

FIRST-PRINCIPLES STUDY OF HALF-METALLIC FERROMAGNETISM IN (1 1 1) SURFACE OF CsSe

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Abstract

The electronic and magnetic properties of bulk CsSe in CsCl and NaCl structures have been investigated by employing first-principles method. The result reveals that the compounds have half-metallic ferromagnets at the equilibrium lattice constant with large half-metallic band gaps of 4.36 eV (CsCl-type) and 7.34 eV (NaCl-type) respectively. We have examined the half-metallicity in (111) surface of CsSe in CsCl-type structure and found that for both Cs- and Se-terminated surfaces, the half-metallic property was retained.

Keyword: Spintronics, HM ferromagnet, CsSe, Electronic structure, Surfaces.

1. INTRODUCTION

Past decades have experienced intensified efforts in areas of spintronics (known also as magnetoelectronics) which has shown rapid and novel development on ferromagnetic materials suitable for spin injection into a semiconductor, and of which half-metallic (HM) ferromagnet is one of the most prominent classes of such materials [1]. HM ferromagnetic compounds exhibits a metal character in one spin channel and a semiconductor (or insulator) character in the other spin channel so that the conduction electrons at the Fermi level keeps a 100% spin polarization ratio, attracts research interest due to their potential applications in spintronic devices for information storage, logic and sensor applications. In 1983, de Groot *et al.* [2] first reported HM behaviour in Heusler alloy NiMnSb from first-principle calculations, and since then the trend to searching for half-metals properties of ternary compounds of similar structure began. Compounds of transition metal series presents sp element as vital for stabilizing HM ferromagnetism [3]. Compounds without a transition metal in their structure have shown HM ferromagnetism [4]. Several half-metallic materials have been predicted theoretically, e.g. Heusler compounds [5-9], diluted magnetic semiconductors [10], binary compounds [11], metallic oxides [12], and layered perovskites [13]. Many fundamental properties of materials are determined from the nature of their surface. A spin injection process is affected by the atomic scale structure at the interface. The atoms on the surface have a different environment to the bulk, and may adopt different geometrical arrangements with different electronic properties as a result. As reported in recent paper [14], the (0 0 1) and (1 1 1) surfaces of RS-type BaC retained their bulk HM property. However, in the case of ZB-type CrP, the HM property disappeared in the P-terminated (0 0 1) surface and is preserved in the Cr-terminated (0 0 1) surface [15, 16]. A more recent research has shown that the half-metallicity of CsCl-type structure RbS and KS is preserved at their (1 1 1) surfaces [17]. Just recently, Bialek and Lee [4] reported half-metallic properties of (0 0 1) and (1 1 0) surfaces of CsSe in CsSe and ZB structures. However, according to [4] processes important for a performance of electronic devices occurs at surfaces, and computational studies of the electronic and magnetic properties of surfaces are often challenging.

Designing a material is a long way from its possible application in electronic devices. Most often perfectly periodic compounds are investigated during the process of designing, while it is a well-known fact that a break in periodicity may considerably change the properties of a perfect crystal. Thus, since not every surface retains or keeps its bulk half-metallic (HM) property, it is very important to investigate the surface properties for the application of HM ferromagnetism in (1 1 1) surface of CsSe since it has not yet been reported, to the best of our knowledge, in literature. In this paper we discuss, firstly

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the bulk electronic structure of CsSe in CsCl- and NaCl-type structures by means of first-principles pseudopotentials and plane-wave basis set method, and secondly the (1 1 1) surface property of CsSe CsCl-type, since the retaining of HM character for surfaces is very important to practical applications in spintronics. Nevertheless, our present work demonstrates that the CsCl-type structure exhibits lower symmetry than its constituent member at the bulk state.

The rest of this paper is structured as follows: In Section 2, the computational method is explained. Section 3 presents the results and discussion. Finally, the paper ends with concluding remarks in Section 4.

