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Research articles

First-principles study of half-metallic properties in RbCaNZ (Z = O, S, and Se) quaternary Heusler compounds

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ABSTRACT

On the basis of first principles calculations, the electronic structures and magnetic properties of quaternary Heusler alloys RbCaNZ (Z = O, S, and Se) were studied. The negative formation energies indicated that all these compounds were thermodynamically stable and thus may be experimentally synthesized at appropriate conditions in the future. The results showed that Y_I structure was the most favorable configuration among the three possible structures. All compounds were found to be half-metallic ferromagnets. The characteristic of energy bands and origin of half-metallicity were also verified. The total magnetic moments of RbCaNZ (Z = O, S, and Se) compounds were obtained $2\mu_B$ per formula unit, which were in an agreement with Slater-Pauling rule ($M_{tot} = 12 - Z_{tot}$). Half-metallicity was preserved at ranges of 5.06–8.36 Å, 5.96–8.81 Å, and 6.13–8.73 Å for RbCaNO, RbCaNS, and RbCaNSe compounds, respectively, which show that these quaternary Heusler compounds may be potential candidates in spintronic applications.

1. Introduction

Nowadays, materials with a high spin polarization at the Fermi energy are interesting for spintronic applications due to their potential to be used in devices with improved magnetoresistance and low signal-to-noise ratio. In particular, half-metallic (HM) ferromagnets in which one of the two spin channels is metallic and the other is semiconducting or insulating, leading to 100% spin polarization at the Fermi level, are interesting and favorable in spintronics. First, half-metallicity was predicted in NiMnSb half-Heusler alloy by de Groot et al. in 1983 [1]. Several numbers of new HM materials have been theoretically predicted in Heusler alloys [2–7], ferromagnetic metallic oxides [8–10], dilute magnetic semiconductors [11,12], and zincblende transition-metal pnictides and chalcogenides [13–17]. The high spin-polarizations have also been experimentally measured for some of the alloys [18–23]. Studies mainly have focused on Heusler alloys due to their large magnetization, relatively easy synthesis, and high Curie temperature. The Heusler structure consists of four interpenetrating face-centered-cubic (FCC) lattices with four unique crystal sites namely A(0,0,0), B(1/4,1/4,1/4), C(1/2,1/2,1/2), D(3/4,3/4,3/4) in Wyckoff coordinates. X_2YZ Heusler compounds are characterized with two different crystallization types [24,25]. In $AlCu_2Mn$-type structure, two X atoms are located at A and C sites, while Y and Z atoms are placed at B and D sites, respectively. In $CuHg_2Ti$-type structure, two X atoms are located at A and B sites, whereas Y and Z atoms are located at C and D sites, respectively.

However, in some ternary Heusler compounds, disordering effects usually destroy half-metallicity and influence the magnetoresistance ratio [24,25]. To overcome this disadvantage, recently, several efforts have been made to investigate the quaternary Heusler alloys XX′YZ (X, X′, and Y are transition metals, and Z is a main-group element) instead of the ternary ones (X_2YZ and XYZ). In these compounds, the valence of X′ is lower than that of X atoms, and the valence of Y element is lower than that of both X and X′. XX′YZ quaternary Heusler compounds crystallize in the LiMgPdSn-type crystal structure [26,27] with $F\bar{4}3m$ symmetry.

In the early studies, many scientists have focused on verification of HM characteristic in quaternary Heusler alloys including magnetic transition-metal elements, such as quaternary Heusler ferromagnets NiFeMnGa and NiCoMnGa [28], NiCoCrGa [29], CoFeCrZ (Z = Ga, Ge, Al, and Si) [30], CoFeTiZ and CoFeVZ (Z = Al, Ga, Si, Ge, As, and Sb) [31], CoFeTiSb [32], and ZrFeTiAl, ZrFeTiSi, ZrFeTiGe, ZrNiTiAl [33], CoMnTiZ (Z = P, As, and Sb) [34], CoRhYZ (Y = Sc, Ti, Cr, and Mn; Z = Al, Si, and P) [35], and CoRuTiZ (Z = Si, Ge, and Sn) [36].

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Until now, there are few studies on d^0 quaternary Heusler systems which do not include transition metals. Compared with the alloys including transition metals with large stray fields, these d^0 materials are more meaningful in real applications because of their smaller magnetic moments. Recently, Du et al. [37] studied the electronic structures and magnetic properties of quaternary alloys KCaNX (X = O, S, and Se) with full-Heusler structure in which all the compounds were found to be HM ferromagnetic materials. Besides, Bouabça et al. [38] investigated the structural, electronic, magnetic, and thermal properties of new quaternary Heusler alloys CsSrCZ (Z = Si, Ge, Sn, P, As, and Sb). Their results showed that CsSrCZ (Z = Si, Ge, Sn) compounds had a nearly HM characteristic and CsSrCZ (Z = P, As, Sb) compounds were true HM ferromagnets. In this regard, we decided to verify HM characteristic in RbCaNZ (Z = O, S, and Se) quaternary Heusler compounds. To the best of our knowledge, there is no study on these alloys in the literature. The computational method is presented in Section 2. Results and discussion are presented in Section 3. A summary of the results is given in Section 4.

