First principles study on d^0 half-metallic properties of full-Heusler compounds $RbCaX_2$ (X = C, N, and O)*

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A first-principles approach is employed to study the structural, electronic, and magnetic properties of $RbCaX_2$ (X = C, N, and O) full-Heusler compounds. It is observed that $RbCaN_2$ and $RbCaO_2$ are new d^0 half-metals with an integer magnetic moment of 3 μ_B and 1 μ_B in their ferrimagnetic ground states, respectively, while $RbCaC_2$ is a common metallic compound. Analysis of the density of states of these compounds indicates that the magnetic moment and furthermore, the half-metallicity primarily originate from the spin-polarization of the p-like states of N and O atoms. The half-metallic (HM) gaps of $RbCaN_2$ and $RbCaO_2$ are notably large; thus, the half-metallicity is robust against lattice distortion. Such materials are suitable to be grown on various semiconductor substrates. In addition, for $RbCaN_2$ and $RbCaO_2$, four possible terminations of the surface are also calculated.

Keywords: d^0 half-metallicity, electronic structure, full-Heusler compound

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1. Introduction

Different from the conventional half metallic materials, d electrons provide the primary magnetic moments for transition metals.[1–5] In recent years, as a new class of potential materials in spintronic devices, considerable attention has been devoted to 100% spin-polarization in systems without transition. This new class of materials is usually called sp or d^0 half metallic materials. From an application point of view, these materials are very promising; d^0 half-metallic materials exhibit many interesting features, such as a rather large HM gap and a high Curie temperature, and are robust to the change of the lattice parameter.

A first-principles investigation of the d^0 half-metallic in ZB-CaP, CaAs, and CaSb has been proposed by Kusakabe *et al.*[6] The magnetic order of calcium pnictides is carried by the p-electrons without any direct involvement of the d-electrons. Since then, many studies with different methods on d^0 half-metallic materials with a zinc–blende structure were performed, such as I–V, II–V, and II–IV compounds.[7–12] In detail, on the basis of *ab initio* calculations employing the density functional theory (DFT), Sieberer *et al.*[7] predicted that all I/II–V compounds have a tendency toward a ferromagnetic ground state. Furthermore, using the mean-field approximation and random-phase approximation, Gao *et al.*[8,9] predicted that ZB–CaC, SrC, and BaC exhibit robust d^0 half-metallic ferromagnetism with Curie temperatures higher than room temperature. Additionally, in several studies, alkali and alkaline earth metals with C/N/O-elements in various structures were also predicted to be HM materials.[13–18]

Moreover, due to their high Curie temperature T_c, high magnetic moments, and their ability to be easily synthesized in reality, Heusler compounds[19] have also attracted considerable research interest in the spintronic field. Until now, to the best of our knowledge, there have only been a few predictions in the field of d^0 half-metallic materials based on the Heusler structure. Furthermore, a very large pool of interesting materials is waiting for exploration. Chen *et al.*[20] and Malsawmtluanga *et al.*[21] reported that GeKCa and SnKCa were d^0 half-metallic materials in the half-Heusler structure with magnetic moments of 1 μ_B per formula unit. Białek *et al.*[22] have investigated the surface properties of GeKCa and SnKCa by first principle calculations and showed that their bulk half-metallicity is destroyed at the surfaces, terminated with metal atoms. Umamaheswari *et al.*,[23,24] Lakdja *et al.*,[25,26] Rozale *et al.*,[27,28] and Wei *et al.*[29] also predicted ferromagnetism on the half-Heusler $RbSrX$ (X = C, Si, and Ge), $XCsBa$ (X = C, Si, and Ge), $XCaC$ (X = Li and Na), and $XRbCs$ (X = N, P, and As).

