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Search for new half-metallic ferromagnets in zinc blende CaSi and CaGe by first-principles calculations

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Abstract

We present an investigation on the electronic structure and ferromagnetism for the hypothetical zinc blende (ZB) CaSi and CaGe by using first-principles full-potential linearized augmented plane-wave (FP-LAPW) calculations. It is found that ZB CaSi and CaGe are half-metallic (HM) ferromagnets without any transition-metal component; they have a magnetic moment of $2.000 \mu_B$ per formula unit. Analysis of the density of states and magnetic moment indicates that their magnetism mainly originates from the spin polarization of anion p states and the hybridization between the anion p states and the Ca d states. We also find that the half-metallicity can be maintained even when the lattice constant of ZB CaSi and CaGe is compressed up to 8% and 5%, respectively. The absence of the transition-metal atoms makes ZB CaSi and CaGe attractive not only as materials for possible spintronics devices but also as model objects for the study of new mechanisms of the formation of half-metallic ferromagnetism in s-p electron systems.

1. Introduction

Half-metallic (HM) ferromagnets, where one spin direction behaves like a metal and the other is semiconducting, resulting in 100% spin polarization, are attracting more and more attention and they are believed to be promising as ideal components of spintronics devices [1]. Since the first theoretical prediction of HM ferromagnets in half-Heusler compounds of NiMnSb and PtMnSb by de Groot and collaborators [2] in 1983, more HM ferromagnets have been predicted theoretically or confirmed experimentally. So far, in addition to the half-Heusler compounds, HM ferromagnets also exist in full-Heusler compounds such as Co₂MnSi and Co₂MnGe [3], in metallic oxides such as CrO₂ [4] and Fe₃O₄ [5], in perovskite compounds such

as $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [6] and $\text{Sr}_2\text{FeMoO}_6$ [7], and in diluted magnetic semiconductors (DMSs) such as Mn-doped GaN [8] and Mn-doped Ge [9]. Many works have been undertaken to develop new HM ferromagnets, especially the remarkable one by Akinaga *et al* [10]: his group first predicted CrAs in the zinc blende (ZB) structure to be a half-metal, then they grew it in thin films and found that it has a high Curie temperature (>480 K). This work motivated intensive studies on the transition-metal chalcogenides and pnictides [11–16]. Most of them are found to be HM ferromagnets: the majority spin (spin-up) electrons are metallic, and there is an energy gap around the Fermi level in the bands for the minority spin (spin-down) electrons. In experiments, ZB CrSb and MnAs films or multilayers have been grown successfully by means of molecular-beam epitaxy [17, 18], although their stablest phase is the NiAs structure not the ZB structure [14, 15]. Moreover, ZB Mn–IV compounds such as MnC [19], MnSi and MnGe [20] near their equilibrium lattice constants are also found to be HM ferromagnets, and interestingly, MnC shows opposite behaviour: the minority electrons are metallic and an energy gap opens in the majority spin bands.

