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Investigation on Structural, Elastic, Electronic and Vibrational Properties of LiTiAl Half-Heusler Compound Using First Principles Methods

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Abstract. Heusler alloys are particularly noticeable in spintronics and thermoelectric applications. The researches on new and better thermoelectric materials are increasing rapidly due to the energy crisis and environmental pollution which are frequently discussed in recent times. Thermoelectric materials are seen as potential ways to solve these problems. Half-Heusler materials are considered thermoelectric materials due to their large temperature stability. Typically, half-Heusler crystallizes in a face-centered cubic structure with alloys $F\bar{4}3m$ space group (No.216). In this study, the structural, elastic, electronic and vibrational properties of the Li-based LiTiAl compound with 8 electrons in the primitive cell were investigated using the VASP package program using the first principles methods. The 700 eV cutoff energy and 15x15x15 k-points were used in calculations. The lattice constant has been calculated as 6.191Å. The obtained structural parameteres are convenient with the results of literature. Band structures, total and partial density states graphs are drawn as electronic properties. From these calculations, the band gap of this compound was found to be 9.55 meV. Elastic constants were calculated from stress-strain rate. The calculated elastic constants show that this compound is mechanically stable. Phonon frequencies are calculated and the structure is found dynamically stable.

Keywords: LiTiAl, Half-Heusler, Vibrational properties, DFT, GGA-PBE.

LiTiAl Yarı-Heusler Alaşımının Yapısal, Elastik, Elektronik ve Titreşimsel Özelliklerinin İlk İlkeler Yöntemleri Kullanılarak İncelenmesi

Özet. Heusler alaşımları özellikle spintronik ve termoelektrik uygulamalarda önemli ölçüde dikkat çekmektedir. Son zamanlarda sıklıkla tartışılan enerji krizi ve çevresel kirlilikten dolayı yeni ve daha iyi termoelektrik malzemelerdeki araştırmalar hızla artmaktadır. Termoelektrik malzemeler bu problemlerin çözümü için potansiyel yollardan biri olarak görülmektedir. Yarı-Heusler malzemelerde büyük sıcaklık kararlılıklarından dolayı termoelektrik malzemeler olarak düşünülmektedir. Tipik olarak yarı-Heusler alaşımlar $F\bar{4}3m$ uzay gruplu (No.216) yüzey merkezli kübik yapıda kristallenir. Bu çalışmada ilkel hücresinde 8 elektrona sahip Li tabanlı LiTiAl bileşiğinin yapısal, elastik, elektronik ve titreşimsel özellikleri ilk ilkesel yöntemler kullanan VASP paket programı kullanılarak incelenmiştir. Hesaplamalarda 700 eV kesilim enerjisi ve 15x15x15 k-noktası kullanılmıştır. Örgü sabiti 6.191Å olarak hesaplanmıştır. Elde edilen yapısal parametreler mevcut literatür sonuçları ile uyumludur. Elektronik özellikler olarak band yapısı, toplam ve kısmi durum yoğunluğu grafikleri çizilmiştir. Bu hesaplardan bu bileşiğin band aralığı 9.55 meV olarak bulunmuştur. Elastik sabitleri zor-zorlanma oranından hesaplanmıştır. Hesaplanan elastik sabitleri bu bileşiğin mekaniksel olarak kararlı olduğunu göstermiştir. Fonon frekansları hesaplanmıştır ve yapı kararlı olarak bulunmuştur.

Anahtar Kelimeler: LiTiAl, Yarı-Heusler, Titreşimsel özellikler, DFT, GGA-PBE.

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1. INTRODUCTION

Heusler and Half-Heusler (HH) alloys have been attracted precious interests in novel materials in the materials science technology [1-7]. The HH alloys have potential many applications in spintronics and green-energy related fields, such as solar cells. In recent years, there is a strong demand for new optoelectronic devices. HH alloys have band gaps that can be tuned from 0 to 4 eV by changing their chemical composition [7].