Recently, the bulk and surface half-metallicity of full-Heusler compounds $KCaX_2$ (X = C, N, and O) have been investigated by Rozale *et al.*[30] and Białek *et al.*,[31] respectively. Furthermore, Umamaheswari *et al.* have predicted $RbCaN_2$ and $RbCaO_2$ to be HM materials.[32] However, the effects of the lattice parameters on the electronic structure and the surface properties of the materials were neglected in the discussion. The origin of the magnetism, especially the

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half-metallicity, should be explained in a more detailed way based on the electronic arrangement. In this paper, we calculated the electronic structures and magnetic properties of the RbCaX_2 compounds in the full-Heusler structure. Our calculations show that the $RbCaN_2$ and $RbCaO_2$ compounds are both typically half-metallic materials with a large HM gap. In addition, the stability of the half-metallicity and the d^0 surface half-metallic properties of the materials, which were neglected in the discussion of Umamaheswari's work, have been addressed based on the electronic structures. The origins of the magnetism and half-metallicity have been discussed in detail based on the electronic arrangement.

2. Computational details

The CASTEP code was used to calculate the band structures, density of states (DOS), and the total energy. The CASTEP code is based on the density functional theory (DFT) plane-wave pseudo-potential method.[33,34] During our calculations, the ultrasoft pseudo-potential[35] was used to describe the interactions between the valence electrons and the atomic core, and the exchange–correlation potential was dealt with by the generalized-gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerh (PBE).[36,37] The cut-off energy of the plane wave basis set is 450 eV for all of the cases. For the Brillouin zone integration, we use $13\times13\times13$ k meshes for the bulk $RbSrN_2$ and $10\times10\times1$ k meshes for the (001) surfaces, respectively. The calculations continue to ensure good convergence until the energy deviation is less than 1×10^{-6} eV/atom. The (001) surfaces of $RbCaN_2$ and $RbCaO_2$ were studied by adopting a slab model that included 11 atomic layers for both, which were terminated. One 15-Å vacuum was applied to avoid the interaction of adjacent slabs.

3. Results and discussion

From the structural point of view, Heusler compounds (molecular formula X_2YZ) have two possible structures, namely, a Cu_2MnAl-type structure and an $HgCu_2Ti$-type structure. In the former, the atomic sites are as follows in Wyckoff coordinates: X(A) (0, 0, 0), Rb(B) (1/4, 1/4, 1/4), X(C), (1/2, 1/2, 1/2), and Ca(D) (3/4, 3/4, 3/4), and in the latter, X(A) (0, 0, 0), X(B) (1/4, 1/4, 1/4), Rb(C) (1/2, 1/2, 1/2), and Ca(D) (3/4, 3/4, 3/4). The two possible prototype structures for crystallization of the full-Heusler compounds Cu_2MnAl and Hg_2CuTi are displayed in Figs. 1(a) and 1(b). To find the more favorable structure in RbCaX_2, the total energy is minimized according to two possible prototype structures, as shown in Fig. 2. It can be observed that all of the compounds have a lower total energy in the Cu_2MnAl-type structure than in the Hg_2CuTi-type structure at the equilibrium lattice constant. Thus, from the point of view of the total energy, the Cu_2MnAl-type structure is energetically more favorable for RbCaX_2. The achieved equilibrium lattice constants are 6.64 Å, 6.47 Å, and 6.34 Å for RbCaX_2 (X = C, N, and O) with the Cu_2MnAl-type structure, respectively.

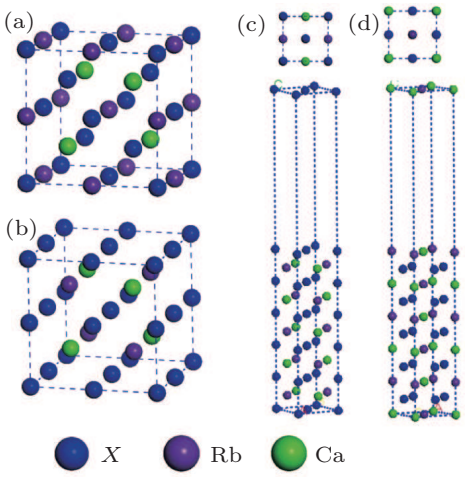


Fig. 1. (color online) (a) and (b) Possible prototype structures of crystallization for the full-Heusler compounds: the Cu_2MnAl-type and Hg_2CuTi-type. (c) and (d) Top and side views of eleven layer surfaces of RbCaX_2: (c) X-terminated surface, and (d) Rb–Ca terminated surface.