The HM ferromagnets of ZB transition-metals chalcogenides and pnictides mentioned above, as well as Mn–IV compounds, are all based on transition metals, and their half-metallicities originate from the ZB symmetry induced p–d hybridization and the bonding–antibonding splitting that have been reported by [11, 14, 16]. However, remarkably, HM ferromagnets excluding transition metals were first reported in 2004 by Geshi and co-workers [21]. They predicted that ZB Ca pnictides (i.e. CaP, CaAs and CaSb) are HM ferromagnets. These compounds do not contain transition-metal atoms and therefore the mechanism of ferromagnetism is different from both the double exchange and the p–d exchange that are important in magnetic 3d compounds. Here the crucial role is played by the spin polarization of the p states of the pnictides. Then Kusakabe *et al* [22] investigated the band structure of ZB CaAs using a first-principles calculation and found the band is curiously flat. The hybridization of the p states of As with the d states of Ca is shown to be essential for the formation of a flat band made of localized orbitals. They also discussed the connection from the first-principles result to a solvable Hubbard model with a flat band. To confirm the stability of ferromagnetism against lattice distortion of ZB CaAs, in 2005, Geshi *et al* [23] studied the tetragonally distorted structures and found two minimal energy structures. Ferromagnetism remains in a minimal structure. They also provided a possible fabrication of this structure on an InSb substrate. Motivated by these studies, several research groups [24–26] investigated the other ZB II–V compounds. Sieberer *et al* [24] systemically studied the II–V compounds excluding Bi, and found that MgN and MY (M = Ca, Sr, and Ba; Y = N, P, As and Sb) are all HM ferromagnets. Meanwhile, they mentioned that HM ferromagnetism also exists in the ZB I–V compounds. More importantly, they estimated the Curie temperature of ZB CaAs within the mean-field approximation (MFA). The predicted Curie temperature of 680 K considerably exceeds room temperature, which makes ZB CaAs a possible candidate for practical spintronics applications. Later, Yao *et al* [25] investigated the ZB II–Bi compounds with first-principles calculations and it was shown that CaBi, SrBi and BaBi are all HM ferromagnets. The origin and the stability of HM ferromagnetism were also discussed. In [26], Volnianska *et al* extended the analysis of ZB structure of Ca pnictides to the NiAs structure. They found that in the NiAs structure only CaN is ferromagnetic, and it is also a half-metal. Very recently, Geshi *et al* [27] systemically investigated CaN and SrN again. Their first-principles calculations indicated that for both CaN and SrN the rock salt (NaCl) phase is the most stable among all the four possible phases (ZB, CsCl, wurtzite and NaCl), and that the four phases for CaN and SrN are all HM ferromagnets. They further confirmed the structural stability of CaN having the NaCl structure by performing first-principles molecular dynamics simulations, and they also proposed a synthesis process for CaN with NaCl structure based on first principles.

In a word, the previous studies on binary HM ferromagnets excluding transition metals were all focused on the II–V compounds. These works motivated us to search for new HM ferromagnets that do not contain transition metals. One naturally asks if the ZB II–IV compounds are also HM ferromagnets. In fact, the II–IV compounds MX ($M = \text{Ca, Sr}$ and Ba ; $X = \text{Si, Ge}$ and Sn) have been previously prepared in experiments, but they belong to the CrB-type structure [28]. The reversible hydriding and dehydriding properties of CaSi have suggested potential applications of metal silicides for hydrogen storage [29, 30]. To the best of our knowledge, there are no experimental and theoretical studies on the other possible phases of CaSi and CaGe. Therefore, in this paper we investigate the electronic structure and the ferromagnetism for CaSi and CaGe in the hypothetical ZB structure theoretically, using the first-principles full-potential linearized augmented plane-wave (FP-LAPW) method. It is shown that both ZB CaSi and CaGe are HM ferromagnets without any transition-metal component, with a magnetic moment of $2.0000 \mu_B$ per formula unit. The magnetism mainly originates from the spin polarization of anion p states and the hybridization between the anion p states and the Ca d states, and the half-metallicity can be maintained even when the lattice constant of ZB CaSi and CaGe is compressed up to 8% and 5%, respectively.

2. Computational method

The first-principles FP-LAPW method implemented in the Wien2k package [31], which has no shape approximation in the charge, potential and wavefunction expansions, was used to perform the geometry optimization and the electronic structure calculations for ZB CaSi and CaGe. We adopted the generalized gradient approximation in the scheme of Perdew–Bueke–Ernzerhof (GGA–PBE) [32] for the exchange–correlation functional. The radii R_{mt} of the muffin tins were chosen to be approximately proportional to the corresponding ionic radii and as large as possible, but not overlapped. We took $R_{\text{mt}}K_{\text{max}}$ as 8.0 and made the expansion up to $l = 10$ in the muffin tins. For the Brillouin zone integration, we used 3000 k -points in the first Brillouin zone. The self-consistency calculations were considered to be converged only when the energy difference between input and output energy was less than 10^{-5} Ryd per formula unit.

