Journal of Magnetism and Magnetic Materials 350 (2014) 167–173

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Ab-initio investigation of half-metallic ferromagnetism in half-Heusler compounds XYZ (X=Li, Na, K and Rb; Y=Mg, Ca, Sr and Ba; Z=B, Al and Ga)

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ARTICLE INFO

Article history:
Received 16 May 2013
Received in revised form
30 August 2013
Available online 16 September 2013

Keywords:
Half-Heusler alloys
Half-metallic ferromagnetism
First principles calculation
TB-LMTO method

ABSTRACT

The structural, electronic and magnetic properties of XYZ compounds (X=Li, Na, K and Rb; Y=Mg, Ca, Sr and Ba; Z=B, Al and Ga) in half-Heusler phase are studied by first principles calculations within density-functional theory. From the spin-polarized calculations, it is found that the compounds XCaB, XSrB, XBaB and LiBaGa are ferromagnetic and metallic whereas the other compounds XMgB, XYAl and XYGa except LiBaGa are non-magnetic and metallic. Among the compounds which exhibit ferromagnetism, XCaB and XSrB (X=Li, Na, and K) exhibit half-metallic (HM) property with an integer magnetic moment of 2.0μ_B per formula unit at their equilibrium volume. However, other compounds such as RbCaB, RbSrB and XBaB (X=Li, Na, K and Rb) are so-called nearly HMFs and exhibit HMF property at their expanded volume. The magnetic moment mainly originates from the strong spin-polarization of *np* electrons of Z (B and Ga) atoms and partial involvement of *nd* electrons of Y atoms. The robustness of half-metallicity against the lattice constant is also calculated. The absence of transition-metal atom makes these compounds important model systems for the study of origin and properties of half-metallic ferromagnetism of *s–p* electron systems.

1. Introduction

Rapid development of modern material science has intensified the research interest in the field of spintronics. One of the most important materials for spintronics is half-metallic materials including half-metallic ferromagnets (HMFs) and half-metallic antiferromagnets. In HMFs, one of the two spin channel is semiconducting with a gap at the Fermi level E_F, leading to 100% spin-polarization at E_F, whereas the other one behaves like a metal. The concept of HM ferromagnet was first predicted by de Groot et al. [1] on the basis of band structure calculations for NiMnSb and PtMnSb half-Heusler alloys. Since then, several different classes of HM ferromagnets have been predicted theoretically or confirmed experimentally such as full and half-Heusler alloys [2], transition metal oxides [3], perovskite manganites [4], zinc-blende (ZB) transition-metal pnictides [5,6], and transition-metal chalcogenides [7,8]. Transition metal pnictides (CrAs) and chalcogenides (CrTe) crystallize in NiAs phase, however they exhibit HM property in ZB phase. ZB CrAs, CrSb and MnAs films are fabricated on GaAs substrate using molecular-beam epitaxy method. These studies inspired many research groups to search for existence of HMFs in other possible structures.

Nowadays Heusler compounds have attracted great interest in the field of spintronics due to their high curie temperature and the structural similarity to conventional semiconductors with ZB structure. The theoretical and experimental studies on Co_2, Mn_2 and Fe_2 based full-Heusler compounds showed that they exhibit half-metallic property [9–11]. Also half-Heusler compounds, like XMZ (X=Fe, Co and Ni; M=Ti, V, Nb, Zr, Cr, Mo and Mn; Z=Sb and Sn) [12], NiCrZ (Z=Al, Ga, In, P, As, Sb, S, Se and Te) [13–15] and hypothetical NiVM (Z=P, As, Sb, S, Se and Te) [16] have been predicted to be HMFs from first principles calculations. In the above mentioned HMFs, the magnetic moment is mainly due to the presence of localized *d* electrons of transition metals.

Recently, several studies have been analyzed and proposed an unusual class of FM materials excluding transition metals and rare earth elements, increasing the research interest in the field of spintronics. For example, Kenmochi et al. [17,18] have reported that C and N doped AeO (A=Mg, Ca, Sr and Ba) compounds shows HMF's. Kusakabe et al. [19] and Geshi et al. [20] analyzed the HMF property of calcium pnictides in ZB structure. Several studies have been carried out for alkali and alkaline earth metal compounds with *sp* elements e.g., I–V, II–V, I–VI, I–IV and II–IV compounds in ZB, rocksalt, CsCl and wurzite structures [21–26] and these class of compounds are named as *sp* or d^0 HMFs. These facts motivated us to search for new HMFs in half-Heusler alloys without transition metals. To the best of our knowledge there has been a little work on HMFs with Heusler structure excluding transition metal.

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http://dx.doi.org/10.1016/j.jmmm.2013.09.019

Recently half-metallic ferromagnetism in half-Heusler compounds such as GeKCa, SnKCa [27], XCsBa (X=C, Si and Ge) [28], SrRbX (X=C, Si and Ge) [29] and $KCaX_2$ (X=C, N and O) [30] have been investigated by first principles calculations.

In this work, the structural, electronic and magnetic properties of XYZ (X=Li, Na, K and Rb; Y=Mg, Ca, Sr and Ba; Z=B, Al and Ga) compounds in half-Heusler structure have been studied using TB-LMTO method. In particular, the half-metallic property of these compounds are investigated by both spin-polarization and non-spin-polarization calculations. The rest of this paper is organized as follows: in Section 2, the computational details of the calculations and crystal structure of half-Heusler compounds are described; in Section 3, the results are discussed. Finally, conclusion is given in Section 4.