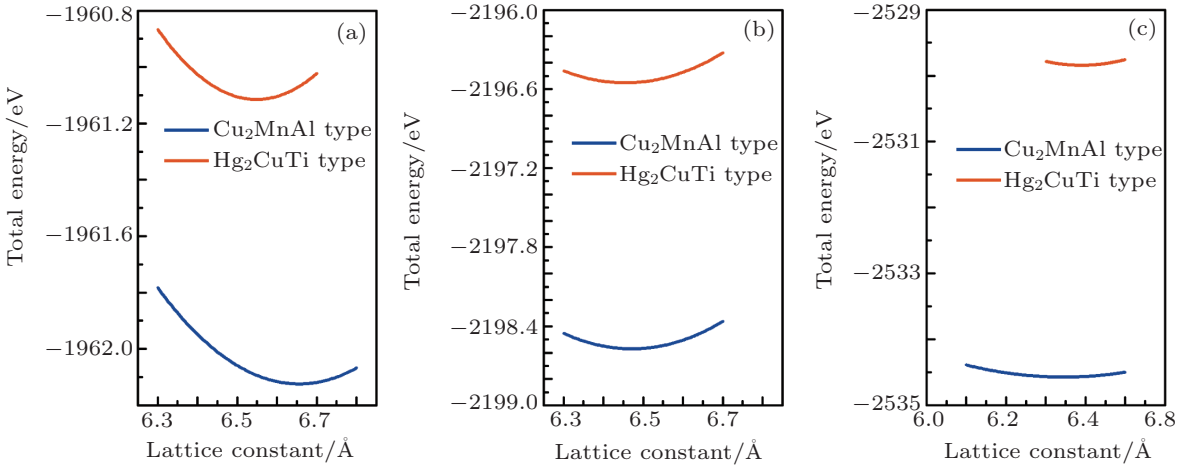


Fig. 2. (color online) The calculated total energies as a function of the lattice constants for $RbCaC_2$ (a), $RbCaN_2$ (b), and $RbCaO_2$ (c) with Hg_2CuTi-type and Cu_2MnAl-type structures.

Note that not all of the Heusler alloys can be synthesized and form a stable phase. To examine whether the Cu_2MnAl-type $RbCaX_2$ compounds can be synthesized in the experiment and the phase stability, the formation energy $E_{formation}$ was calculated by subtracting the sum of the equilibrium total energies for constituent elements from the equilibrium total energies of the corresponding compound under current study. Using the formula: $E_{formation} = (E_{tol}-2E_X-E_{Rb}-E_{Ca})$, we find that the $E_{formation}$ of the $RbCaN_2$ and $RbCaO_2$ compounds are -1.39 eV and -0.83 eV, respectively; however, the $E_{formation}$ of the $RbCaC_2$ compound is 5.73 eV. Note that the negative eV indicates that the compound is energetically stable. Thus, it is possible to synthesize the $RbCaN_2$ and $RbCaO_2$ compounds with Heusler structure experimentally.

