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First-Principles Calculation of structural, electronic and magnetic properties of half-Heusler LiCaC and NaCaC compounds

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ABSTRACT

The structural, electronic and magnetic properties of LiCaC and NaCaC compounds in half-Heusler structure have been studied using local density approximation (LDA) based on density functional theory (DFT). From the total energy calculation, it is found that the compounds LiCaC and NaCaC are stable in ferromagnetic phase. The spin-polarized electronic band structure and density of states of these compounds show that the minority spin channel has metallic nature and the majority spin channel has a semiconducting gap of 2.27 and 2.0 eV for LiCaC and NaCaC respectively, resulting in a stable half-metallic ferromagnetic (HMF) behavior with magnetic moment of 1 μ_B per formula unit. Analysis of density of states of these compounds indicates that the magnetic moment mainly originates from the strong spin-polarization of 2p like states of C and the hybridization between the C-2p like states and the Ca-3d like states. The robustness of half-metallicity against the lattice constant is also calculated. Presence of HMF in LiCaC and NaCaC compounds without any transition metal makes these compounds promising materials for spintronic applications.

1. Introduction

A rapid growth of spintronics intensified the research interest in the search for novel magnetic materials such as new magnetic semiconductor materials and metallic magnetic materials. These novel magnetic materials have peculiar property known as half-metallic ferromagnetism (HMF) and these materials are considered as potential candidates for spintronics applications [1–6]. In HMFs, one of the two spin channel is semiconducting with a gap at the Fermi level (E_F); whereas the other one behaves like a metal leading to 100% spin polarization at E_F. HMF was first discovered in 1983 by de Groot et al. when calculating the band structure of half-Heusler compound NiMnSb [7]. So far, transition metal based compounds have been widely studied due to localized d-electrons of a partially filled atomic shell [8–14]. In recent years, spin-polarization in systems without transition metal attracts increasing research interest as potential materials in spintronic devices. This new class of materials are known as sp or d^0 HM materials.

First Kusakabe et al. [15] reported the existence of HMF in ZB-CaP, CaAs and CaSb excluding the transition metals with a magnetic moment of 1.0 μ_B per formula unit. The magnetic order is carried by the anion p electrons without any direct involvement of d electrons of cation as in HM ferromagnets with 3d electrons. Since then, there have been more studies on HMF in the ZB structure, for example, IIA–IVA, IIA–VA, and IA–VA compounds including CaC, CaN, and LiP [16–21]. In all these compounds, the partially occupied p band of the anion atom is responsible for the ferromagnetism in these compounds. Furthermore, using the mean field approximation and random phase approximation, Gao et al. [18] predicted that the Curie temperature of MC (M = Ca, Sr and Ba) compounds in the ZB structure may exceed room temperature. Several works were focused on alkali and alkaline earth metals with C, N and S [22–27] in various structures and predicted the existence of half-metallicity.

Heusler-based compounds [28] have attracted considerable research interest in the spintronic field, due to their high Curie temperature, and also due to their similarity to the conventional zinc-blende semiconductors. It is of great interest to merge magnetic properties of the sp-HM compounds with the properties of Heusler-type structure. To the best of our knowledge there has been a little work on HMF in Heusler structure excluding transition metals. GeKCa and SnKCa were found to be HMFs in the half-Heusler structure with a large HM gap of 0.28 eV and 0.27 eV respectively [29]. The calculated magnetic moment of 1.00 μ_B per formula unit for both GeKCa and SnKCa mainly originates from the Ge (Sn) atom. Recently, Białek et al. [30] investigated the magnetic properties of (0 0 1) surfaces of GeKCa and SnKCa compounds in the half-Heusler structure and they found that the magnetic properties of the surfaces terminating with layers containing Ge and Sn atoms are enhanced compared with the properties of the

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bulk. Lakdja et al. and Rozale et al. [31,32] predicted that XCsBa and RbSrX (X=C, Si and Ge) compounds in half-Heusler structure exhibit HM ferromagnetism with a magnetic moment of 1 μ_B.

