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# Half-metallic ferromagnetism in the half-Heusler compounds GeKCa and SnKCa from first-principles calculations

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ABSTRACT

The structural, electronic and magnetic properties of the compounds GeKCa and SnKCa with half-Heusler structure excluding transition metals are investigated by using the first-principles pseudopotential plane wave method based on density functional theory. From the calculated total energies of three possible atomic arrangements we obtain the most stable structure for GeKCa and SnKCa where Ge (Sn), K and Ca occupy the (0, 0, 0), (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) positions, respectively. It is shown that both GeKCa and SnKCa with the most stable atomic arrangement exhibit half-metallicity with large half-metallic gaps (0.28 and 0.27 eV, respectively) and with an integer magnetic moment of 1.00 $\mu_B$ per formula unit. The magnetic moment mainly originates from Ge (Sn) p electrons, and the ferromagnetic state is more favourable in energy than the antiferromagnetic state for both compounds. We also find that the half-metallicity can be maintained up to the lattice contraction of 10% and 13% for GeKCa and SnKCa, respectively.

## 1. Introduction

A highly spin-polarized current injection into semiconductors is required for the realization of spintronic devices such as the spin valve, the spin current diode, and the spin filter, and so on. Half-metallic (HM) ferromagnets are seen as the most promising candidates of spin-injector materials, because their electronic structure is metallic in only one of the two spin channels, which results in complete (100%) spin polarization at the Fermi level. Since de Groot et al. [1] firstly predicted in 1983 the HM ferromagnet of NiMnSb (a half-Heusler alloy with $C1_b$ structure), more and more HM ferromagnets have been predicted theoretically or confirmed experimentally in some classes of compounds such as the half-Heusler alloys, the full-Heusler alloys, the perovskites, the chromium dioxide, the magnetite, and the zinc-blende (ZB) and wurtzite transition-metal pnictides and chalcogenides (see the recent reviews on HM-FMs in Refs. [2–4] and references therein).

HM ferromagnets with half-Heusler and full-Heusler structures have attracted considerable research interest because of their high Curie temperatures and structural similarity to conventional semiconductors with zinc-blende structure (see the following structural description in Section 3), e.g., the full-Heusler compounds $Co_2MX$ (M = Mn, Fe and Cr; X = Si, Ge and Sn) with $L2_1$ structure have been found to be HM ferromagnets by some theoretical and experimental research groups [5–9]. The measured Curie temperatures are 985 K for $Co_2MnSi$, 905 K for $Co_2MnGe$ [10] and 1100 K for $Co_2FeSi$ [9]. Based on the mean field approximation or the random phase approximation, the estimated Curie temperatures of most of the $Co_2MZ$ compounds considerably exceed the room temperature [11,12]. For half-Heusler compounds, CoMnX (X = P, As and Sb) [13–15], FeCrSb, FeMnSb [14], NiCrZ (Z = P, Se and Te) and NiVAs [16–18] have also been predicted to be HM ferromagnets. Theoretically, the above-room-temperature ferromagnetism in NiCrZ and NiVAs were predicted by Şaşıoğlu et al. [18].

Unlike the HM full-Heusler alloys, however, few HM half-Heusler ones have been synthesized experimentally. Therefore, it is important to search for new HM ferromagnets with half-Heusler structure on the one hand, and on the other hand, the HM ferromagnets mentioned above all contain transition metals which provide the main magnetic moments. Recently, HM ferromagnets excluding transition metals have been predicted theoretically, e.g., the graphene nanoribbon [19] and the alkaline-earth carbides and nitrides with zinc-blende and rocksalt structures [20–24], and some of them have been confirmed experimentally [25]. For these HM ferromagnets excluding transition metals, the C or N p electrons provide the main magnetic moments, and they are usually called sp or $d^0$ half-metals [20–24].

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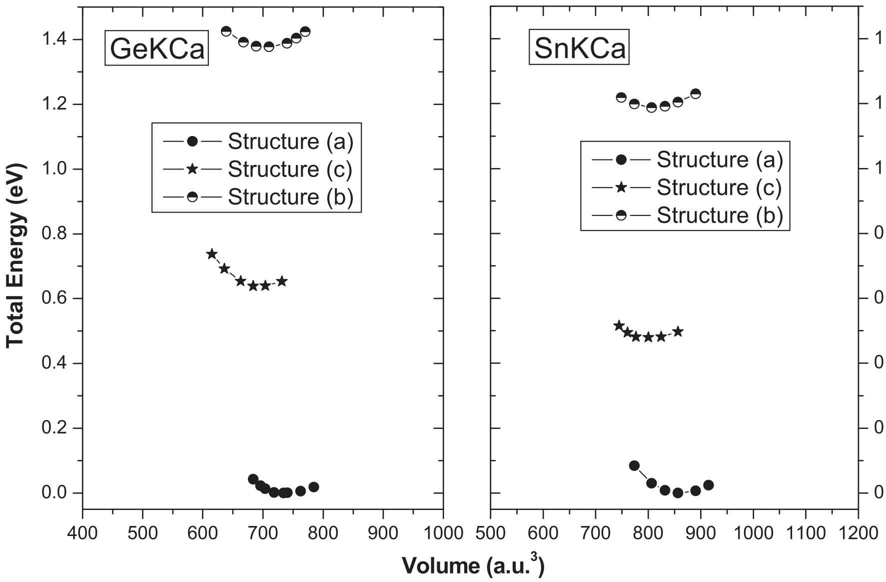