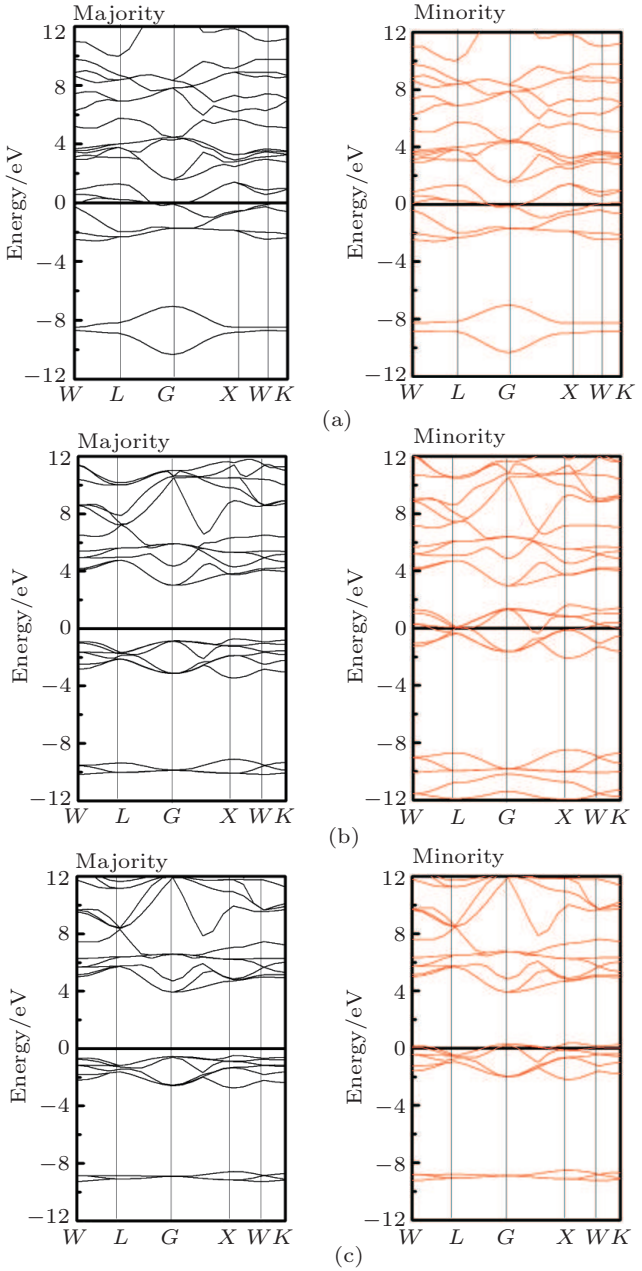


Fig. 3. (color online) Majority-spin and minority-spin band structures of $RbCaC_2$ (a), $RbCaN_2$ (b), and $RbCaO_2$ (c).

The electronic structures of the $RbCaX_2$ compounds along the main symmetry directions in the irreducible Brillouin zone are shown in Fig. 3. For $RbCaC_2$, we can see that both the majority- and minority-band structures show a metallic overlap with the Fermi level (E_f), which indicates that $RbCaC_2$ is a common metallic material at its own equilibrium lattice constant. However, for $RbCaX_2$ (X = N and O), the Fermi levels are located at a band gap in the majority spin direction and have an intersection with the valence bands in the minority spin direction, which indicates that the $RbCaX_2$ (X = N and O) compounds are half-metallic materials. We can see that the energy gap in these compounds is an indirect band gap (G–X) and that the indirect band gap is equal to 3.71 eV and 4.39 eV for $RbCaN_2$ and $RbCaO_2$, respectively. The spin-flip gaps (HM gap), which are the minimum energy required to flip a minority-spin electron from the valence band maximum edge to the majority-spin Fermi level, are the most proper indication of the half-metallicity of a material.[37] The width of the HM gaps are E_{HM-gap} ($RbCaN_2$) = 0.71 eV and E_{HM-gap} ($RbCaO_2$) = 0.49 eV, respectively. This value is quite a lot larger than most of the half-metallic Heusler compounds with 3d transition metals; it is also larger than the previously d^0 half-metallic Heusler compounds $KCaN_2$ (0.16 eV) and $KCaO_2$ (0.30 eV), which indicates that the half-metallicity of the $RbCaX_2$ (X = N and O) compounds is very stable.

Figure 4 shows the calculated total and partial density of states (DOS) of the $RbCaX_2$ (X = N and O) compounds to further understand the origin of the magnetism and half-metallicity. In a range of -4 eV$\sim$ 2 eV/-4 eV$\sim$ 1 eV, the DOS of the Rb and Ca atoms with s, p, and d orbitals have little distribution for both spin channels. The states around -4 eV$\sim$ 2 eV/-4 eV$\sim$ 1 eV can mainly be traced to the covalent hybridization between the p-states of N(A)/O(A) and N(C)/O(C). The origin of the gap is similar to those of sp HM ferromagnets of alkaline-earth nitrides and carbides and mainly attributed to the covalent hybridization between the p-states of N(A)/O(A) and N(C)/O(C).[8,9] The calculated total magnetic moment of the $RbCaN_2$ ($RbCaO_2$) compound is 3 μ_B (1 μ_B). This can be explained from the electronic arrangement: there are 13 (15) valence electrons in $RbCaN_2$/$RbCaO_2$ compounds (Rb: $5s^1$; Ca: $4s^2$; N: $2s^2$, $2p^3$; O: $2s^2$, $2p^4$) that contribute to the bond formation and magnetism. In detail, 4 valence electrons occupy the N-2s and O-2s states in the lowest energy states. 6 of the remaining 9 (11) valence electrons occupy the majority spin p states of N/O, which results in the 6 fully filled majority spin bands. The remaining 3 (5) valence electrons partially occupy the 6 lowest minority spin bands by leaving 3 (1) holes, which are responsible for the magnetic moments of 3 μ_B (1 μ_B), respectively. Further, for $RbCaN_2$/$RbCaO_2$, the atomic magnetic moments are 1.62 μ_B/0.56 μ_B for N(A and C)/O(A and C), -0.16 μ_B/-0.08 μ_B for Rb(B), and -0.08 μ_B/-0.04 μ_B for Ca(D), respectively. The magnetic moment of the N(A and C)/O(A and C) atom is antiparallel