The most-well known semi-Heusler compound is NiMnSb [8]. In 1983, de Groot's group [9] showed using first-principles electronic structure properties that this compound is in reality half-metallic, i.e. the minority band is semiconducting with a gap at the Fermi level E_F, leading to 100% spin polarization at E_F.

The analysis of lattice parameters, band gaps and static dielectric constants of half-Heusler compounds at ambient pressure are investigated and demonstrated as new candidates for the optoelectronic devices by Mehnane et al. [7]. The structural, electronic and optical properties of half-Heusler compounds of I-II-V and I-III-IV types using first principles calculations based on the density functional theory by Kacimi et al. [10]. Recent progress and advances in the half-Heusler compounds are briefly reviewed by Xie and his friends [11]. Kieven and Klenk present their first principles calculations results in order to find potential of HH materials to use in optoelectronic devices [12]. In addition to, there are some remarkable studies about topological insulators. To exemplify, Xiao and his friends [13] explore the feasibility of converting ternary half-Heusler compounds into a new class of three-dimensional topological insulators.

In this work, we have been discussed the structural, elastic, electronic, vibrational and thermodynamic properties of the LiTiAl HH alloy by analyzing first principles results. LiTiAl is a one of the compound from I-III-IV type-HH alloy that has eight valance electrons and including a large number of semiconductors with energy gaps vary in a wide range [11]. In this study, lattice parameter is quite convenient with literature and also the structure is dynamically stable considerable as vibrational part of the study.

2. METHOD of CALCULATION

Generally, HH alloys XYZ crystallize in a non-centrosymmetric structure corresponding to the space group $F\bar{4}3m$ (Space number: 216) [14]. The first principles calculations are performed using density functional theory within the Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) [15, 16] as implemented in the Vienna Ab-initio Simulation Package (VASP) [17-20]. For the plane-wave basis set, the kinetic energy cutoff is taken to be 700 eV. The numerical integration of Brillouin zone for optimization, elastic and optical properties is applied using a $15\times15\times15$ Monkhorst-Pack k-points sampling procedure for HH-LiTiAl alloy while $42\times42\times42$ k-points for band structure and $20\times20\times20$ k-points for partial density of states are employed. Phonon frequencies are calculated via the PHONOPY program [21], which uses the force constants obtained from the VASP package code. The phonon account was made using a $2\times2\times2$ supercell containing 24 atoms. Since the phonon spectrum obtained does not contain any virtual branches, the structure is found dynamically stable.

3. RESULTS and DISCUSSIONS

3.1. Structural and elastic properties

To understand the properties of these materials, atomic positions are important to identify the crystal lattice.

The structural and elastic properties are discussed in this section. Heusler alloys are defined as the ternary intermetallic compounds in I-III-IV type-HH groups. The crystal structure of LiTiAl HH alloy is shown in Fig. 1 in which the Li-atoms are green color, Ti-atoms are purple and Al-atoms are brown ones.

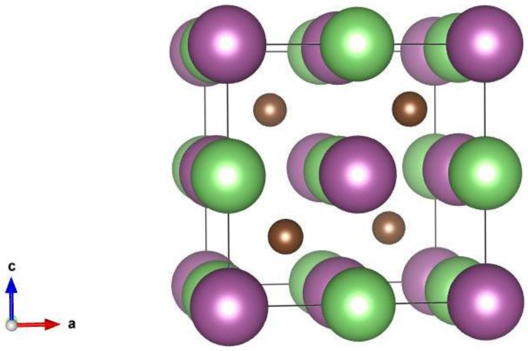


Figure 1. The crystal structure of LiTiAl HH alloy.

We have studied the properties using GGA-PBE method and presented the results for elastic parameters with Table 1. There is one study to compare lattice constants. According to the reference study [22], the optimized lattice constant as determined using the GGA method proposed by Engel and Vosko [23] is found to 5.895 Å. Our optimized lattice constant with GGA-PBE method is obtained as 6.191 Å. These values are quite compatible with together. Our calculated value of lattice constant is 0.047 percentage of value difference greater than the given reference value.