3. Results and discussion

First, in order to determine the equilibrium lattice constants of the hypothetical ZB CaSi and CaGe, we calculated the total energy as a function of the volume for the paramagnetic and ferromagnetic configurations of ZB CaSi and CaGe. Figure 1 shows the calculated results. We find, for both ZB CaSi and CaGe, that the ferromagnetic state is more favourable in energy than the corresponding paramagnetic state. The predicted equilibrium lattice constants in the ferromagnetic state of ZB CaSi and CaGe are 6.84 and 6.88 Å, respectively.

Then, the spin-polarized total and main partial density of states (DOS) of ZB CaSi at its equilibrium lattice constant of 6.84 Å are presented in figure 2. We do not give the partial DOS of Ca s and p states and Si s states, because their values are very small in the energy range from -2 to 6 eV. From figure 2(a) we can see, similar to ZB MnC [19] and ZB CaAs [21–24] but in contrast to ZB transition-metals chalcogenides and pnictides [11–16], that the minority spin electrons are metallic and there is an energy gap of about 1.88 eV around the Fermi level for the majority spin bands. Therefore, ZB CaSi behaves like a half-metal. We note that the top of the majority spin valence bands is located at about -0.13 eV and the bottom of the majority spin conduction bands at about 1.75 eV, so the gap for creating a majority spin hole at the top of the majority spin valence bands by exciting a majority spin electron into the conducting majority spin bands is 0.13 eV, and the gap for a majority spin electron at the bottom of the majority spin

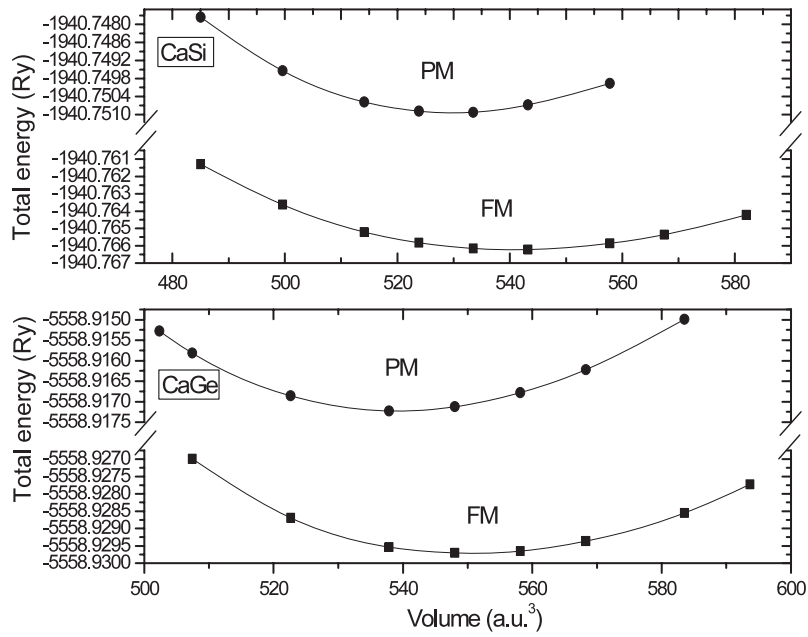


Figure 1. Total energy as a function of volume per formula unit for the ferromagnetic (FM) and paramagnetic (PM) configurations of ZB CaSi and CaGe.