to that of the Rb(B) atom, which is a typical characteristic of half-metallic (HM) ferrimagnets.

Here, we will study the robustness of the half-metallicity with respect to the lattice constant. The surroundings (e.g., the temperature) and the preparation methods (e.g., the growth of thin film materials) usually make the lattice of the half-metallic materials change and cause the lattice constant to deviate from the ideal one, which may affect their half-metallicity. The DOSs at different lattice constants were investigated for the $RbCaN_2$/$RbCaO_2$ compounds. As shown in Fig. 5, we find that the electronic structures are similar to those at the equilibrium lattice constants, and both the valence band and conduction band shift upwards with the decrease of the lattice constants. From the figure, it can be observed that the half-metallicity could be kept until the lattice constants are compressed to a critical value of 5.37 Å and 4.94 Å for the $RbCaN_2$/$RbCaO_2$ compounds, respectively. This means that the half-metallicity is preserved up to a contraction of the lattice constant by 17% and 22% for $RbCaN_2$/$RbCaO_2$, respectively.

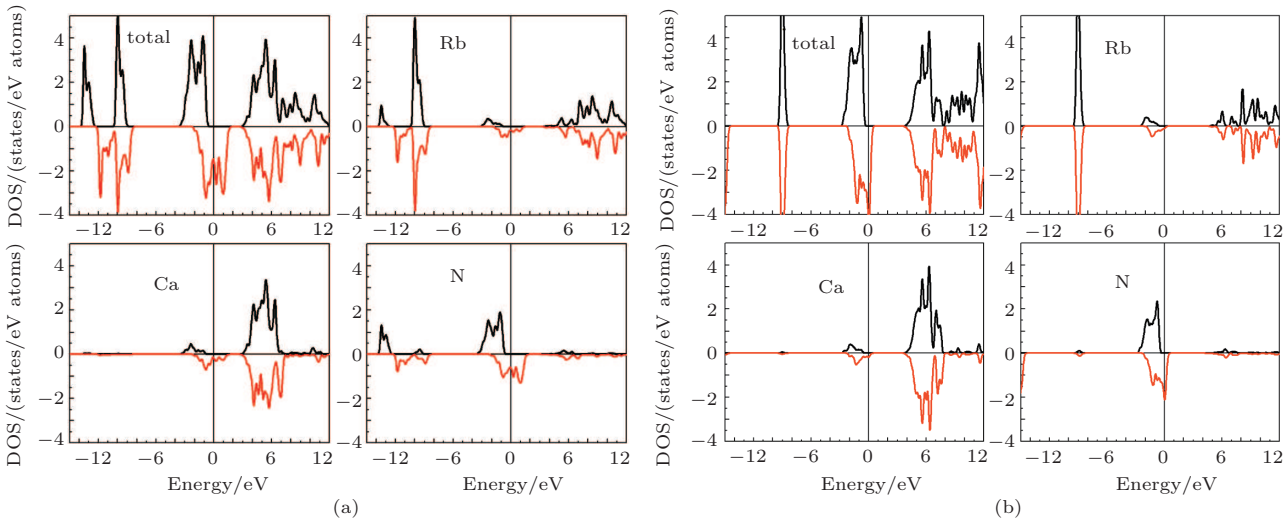


Fig. 4. (color online) The calculated total and partial DOS plots for $RbCaN_2$ (a) and $RbCaO_2$ (b).

