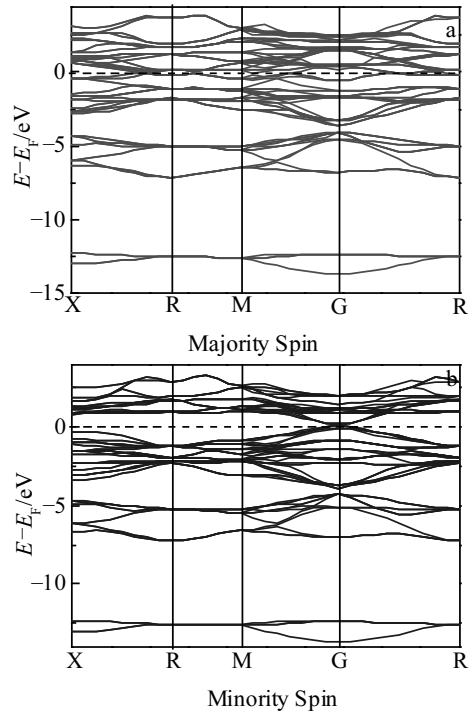

Fig.3 Calculated majority spin (a) and minority spin (b) band structures for Cr_2VAs at its equilibrium lattice constant (the horizontal dashed line in zero energy represents the Fermi level)

Table 1 Calculated equilibrium lattice constant, physical nature, gap width, spin polarization, total and atom magnetic moments of various alloys

Alloy	a_{cal}/nm	Nature	Gap width/eV	Spin polarization ratio/%	$m_{Cr(A)}/\mu_B$	$m_{Cr(C)}/\mu_B$	m_V/μ_B	m_{Mn}/μ_B	m_{sp}/μ_B	m_{tot}/μ_B
Cr_2VP	0.5700	Metal	-	50.3	1.56	1.56	–1.16	-	–0.12	1.84
Cr_2VAs	0.5854	Nearly half-metal	0.088	77.8	1.80	1.80	–1.46	-	–0.14	2.00
Cr_2VSb[21]	0.6073	Half-metal	0.51	100	–2.02	–2.02	1.88	-	0.16	–2.00
Cr_2MnP[21]	0.5590	Metal	-	52.86	–0.494	1.033	-	–0.384	0.016	0.204
Cr_2MnAs[21]	0.5778	Nearly half-metal	0.129	94.61	–1.015	1.722	-	0.779	0.034	0.018

electron direction, and the Fermi level passes through the overlap regions. Therefore, the majority spin band structure exhibits metallic nature. Different from majority spin band, the minority spin bands almost all have an energy gap (Fig.2b), except at G(Γ). That is, the top of valence bands just touch the bottom of conduction bands only at G (Γ), which indicates the metallic nature, as listed in Table 1. The majority spin band of Cr_2VAs, as shown in Fig.3a, is similar to that of Cr_2VP, which also exhibits metal nature. However, for the minority spin band of Cr_2VAs alloy (Fig.3b), a small semiconducting band gap near the Fermi level is observed, with a gap width of 0.088 eV. As is known, the electron spin polarization (P) at the Fermi level (E_F) of a material is defined by:

$$P = \frac{\rho_{\uparrow}(E_F) - \rho_{\downarrow}(E_F)}{\rho_{\uparrow}(E_F) + \rho_{\downarrow}(E_F)} \quad (1)$$

Here, $\rho_{\uparrow}(E_F)$ and $\rho_{\downarrow}(E_F)$ are the spin dependent density of states at E_F; ↑ and ↓ are the majority spin band and minority spin band, respectively. Below the Curie temperatures in common ferromagnetic materials, P often gives a value less than 1. Full spin-polarized behavior of electrons at Fermi level, or say P=100%, appear only when $\rho_{\uparrow}(E_F)$ or $\rho_{\downarrow}(E_F)$ equals zero. In the current work, the P values are determined as 50.3% and 77.8% (as listed in Table 1). The results indicate that Cr_2VP is metal materials while Cr_2Vas is half-metal materials.