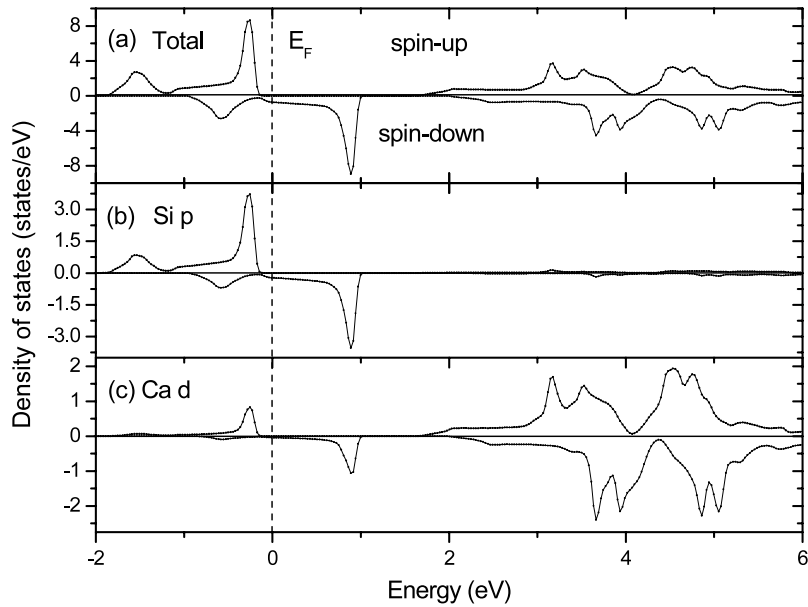


Figure 2. The spin-polarized total and main partial DOS of ZB CaSi at its predicted equilibrium lattice constant.

conduction bands is 1.75 eV. Therefore, the minimal energy gap for a spin excitation, or the HM gap [12–14], is 0.13 eV, the smaller one of the two gaps. Moreover, from figure 2 we can

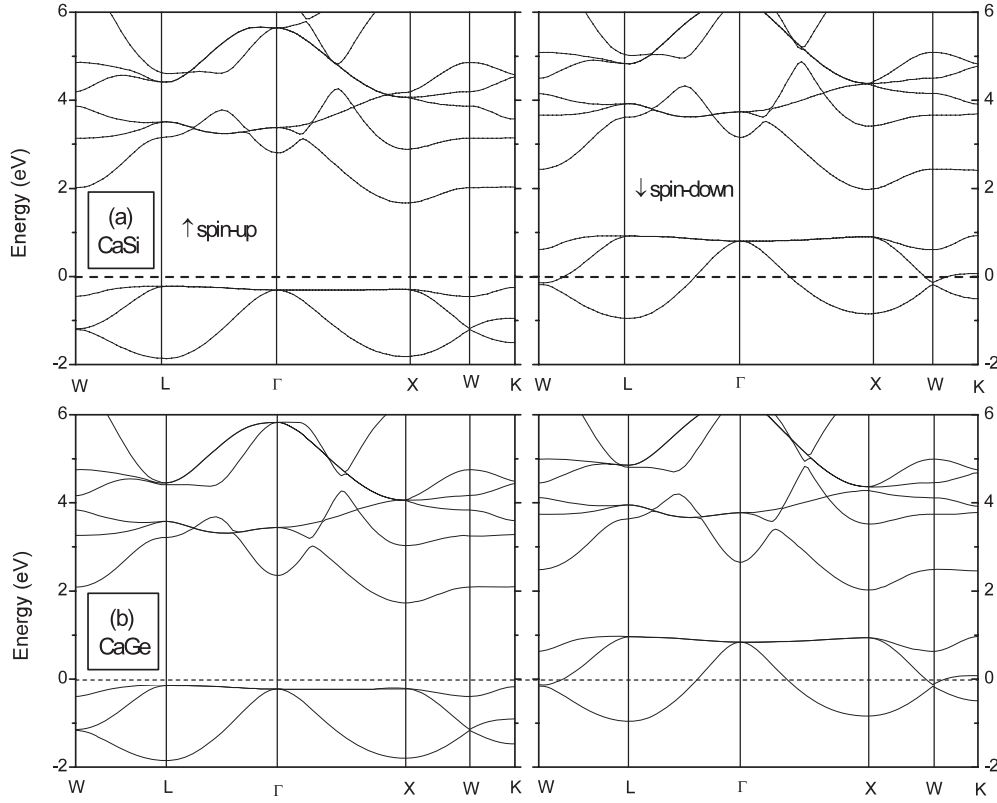


Figure 3. Spin-polarized band structure of ZB CaSi and CaGe at their equilibrium lattice constant. The horizontal dashed line indicates the Fermi level at 0 eV.