2. COMPUTATIONAL METHOD

In this work, all the calculations were implemented using spin-polarized density-functional theory (DFT) in the Quantum-ESPRESSO package [18], which is based on the plane-wave pseudopotential basis set method. DFT has been proven to give the correct equilibrium structure of binary alloys in the vicinity of the Fermi level E_F . In the present calculations, a plane-wave basis set with a kinetic-energy cutoff of 65 Ry is used in combination with Norm-Conserving pseudopotential and Perdew-Burke-Ernzerhof (PBE) exchange-correlation with the local density approximation. The convergence threshold for energy in the calculations is chosen to be 10^{-6} . The occupation state is set to smearing, and the value of Gaussian spreading for Brillouin-zone (BZ) integration is 0.05 eV, K-points are generated automatically with the size of $8 \times 8 \times 8$ for the bulk compounds, and K-Point of $8 \times 8 \times 1$ supercell was adopted for CsCl (1 1 1) surface of CsSe. The equilibrium lattice parameters were calculated through the ground state total energy; starting by performing single-point self-consistent calculations, followed by nonself consistent calculations of the $8 \times 8 \times 8$ uniform grids which allow both the calculation of the electronic and band structures in CsSe. The energy-volume data generated were fitted to obtain the equilibrium lattice parameters using the method proposed by Birch–Murnaghan [19]:

$$\Delta E(V) = E - E_0 = BV_0 \left[\frac{V_0}{B'} + \frac{1}{1-B'} + \frac{V_0}{B'(B'-1)} \right] \quad (1)$$

where V_0 , E_0 , B and B' are the equilibrium volume at zero pressure, equilibrium energy, bulk modulus and pressure derivative respectively. Here, the (1 1 1) surface is polar with two types of termination namely Cs-terminated and Se-terminated surfaces. The asymmetric slabs consisted of 15 atomic layers of which 10 atomic layers were fixed at bulk positions with 5 relaxed top layers. Moreso, while relaxed layers on one side mimic the surface, the fixed layers on the other side mimic the bulk region. The distances between successive atomic layers are 3.084 Å. The spin exchange energies are accounted for using the method of [20]:

$$H = -\sum_{ij} J_{ij} S_i \cdot S_j, \quad (2)$$

where $J_{ij} < 0$ implies an antiferromagnetic ground state, $J_{ij} > 0$ indicates a ferromagnetic ground state and H is the spin Hamiltonian. The CsSe CsCl-type structure retains its half-metallic properties in a wide range of lattice constants [21] and so we have assumed that the relaxation and reconstruction will not influence much the electronic properties of the (1 1 1) surface calculation.

3. RESULTS AND DISCUSSIONS

3.1 The properties of bulk CsSe in CsCl and NaCl structure.

Firstly, we calculated the total energy as a function of lattice constant in NaCl- and CsCl-type structures for both spin-polarization (FM phase) and non-spin-polarization (NM phase). The optimized CsSe (in CsCl and NaCl structures) is shown in Fig. 1 while in Fig. 2, we present the curves of total energy versus lattice constant for bulk CsSe (CsCl and NaCl). All the calculations are performed in both FM and NM phases. The calculated results indicate that the FM states are more stable than NM states for both compounds. The equilibrium lattice constants for CsCl and NaCl are 8.242 a.u. (4.36Å) and 13.599 a.u. (7.19Å) respectively. The obtained lattice constants are in good agreement with that in Ref. [21]. Therefore the following calculations are performed, based on the theoretical equilibrium lattice parameters in CsSe NaCl states and CsSe CsCl states respectively.

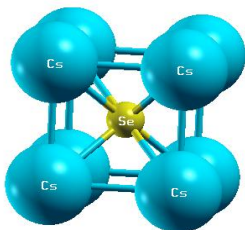


Fig. 1 (a): Bulk CsSe in CsCl-type structure

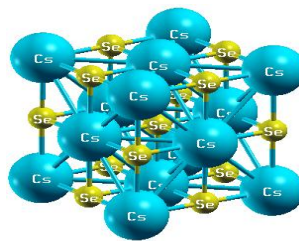
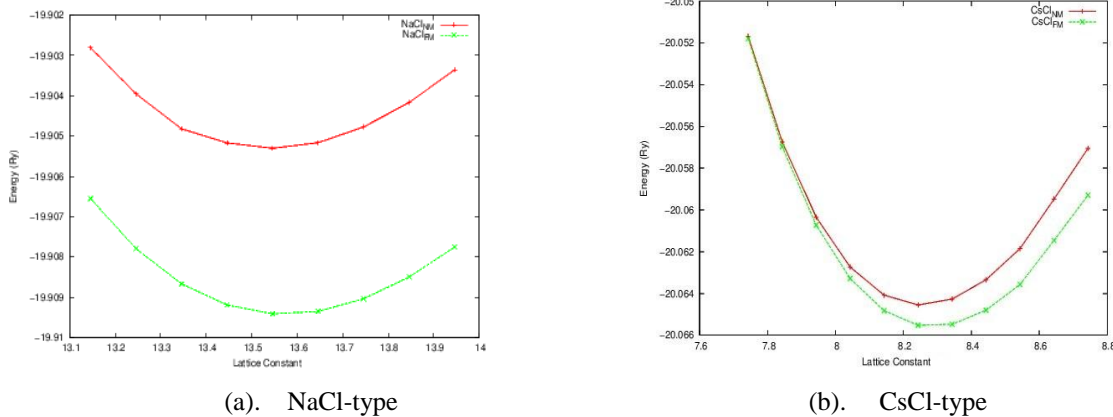