In this paper, using the First-Principles Calculation the structural, electronic and magnetic properties of LiCaC and NaCaC compounds in half-Heusler structure are studied. It is found that ferromagnetic phase have lower energy than the non-magnetic phase. The organization of this paper is as follows. In Section 2, method of calculation and crystal structure is described briefly. In Section 3, results of the calculations and their discussions are given. Section 4 summarizes the results.

2. Computational method

The electronic and magnetic properties LiCaC and NaCaC compounds have been investigated through the First-Principles Calculation by using the efficient computational scheme offered by Andersen's tight-binding linear muffin-tin orbital (TB-LMTO) method. This method has been described well in the literature [33]. In this method, the total energy and electronic structure are calculated based on the density functional theory (DFT) within the local density approximation (LDA) [34]. Exchange and correlation contributions to both the atomic and crystalline potentials have been included through the von Barth–Hedin scheme [35]. Atomic sphere approximation (ASA) has been used. The Wigner–Seitz sphere is chosen in such a way that the potential discontinuity at the sphere boundary is minimum and the charge flow between the atoms is in accordance with the electro-negativity criteria. The density of states (DOS) was calculated by the tetrahedron method [36]. The Brillouin zone integration is performed by the usual tetrahedron technique. A mesh of $16\times16\times16$ was taken in the irreducible wedge of Brillouin Zone. E and $\mathbf{k}$ convergence are also checked carefully. Scalar-relativistic Kohn–Sham equations were solved taking all relativistic effects into account except for the spin-orbit coupling.

The half-Heusler compounds have the general formula XYZ and crystallize in non-centrosymmetric cubic MgAgAs ($C1_b$) structure with the space group F-43m. The structure of these compounds arises from three interpenetrating fcc lattices of X, Y, and Z atoms and the corresponding Wyckoff positions are $\mathbf{r_1}$ =(0.5, 0.5, 0.5), $\mathbf{r_2}$ =(0, 0, 0), and $\mathbf{r_3}$ =(0.25, 0.25, 0.25). There are six ways to distribute the X, Y, and Z atoms over the three sublattices. For symmetry reasons, exchange of atoms at $\mathbf{r_1}$ and $\mathbf{r_2}$ results in an equivalent structure. Therefore by interchanging the positions of atoms in cubic ($C1_b$) structure only three phases (α, β and γ) are formed. i.e., X, Y, and Z atoms are arranged at different positions ($\mathbf{r_1}$, $\mathbf{r_2}$, $\mathbf{r_3}$), ($\mathbf{r_3}$, $\mathbf{r_1}$, $\mathbf{r_2}$) and ($\mathbf{r_2}$, $\mathbf{r_3}$, $\mathbf{r_1}$) respectively. The crystalline structure ($C1_b$) of these materials is discussed well in literature [37–41].

3. Results and discussion

3.1. Total energy calculation

In order to find the most favorable phase in half-Heusler structure, total energy is minimized according to three atomic arrangements (α, β, and γ-phases). The total energy calculation reveals that both the compounds are having lower energy in α-phase than the other two phases (β and γ). Fig. 1 shows the calculated results. To determine the equilibrium lattice constants, bulk modulus of the hypothetical LiCaC and NaCaC compounds (α-phase), the total energies are calculated as a function of relative volume for both nonmagnetic (NM) and ferromagnetic (FM) states and fitted to Birch equation of state [42]. Towards the stability of ferromagnetism, the total energy difference between the FM and NM state ($\Delta E = E_{NM} - E_{FM}$) is calculated. The calculated equilibrium lattice constant, bulk modulus and ΔE values are summarized in Table 1. From the calculation, it is found that for both the systems the FM phase has lower energies than the NM phase and it indicates the stability of FM phase ($\Delta E > 0$). Furthermore, LiCaC has the smallest cell volume and highest bulk modulus, indicating that the bonding is the strongest due to the smaller interatomic distances. In order to study stability of these hypothetical compounds, formation energy (ΔH) is calculated and the values are given in Table 1. The –ve value indicates that these compounds will not decompose once they have been formed.