see that the total DOS around the Fermi level is mainly composed by the Si p states and the Ca d states. There is a large exchange splitting around the Fermi level between the majority and minority spin bands for the Si p states, and the Si p states are hybridized with the Ca d states. The spin polarization of Si p states and the remarkable hybridization between the Si p states and the Ca d states provide the magnetism in ZB CaSi. This is consistent with our calculated magnetic moments: the Ca atom, the Si atom and the interstitial area are 0.196, 0.879 and 0.925 μ_B , respectively, i.e., the atomic spin magnetic moments mainly originate from the Si atom. The large moment in the interstitial region is yielded mainly by p states of Si hybridized with d states of Ca, because most of the d states are in the muffin-tin spheres of Ca atoms. It should be noted that magnetic moment induced mainly by the spin splitting of anion p states in organic magnets has also been found in our previous work [33]. Also, the calculated total magnetic moment in ZB CaSi, 2.000 μ_B per formula unit, is just a typical character of HM ferromagnets.

In order to further investigate the electronic structure of ZB CaSi, we give the corresponding spin-polarized band structure at the equilibrium lattice constant, which is shown in figure 3(a). It also indicates the HM character of ZB CaSi. From figures 3(a) and 2, we find, for both majority and minority spin bands, that the three lowest bands mainly originate from the hybridized Si p states and Ca d states. The three lowest majority spin bands are fully filled while the minority spin ones are partly filled because of the interaction between the Si p states and the Ca d states. This can be explained from the electronic arrangements: in ZB

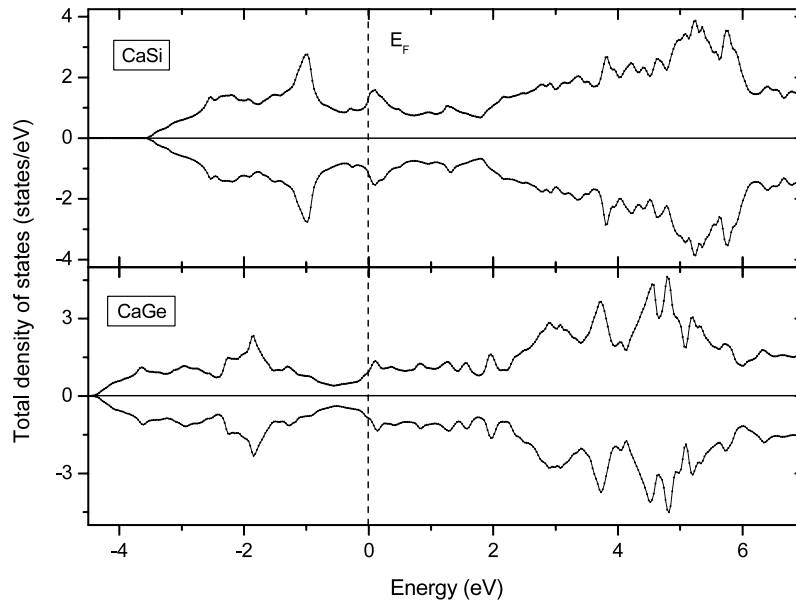


Figure 4. The spin-polarized total DOS of CaSi and CaGe in the CrB-type structure.

CaSi, six valence electrons (Ca:4s²; Si:3s²3p²) contribute to bond formation and magnetism; two of them occupy the Si s states in the lowest energy (about -7 eV, not shown in figure 2). Three of the remaining four valence electrons, including about 2.48 Si p electrons and 0.52 Ca d electrons, occupy the majority spin p states of Si and d states of Ca, respectively, which results in the three majority spin fully filled bands. Meanwhile, about 0.62 Si p electrons and 0.06 Ca d electrons partly occupy the three lowest minority spin bands. Therefore, the three minority spin bands are partly filled, which provides the main magnetic moment. Moreover, because of the tetrahedral coordinated environment in the ZB structure, these bands around 3.5 and 5.0 eV for both majority and minority spin channels are mainly formed by the Ca e_g states and t_{2g} states, respectively.