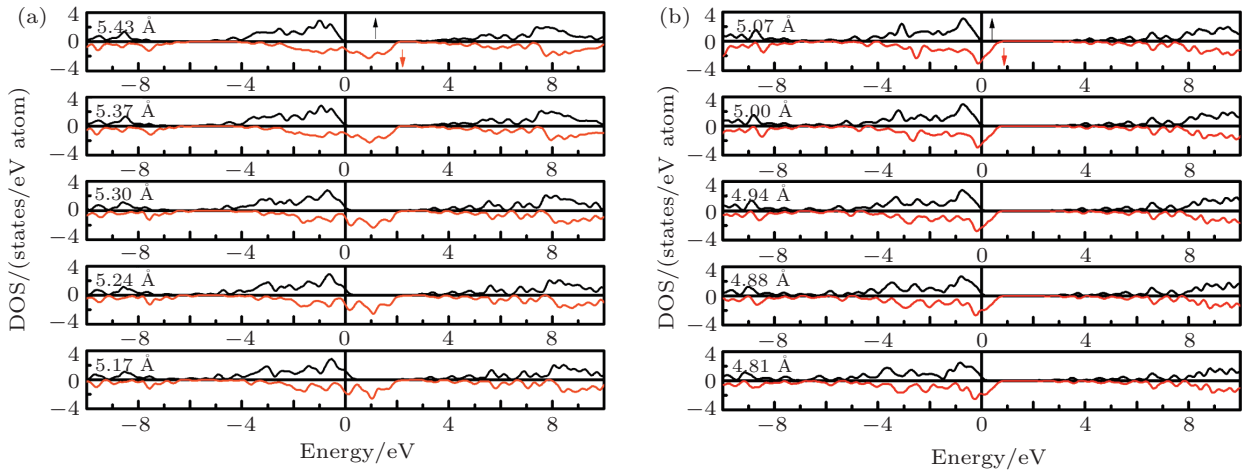


Fig. 5. (color online) The calculated total DOS at different lattice constants for $RbCaN_2$ (a) and $RbCaO_2$ (b).

Considering the application of these compounds in electronic devices, one cannot forget a description of the surface properties of the materials. The electronic properties of surfaces usually differ from those of the bulk. How much different the surface properties are from those of the bulk depends on, among other factors, surface termination. The surface usually destroys the half-metallicity and decreases the spin polarization[22,31] in practical spintronic applications. The corresponding crystal structures are also shown in Figs. 1(c) and 1(d). Finally, we calculated the surface electronic structure to check the half-metallic properties of the $RbCaN_2$/$RbCaO_2$ compounds, as shown in Figs. 6 and 7. For $RbCaN_2$, we can see that the N terminated (001) surface is still half-metallic; however, the half-metallic gap in the majority spin direction is destroyed by the Rb–Ca terminated (001) surface. The calculated spin polarization ratio is 66.7% at the Rb–Ca terminated (001) surface and loses the 100% spin polarization rate of the bulk state. However, for $RbCaO_2$, both the O and Rb–Ca terminated (001) surfaces are still half-metallic.