3.2. Electronic structure and magnetic properties

The electronic band structure of ferromagnetic LiCaC and NaCaC compounds at their equilibrium lattice constant have been obtained using spin-polarized calculations. Due to the similarity of the electronic structure of these compounds, spin-polarized band structure for LiCaC only is shown in Fig. 2. From the band structure it is observed that there is strong spin-polarization of energy states around the Fermi level. In addition to that, it can be seen that the minority-spin channel is metallic whereas in the majority-spin channel there is an energy gap around the Fermi level making these systems to be HM ferromagnets. Also it can be seen that the energy gap in these compounds is direct band-gap (X–X) and the Fermi level locates just above the top of the valence band at the X point of high symmetry in the Brillouin zone, the direct band-gap is equal to 2.27 and 2.0 eV for LiCaC and NaCaC respectively. The HM gap which is determined as the minimum between the

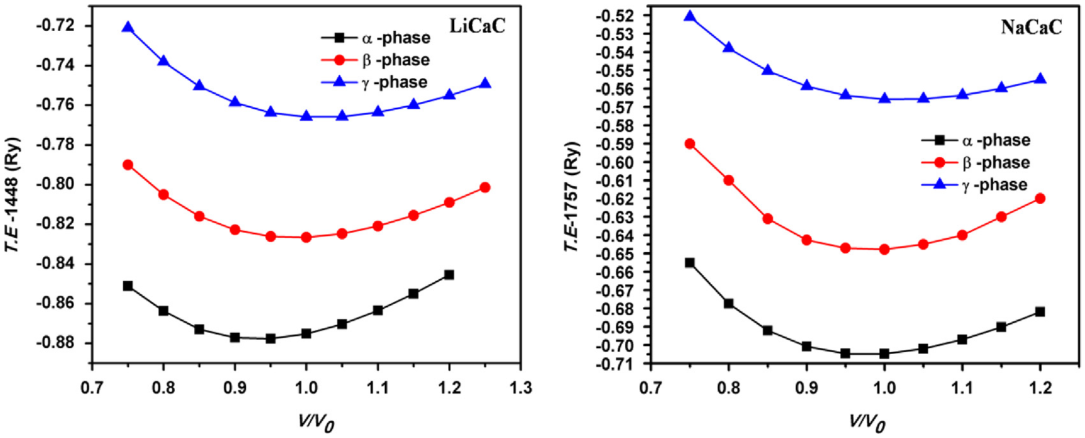

Fig. 1. Volume optimization for LiCaC and NaCaC compounds.

lowest energy of majority (minority) spin conduction band with respect to the Fermi level and the absolute values of the highest energy of the majority (minority) spin valence band is 0.53 and 0.48 eV for LiCaC and NaCaC respectively. HMF property of these compounds is in contrast to the properties of half-metallic ZB transition-metal pnictides and chalcogenides, in which the majority-spin channel is metallic, while there is a semiconducting gap in the minority-spin channel. The overall band structure profiles for NaCaC is similar to LiCaC.

In order to understand the origin of HMF in LiCaC and NaCaC compounds, the spin-polarized total and partial density of states (DOS) at their equilibrium lattice constant are calculated and plotted in Fig. 3 for LiCaC. Comparing the DOS with the band structure (Fig. 2), for both majority and minority spin bands, the lower most band around −8 eV corresponds to 2s-like state of C and the topmost valence band mainly originates from the hybridized C-2p like states and Ca-3d like states. The three topmost valence band in majority spin states are fully filled and exhibit semiconducting nature; whereas, in the minority spin states, these states are partially filled and these bands cross the Fermi level exhibiting metallic nature. It can be explained from the electronic arrangements: there are seven valence electrons in these compounds (Li/Na: $2s^1/3s^1$; Ca: $4s^2$; C: $2s^2$, $2p^2$) which contribute to bond formation and magnetism; two of them occupy the C-2s states in the lowest energy states. Three of the remaining five valence electrons, occupy the majority spin 2p states of C which results in the three fully filled majority spin bands. Meanwhile, remaining two electrons partially occupy the three lowest minority spin bands by leaving one hole, which provides the main magnetic moment of 1 μ_B/f.u. Moreover, the magnetic state is not an itinerant electron state but rather a localized one where unpaired spin states are located in well-defined orbitals. Here

Table 1
Lattice parameter (a) in Å, bulk modulus (B_0) in GPa, total energy difference (ΔE) in meV, formation energy (ΔH) in meV and exchange splitting energy (Δx) in eV, and total and partial magnetic moments in μ_B for LiCaC and NaCaC compounds.