In figure 3(b), we give the spin-polarized band structure of ZB CaGe at its equilibrium lattice constant of 6.88 Å. It shows that ZB CaGe is also a HM ferromagnet although its HM gap (0.05 eV) is smaller than that of ZB CaSi (0.13 eV). We do not discuss the electronic structure and the magnetism of ZB CaGe here because of the close similarity between ZB CaSi and CaGe.

In the introduction of this paper, we mentioned that ZB CrAs and CrSb have been realized only in the form of thin films through epitaxial growth, because their ZB phases are theoretically 0.9 and 1 eV unstable with respect to their ground-state NiAs phases [10, 14]. CaSi and CaGe have been previously prepared in experiments [28]. But they belong to the CrB-type structure. So it is important to study the structural stabilities of CaSi and CaGe for the possible experimental synthesis of ZB CaSi and CaGe films. We further performed the total energy and electronic structure calculations for CaSi and CaGe in the experimental CrB phase [28]. The calculated total DOS is presented in figure 4. It is shown that both CaSi and CaGe in the CrB-type structure are non-magnetic and metallic. The calculated total energies indicate that the ZB phases of CaSi and CaGe, respectively, are about 1.74 and 2.11 eV unstable with respect to their CrB phases, which confirms the fact that CaSi and CaGe previously prepared in experiment have the CrB-type structure [28]. Compared with the values of 0.9 and 1 eV

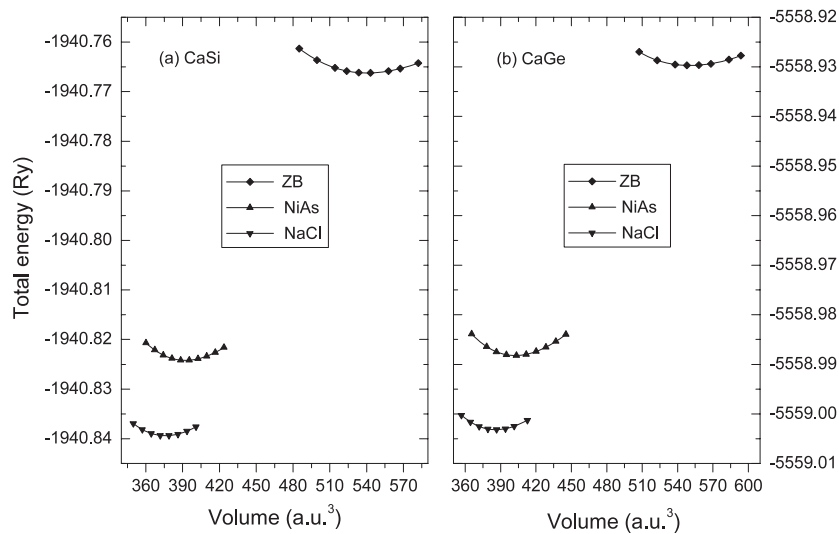


Figure 5. Total energy as a function of volume per formula unit in the ZB, NiAs and NaCl phases for both CaSi and CaGe in the ferromagnetic state.

for CrAs and CrSb, respectively, the total energy differences of 1.74 and 2.11 eV for CaSi and CaGe are large, and thus it may be difficult to grow ZB CaSi and CaGe films or multilayers. Therefore, we in the following investigate the other possible structures of CaSi and CaGe to examine if there is HM ferromagnetism in more stable structures.

Figure 5 gives the calculated total energy as a function of volume per formula unit in the ZB, NiAs and NaCl phases for both CaSi and CaGe in the ferromagnetic state. It is clear, for both CaSi and CaGe, that the NaCl phase is more stable in energy than the NiAs and ZB phases. The optimized equilibrium volumes of NiAs and NaCl phases for CaSi (CaGe) per formula unit are about 392 (402) and 376 (386) au^3 , respectively. And the calculated differences in total energy between the ZB and the NaCl phases for CaSi and CaGe per formula unit are about 0.99 and 1.00 eV, respectively. However, unfortunately, our band structure and magnetic moment calculations indicate that both CaSi and CaGe in the equilibrium NiAs and NaCl phases do not have HM character. Therefore, for CaSi and CaGe, HM ferromagnetism only exists in the ZB structure.

