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Bensaid Djillali (✉ djizer@yahoo.fr)

Faculté des sciences et technologie université aintemouchente

Doumi Bendouma

Universite Dr Tahar Moulay de Saida

Sohail Ahmad

king khalid university

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The lithium (Li) doping effect for enhancing thermoelectric and optoelectronic performances of Co₂NbAl

Djillali Bensaid^{1*}, Doumi Bendouma², Sohail Ahmad³

¹faculty of Science and technology , University Belhadj Bouchaib, BP 284, Ain-Temouchent, 46000, Algeria

² DrTahar Moulay University of Saida, 20000 Saida, Algeria

³Department of Physics, College of Science, P O Box 9004 King Khalid University Abha,
Saudi Arabia

Abstract

Cobalt -rich Heusler compounds represent a very interesting family among Heusler alloys due to their performance in the field of spintronics and magnetic devices. The quaternary Heusler created by swapping of an anti-atom site by an alkali element improves the performance of physical properties for new applications. In this study, the electronic structures and magnetic properties before and after swapping cobalt (Co) by lithium (Li) in the Co₂NbAl compound have been investigated using first-principle computational calculations. Our findings revealed that the swapping Co antisite by Li keeps the half-metallic character in the CoLiNbAl. Analysis of band structures show that ternary Heusler compound is ferromagnetic half-metallic with half metallic gap (band gap in minority channel) equal 0.134 eV but the swapping Co with Li leads the material to change its behavior and becomes a semiconductor with a gap equal 1.043 eV using HSE06 approach. The results of optical and thermoelectric properties such as absorption coefficient, reflectivity or thermopower and figure of merit are very interesting in the optoelectronic field and encourages the researchers to realize photovoltaic cell and thermoelectric generator with a higher efficiency. These interesting features suggest that Co₂NbAl and LiNbAlCo Heusler compounds could be good candidates for applications of antiferromagnetic spintronics and optoelectronics in commercial semiconductor industry.

Keywords:

Co-based Heusler alloys; Half-metallic ferrimagnetics; Hybrid functional; quaternary semiconductor Heusler alloy

Corresponding author. Tel.: +213 542 695 480

E-mail address: djillali.bensaid@cuniv-aintemouchent.dz (D. Bensaid). djizer@yahoo.fr

Introduction

Heusler alloys have undergone rapid growth in the last decade, due to their outstanding performance in technological and spintronics applications. The spintronic devices are based on the exceptional nature of the electronic structures and semi-metallic properties of this type of materials. There are several applications of these devices such as the giant magnetoresistance spin valves [1], magnetic tunnel junctions [2], spin-injecting [3] and spin-transfer torque devices [4]. Theoretical and experimental research focuses on Heusler alloys due to the diversity of their functional characteristics. From a purely theoretical point of view most of the Heusler alloys have the same crystallographic structure and some of them even are very close in composition and electronic structure [5–7]. These characteristics can minimize the mismatching of lattice and electronic structure. Another very important point is the crystallographic similarity between most of the Heusler alloys and semiconductors, because we can distinguish them in two groups the diamond or zinc blend structure. Several investigations have been made in the literature to switch from a Heusler semiconductor to a diluted magnetic semiconductor. Recently, it has been found that the diluted magnetism in semiconductor with Heusler structure can be induced by the atomic anti-site disorder between the different crystallographic sites [8]. The replacement of cobalt which resides in a 4c atomic site by an alkali metal atom leads to two very important consequences such as the destruction of the half metallicity caused by the opening another gap in the majority spin leading to a semiconductor material. In this study, we have analyzed the effect of anti-site disorder of lithium (Li) on the structural parameters, dynamic stability, the electronic structures and magnetic properties of the Co_2NbGa alloy.

METHODOLOGY

The first-principle calculations of the density functional theory (DFT) via the full-potential linearized augmented plane wave method (FP-LAPW) implemented in the WIEN2k software [9] are employed to predict the structural, electronic, magnetic, optical and thermal properties of Li doped Co_2NbGa alloy. The generalized gradient approximation (GGA-PBE) proposed by Perdew–Burke–Ernzerhof [10] is considered as exchange-correlation potential for our calculations. The muffin-tin sphere radii of 2.3, 2.05, 2.1, and 2.0 a.u for Li, Nb, Al and Co were used for calculations, respectively. The $2s^1$, $5s^2 4d^4$, $3s^2 3p^1$, and $4s^2 3d^7$ respectively for Li, Nb, Al and Co are considered as valence states due to their high energies.

