Journal of Physics and Chemistry of Solids 112 (2018) 190–199

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

Magneto-electronic, thermal, and thermoelectric properties of some Co-based quaternary alloys

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ARTICLE INFO

Keywords:
Ductile
Grüneisen parameter
Half-metallic
Seebeck coefficient
Spin-polarized

ABSTRACT

In this study, quaternary Heusler alloys CoFeCrZ (Z = Si, As, Sb) were investigated based on the modified Becke–Johnson exchange potential. The electronic structures demonstrated that CoFeCrZ (Z = Si, As, Sb) alloys are completely spin polarized with indirect bandgap and has an integer magnetic moment according to the Slater–Pauling rule. Pugh's and Poisson's ratios showed that these materials are highly ductile with high melting temperatures. The thermal properties comprising the thermal expansion coefficient, heat capacity, and Grüneisen parameter were evaluated at various pressures from 0 to 20 GPa. The Grüneisen parameter values indicated the strong anharmonicity of the lattice vibrations that predominated in these compounds. We also studied the dependency of the thermoelectric transport properties on the temperature, i.e., the thermal conductivity and Seebeck coefficient. These alloys exhibited low lattice thermal conductivity and good Seebeck coefficients at room temperature. The half-metallic structures of these compounds with large band gaps and adequate Seebeck coefficients mean that they are suitable for use in spintronic and thermoelectric device applications.

1. Introduction

In recent decades, quaternary Heusler alloys have attracted much interest due to their excellent properties such as high spin-polarization and half-metallic ferromagnetism, where they have possible uses in spintronic and thermoelectric applications [1–4]. In spintronic applications, magnetic materials with high spin polarization are crucial for improving the performance of spintronic devices such as spin filters, spin injectors, and spin valves [5]. Half-metallic ferromagnets are considered to be the most promising candidates for uses in thermoelectrics, where these materials are highly spin-polarized because their band structure is metallic in one of the two spin channels and semiconducting or insulating in the other, which results in complete (100%) spin polarization of the electrons at the Fermi level [6–11]. In terms of applications, the main prerequisite is that half-metallic ferromagnets should have a high Curie temperature. The Co-based Heusler alloys are of particular interest because they have a reasonably high Curie temperature and varying magnetic moments [12–14]. Co-based Heusler alloys have attracted much attention due to their theoretically predicted half-metallic nature and experimentally observed high-spin polarization values with high Curie temperatures [15,16]. Therefore, these multifunctional alloys can have many more applications compared with other materials. Thus, in this study, we investigated the magneto-electronic and thermoelectric properties of quaternary Heusler alloys.

2. Computational details

In this study, all of the calculations were performed according to the full-potential linearized augmented plane-wave method embedded in WIEN2k [17] based on density functional theory. The density functional theory requires that the total energy E[ρ(r)] is a unique functional of the electron density ρ(r) and the minimization of E[ρ(r)] with respect to ρ(r) yields a set of single-particle-like equations, where their solutions provide the ground-state energy and charge density. The exchange-correlation function was treated using the generalized gradient approximation [18] and modified Becke–Johnson (mBJ) [19] exchange-correlation function. The precise size of the basis set, i.e. the convergence parameter $R_{MT}K_{max}$, was fixed to 7.0. The cut-off energy as the separation between the core and valence states was set to −6 Ry. To ensure self-consistent calculations, 3500 k-points were used in the entire Brillouin zone, which corresponded to 120 k-points in the irreducible wedge of the Brillouin zone. Self-consistent iteration was achieved by convergence of the total energy/cell of the system to less than 0.0001 Ry and the charge difference to less than 0.0001 e/a.u.^{3} per unit cell. The analysis of the transport properties involved a bulky *k*-point mesh to obtained more acceptable results, so a 50 × 50 × 50 *k*-point mesh was

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https://doi.org/10.1016/j.jpcs.2017.09.023
Received 3 June 2017; Received in revised form 2 August 2017; Accepted 15 September 2017
Available online 21 September 2017

used. The BolzTrap code [20] under the constant relaxation time approximation for the charge carriers was employed to compute the transport properties of the compounds.

3. Results and discussion

The results obtained from the calculations are discussed in the following.

3.1. Structural, electronic, and magnetic properties

In Heusler alloys, the physical properties depend robustly on the positions of the atoms in the crystal, where even slight disorder can greatly change their electronic structure. If the atoms are positioned at their specific sites, the resulting structure will be well ordered. Therefore, a careful study of the crystal structure is required to predict or investigate the properties of Heusler alloys. The electronic structure, magnetic, and transport properties exhibit great variations from the actual physical properties if any disorder is present in the structure. Thus, in order to minimize the disorder, we checked the structural stability in all of the possible structures. Quaternary Heusler alloys mostly have the prototype LiMgPdSn structure [21,22] with the space group of *F-43m* (No. 216), and they possibly crystallize in three different structures, i.e., YI, YII, and YIII. The Wyckoff positions in the YI-type structure are 4a (0, 0, 0), 4b (1/2, 1/2, 1/2), 4c (1/4, 1/4, 1/4), and 4d (3/4, 3/4, 3/4), which are occupied by the Z (Si, As, Sb), Cr, Fe, and Co atoms, respectively. The atomic positions in the YII and YIII structure types have been discussed previously [23,24]. To determine the ground state energies for these materials, we performed volume optimization in all three non-equivalent structures in the ferromagnetic phase. The optimized lattice constants for CoFeCrZ (Z = Si, As, Sb) were 5.706 Å, 5.742 Å, and 5.764 Å, respectively. For CoFeCrSi, the optimized lattice constant was nearly equal to the experimental value of 5.69 Å [12]. As shown in Fig. 1, the YI structure had the lowest total energy, thereby indicating that the YI structure is the preferred crystal structure in all three possible configurations. Thus, we treated the YI structure as the stable state for the electronic structure calculations for these alloys.