In order to check the variation feature of electron structure, we compare the atom-projected partial density of states (PDOS) with the corresponding total density of states (DOS) for Cr_2VP and Cr_2VAs, as shown in Fig.4. For the Cr_2VP and Cr_2VAs full-Heusler alloys, the sharp peak between the energy intervals of −14 and −12 eV arises from P, Cr, and V atoms. In the energy interval of −8 and −4 eV, the two consecutive DOS peaks consist mainly of Cr, V and P atoms, which indicates that the hybridization of p-d electrons occurs. The DOS peaks between energy intervals of −4~0 eV for majority and minority spin bands mainly come from Cr and V atoms, which commonly indicate d-d hybridization. Furthermore, between 0 and 4 eV energy intervals, most DOS arises from Cr and V atoms, together with some contributions from Z (Z=P, As).

Fig.5 shows the PDOS of Cr_2VZ (Z=P, As) at their respective equilibrium sates. The total DOS in the range of −8~−4 eV mainly originates from p electrons of Z (Z=P, As) atoms, along with a few 3d electrons of Cr and V in both bands. These DOS peaks are the bonding peaks originating

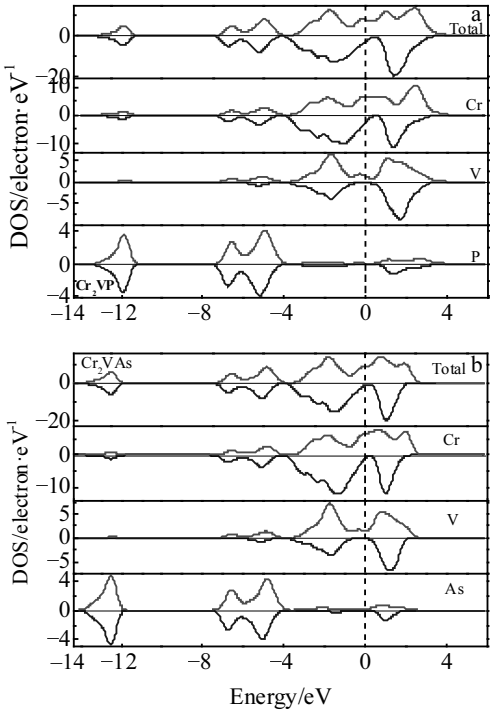

Fig.4 Calculated spin-polarized total and partial DOS for Cr_2VP (a) and Cr_2VAs (b) at their equilibrium sates

from the p-d hybridization between the Cr, V and the Z atoms. At the same time, the p-d hybridization between the Cr, V and Z atoms also generates the anti-bonding peaks, which is in the energy range of 0~2 eV for the majority (minority) spin band above the Fermi level. The peaks between −8 and −4 eV in both side bands become somewhat asymmetry. Such behavior can be well explained in terms of the state hybridization between the 3d electrons of Cr, V and the 2p electrons of Z atoms. Moreover, the DOS between −4 and 4 eV is mainly from Cr(A) 3d, Cr(C) 3d and V 3d electrons. It can also be seen that the Cr and V atoms in the current alloys exhibit spin splitting. For Heusler alloys, the gap is thought to origin from the covalent hybridization between the lower energy d electrons of the higher-valence transition metal atom and the higher-energy d states of the lower-valence transition metal atom. The energy gap in the minority spin band should be due to the hybridization among the Cr 3d and V 3d electrons. A further analysis reveals that the Cr 3d electron splitting is