**Fig. 1.** The calculated ferromagnetic total energy as a function of volume per formula unit for the three possible atomic arrangements of both GeKCa and SnKCa with half-Heusler structure. Note that the total energies are the relative values to the most stable structure (a).

To the best of our knowledge, there have been no reports on HM ferromagnets with half-Heusler structure excluding transition metals. In this paper, we use the first-principles calculations to investigate the structural, electronic and magnetic properties for the compounds GeKCa and SnKCa with half-Heusler structure. It is found that both GeKCa and SnKCa with the most stable atomic arrangement show HM ferromagnetism with large HM gaps (0.28 and 0.27 eV, respectively) and with an integer magnetic moment of

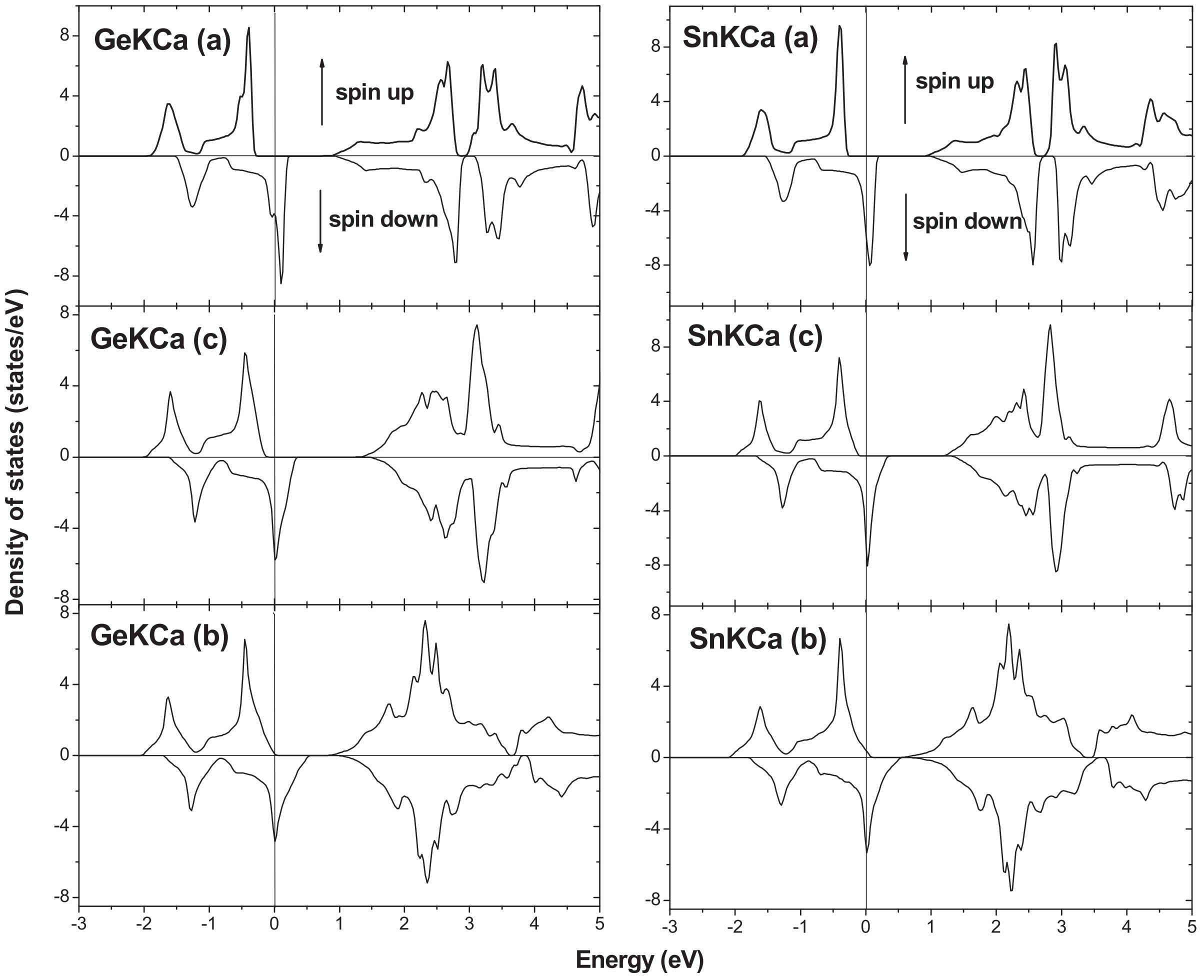

**Fig. 2.** The spin-projected total density of states of the three possible atomic arrangements (a), (b) and (c) for both GeKCa and SnKCa.