The densities of states were performed by the tetrahedral integration method, where the $R_{\text{MT}} \times K_{\text{max}} = 7$ was used for the number of plane waves, and the expansion of the wave functions was set to $l_{\text{max}} = 10$ inside of the muffin tin spheres. The k-point mesh for sampling the Brillouin zone is performed by a Monkhorst-Pack scheme of $12 \times 12 \times 12$ point mesh. The 10^{-6} eV value for criterion convergence is used for the total energy. To determine the band gaps, optical properties, and dielectric constants we have used the screened hybrid Heyd-Scuseria-Ernzerhof (HSE06) [11] exchange-correlation functional with a $4 \times 4 \times 4$ k-mesh. To obtain accurate results for transport properties, we have used the BoltzTraP code [12] with a high k-point density of $20 \times 20 \times 20$ mesh and a constant relaxation-time approximation.

3. RESULTS AND DISCUSSIONS

3.1. Structural properties and dynamical stability

The Co_2NbAl Heusler compound is 2:1:1 stoichiometric ternary intermetallic with inverse Heusler structure. This material crystallizes in the cubic structure with AgLi_2Sb as prototype structure with space group $F\bar{4}3m$ No. 216, its primitive cell is described by four interpenetrating fcc sublattices, which contains three atoms Co, Nb and Al that form the base of this primitive cell. The substitution of cobalt (Co) by lithium (Li) in Co_2NbAl generates a quaternary LiNbAlCo compound with the same space group of $F\bar{4}3m$ No. 216 in the LiMgPdSn prototype.

Due to the symmetry described by the space group of $F\bar{4}3m$, the exchange of atoms between the Wyckoff positions 4a and 4b or 4c and 4d does not change and finally the LiMgPdSn type structure presents a primitive fcc cell with a base containing four atoms. The Figure 1 presents

the structure of Co₂NbAl and LiNbAlCo compounds, where the Co atom has been replaced by Li atom.

The formation energy is the indicator factor for structural stability. The formation energy of quaternary Heusler compounds is given by the following expression:

$$E_F = E_{XX'YZ} - (E_X + E_{X'} + E_Y + E_Z) \quad (1)$$

In Table 1, we have summarized the values of formation energies. The formation energy of our quaternary Heusler is negative value, which means that the LiNbAlCo are thermodynamically stable and can be obtained in equilibrium conditions. We noted that the formation energy of our ternary material is in agreement with the result found by Shakeel Ahmad Sof et al., [13].

Our lattice constant of LiNbAlCo compound has an accuracy of 98.51 % compared to the value calculated in the reference [14]. In the cubic lattice of LiNbAlCo, when the Co atom is replaced by the Li less electronegative atom, the lattice parameter increases slightly due to the ionic nature of the bond between the Co-Li couple. Consequently, the hardness of material decreases.

Electronic band structures and densities of states

For the electronic band structures of Co₂NbAl material, the GGA-PBE approach is used to describe the half-metallicity. Our calculated band structures in both spin up and down along high symmetry directions of the Brillouin zone (BZ) are shown in Figure 2(a). From this curve, we see clearly that a gap occurs in the minority-spin bands, while the majority-spin bands have a metallic nature, generating a half-metallic behavior in Co₂NbAl material. For minority-spin channels, the electronic states near the conduction band minima (CBM) are mainly contributed by the d states of Co and Nb atoms. These states near to Fermi level are responsible for opening the gap in minority-spin states. In addition, the effect of d-d hybridization states of Co and Nb atoms, are contributed in the valence band (BV) in the energy ranges of -2.9 to -0.56 eV and -3.45 to -1.3 eV for spin down and spin up channels, respectively.

For Co₂NbAl, we have found a half-metallic ferromagnetic band gap $E_g(\text{HMF})$ value of 0.497 eV and a half-metallic gap $E_g(\text{HM})$ of 0.02 eV this last one is very important factor to use half metallic materials in spintronic applications. Our result of $E_g(\text{HMF})$ shows excellent agreement compared to the available theoretical value [13] given in Table 1. We have found a total magnetic moment of 1.989 μ_B for Co₂NbAl compound, which is very significant with

respect to the value of magnetic moment given by the Slater-Pauling rule. The cobalt (Co) atom has a main contribution to the total magnetic moment ~~thanks~~ owing to its partially filled d states. The deviation of calculated magnetic moment is 0.55 % from the value found by Srikrishna et al., [15]. Moreover, a good agreement of the magnetic moment of Co is mentioned.