Table 1. The second order elastic constants (C_{ij}), bulk modulus (B), shear modulus (G) and the ratio of G/B of LiTiAl HH alloy.

LiTiAl	C_{11} **[GPa]**	C_{12} **[GPa]**	C_{44} **[GPa]**	B **[GPa]**	G **[GPa]**	B/G
Present work (GGA-PBE)	63.26	41.59	22.85	48.82	10.83	4.5

The elastic constants depict that the response of the crystal to external forces and examine the crucial factor in determining the strength and resistivity of the materials. Within the light of considering this fact, the second order elastic constants are calculated.

To obtain the elastic constants through the first-principles modeling of materials from their known crystal structures, there are basically two common methods [24, 25] an approach based on analysis of the total energy of properly strained states of the material in the volume conserving technique and an approach based on the analysis of changes in calculated stress values resulting from changes in the stress-strain technique. In this study, the stress-strain technique has been used to obtain the second-order elastic constants (C_{ij}) of LiTiAl HH alloy. The stress-strain technique is based on constructing a set of linear equations from stress–strain tensors for several deformations of the unit cell. This set of equations represents a general form of Hooke's law and can be solved with respect to the second-order elastic constants.

$$\sigma_i = \sum_{j-1}^{6} C_{ij} \varepsilon_j \tag{1}$$

Equation (1) describes that the linear dependency of stress component σ_i (i = 1–6) and applied strain ε_j (j = 1–6) under a small deformation. Here C_{ij} are the elastic constants of the crystal and its structure has been fully relaxed under a given set of exchange-correlation potential functions and obtained an equilibrium structure with a minimum total energy. The Born's stability criteria's [26] should be satisfied for the stability of lattice. The known Born's stability conditions of cubic crystals are: $C_{11}>0$, $C_{11}-C_{12}>0$, $C_{44}>0$, $C_{11}+2C_{12}>0$ and $C_{12}<B<C_{11}$ for mechanical stability. According to the Born's stability conditions, LiTiAl HH alloy is mechanically stable using the second order constants for calculations.

As it is known, the bulk modulus (*B*) determines the resistance of material fracture and the shear modulus (*G*) represents the resistance to plastic deformation. The *B/G* ratio is relevant to ductile/brittle behavior for solids. It is well-known that the critical value is 1.75 and/or greater than that value the material is regarded as ductile [27-29]. LiTiAl HH alloy indicates that the ductile behavior due to the fact that the present value of *B/G* is 4.5.

3.2. Electronic properties

Electronic structure calculations have been performed to evaluate the electronic properties of LiTiAl HH alloy along the high symmetry directions in inclusion of total density of states (DOS) with band structure calculated by GGA scheme as presented in Figure 2.

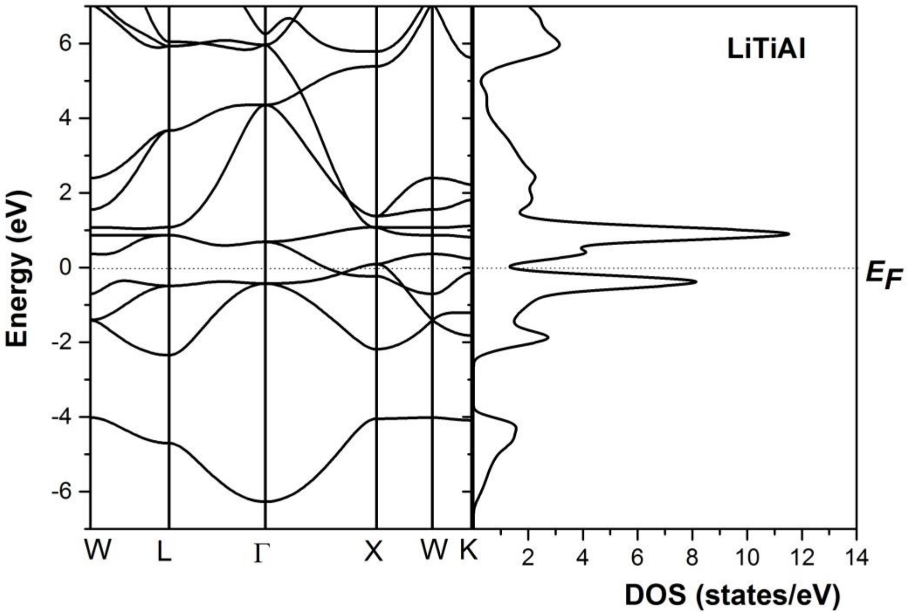


Figure 2. The band structure and density of states of LiTiAl HH alloy.