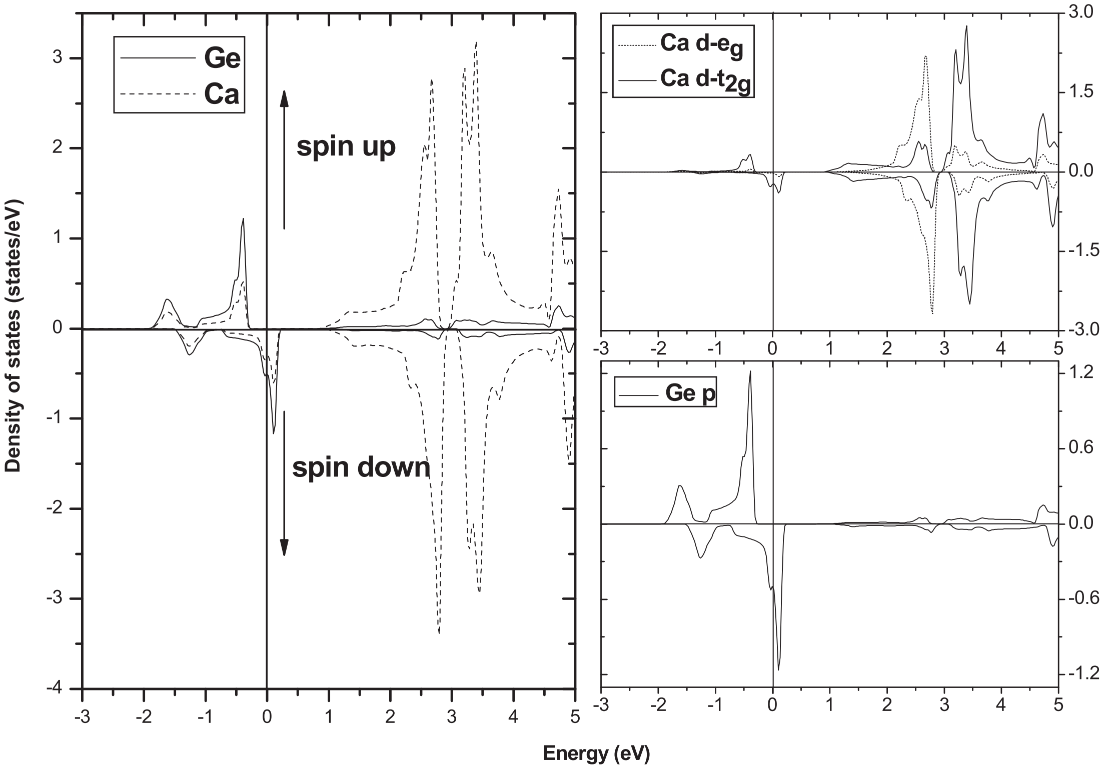

**Fig. 3.** The spin-projected partial density of states for GeKCa with structure (a).

$1.00\ \mu_B$ per formula unit, and the atomic magnetic moment mainly originates from Ge (Sn) p electrons. We also find that the half-metallicity can be maintained up to the lattice contraction of 10% and 13% for GeKCa and SnKCa, respectively.

## 2. Computational method

The geometry optimization and electronic structure calculations are performed by using the first-principles pseudopotential plane wave method, as implemented in the CASTEP package [26]. This is based on the density functional theory in describing the electron–electron interaction and a pseudopotential description of the electron–core interaction. The interactions of the electrons with the ion cores are represented by the Vanderbilt-type ultrasoft pseudopotentials for Ca, K, Ge and Sn atoms. The plane-wave basis set cutoff is set as 500 eV, which is sufficient to lead to a good convergence. The summation over the Brillouin zone is carried out with a k-point sampling using a Monkhorst-pack grid with parameters of $12 \times 12 \times 12$. We adopt the generalized gradient approximation (GGA) in the scheme of Perdew–Bueke–Ernzerhof (PBE) [27] for the exchange–correlation functional.

