Half-metallic ferromagnetism in the RbSe and CsTe compounds with CsCl structure: A first-principles study

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Abstract
We investigate the electronic structures and magnetic properties of RbSe and CsTe compounds in CsCl, RS and ZB structures by using first-principles calculation. It is shown that these two compounds exhibit half-metallic ferromagnetism with an integer magnetic moment of 1.00 μB per formula in all the three structures. Total energy calculations indicate the CsCl phase is more stable than the other two phases. We investigate these two compounds with CsCl structure in detail. The ferromagnetism results mainly from the spin-polarization of p states of anion Se (Te) for the two compounds. The half-metallicities of RbSe and CsTe compounds can be preserved up to 2.5% and 0.8% compression of lattice constants with respect to their equilibrium lattices, respectively.

Keywords: Half metallic, First-principles calculation, Magnetic property, Electronic structure

1. Introduction
The new and rapidly developing field of spintronics, in which the spin degree of freedom of the electrons is used in addition to the charge of the electrons, has provided strong motivation to search novel half-metallic materials [1].

Half-metallic magnets, are seen as the most promising candidates of high-spin-polarization materials, because their band structure is metallic in one
of the two spin channels and semiconducting or insulating in the other one, which results in complete (100%) spin polarization of electrons at the Fermi level.

In 1983, de Groot et al. [2] predicted the first half-metallic ferromagnet of the half-Heusler alloy NiMnSb. Since then, a number of new half-metallic materials, such as CrAs, NiMnSb, Co2MnAl, etc. [3, 4], have been initially predicted theoretically by first-principle calculations and later verified by experiments.

Half-metallic properties are present in various perovskite structures [5, 6], Heusler compounds [7, 8, 9, 10], dilute magnetic semi-conductors [11] and metallic oxides [12, 13]. All these materials contain transition metal atoms. Recently, calcium pnictide compounds such as CaP, CaAs, and CaSb with zinc-blende structure were reported to be half-metallic ferromagnets with magnetic moment of 1.0 $\mu_B$. These pnictides do not include any transition-metal atoms and ferromagnetism does not arise from the p-d exchange and the double exchange which are significant in 3d transition-metal compounds [14]. Here the spin polarization of the s and p states makes main contribution to the half-metallic ferromagnetism. This kind of materials is then considered as the sp half-metallic ferromagnets. It is well known that the ferromagnets with large magnetic moment would give rise to more stray flux, which can lead to more energy losses in devices [15]. So sp half-metallic ferromagnets such as CaC and CaN are more meaningful, because they possess small values of magnetic moment (1 or 2 $\mu_B$ per formula unit [16, 17]) compared to those of d half-metallic ferromagnets such as CrAs and CrTe (3 or 4 $\mu_B$ per formula unit [18]). Later, alkali metal pnictides with rocksalt structure [19] and alkali metal LiS, NaS and KS [20] were reported to be half-metallic ferromagnets.

These studies motivated us to search for new sp half-metallic materials which do not contain 3d transition metals. To the best of our knowledge, there is no experimental and theoretical study about the RbSe and CsTe compounds. In the present work, we report the theoretical investigation of the electronic structure and magnetism for ZB, RS and CsCl structures about the two alloys. We predict that the two alloys are HM ferromagnets with an magnetic moment of 1.0 $\mu_B$ in all the three structures. The CsCl structure are energetically the most stable structure for the two alloys.
2. Method of calculations

We have carried out density functional calculation using the scalar relativistic version of the full-potential local-orbital (FPLO) minimum-basis band-structure method \[21, 22\]. For the present calculations, the site-centered potentials and densities are expanded in spherical harmonic contributions up to \( l_{\text{max}} = 12 \). The Perdew-Burke-Ernzerhof 96 of the generalized gradient approximation (GGA) is used for exchange-correlation (XC) potential \[23\]. For the irreducible brillouin zone, we use the \( k \) meshes of 20×20×20 for all the calculations. The convergence criteria of self-consistent iterations is set to 10\(^{-6}\) to the density and 10\(^{-8}\) Hartree to the total energy per formula unit.

3. Results and discussions

CsCl, RS and ZB phases are three different crystal structures. CsCl structure has the space group Pm\( \bar{3} \)m (no. 221); RS has the space group Fm\( \bar{3} \)m (no. 225); ZB has the space group F4\( \bar{3} \)m (no. 216). Rb(Cs) and Se(Te) are located at (0,0,0) and (0.5,0.5,0.5); (0,0,0) and (0.5,0.5,0.5); (0,0,0) and (0.25,0.25,0.25) of these two compounds in the three structures, respectively.