2. Computational method

Full potential linearized augmented plane-wave (FPLAPW) method implemented inWIEN2k [39] was employed to study electronic and magnetic properties of RbCaNZ (Z = O, S, and Se) quaternary Heusler alloys. The exchange and correlation potential was treated using generalized gradient approximation (GGA) within the parameterization of Perdew–Burke– Ernzerhof [40]. The muffin-tin sphere radii (R_{MT}) were chosen 2 *a.u.* for Rb, Ca, N, and Z = (O, S, and Se). The basis functions are expanded into the spherical harmonic functions within the muffin-tin sphere and the Fourier series within the interstitial region. For the wave function expansion inside muffin-tin spheres, the maximum value of the orbital momentum (l_{max}) was assumed equal to 10 and the plane wave cut-off (K_{max}) was chosen as $8.0/R_{MT}$ for the expansion of the wave functions in the interstitial region. The largest vector in the charge density Fourier expansion, G_{max}, was chosen to be 12. The separation energy was limited by $-6\,Ry$ value. In the self-consistent calculations, the charge convergence value was set to 0.00001 e.

3. Results and discussion

3.1. Structural properties

XX′YZ quaternary Heusler compounds crystallizing in the LiMgPdSn-type structure are resulted from the X_2YZ ternary Heusler structure when one X atom is substituted by another atom X′. In general, there are three types of nonequivalent configurations for the quaternary Heusler structure XX′YZ: type Y_I such as X (0, 0, 0), X′ (0.25, 0.25, 0.25), Y (0.5, 0.5, 0.5), Z (0.75, 0.75, 0.75); type Y_{II} such as X (0, 0, 0), X′ (0.25, 0.25, 0.25), Y (0.5, 0.5, 0.5), Z (0.75, 0.75, 0.75); and type Y_{III} such as X (0.25, 0.25, 0.25), X′ (0.75, 0.75, 0.75), Y (0, 0, 0), Z (0.5, 0.5, 0.5). For instance, the crystal structure of RbCaNO compound in the three types is shown in Fig. 1. Afterward, the total energy values as functions of unit cell volume for all compounds in three structures were calculated and fitted to the Murnaghan equation of state [41] and the obtained energy-volume curves are shown in Fig. 2. Here, only the results for ferromagnetic (FM) state are shown because antiferromagnetic (AFM) and nonmagnetic (NM) states have relatively high energy differences compared with FM state. According to Fig. 2, the Y_I structure is energetically favorable than other two structures indicating that Y_I structure is the ground state structure in the three compounds. Hence, further results mainly focused on this structure. Furthermore, the bulk equilibrium parameters including the lattice parameter, bulk modulus, and derivative of bulk modulus are listed in Table 1 for RbCaNZ (Z = O, S, and Se) compounds in three structures. As can be seen, the lattice constants increase with increasing the covalent radius of Z anion from O (6.21 Å) → S (6.68 Å) → Se (7.04 Å) in the three structures [37].

The value of bulk modulus (B) is a criterion of incompressibility of a substance or resistance against compression. It can be formally defined by equation:

$$B = -V\frac{dP}{dV} \tag{1}$$

where P is pressure, V is volume, and dP/dV denotes the derivative of pressure with respect to volume. According to Table 1, with increasing lattice constant along O → S → Se, B decreases indicating that compressibility increases and the substance gets softer. In fact, the bulk modulus inversely relate to the equilibrium volume of unit cell (V_0) as $B \propto V_0^{-1}$.

Derivative of bulk modulus (B') is a dimensionless parameter. This parameter for RbCaNZ (Z = O, S, and Se) alloys is higher than 4. If B' is greater than 4, the material becomes softer with increasing the compression.

The cohesive energy (E_C) of a solid is the energy required to break the atoms of the solid into isolated atomic species and is defined as:

$$E_C^{RbCaNZ} = E_{tot}^{RbCaNZ} - (E_{Rb} + E_{Ca} + E_N + E_Z) \qquad ; Z = \text{O, S, and Se} \tag{2}$$

where E_{tot}^{RbCaNZ} is the equilibrium total energy of RbCaNZ compounds, and E_{Rb}, E_{Ca}, E_N, and E_Z are the total energies of the atomic components in the isolated state. The relatively high cohesive energies (Table 1) for all compounds mean that RbCaNZ (Z = O, S, and Se) alloys are stable due to the high energy of the chemical bonds. Fur-

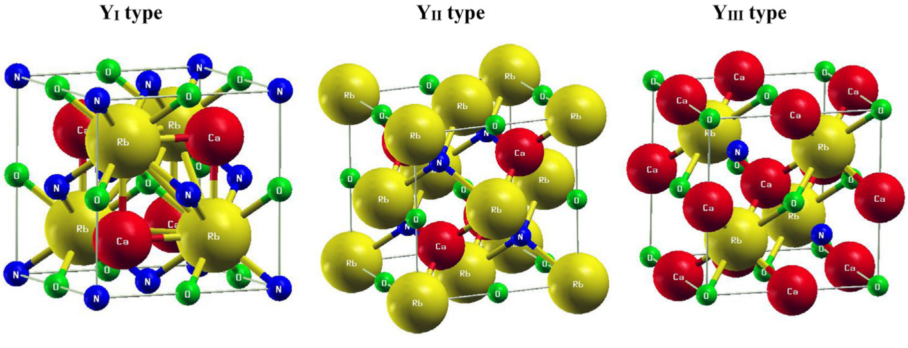

Fig. 1. Crystal structure of RbCaNO quaternary Heusler compound in the three structures.