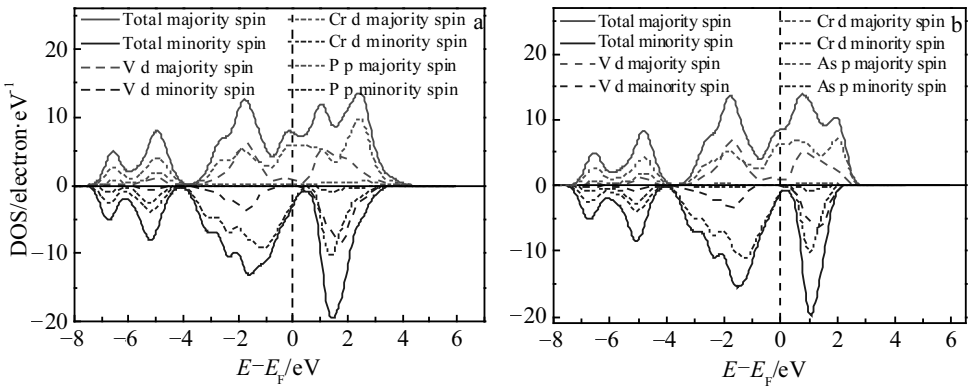

Fig.5 Partial DOS of Cr-d, V-d, and As-p for Cr_2VP (a) and Cr_2VAs (b) at their equilibrium sate

dominant in the occurrence of energy gap, based on the similarity of gap of Cr partial DOS and total DOS.

The total and partial magnetic moments of alloys at their equilibrium states are listed in Table 1. The magnetic moment per formula unit for Cr_2VAs is 2.00 μ_B, while for Cr_2VP, the value is 1.84 μ_B. The integral magnetic moment of a half-metallic full-Heusler alloy follows the general Slater-Pauling rule, that is $M_t = Z_t - 24$. Here, M_t is the total magnetic moment per formula unit and Z_t is the total number of valence electrons. The Cr_2VAs has 22 valence electrons, so the total magnetic moments should be 2.00 μ_B. This reveals the anti-parallel magnetic alignment of Cr(A) or Cr(C) and V or P/As atoms. For the Cr_2VZ, four V atoms and four Z atoms serve as the first neighbors of Cr(A) or Cr(C) atoms. While for V or Sb atoms, they are enclosed by four Cr(A) and four Cr(C) atoms. The anti-parallel arrangement of magnetic moments for Cr(A) or Cr(C) and V indicates that Cr_2VZ becomes a ferrimagnetic magnet. From Table 1, it can be seen that the magnetic moment of Cr atom is the largest in Cr_2VZ (Z=P, As), while that of Sb atom has a negligible effect on the total spin magnetic moments in the current alloys.

3 Conclusions

1) The calculated results of the total energy show that ferri-magnetic configuration is the most stable.

2) The Cr_2VP full-Heusler alloy is a common ferrimagnet, while for Cr_2VAs one, the total magnetic moment is −2 μ_B per formula unit at their stable states.

3) The occurrence of energy gap in the minority spin band is analyzed based on the hybridization between the Cr 3d and the V 3d electrons.

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Cr_2VZ (Z=P, As)全赫斯勒合金的能带结构、半金属性与磁性研究

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摘　要：采用基于密度泛函理论的第一性原理计算方法，研究了 Cr_2VZ (Z = P, As)全赫斯勒合金的能带结构、半金属性及其磁性。结果表明，当 Cr_2VZ (Z = P, As)处于亚铁磁性时，结构处于稳定态。同时确定了 Cr_2VAs 的单位结构的总磁矩为–2 μ_B，计算结果符合 Slater-Pauling 规则。Cr_2VP 在稳定态属于普通铁磁体。采用 Cr 3d 与 V 3d 电子的杂化解释了自旋向下能带出现带隙的原因。当 Cr_2VP 和 Cr_2VAs 合金的晶格常数分别在 0.5700~0.5900 nm 和 0.5704~0.6054 nm 范围内变化时，二者的半金属性能够保持。本研究成果能够为 Cr_2VZ (Z = P, As) 合金的实际应用提供一些帮助。

关键词：第一性原理；全赫斯勒合金；半金属性；Slater-Pauling 规则

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