We calculate the ferromagnetic (FM) and paramagnetic (PM) states total energies as a function of lattice constants for RbSe and CsTe in the three structures. The results are shown in Figure. 1. Note that the total energy in the PM state is the relative value to that in the FM state. Moreover, the FM state is more stable than the PM state. From Fig. 1, we find that the FM CsCl structures are energetically the most atable structures for both RbSe and CsTe compounds.

Table 1 presents the optimized lattice constants and the calculated total magnetic moments per formula unit at equilibrium lattices for the two compounds in the three structures. Half-metallic gaps, the formation and cohesive energies are also listed in Table 1.

The formation energy \((E_f)\) and cohesive energy \((E_c)\) indicating thermal stability of a compound can be calculated using the following formulas:

\[
E_f = E_{\text{tot}}^{\text{RbSe}} - [E_{\text{bulk}}^{\text{Rb}} + E_{\text{bulk}}^{\text{Se}}] \tag{1}
\]

\[
E_c = E_{\text{tot}}^{\text{RbSe}} - [E_{\text{iso}}^{\text{Rb}} + E_{\text{iso}}^{\text{Se}}] \tag{2}
\]

where \( E_{\text{tot}}^{\text{RbSe}} \) is the total energy of the RbSe compound, \( E_{\text{bulk}}^{\text{Rb}} \) and \( E_{\text{bulk}}^{\text{Se}} \) refers to the total energy per atom of each elemental bulk. \( E_{\text{iso}}^{\text{Rb}} \) and \( E_{\text{iso}}^{\text{Se}} \) are the
energies of an isolated Cs and Se atoms, respectively. It is same for the CsTe compound, just replace Rb or Se by Cs or Te in the relevant position. The negative values of the formation energy and cohesive energy, listed in Table 1 for this two alloys in the three structures, indicate that these two compounds are energetically stable.

The calculated spin-polarized total densities of states (DOS) are plotted in Figure 2 for the RbSe and CsTe in the three structures at their optimized lattice parameters. The total DOS of the RbSe and CsTe compounds in the same types are generally similar in shape. It is clear that there is an energy gap at Fermi level in the spin-up states, while the spin-down states are metallic. The energy gap seen in the spin-up band causes 100% spin polarization at Fermi level and half-metallic ferromagnetism. Non-zero spin flip gap proves that these two compounds with the three structures are true half-metallic ferromagnets.

Since the CsCl structure is energetically the most stable one among the three structures, next we will discuss the properties of RbSe and CsTe in this structure. The values of the valence band maximum (VBM), conduction band minimum (CBM) and band gap are given in Table 2 for the two compounds in CsCl structure. The energy required to create a spin hole at the top of the spin-up valence bands by exciting a spin-up valence band electron into the spin-down conducting bands means the spin flip gap which is equal to the absolute value of the valence band maximum. Figure 3 shows the calculated results of total and partial DOS of RbSe and CsTe in CsCl structure. As for RbSe, the energy region below -8.0 eV consists mainly of Rb-p and Se-s electrons. The density of states near the Fermi level are originated mainly from the Se-p orbitals, with relatively small contribution of the Rb-s and Rb-d states. In the case of CsTe, the energy region below -6.0 eV consists mainly of Cs-p and Te-s electrons. The density of states near the Fermi level are originated mainly from the Te-p orbitals, with relatively small contribution of the Cs-s and Cs-d states. The calculated values of the total and partial magnetic moment of these two compounds in CsCl structure are listed in Table 2. The values of the total magnetic moments are evaluated to be 1.0 $\mu_B$ for the two compounds. The formula $M_{tot} = n - 8$ can be used to calculate the total magnetic moment, where $n$ is the sum of valence electrons per formula unit. For the two compounds, the main contribution to the total magnetic moment comes from the Se/Te atom, while the contribution of Rb/Cs atom is very small.

The band structure of RbSe and CsTe compounds at their optimized lat-
tice constant for the spin-up and spin-down electrons is plotted in Figure. 4 and Figure. 5. Definitely, these two compounds exhibit HM characteristics: the spin-down band structure is metallic, and there is an energy gap in the spin-up band structure. The energy gap can be determined from the difference between the energies of the lowest unoccupied band at the Γ point and the highest occupied band at the M point.