## 3. Results and discussion

The $L2_1$ structure of full-Heusler $X_2YZ$ compounds can be regarded as four interpenetrating fcc (face-centered cubic) sublattices, and the X atoms are located at A (0, 0, 0) and C (1/2, 1/2, 1/2), the Y atom is located at B (1/4, 1/4, 1/4) and Z atom occupies D (3/4, 3/4, 3/4) in the Wyckoff coordinates [5]. The $L2_1$ structure becomes the $C1_b$-type structure of half-Heusler XYZ compounds when the X position (0.5, 0.5, 0.5) is vacant, and the appropriate description for the $C1_b$ structure is a zinc-blende XZ lattice stuffed

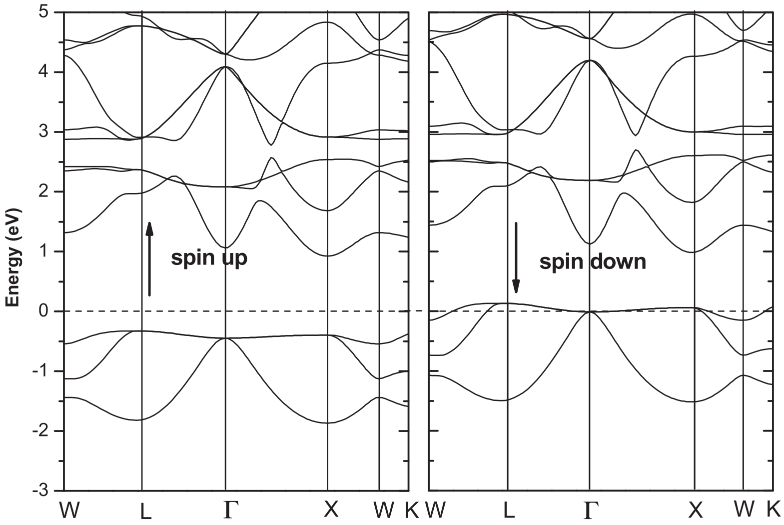

**Fig. 4.** Spin-polarized band structure of GeKCa with structure (a) at its predicted equilibrium lattice constant.

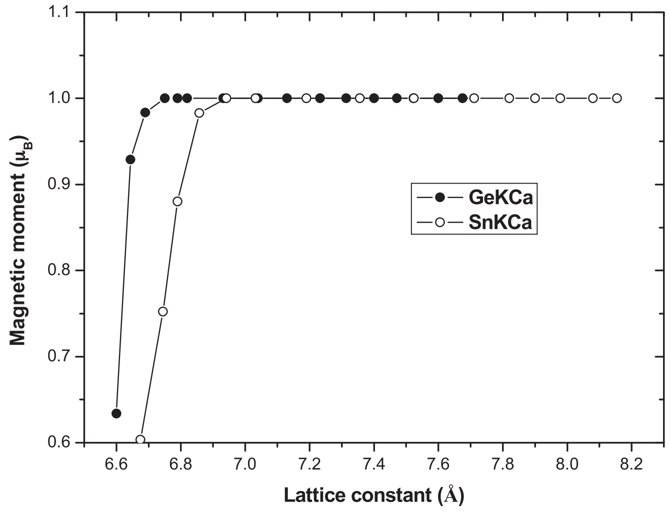

**Fig. 5.** Total magnetic moment per formula unit as a function of lattice constant for GeKCa and SnKCa with the most stable atomic arrangement.

with Y atoms in an ordered way. Meanwhile, there are three possible types of atomic arrangement in the $C1_b$ structure of half-Heusler compounds [28]: (a) X (0, 0, 0), Y (1/4, 1/4, 1/4), Z (3/4, 3/4, 3/4); (b) X (1/4, 1/4, 1/4), Y (0, 0, 0), Z (3/4, 3/4, 3/4) and (c) X (0, 0, 0), Y (1/2, 1/2, 1/2), Z (3/4, 3/4, 3/4). The investigation for the three possible atomic arrangements is very necessary, because in some experiments, it was shown that the structure of half-Heusler compounds depends greatly on the partial disorder [28–30].

First, we perform the calculations of total energy as a function of the volume per formula unit for the ferromagnetic state of the three possible atomic arrangements for both GeKCa and SnKCa (Fig. 1). It is found that both GeKCa and SnKCa with structure (a), where Ge (Sn), K and Ca occupy the (0, 0, 0), (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) positions, respectively, have the lowest total energy, and thus this atomic arrangement is most stable. The calculated equilibrium lattice parameters with the most stable atomic arrangement are 7.58 and 7.99 Å for CaKGe and SnKCa, respectively.