2. Method of calculation and crystal structure

Geometry optimization, electronic structure and magnetic properties of XYZ (X=Li, Na, K and Rb; Y=Mg, Ca, Sr and Ba; Z=B, Al and Ga) compounds are performed by tight binding linear muffin tin orbital (TB-LMTO) method within the local spin density approximation (LSDA). A detailed description of this method, including its applications can be found elsewhere [31,32]. Exchange and correlation contributions to both the atomic and crystalline potentials have been included through the von Barth–Hedin scheme [33]. The Wigner-Seitz sphere is chosen in such a way that the atomic sphere boundary potential is minimum and the overlap of the interstitial and atomic sphere remains within the limits of the atomic sphere approximation (ASA). Without disturbing the crystal symmetry, empty spheres are included in appropriate positions to have close packing. In this calculation, we have kept the maximum overlap between atomic spheres as approximately 16%. The density of states (DOS) were calculated by the tetrahedron method. The Brillouin zone (BZ) integration is performed by the usual tetrahedron technique [34]. A mesh of $8\times8\times8$ was taken in the irreducible wedge of Brillouin Zone. E and 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*. Also these compounds are called as half-Heusler or Juza–Nowotny compounds which belong to the class of filled tetrahedral compounds (FTC) [35]. 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 $\mathbf{r_3}=(0.25, 0.25, 0.25)$. The atoms X at $\mathbf{r_1}$ and Y at $\mathbf{r_2}$ form a rocksalt lattice and Z atom is found at $\mathbf{r_3}$ in the centres of tetrahedra formed by X and Y atoms. In general, 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 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, Z atoms are arranged at different positions (r_1, r_2, r_3), (r_3, r_1, $\mathbf{r_2}$) and ($\mathbf{r_2}$, $\mathbf{r_3}$, $\mathbf{r_1}$) respectively. Some experimental studies show that the structure of half-Heusler compounds depend on the atomic disorderness, therefore the investigation of XYZ compounds in the three possible arrangements is necessary. The crystalline structure ($C1_b$) of this type of material is discussed well in literature [36,37].

3. Results and discussion

3.1. Total energy calculation and related properties

In order to determine the equilibrium lattice constants of hypothetical XYZ compounds in half-Heusler phase, the total energy as a function of relative volume for three possible atomic arrangements (α, β and γ) are calculated. It is found that all the compounds are most stable in α-structure than other structures (β and γ). Both the spin-polarization (FM phase) and non-spin-polarization (NM phase) calculations have been performed for the XYZ compounds in the stable α-structure. For illustration, the total energy curve with respect to relative volume of LiCaB in α, β and γ structures and NM and FM phases in cubic α-structure are given in Fig. 1(a–b). The total energy difference between NM and FM phases in α-structure ($\Delta E=E_{NM}-E_{FM}$) is given in Table 1(a–c). The positive value of ΔE indicates that the FM state is more favorable than the NM state in XYB (Y=Ca, Sr and Ba) and LiBaGa compounds, whereas for XMgB, XYAl and XYGa except LiBaGa compounds, ΔE value is zero. In other words, there is no spin-polarization of energy states around the Fermi level in these compounds and they are non-magnetic.

The calculated total energies as a function of relative volume were fitted to the Birch equation of state [38] to obtain the equilibrium lattice constant and bulk modulus. In order to study the stability of these hypothetical compounds, the estimation of formation energy (E_f) of these compounds is very important. It is calculated using the relation $E_f=E_{XYZ}-(E_x+E_y+E_Z)$ where E_{XYZ} is the total energy of compound XYZ and E_x, E_y and E_Z are total energy of pure elemental constituents in the compound XYZ and

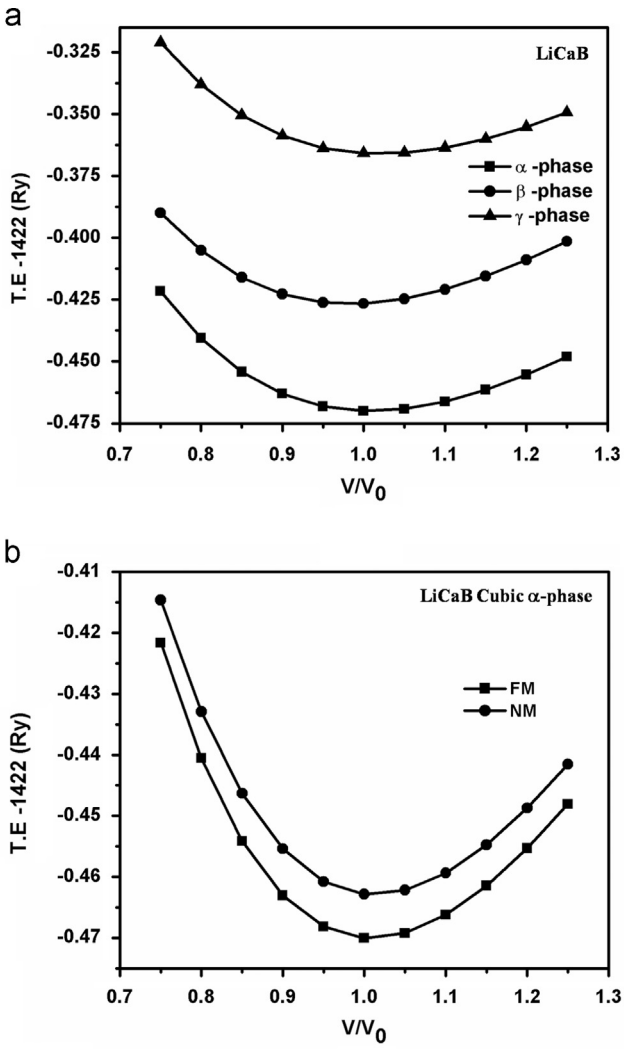

Fig. 1. Total energy per molecule as a function of relative volume for (a) cubic α, β and γ-structure and (b) NM and FM states of cubic α-structure of LiCaB.