In order to study the stability of the half-metallicity along with the variation of the interatomic distances, we further calculated the total magnetic moment with the contraction of lattice constant (see Figure. 6). From Figure. 6, we can see that the total magnetic moments keep an integer value of $1.0 \mu_B$ per formula unit the lattice constants are contracted to be 4.063 and 4.585 Å for RbSe and CsTe, respectively. The half-metallicities of RbSe and CsTe can be preserved up to 2.5% and 0.8% compression of lattice constants with respect to their equilibrium lattices, respectively. In addition, we also reveal that RbSe and CsTe are still HM when their lattice constants are expanded appropriately. The changes of magnetic moments for RbSe and CsTe compounds under pressure are given in Figure. 7. As can be seen from it, the magnetic moments keeps $1.0 \mu_B$ when pressure in the range from 0 to 2.12 GPa and 0 to 0.29 GPa for RbSe and CsTe compounds, respectively.

4. Conclusions

In conclusion, we have used first-principle FPLO method to investigate the electronic structures and magnetic properties of RbSe and CsTe compounds with CsCl, RS and ZB structures. This two compounds exhibit the half-metallic character with magnetic moment of $1.0 \mu_B$ in all the three structures. These ferromagnetic compounds do not include and 3d transition metal element and the magnetism mainly arises from the spin polarization of the Se-p/Te-p states. The compounds with CsCl structure are energetically more stable than the other two structures, which makes them more promising materials for future spintronic applications.
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Table 1: The calculated equilibrium lattice constants, magnetic moments, half-metallic gap ($E_g$), formation ($E_f$) and cohesive ($E_c$) energise for the RbSe and CsTe compounds with the three different structures.

| Compounds     | a (Å) | m ($\mu_B$) | $E_g$ (eV) | $E_f$ (eV) | $E_c$ (eV) |
|---------------|-------|-------------|------------|------------|------------|
| RbSe-CsCl     | 4.167 | 1.00        | 0.06       | -1.92      | -5.50      |
| RbSe-RS       | 7.087 | 1.00        | 0.30       | -1.68      | -5.26      |
| RbSe-ZB       | 7.908 | 1.00        | 0.57       | -1.39      | -4.97      |
| CsTe-CsCl     | 4.621 | 1.00        | 0.02       | -1.61      | -5.02      |
| CsTe-RS       | 7.874 | 1.00        | 0.21       | -1.37      | -4.77      |
| CsTe-ZB       | 8.794 | 1.00        | 0.41       | -1.10      | -4.50      |
Table 2: Valence band maximum (VBM), conduction band minimum (CBM), band gap and the total and partial magnetic moments for these two compounds in CsCl structure. Rb(Cs) and Se(Te) are represented by the number 1 and 2.

| Compounds | VBM (eV) | CBM (eV) | Band gap (eV) | $M_{tot}$ ($\mu_B$) | $M_1$ ($\mu_B$) | $M_2$ ($\mu_B$) |
|-----------|----------|----------|---------------|---------------------|----------------|----------------|
| RbSe      | -0.06    | 3.40     | 3.46          | 1.00                | -0.011         | 1.011          |
| CsTe      | -0.02    | 3.28     | 3.30          | 1.00                | -0.010         | 1.010          |
Figure 1: Total energy as a function of lattice constant of RbSe and CsTe compounds in the three structures. PM and FM correspond to paramagnetic and ferromagnetic calculations, respectively.
Figure 2: The total density of states for RbSe and CsTe compounds in the three structures at their equilibrium lattice constants.
Figure 3: The total and partial DOS plots of RbSe and CsTe at their equilibrium lattice constants. The zero energy value is in correspondence to the Fermi level. Positive values of DOS represent spin-up electrons, negative values represent spin-down electrons.
Figure 4: Spin-up and spin-down band structure for RbSe at the equilibrium lattice constant. Arrows ↑ and ↓ represent the spin-up and spin-down states respectively.
Figure 5: Spin-up and spin-down band structure for CsTe at the equilibrium lattice constant. Arrows $\uparrow$ and $\downarrow$ represent the spin-up and spin-down states respectively.
Figure 6: Total magnetic moments per formula unit as a function of lattice constants for RbSe and CsTe. The dashed lines indicate the equilibrium lattice constants.
Figure 7: The changes of magnetic moments of RbSe and CsTe under pressure, zero pressure is in correspondence to equilibrium lattice constants.