Compounds	a	B_0	ΔE	ΔH	Δx	$M_{Li/Na}$	M_{Ca}	M_C	M_I	M_{TOT}
LiCaC	5.66	55	146	−8.62	−0.81	0.07	0.11	0.82	−0.01	1.0
NaCaC	5.97	52	137	−7.84	−0.78	0.06	0.10	0.85	−0.01	1.0

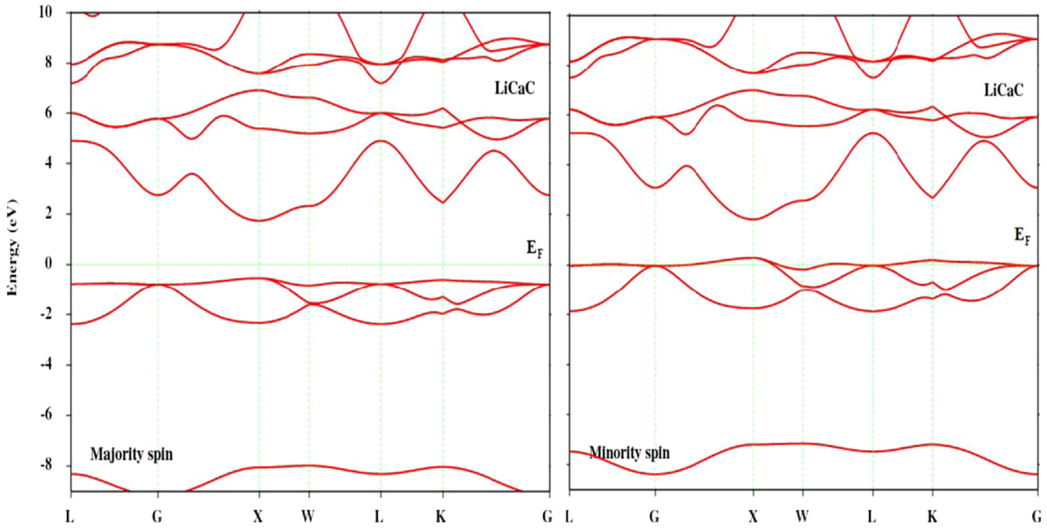

Fig. 2. Spin-polarized band structure for LiCaC.

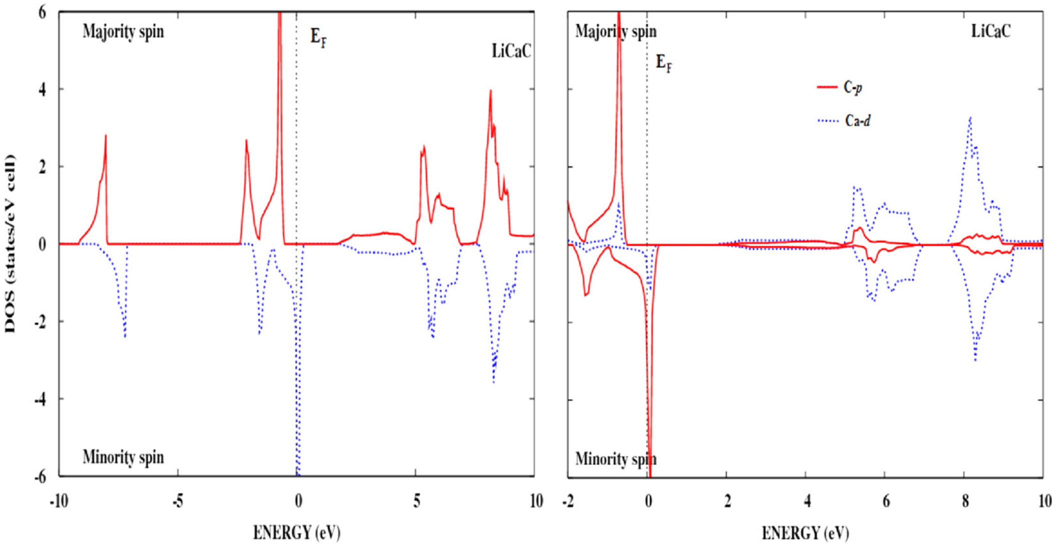

Fig. 3. Spin-polarized total and partial DOS of LiCaC.