Fig. 1 (b): Bulk CsSe in NaCl-type structure



(a). NaCl-type

(b). CsCl-type

Fig. 2: (a) The total energies per unit cell as a function of lattice constants for NaCl in FM and NM phase. (b) The total energies per unit cell as a function of lattice constants for CsCl in FM and NM phase.

The electronic band structures and total density of states (DOS) for CsCl and NaCl are shown in Fig. 3 and Fig. 4 respectively. The calculated electronic band structure along the high symmetry points of the Brillouin zone (BZ) with Fermi energy set to zero (broken-line) shows degeneracy at gamma points (G) in the bands along the $W \rightarrow L \rightarrow G \rightarrow X \rightarrow W \rightarrow K$ directions in Fig. 3(a), and also in the $R \rightarrow G \rightarrow X \rightarrow M \rightarrow G$ directions in Fig. 3(b) respectively. However, at these G points an electron can be projected from the lowest energy state to the highest energy state without any change in crystal momentum. As can further be observed from the total DOS of Fig. 4, the spin-down DOS crosses the Fermi level showing a metallic behaviour. However, there is a large band gap around the Fermi level for each compound in the spin-up band structure which shows an insulating behaviour. Consequently, these compounds keep an ideal 100% spin-polarization of conduction electrons at the Fermi level. This indicates that they are HM ferromagnets. From the partial DOS, one can see that the DOS located at the Fermi level are originated exclusively from the 4p orbitals of Se. The HM band gap is defined as the minimum between the lowest energy of majority (minority) spin conduction bands with respect to the Fermi level and the absolute values of the highest energy of the majority (minority) spin valence bands. Thus, the compounds NaCl and CsCl have HM band gaps of 3.37 eV and 3.46 eV, respectively. The HM band gaps are so large that these compounds may probably keep their HM property at room temperature.