The Fig. 2 indicates clearly that the LiTiAl HH alloy portrays the metallic nature of the compound due to the fact that at around Fermi level (E_F) that is set to the zero band structures have been nested. According to the DOS, there is no band gap and also it could be concluded from band structures.

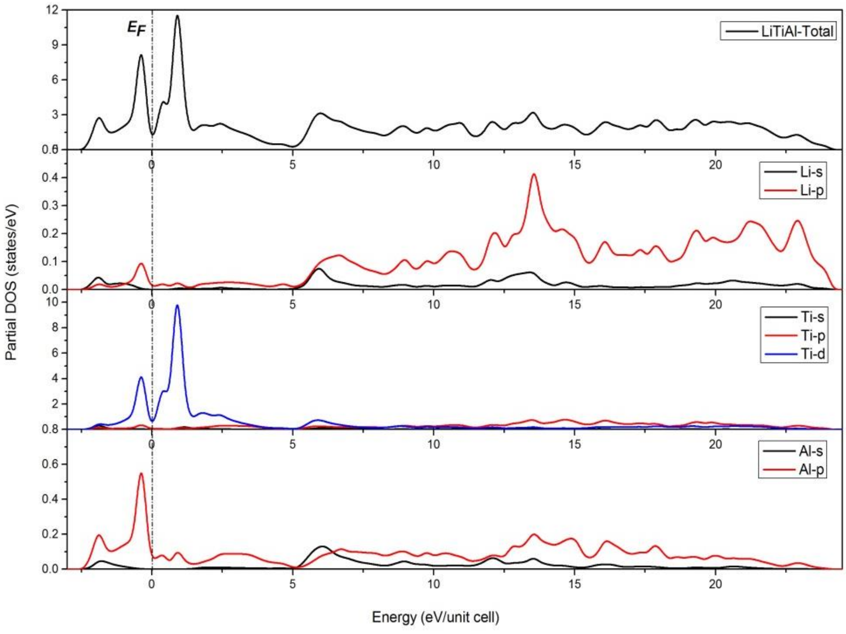


Figure 3. The partial and total density of states of LiTiAl HH alloy.

We have presented the total density of states (TDOS) and partial density of states (PDOS) of LiTiAl HH alloy in Figure 3. As it is clearly shown from Figure 3, under the conventional GGA model, the contribution to the lower valance bands and Fermi energy level are mainly Al-p states and Ti-d states. The calculated whole width of valance band is nearly 25 eV. The conduction bands are mainly from Li-p states and partially Al-p states. Ti-d states have a maximum nearly at around 1.5 eV. The LiTiAl HH alloy has a metallic behavior due to the fact that it has no band gap.