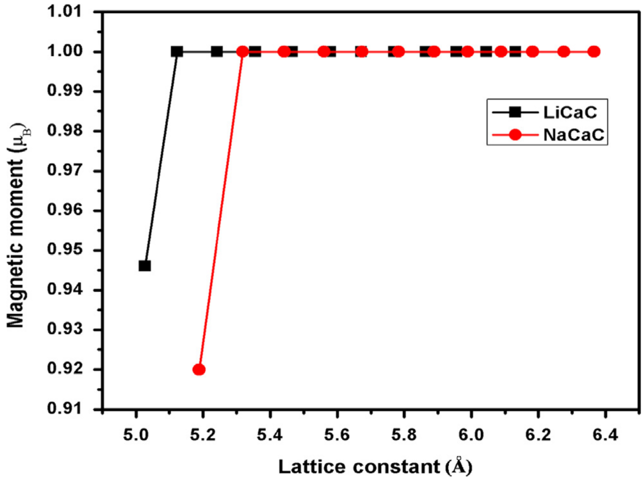

Fig. 4. Total magnetic moment (μ_B) as a function of lattice constant (Å) for LiCaC and NaCaC compounds.

HMF is formed due to the spontaneous spin-polarization of 2p states of C atom. In this case ferromagnetism arises due to exchange splitting of the 2p states of C atom. The exchange splitting energy (Δx) is defined as the average energy difference between majority spin and minority spin bands and is given in Table 1.

From the spin-polarized calculations, the total and partial magnetic moment for these compounds are calculated and summarized in Table 1. HMF property of the compounds LiCaC and NaCaC has been confirmed from the integer value of total magnetic moment of 1.00 μ_B per formula unit. In other words these compounds exhibit 100% spin polarization around the Fermi level at their equilibrium volume. From the partial magnetic moment, it can be observed that the main contribution comes from the C atom, whereas the moments from other atoms are small. In the above mentioned compounds, HMF is mainly induced by spin polarization of 2p like states of C slightly hybridized with 3d like states of Ca. Although the Ca atom provides small magnetic moment to total magnetic moment, it plays an essential role in the origin of magnetism. This mechanism of HMF in sp systems is different from transition metal based HMF [14,43], for which their high spin states are ferromagnetically aligned via the double exchange mechanism or by the p–d exchange mechanism. This is the origin of magnetism of transition-metal pnictides and chalcogenides in the ZB structure.

The calculations are extended to investigate the robustness of half-metallicity with respect to lattice constant, since the distortion of the lattice at the interface between the film and the substrate can often occur when materials are to be grown as epitaxial films or heterostructures. The variation of total magnetic moment with respect to contraction of lattice is calculated for LiCaC and NaCaC compounds and it is shown in Fig. 4. From the figure, it can be seen that the total magnetic moment remains an integer value until the lattice are compressed to critical value of 5.12 Å and 5.31 Å for LiCaC and NaCaC respectively. This indicates that the half-metallicity is preserved up to a lattice contraction of 9.5% for LiCaC and 11% for NaCaC. In other words, the half-metallicity of these compounds can be retained when they are grown over ZB-GaAs or ZnSe substrates by molecular beam epitaxial method.

4. Conclusion

To conclude, the possibility of magnetization in LiCaC and NaCaC compounds in MgAgAs ($C1_b$) structure is studied based on TB-LMTO-ASA method within the density functional theory. The total-energy calculations show that in LiCaC and NaCaC, the ferromagnetic state is more favorable than non-magnetic state. The spin-polarized calculations show that the compounds exhibit HMF property with a magnetic moment of 1.00 μ_B per formula unit and it mainly originates from the spin-polarized 2p-like states of carbon atom. These systems have large HM gaps of 0.53 and 0.48 eV and their half-metallicities can be retained for lattice compression up to 9.5% and 11% for LiCaC and NaCaC respectively. Hence, these materials could be grown epitaxially on appropriate substrates. The absences of transition-metal atoms make these compounds important model systems for the study of the origin and properties of the HM ferromagnetism in sp electron systems.

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