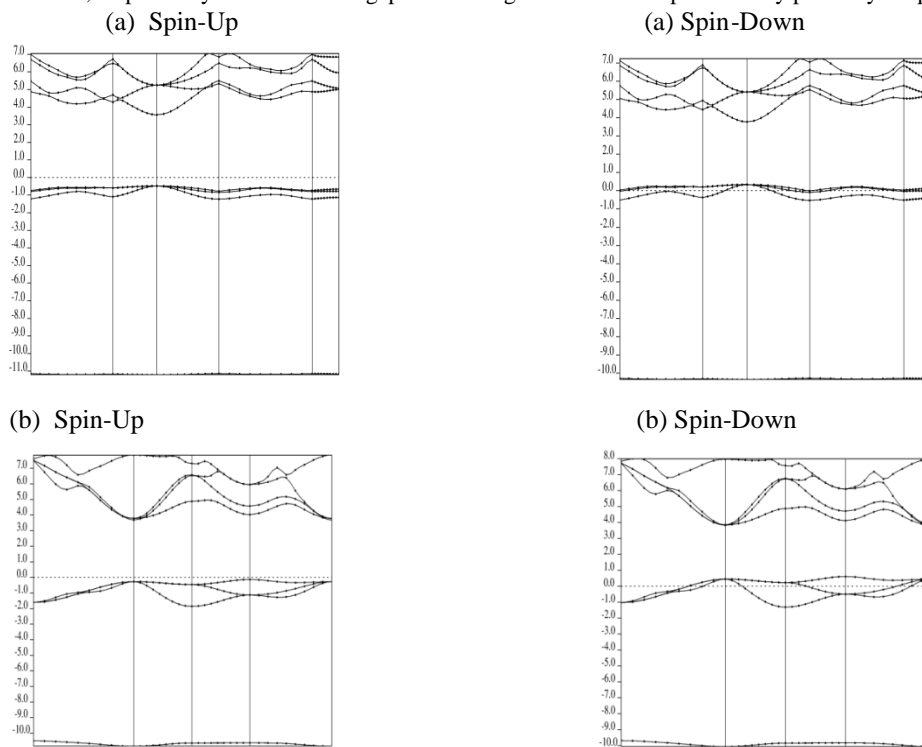


Fig. 3: (a) Band structure of bulk CsSe (NaCl-type), high symmetry directions are from left to right W, L, G, X, W, K. (b) Band structure of bulk CsSe (CsCl-type), high symmetry directions are from left to right R, G, X, M, G.

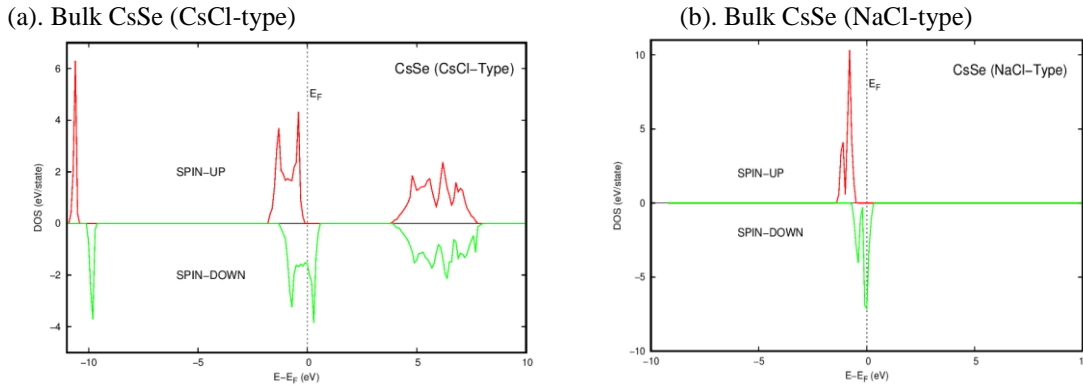


Fig. 4: (a) The total density of states of CsSe CsCl-type structure.
 (b) The total density of states of CsSe NaCl-type structure.

3.2 The (1 1 1) surface study of CsSe CsCl-type structure

To simulate the (1 1 1) surfaces of CsSe in CsCl-type structure, the bulk equilibrium lattice constant 4.36 Å is used. We have chosen the CsCl-type structure for our surface study since it can be observed in Fig. 2 as being the most stable of the two type structures. We adopted a slab model containing 15 atomic layers. In order to avoid the interactions of neighbouring slabs, a 16 Å vacuum is added above the surface. Each layer includes only one kind of atoms, thus there are only two types of terminations which are the Cs (CsCl)-terminated and Se-terminated surfaces for CsCl. To obtain the equilibrium structure of these slabs, we relax the first five layers of the slab and fix the others and then optimize the slabs by the total energy and atomic force calculations. After optimization, we realize that the significant change only occurred in the top three layers. Moreover, previous studies also indicated that the slabs of thirteen to fifteen layers are adequate to study the properties of the surface in some CsSe materials [22, 23]. For the Cs/Se-terminated of CsCl, the surface atomic layers move towards the center of the slabs while the second atomic layers move towards the vacuum. However, the positions of third layer atoms change much less than the surfaces and the second layers, revealing that our model is sufficient for the calculations. Moreso, Fig. 5 shows the spin-polarized atomic DOS of the Cs-terminated (1 1 1) surface for the relaxed slabs of the CsCl structure while Fig. 6 shows the corresponding DOS of Se-terminated surface. The DOS results reveal that the majority carriers are in the spin-up directions. In the obtained results of Fig. 5 and Fig. 6, the spin-up DOS lies below the Fermi level while the spin-down DOS crosses the Fermi level. These shows that the (1 1 1) terminated surface investigation in our current work display half metallic behaviour in CsSe CsCl. In addition, the trend exhibited by the spin-up and spin-down peaks in the DOS terminated surfaces of Fig. 5 and Fig. 6 are indications that the slab model of 15 atomic layers used in this study was large enough for convergence and accuracy of our calculations which has shown half metallicity in agreement with other reported surfaces [4].