It is well known that the band structure is vital for determining the thermoelectric properties because these properties depend greatly on the band structure. Therefore, it is very important to estimate the band gap (E_g) accurately, so the mBJ potential was used with the generalized gradient approximation to predict the band gaps accurately and close to the experimental values [25,26]. The intended spin-polarized band structures of the CoFeCrZ (Z = Si, As, Sb) compounds at the equilibrium lattice constant are presented in Fig. 2, which shows that the majority-spin (spin-up) band was metallic in all of the alloys, where the energy bands crossed the Fermi level (E_F) at various symmetry points, and the semiconducting behavior followed in the minority spin (spin-down) band around the E_F. The valence band maximum was located at the Γ point and the conduction band minimum at the X point, thereby demonstrating that

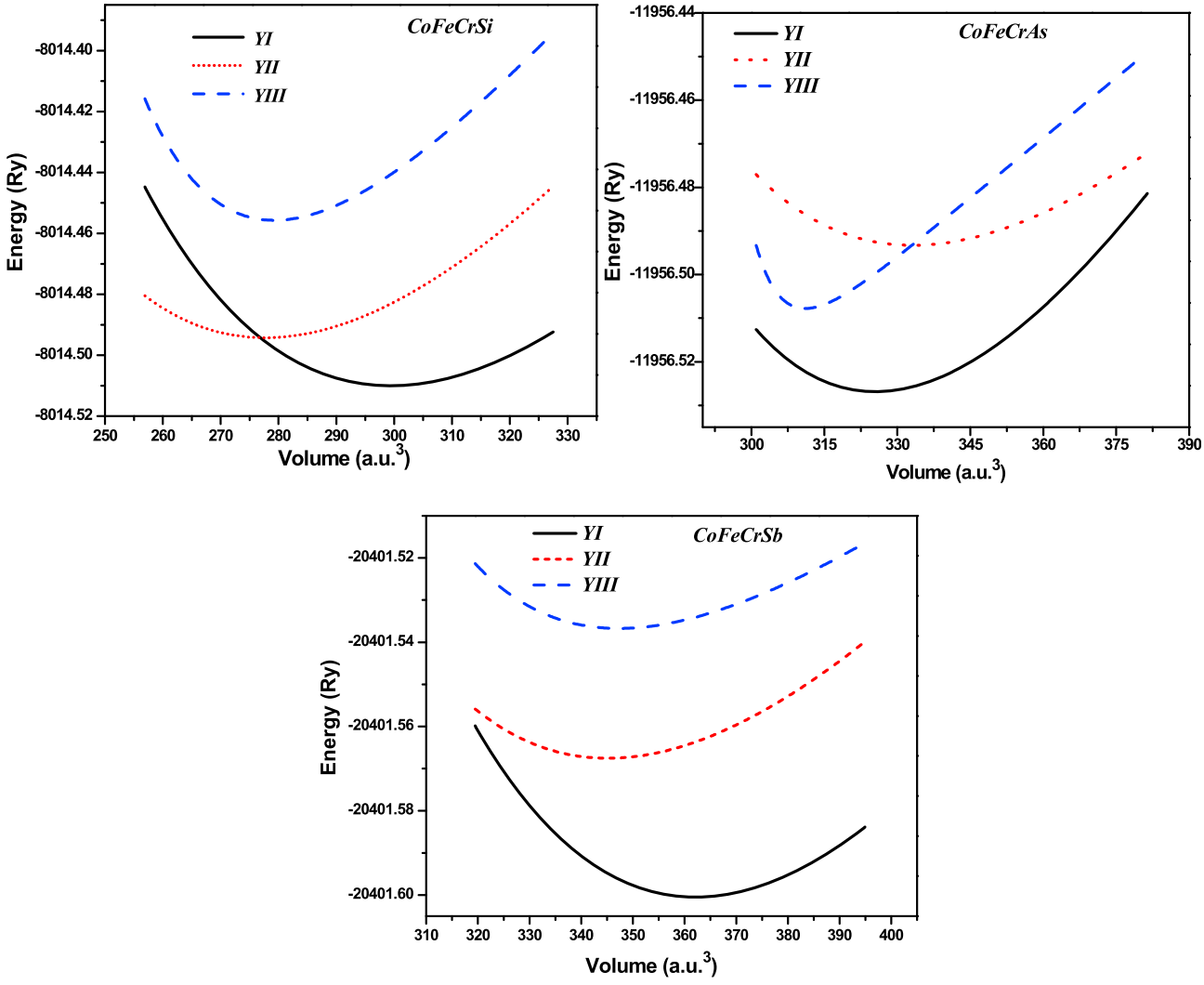

Fig. 1. Total energy–volume curves for CoFeCrSi, CoFeCrAs, and CoFeCrSb in the YI, YII, and YIII structure types.