We further calculate the electronic structure and the magnetic moment for the half-Heusler compounds GeKCa and SnKCa with three possible atomic arrangements. Fig. 2 presents the spin-polarized total density of states (DOS) of GeKCa and SnKCa at their respective equilibrium lattice constants. One can see that for both GeKCa and SnKCa with all the three atomic arrangements except SnKCa with structure (b), there is an energy gap around the Fermi level in the majority-spin (spin-up) channel while the minority-spin (spin-down) channel is strongly metallic, that is to say, they exhibit a true HM characteristic with 100% spin-polarization around the Fermi level. For SnKCa with structure (b), the majority-spin DOS touches the Fermi level a little, and thus it shows nearly half-metallicity. The calculated total magnetic moment per formula unit is 0.98 $\mu_B$ for SnKCa with structure (b), and 1.00 $\mu_B$ for GeKCa with structures (a), (b) and (c) and SnKCa with structures (a) and (c), which also confirm the nearly half-metallicity and true half-metallicity, respectively. So both GeKCa and SnKCa are HM for all the three possible atomic arrangements in the half-Heusler structure, and it can be predicted that the half-metallicity of both GeKCa and SnKCa can be preserved even if the partial disorder occurs in the samples. In the following, we mainly discuss in detail the electronic and magnetic properties for both GeKCa and SnKCa with the most stable structure (a).

Fig. 2 also shows that, for GeKCa and SnKCa with structure (a), the energy gaps around the Fermi level in the majority-spin channel are about 1.21 eV and 1.23 eV, respectively, which are larger than those of NiMnSb (0.5 eV) and CoMnSb (1 eV) [31]. Meanwhile, the HM gap [22–24], which is determined as the minimum between the bottom energy of majority (minority) spin conduction bands with respect to the Fermi level and the absolute values of the top energy of majority (minority) spin valence bands, is 0.28 eV for GeKCa with structure (a) and 0.27 eV for SnKCa with structure (a). These values are smaller than those of zinc-blende CrSb (0.774 eV) [32] and CaC (0.83 eV) [22].

The calculated spin-projected partial DOS of GeKCa with structure (a) in the ferromagnetic state at the equilibrium lattice constant is shown in Fig. 3. Note that we do not give the partial DOS of cation K because its contribution to the total DOS of GeKCa is small. Comparing the total and partial DOS with the band structure (Fig. 4), we can see that, for both majority- and minority-spin

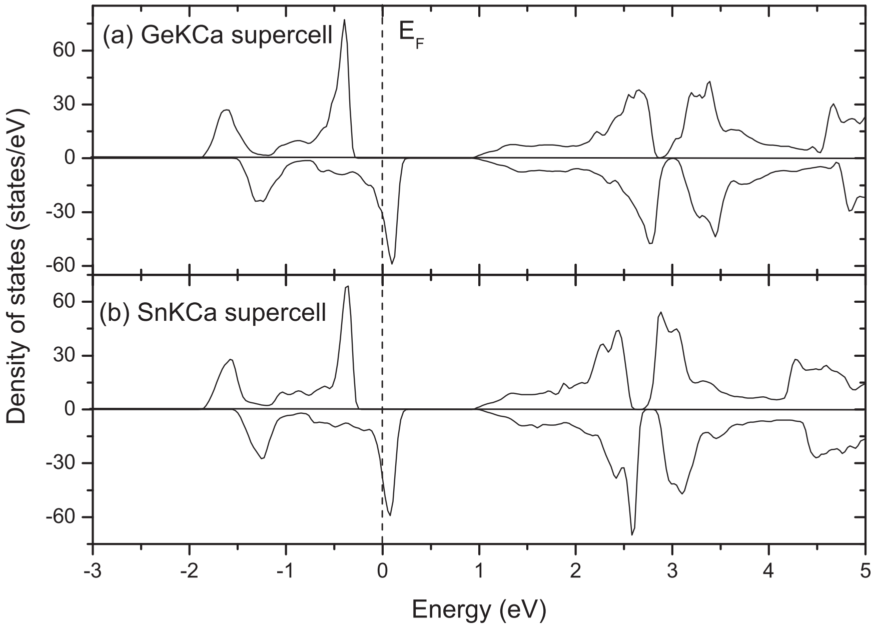

**Fig. 6.** The spin-projected total density of states for the relaxed $1 \times 1 \times 2$ supercells of GeKCa and SnKCa with atomic slightly shift.