The addition of Li instead of Co destroys the half-metallic behavior and hence the LiNbAlCo material becomes a semiconductor with an indirect band gap of value 0.72 eV. This value is in good agreement with the value of reference [XX].

The GGA exchange and correlation functional produces a mistake for the prediction of the value of band gaps in the semiconductors. To correct this mistake and go beyond the GGA, we have used another approach such as the hybrid functional HSE06. This functional provide accurate results for computing bands gaps compared to the experimental data. The calculated electronic structures for LiNbAlCo with PBEsol and HSE06 functional are shown in Figure 3. We can see that the hybrid functional gives the same description of the band structure of reference [14], where our calculated band gap of 1.043 eV is closed to the value of 1.041 eV [14] given in the Table1.

Figure 4 illustrate the total and partial densities of states (DOS). For the valence states, the DOS analysis indicates that region ① is mainly ormed by the 3s orbitals of Al; the second zone ② is primarily dominated by the 3d-Co and 4d-Nb states Furthermore, the d-d hybridization occurs between 3d-Co and 4d-Nb states, which is responsible for the d-d exchange interaction. This interaction type pushes the bands to burst, leading to create the gap. Moreover, the same d-d hybridization phenomenon between d-Co and d-Nb states appears just above the Fermi level in the conduction band. The fourth zone ④ of DOS is dominated by the 3s states of Al and the various weaker states related to the Li atom.

Thermoelectric properties

The Heusler semiconductors are among the best thermoelectric materials because of the presence of a band gap, which plays a very important role to obtain a high thermoelectric power factor and an accurate value of merit. The thermoelectric efficiency is due to many parameters such as the thermoelectric power factor which describes the electronic transport and represents an important feature to determine the class of potential thermoelectric materials. The association of the rigid band approximations and the constant relaxation time

allows evaluating the transport properties of the materials. This combination allows to predict the S and the σ of thermoelectric (TE) materials.

The electrical conductivity ratio to the relaxation time σ/τ as a function of the chemical potential at different temperatures is given in Figs. 5(a). The higher figure of merit is an indicator to obtain a better thermoelectric performance from a material. This can only be achieved if the thermal conductivity is as low as possible. The analysis Figure 5.b shows that the electrical conductivity increases with the increase of the temperature in the two regions of the chemical potential. It reaches a maximum for the p-type region, its value equal 40 w/mK at a room temperature. The electronic thermal conductivity gradually increases with increasing temperature in the range of -0.02 to -0.124 of chemical potential.

Our predicted ZT value based on HSE06 approach in the temperature range from 300–1100 K for LiNbAlCo is very attractive and decreases with the increase of temperature. The Figure 5.d shows the dimensionless figure of merit ZT of Li swapping Co. Due to the significant suppression of thermal conductivity, the ZT reached a value of 1.05 at room temperature.

Optical properties

The processing of optical properties is carried out using the Ehrenreich and Cohen's equation [17] which gives the frequency dependent complex dielectric function. This equation is given by the following relation:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (1)$$

This expression represents the optical response of a material to an external electric field. The Kramers – Kronig relation [18] allows us to determine the real and imaginary part of equation 1. The different optical parameters as the refractive index $n(\omega)$, the extinction coefficient $k(\omega)$, reflectivity $R(\omega)$ and absorption coefficient $\alpha(\omega)$ are calculated from the real and imaginary part of the dielectric function [19-21]. The calculated imaginary part of the dielectric function $\varepsilon_2(\omega)$ with PBE and HSE06 approaches of our compound is depicted as a function of energy in Fig.6 a. For HSE06 approach, the $\varepsilon_2(\omega)$ onset at about 1.04 eV coincides with the critical value of gap, We have depicted an acute peak of value of 31.75 at energy 2.52eV due to the electronic transition. We can attribute this peak to the semiconductor nature with the photon absorption needed to excite the electrons, and we can clearly see from the absorption graph that no absorption is observed when the energy of the photons is below the threshold absorption energy which corresponds to the critical value of gap, where the absorption begins when photon energy is close to the value of the forbidden band. The LiNbAlCo compound has a indirect energy band gap, which connects with the