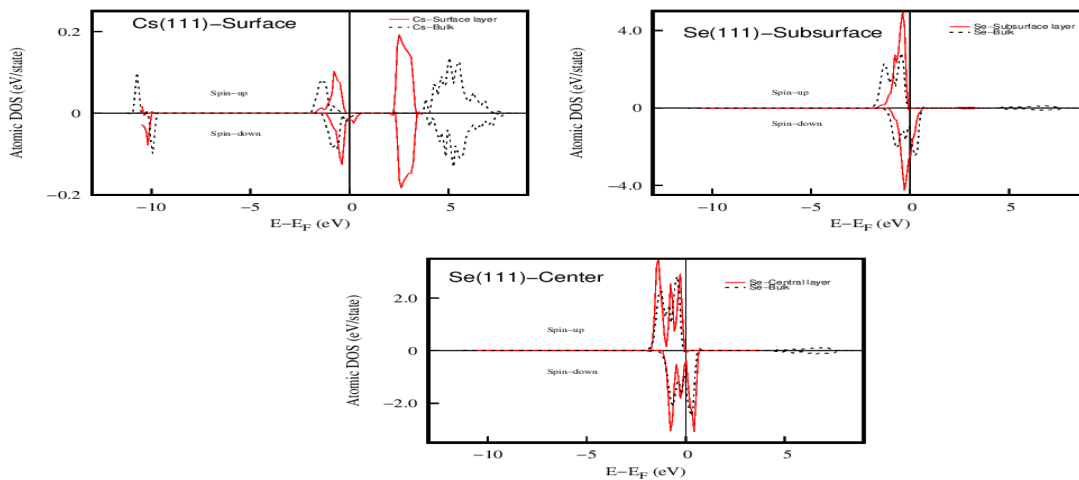


Fig. 5: DOS of Cs-terminated (1 1 1) surface of CsSe.

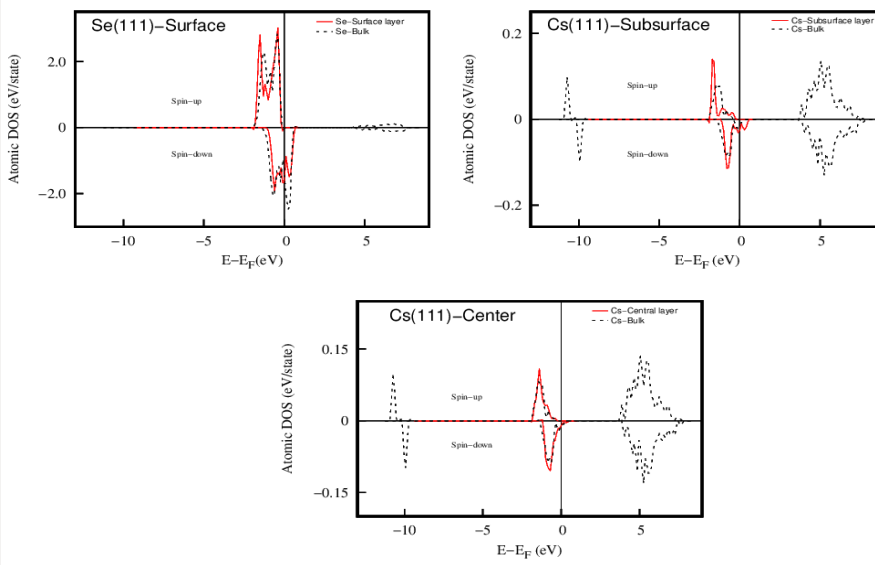


Fig. 6: DOS of Se-terminated (1 1 1) surface of CsSe.

4. CONCLUSION

In conclusion, we have studied the electronic and magnetic properties of bulk CsSe of CsCl- and NaCl-type structures from first-principles calculations. Both structures show that the bulk CsSe exhibit half-metallic (HM) ferromagnetism with large HM band gaps. The surface calculations of CsSe (CsCl-type) from (1 1 1) surfaces of Cs-terminated and Se-terminated results reveals that the surfaces actually retained their bulk HM character. The magnetic moments of atoms at slabs are comparable with those in the corresponding bulk compound. The result reveals that the CsCl-type structure of CsSe shows more stable ground state properties with a magnetic moment of $1 \mu_B/\text{f.u.}$ Our calculations show that the bulk CsSe CsCl structure is more stable than its NaCl-type structure.

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