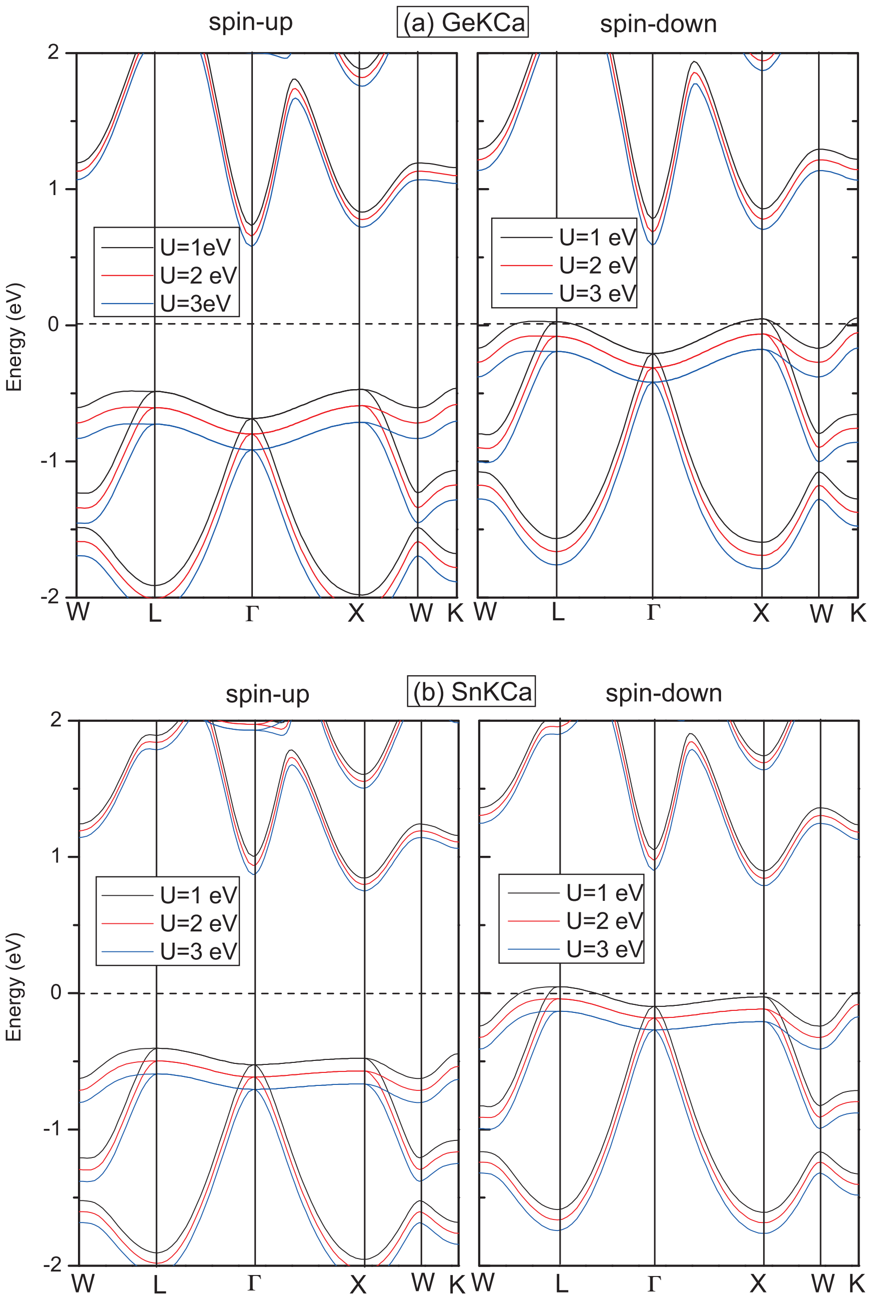

**Fig. 7.** Spin-polarized band structure by GGA + *U* with *U* = 1, 2 and 3 eV for Ge 4p and Sn 5p electrons of GeKCa and SnKCa, respectively.

channels, the three lowest bands mainly originate from the hybridized Ge p states and Ca $t_{2g}$ states. The bands around 2.5 eV are mainly formed by the Ca $e_g$ states and that around 3.5 eV are mainly from the Ca $t_{2g}$ states in both the majority- and minority-spin channels, however, these states locate above the Fermi level and the spin splitting is very weak, so that their contribution to the form of half-metallicity in GeKCa is very small. The half-metallicity is mainly from the spin polarization of the Ge p states and the hybridization between the Ge p states with the Ca $t_{2g}$ states. This mechanism is similar to those of sp HM ferromagnets of alkaline-earth nitrides and carbides [21–23].

Table 1 lists the calculated total and partial magnetic moments for GeKCa and SnKCa with structure (a) at the optimized equilibrium lattice constants. It can be seen that the atomic spin moment mainly originates from the Ge (Sn) atom. This can be explained from the electronic arrangements. There are seven valence electrons in GeKCa (Ca: $4s^2$, Ge: $4s^24p^2$ and K: $4s^1$): two valence electrons occupy the Ge s states in the lowest energy (about 7 eV below $E_F$, not shown in Fig. 3), and three of the remaining five electrons mainly occupy the majority-spin Ge p states and Ca d states, which result in the three majority-spin full filled bands (see Fig. 4). Meanwhile, the remaining electrons make the three minority-spin bands partly

**Table 1**
The predicted equilibrium lattice constant ($a$), the total energy difference between antiferromagnetic and ferromagnetic states per formula unit ($\Delta E$), the total magnetic moment per formula unit ($\mu_{tot}$), the Ca magnetic moment ($\mu_{Ca}$), the K magnetic moment ($\mu_K$), and the $M$ ($M$ = Ge and Sn) magnetic moment ($\mu_M$) at the equilibrium lattice constants for GeKCa and SnKCa with the most stable atomic arrangement.