The large total energy differences between the ZB phase and the ground-state CrB phase, 1.74 and 2.11 eV for CaSi and CaGe, make it difficult for the possible film growth of ZB CaSi and CaGe. But it is still interesting that half-metallicity only exists in the ZB phase among the four phases (CrB, ZB, NiAs and NaCl) for CaSi and CaGe, and the absence of the transition-metal atoms makes ZB CaSi and CaGe attractive not only as materials for possible spintronics devices but also as model objects for the study of new mechanisms of the formation of half-metallic ferromagnetism in s-p electron systems.

Finally, we examine the sensitivity of the HM state to small changes in lattice constant of CaSi and CaGe, because the distortion of the lattice at the interface between the film and the substrate can often occur when materials are grown to be epitaxial films or heterostructures. Figure 6 shows the calculated total DOS of ZB CaSi and CaGe when we compress the lattice constants by 8% and 5%, respectively, with respect to the predicted equilibrium ones. From figure 6 we can see that ZB CaSi and CaGe maintain half-metallicity. Meanwhile, the calculated total magnetic moments per formula unit for ZB CaSi and CaGe with the lattice constant

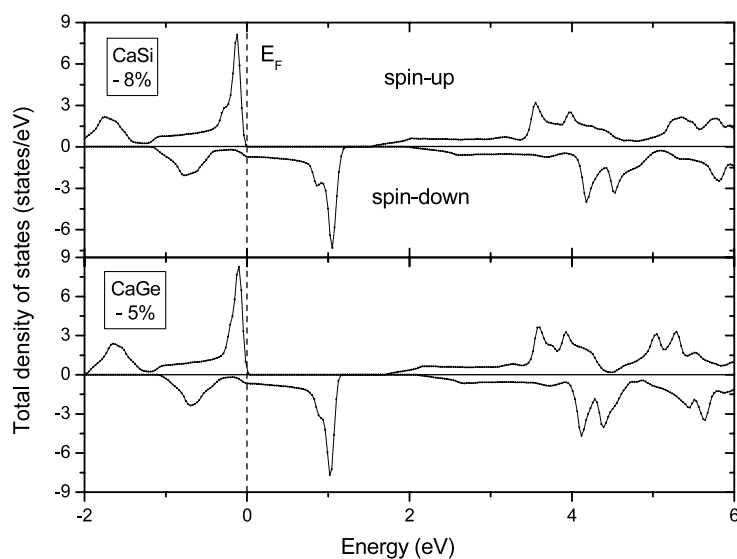


Figure 6. The spin-polarized total DOS of ZB CaSi and CaGe when their lattice constants are compressed by 8% and 5%, respectively, with respect to their equilibrium ones.

contracted by 8% and 5%, respectively, are both $2.0000 \mu_B$, integer multiples of the Bohr magneton. Therefore, ZB CaSi and CaGe are still HM ferromagnets even when their lattice constants are compressed up to 8% and 5%, respectively. Their HM ferromagnetism may be useful in spintronics devices if thin films or multilayers of them can be grown epitaxially on appropriate substrates.

4. Summary

In summary, using the first-principles FP-LAPW method within GGA-PBE for the exchange-correlation functional, we have investigated the electronic structure and ferromagnetism for the hypothetical ZB CaSi and CaGe. Our calculated results show that they are both HM ferromagnets with a magnetic moment of $2.000 \mu_B$ per formula unit, and that the ferromagnetism mainly originates from the spin polarization of anion p states and the hybridization between the anion p states and the Ca d states. We also find that the half-metallicity can be maintained even when the lattice constant of ZB CaSi and CaGe is compressed up to 8% and 5%, respectively. The HM ferromagnetism of CaSi and CaGe may be useful in spintronics devices if thin films or multilayers of them can be grown epitaxially on appropriate substrates, and the absence of the transition-metal atoms makes ZB CaSi and CaGe attractive not only as materials for possible spintronics devices but also as model objects for the study of new mechanisms of the formation of half-metallic ferromagnetism in s-p electron systems.

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