3.3. Vibrational and thermodynamic properties

The stability of lattice dynamics turn outs more featured properties of materials under zero and finite pressure. Phonon frequencies of materials give an idea for the vibrational properties to determine the lattice dynamical stability , thus, the phonon frequencies of LiTiAl HH alloy of in the MgAgAs ($C1_b$) structure have been computed using the PHONOPY code [30, 31] that is based on the forces obtained from the VASP. The PHONOPY code calculates force constant matrices and phonon frequencies using the density functional perturbation theory as described in Ref [31]. The present phonon dispersion curves along several high symmetry directions using a $2 \times 2 \times 2$ cubic supercell of 24 atoms are illustrated in Fig. 4. Unfortunately, up to now there have no experimental and other theoretical works exploring the lattice dynamics of these compounds under zero pressure. As LiTiAl compound has three atoms in the primitive cell, in the phonon spectrum has nine phonon branches, including three acoustic branches and six optical branches. One of the remarkable observations is that none of the branch involves a soft mode in the whole Brillouin zone (see Fig. 4). Therefore, it is strongly supports the dynamical stability of this compound in $C1_b$ structure. As shown on the right side of Fig. 4, the phonon spectrum of the LiTiAl HH alloy consists of three groups of bands. The lower modes with frequencies up to 4.5 THz are mixed states composed of the Ti, and Al atoms. In the next two groups of bands, the contributions are not equal to each other. The modes in the range 8.0 -10.5 THz are predominantly determined by the vibrations of the Li atoms, while the vibrations of the Li and Al atoms are dominant in the upper range of 12-14 THz. It can be easily seen that from Fig. 4, there is gap between optical and acoustic branches owing to the mass differences. The general features are consistent with phonon dispersion relations reported for other HH compounds such as ZrNiSn and ZrCoSb compounds [32, 33].

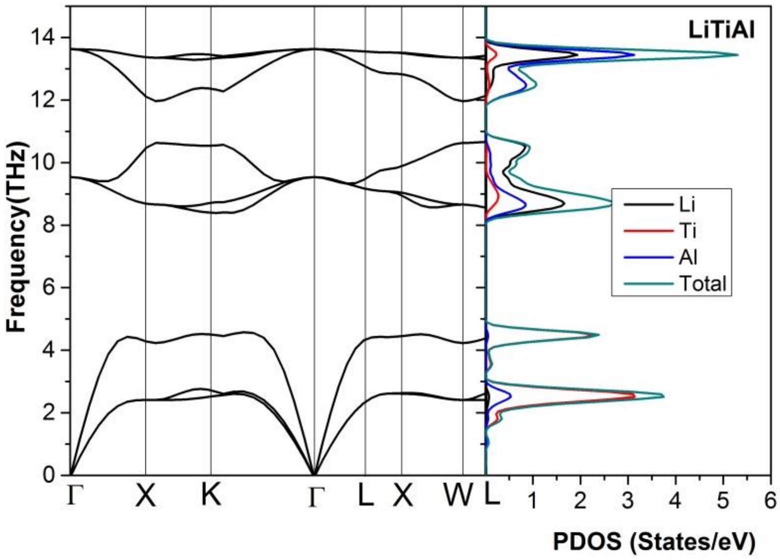
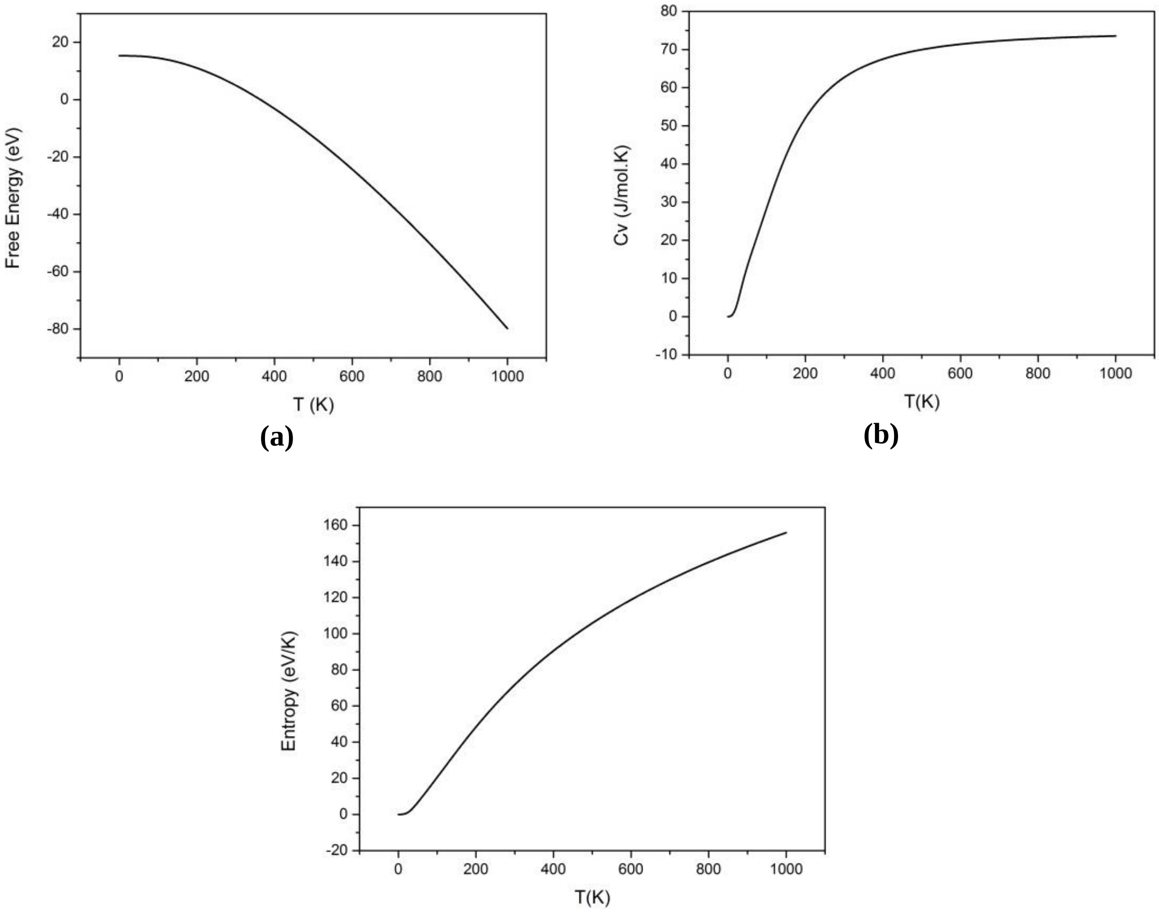