| Compound | $a$ (Å) | $\Delta E$ (meV) | $\mu_{tot}$ ($\mu_B$) | $\mu_M$ ($\mu_B$) | $\mu_{Ca}$ ($\mu_B$) | $\mu_K$ ($\mu_B$) |
|---|---|---|---|---|---|---|
| GeKCa | 7.58 | 41 | 1.00 | 0.87 | 0.10 | 0.03 |
| SnKCa | 7.99 | 43 | 1.00 | 0.88 | 0.10 | 0.02 |

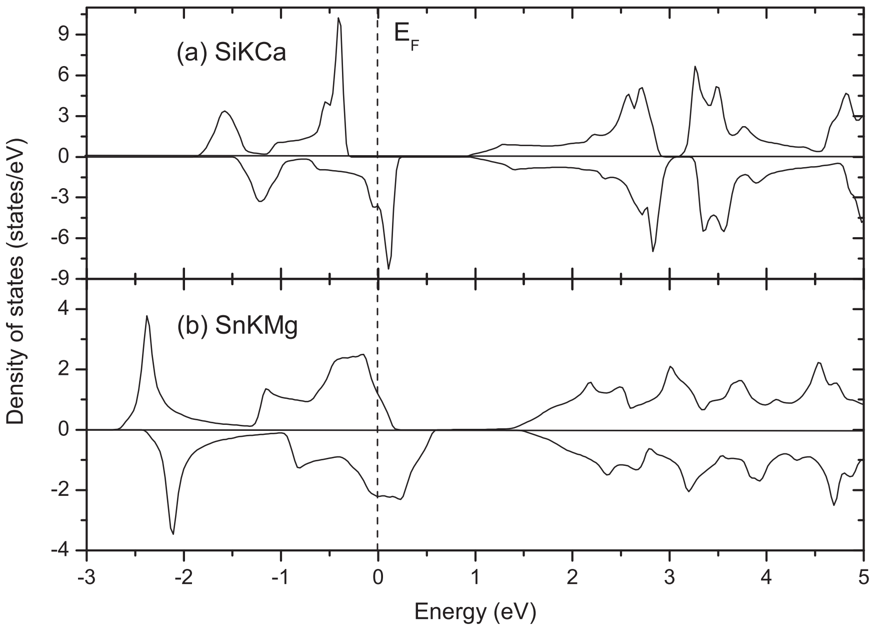

**Fig. 8.** The spin-projected total density of states of SiKCa and SnKMg.

filled, which provides the main magnetic moment. To check if both GeKCa and SnKCa with structure (a) have the ferromagnetic ground state, we perform the total energy calculations for both GeKCa and SnKCa in the ferromagnetic and antiferromagnetic configurations. We construct a 1 × 1 × 2 supercell based on the primitive cell of GeKCa and SnKCa. For the antiferromagnetic configurations, the spins between two Ge (Sn) atoms are antiparallel because the atomic magnetic moments in GeKCa and SnKCa mainly originate from Ge (Sn) atoms. The calculated results indicate that the ferromagnetic state has lower energy than the antiferromagnetic one for both GeKCa and SnKCa, and the total energy differences are about 41 and 43 meV per formula for GeKCa and SnKCa, respectively. So the ferromagnetic state is more favourable in energy than the antiferromagnetic state for both compounds.

We now study the robustness of the half-metallicity with the change of lattice constant, because the lattice distortion is often inevitably introduced in the process of synthesization of materials. Fig. 5 shows the calculated total magnetic moment per formula unit as function of lattice constant. It is found that the magnetic moment is still an integer of Bohr magneton, 1.00 $\mu_B$, when the lattice constant is contracted to be 6.75 Å for GeKCa with structure (a) and 6.94 Å for SnKCa with structure (a), respectively. Therefore, both GeKCa and SnKCa with structure (a) maintain half-metallicity up to 10% and 13% contraction of the lattice constant, respectively, with respect to their equilibrium ones. These are more favourable than the lattice contraction of 2% of CoMnSb [31] and NiMnSn [33].