maximum absorption located in the middle ultraviolet (MUV 4.13–6.20 eV) region and vacuum ultraviolet (VUV 12.4–6.53 eV) region. Therefore, they are could be suitable for the optoelectronic UV optoelectronic device applications including laser diodes (LDs) and light-emitting diodes (LEDs). The static real dielectric constants at the zero frequency $\epsilon_1(0)$ are 57.34 and 14.85 with PBE and HSE06 approaches, respectively. Our value with HSE06 exchange correlation functional is in good agreement with the value found in literature. For deepen the idea on of the optical properties of our compound, the optical absorption as well as the reflectivity of this material for incoming photons were calculated and plotted in Fig. 6 c. From this figure, we can see that the LiNbAlCo semiconductor exhibits a considerable first absorption peak appears in the visible range of light for the incoming photons with the energy about 2.83 eV, where the absorption is about $110 \text{ (} 10^4 \text{ cm}^{-1} \text{)}$ and the reflection is about 60.4 %. The refractive index (n) and extinction coefficient (k) versus photon energy (eV) are displayed in Fig. 6 b and 6 d. The refractive index for PBE (HSE06) approach is 7.57 (3.85) respectively, when the photon energy increases, the refractive index demonstrates the highest peak at 2.12eV and decays sharply to its minimum level.

The energy loss function $L(\omega)$ is signify the lost energy of an electron when of passage in materials. The energy loss function $L(\omega)$ of the LiNbAlCo alloy is illustrated in Figure 6.e . The largest $L(\omega)$ value is 0.421, it is important to mention that the most pronounced peaks are induced by the plasmon excitation, and the energies are considered as plasmon energies with 13.15ev value.

Conclusions

By means of DFT calculations, we have systematically investigated the effect of swapping Li by Co in Co_2NbAl compound on the electronic structure and thermoelectric and optic properties. We note that the half-metallic behavior is destroyed by the addition of Li instead of Co and consequently a new behavior appears which is characterized by an opening of energy located at the level of Fermi in the two spin channels of LiNbAlCo. We have precisely determined the gap energy and dielectric constant by performing ab initio calculations with the hybrid-HSE06 exchange correlation functional. The band structure diagram and the densities of states indicate that the behavior of Co_2NbAl is half metallic, but when in fact the exchange of Co by Li, the material changes its character to semiconductor. The substitution of Co by Li improves the value of ZT which gives considerable performance and leads the LiNbAlCo material to thermoelectric applications with high temperature spin voltage generators. The optoelectronic quality of the material measured by the optical gap and the

various optical parameters such as the refractive index, absorption and dielectric constant suggest that the LiNbAlCo is a promising material for optoelectronic applications such as photovoltaic cells and lithium-based batteries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1: Calculated lattice constant (a), bulk modulus (B), half-metallic ferromagnetic band gap E_g and half-metallic gap for Co_2NbAl and band gap, formation energy, static real dielectric constants for LiNbAlCo .

	a(Å)	B(GPa)	B'	E_g (eV)	ϵ_∞	E_{for} (Ry)
Co_2NbAl	5.9 5.935 ^b	219.45 197.9 ^c	4.54	E_g (HMF) = 0.497 E_g (HM) = 0.02 0.57 ^c , 0.81 ^c		-1.48 ^c
LiNbAlCo	6.0528 5.963 ^a	115.48	4.68	0.72 (PBE) 1.043 (HSE06) 0.465 ^a (PBE) 1.041 ^a (HSE06)	57.34 (PBE) 14.85 (HSE06) 24.2 ^a	-0.356

^a ref 14, ^c ref 13 , ^b ref 15

Table 2 : Calculated total and local magnetic moment (MM) (in μ_B) within the muffin-tin spheres and in the interstitial sites for Co_2NbAl

	MM (Tot)	MM (Co)	MM (Nb)	MM (Al)	MM (interstitial)
Co_2NbAl	1.989 1.35 ^a , 2.00 ^b	1.004 1.02 ^c	0.027	-0.002	-0.044

^a ref 16, ^b ref 15

Fig. 1 crystal structures for ternary Co_2NbAl and quaternary LiNbAlCo

Fig. 2 Projected band structures for a) minority spin c) majority spin and b) total and partial density of states of Co_2NbAl .

Fig. 3 Electronic band structure of LiNbAlCo

Fig.4 the total DOS of LiNbAlCo and the projected DOS on the states associated to Li, Nb, Al and Co.

Fig.5 The calculated transport properties (a) power factor, (b) electrical conductivity, (c) Seebeck coefficient and (d) figure of merit as a function of chemical potential for LiNbAlCo.

Fig.6 a) Real and imaginary part of the dielectric function, b) Absorption c) the reflectivity and refraction constant with GGA and HSE06 for LiNbAlCo.