Figure 4. Phonon frequencies and phonon density of states of LiTiAl.

The temperature dependent properties are calculated through the thermodynamic quantities based on the quasi-harmonic approach and thermal electronic excitation. By using phonon frequencies, the thermodynamic parameters such as heat capacity (C_v), entropy (S), and free energy (F) have been calculated under quasi-harmonic approximation. As illustrated in Fig.5(a) that the free energy decreases with increasing temperature. The contributions from the lattice vibrations to the heat capacity of LiTiAl are illustrated in Fig.5(b). To decrease the probable influence of anharmonicity, the temperature is limited to 1000 K. The contribution from the lattice to the heat capacity follows the Debye model and approaches Dulong–Petit limit at high temperatures. The variations of entropy with the temperature for this HH alloy are given in Fig.5(c) over the same temperature range. It increases with temperature.



(a) (b)

(c)

Figure 5a. Free energy **b.** Heat capacity **c.** Entropy curves with respect to the Temperature (*T(K)*) of HH-LiTiAl alloy

4. CONCLUSION

To sum up, the structural, elastic, electronic, vibrational and thermodynamic properties of LiTiAl HH alloy using first-principles calculations based on the density functional theory with the frame of GGA-PBE. The calculated lattice constants are in good agreement with the existing results from the other related theoretical study that is considered with GGA-EV (Engel-Vosko). Second-order elastic constants and mechanical parameters are obtained and mechanical stability for LiTiAl HH alloy is investigated using the Born's stability criteria. As a result, it has found as mechanically stable. LiTiAl HH alloy exhibits a metallic behavior at zero pressure. In detail, total and partial densities of states of LiTiAl HH alloy are represented and it is shown that main contributions are emerged by Al-p and Ti-d states. Furthermore, vibrational and thermodynamic properties of LiTiAl HH alloy is discussed and determined that LiTiAl HH alloy illustrates as dynamically stable. Finally, we have deduced that our theoretical result for basic physical properties of LiTiAl HH alloy supports that the potential applications is convenient for desiring technological demands.

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