It is necessary to investigate the structural stability for the possible experimental realization of GeKCa and SnKCa. On one hand, we consider the structural distortion, i.e., taking a larger supercell, shifting the atoms to slightly out-of-symmetry positions, and then allowing for relaxation and checking if the atoms will relax to the original structure or e.g. form some super-structure. Here, we construct a 1 × 1 × 2 supercell for both GeKCa and SnKCa. We shift all the atoms to slightly out-of-symmetry positions (deviating from *z* direction by 0.1 Å) and then allow for relaxation. After relaxation, we find that for both GeKCa and SnKCa the supercell with atomic slightly shift has higher energy than that of no atomic shift, and the energy differences are about 6 and 19 meV per supercell for GeKCa and SnKCa, respectively, which means the atoms tend to relax to the original structure. Importantly, the relaxed supercell with atomic slightly shift is still HM and thus the structural distortion does not destroy the half-metallicity in GeKCa and SnKCa (see Fig. 6). The heat of formation is another aspect of structural stability. Referring to rocksalt HM MgN [34], the heats of formation of GeKCa and SnKCa can be expressed as $\Delta H = E_{\text{tot}} - (E_X + E_K + E_{\text{Ca}})$, where $E_{\text{tot}}$ is the total energy of half-Heusler alloy GeKCa or SnKCa per formula unit, and $E_X$, $E_K$ and $E_{\text{Ca}}$ are the total energies of bulk Ge (or Sn), K and Ca per atom, respectively. The calculated heats of formation for GeKCa and SnKCa are −7.14 and −7.67 eV, respectively. The low heats of formation mean GeKCa and SnKCa are thermodynamically stable.

It is interesting to study how the electronic state depends on electron localization especially for the p electrons [34,35]. We calculate the electronic structure for GeKCa and SnKCa by using the GGA + *U* (Hubbard coefficient) scheme [36] for the electronic exchange–correlation functional. Fig. 7(a) and (b) presents the calculated spin-resolved band structure of GeKCa and SnKCa with *U* = 1, 2 and 3 eV for Ge 4p and Sn 5p electrons, respectively. One can see that both GeKCa and SnKCa are still HM when *U* = 1 eV, but the Coulomb interaction *U* on Ge 4p and Sn 5p electrons destroys the half-metallicity (both they become a semiconductor) for both GeKCa and SnKCa when the *U* value reaches 2 eV. We also find that both valence band and conduction band shift to low energy region with the increase of *U* value because of the Coulomb interaction.

Finally, we make an outlook for the possible half-metallicity in more compounds which are similar to those of GeKCa and SnKCa. We optimize the geometry structure and calculated the electronic and magnetic properties at the equilibrium lattice constants for more combinations. It is found from the DOS and magnetic moments that most of the combinations are HM. The same behaviour is not surprising because these combinations are from the same group elements. This phenomena also exists in the half-(full-)Heusler compounds based on transition metals [5,12]. Table 2 collects the equilibrium lattice constants, the magnetic moments and the HM gaps for eight half-Heusler compounds. We find that six of them are HM, and SnKMg and SnLiCa are metallic. As representations, the calculated total DOS at the equilibrium lattice constants for SiKCa and SnKMg are shown in Fig. 8. The two compounds exhibit obvious half-metallicity and metallicity, respectively.

**Table 2**

The calculated equilibrium lattice constant ($a$), the total magnetic moment per formula unit ($\mu_{\mathrm{tot}}$), the electronic conductivity (half-metallic, metallic, or semiconducting), and the half-metallic gap ($E_g$) for some half-Heusler compounds which are similar to GeKCa and SnKCa.

| Compound | $a$ (Å) | $\mu_{\mathrm{tot}}$ ($\mu_B$) | Electronic conductivity | $E_g$ (eV) |
|---|---|---|---|---|
| CKCa | 6.56 | 1.00 | Half-metallic | 0.38 |
| SiKCa | 7.52 | 1.00 | Half-metallic | 0.29 |
| GeKMg | 7.22 | 1.00 | Half-metallic | 0.02 |
| SnKMg | 7.57 | 0.81 | Metallic | — |
| GeLiCa | 6.84 | 1.00 | Half-metallic | 0.03 |
| GeNaCa | 7.16 | 1.00 | Half-metallic | 0.19 |
| SnLiCa | 7.23 | 0.92 | Metallic | — |
| SnNaCa | 7.53 | 1.00 | Half-metallic | 0.08 |

## 4. Conclusion

To summarize, we have investigated the structural, electronic and magnetic properties of the three possible atomic arrangements for both GeKCa and SnKCa compounds with half-Heusler structure by using the first-principles pseudopotential plane wave method implemented with the CASTEP package. The most stable atomic arrangement, where Ge (Sn), K and Ca occupy the (0, 0, 0), (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) positions, respectively, are found for both GeKCa and SnKCa. Both GeKCa and SnKCa with the most stable structure show half-metallicity with the large HM gaps of 0.28 eV and 0.27 eV, respectively. The calculated magnetic moment, 1.00 $\mu_B$ per formula unit for both GeKCa and SnKCa, mainly originates from the Ge (Sn) atom. The half metallicity is found to be robust with respect to the lattice compression and is maintained up to the lattice-constant contraction of 10% and 13% for GeKCa and SnKCa with the most stable structure, respectively.

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