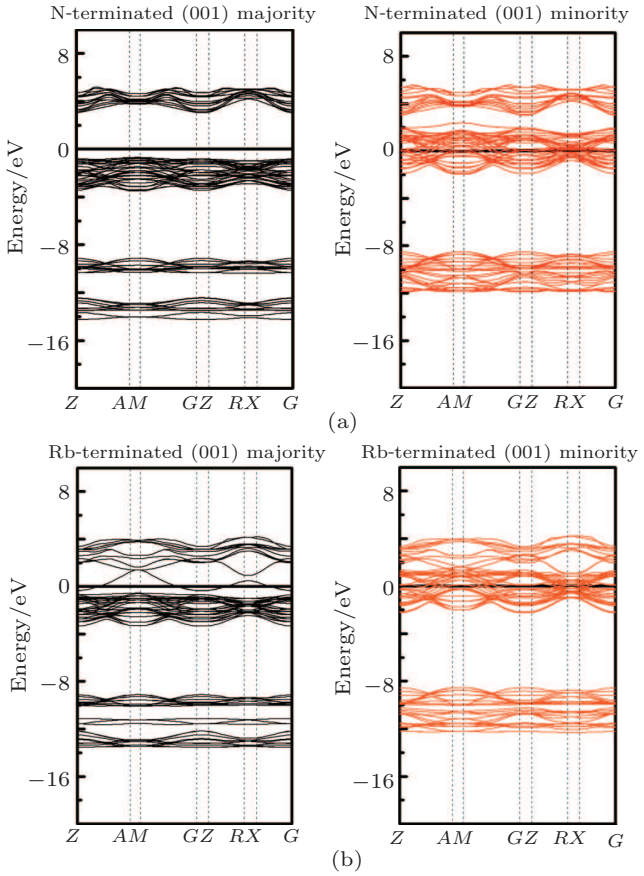


Fig. 6. (color online) Majority-spin and minority-spin band structures of the N and Rb–Ca terminated (001) surfaces of the $RbCaN_2$ compound.

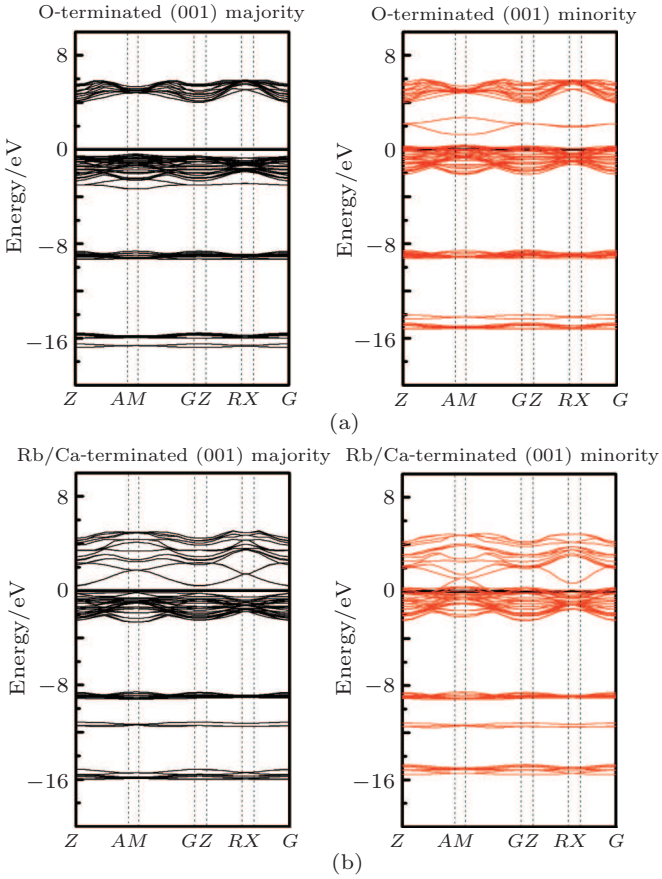


Fig. 7. (color online) Majority-spin and minority-spin band structures of the O and Rb–Ca terminated (001) surfaces of the $RbCaO_2$ compound.

4. Conclusions

To summarize, we have studied the magnetic and half-metallic properties of the $RbCaX_2$ (X = C, N, and O) full-Heusler alloys. d^0 half-metallicity has been predicted in the Cu_2MnAl-type $RbCaN_2/RbCaO_2$ compounds by first-principles calculations, while $RbCaC_2$ is a common metallic compound. $RbCaN_2/RbCaO_2$ compounds have quite large HM gaps, and their half-metallicities are not sensitive to lattice expansion and contraction. In the $RbCaN_2/RbCaO_2$ compounds, the magnetic moments of N(A)/O(A) and N(C)/O(C) atoms are the same and antiparallel to that of the Rb(B) atom; thus, $RbCaN_2/RbCaO_2$ are HM ferrimagnets. The magnetic moments of $RbCaN_2/RbCaO_2$ are 3 μ_B and 1 μ_B, respectively, and they mainly originate from the spin-polarized p-like states of N and O atoms. For the four possible terminations of the surface, the half-metallicity is lost in the case of the Rb–Ca terminated (001) surface of $RbCaN_2$.

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