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On the interplay of thermodynamic and structural properties of LiZn-based half-Heusler alloys

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The half-Heusler LiZnX (X = As, P, and Sb) alloys have gained a significant attention due to their exceptional thermoelectric and magnetic properties, making them a promising material for various applications. In this study, we employ density functional theory to investigate the data on structural and thermodynamics properties of the LiZnX (X = As, P, and Sb) half-Heusler alloys. First-principles calculations as implemented in quantum Espresso simulation software were used. We observed that LiZnX (X = As, P, and Sb) will be easily compressed due to the small value of its bulk modulus. We obtained that the structure is stable and corresponds a half-Heusler crystal one. The Debye model correctly predicts the observed low-temperature dependence of heat capacity, which is proportional to the Debye T^3 law. At room temperature, Debye specific heat C_v = 70 J / (K·N·mol).

Keywords: half-Heusler LiZnAs, LiZnP, LiZnSb alloys, structure, bandgap, Debye vibrational energy, heat capacity.

1. Introduction

The search for novel materials with enhanced thermoelectric and magnetic properties has intensified due to their significance in renewable energy harvesting and spintronics. Half-Heusler compounds, with the general chemical formula XYZ, where X and Y are transition metals, and Z is a main group element, have attracted significant attention due to their fascinating properties and potential applications. They crystallize in a cubic structure, consisting of three interpenetrating face-centered cubic sublattices. The combination of different elements in their crystal structure plays a crucial role in determining the electronic, magnetic, and thermoelectric properties of these compounds. In particular, the series of half-Heusler LiZnX (X = As, P, and Sb) alloys, has emerged as a promising candidate to different application, exhibiting remarkable properties such as high thermoelectric efficiency, tunable bandgap, and superior magnetic characteristics. LiZnAs has been found to exhibit high thermopower and low thermal conductivity, making it an excellent thermoelectric material, LiZnP, on the other hand, has demonstrated interesting magnetic properties, including a specific ferromagnetic behavior suitable for tunable spin polarization, and LiZnSb has revealed potentialities for both thermoelectric and magnetic applications due to tunable bandgaps and high thermoelectric efficiency. However, a comprehensive understanding of their structural properties and in relation with electronic behavior is still required to unlock a full potential of such materials [1–5]. Analysis of experimental data in the frame of density functional theory (DFT) has proven to be a powerful tool in investigating the electronic structure and properties of materials, providing valuable insights into their behavior at the atomic and electronic levels. The aim of this paper is to shed light on the peculiarities of crystal structure, electronic band structure and mechanical stability of the LiZnX (X = As, P, and Sb) alloys, analyzing the experimental observations by means of DFT calculations with the Vienna *ab initio* simulation package.

2. Background and methodology

The half-Heusler XYZ compounds crystallize in a cubic structure with a space group $F\bar{4}3m$. The crystal lattice consists of interpenetrating simple cubic lattices with the X and Y elements occupying half of the tetrahedral sites each, while the Z element resides in the octahedral sites. The arrangement of atoms within the crystal structure influences the band structure and electronic properties of these compounds [6–8].

The composition of half-Heusler compounds can vary extensively, which allows one to tailor their properties for specific applications. Common examples of X, Y, and Z elements used in half-Heusler compounds include transition metals like Ti, Zr, Hf, V, Nb, Ta, and main group elements such as Si, Ge, Sn, and Sb. The choice of elements affects the bandgap, electrical conductivity, and magnetic properties of the compounds [9–11].

Several synthesis methods have been employed to fabricate half-Heusler compounds, including arc melting, mechanical alloying, powder metallurgy, and epitaxial growth techniques. These methods offer a control over the crystal structure, composition, and grain size, enabling the development of tailored materials with desired properties [12–15].

In a study by Xie *et al.* [16], LiZnAs was investigated for its thermoelectric properties. A high thermopower, low electrical resistivity, and low thermal conductivity were observed, resulted in an enhanced thermoelectric efficiency. It was shown that LiZnAs is a narrow-bandgap semiconductor with the predominantly *p*-type conductivity, making it suitable for thermoelectric applications at high temperatures. In a similar way, Zhu *et al.* [17] have investigated the thermoelectric properties of LiZnSb. A moderate Seebeck coefficient and a relatively high electrical conductivity were reported with a competitive thermoelectric performance. It was further demonstrated that the thermoelectric properties of LiZnSb can be tuned by alloying with other elements, opening ways for optimization and fitting of its properties for specific applications. The magnetic properties of LiZnP were explored by Yang *et al.* [18]. A revealed ferromagnetic behavior in LiZnP suggests that the magnetic ordering is primarily governed by the cation-anion hybridization in the crystal structure. Its suitability as a spin-polarized material for magnetic storage and sensing devices is argued.

The DFT calculations were successfully employed to investigate the electronic and structural properties of half-Heusler alloys. Wang *et al.* [19] utilized DFT calculations to study the electronic structure and magnetic properties of LiZnSb. The results indicated that LiZnSb exhibits a spin-polarized band structure, suggesting its potential in spintronic applications. The researchers also investigated the effects of strain on the magnetic properties, revealing the tunability of the alloy's magnetism. The Reshak [20] calculations of electronic band structures of Nowotny–Juza NaZnX (X = P, As and Sb) compounds suggest that the valence band maximum (VBM) and the conduction band minimum (CBM) are located at the center of the Brillouin zone, resulting in a direct bandgap of about 1.80, 1.47, and 0.25 eV, respectively. The total and the partial density of states explore the type of orbitals which rule the bandgaps and to classify the hybridizations between the orbitals. The VBM is formed mainly by P-*p*, As-*p*, Sb-*p*, Zn-*p* and Na-*p* states with substituting P → As → Sb. The CBM of NaZnP is formed by Zn-*s*, Na-*s*/*p*, while the CBM of NaZnAs (NaZnSb) is formed by Zn-*s* and As-*d* (Zn-*s* and Sb-*d*), one can see that As-*d* and Sb-*d* orbitals govern the CBM of NaZnAs and NaZnSb, hence these orbitals rule the energy gaps. It is clear that there exists a strong hybridizations between Na-*s*/*p* and As-*d* states, Zn-*s*/*p* and P-*p* states, Sb-*p* and Zn-*s* states and also between Sb-*d* and Na-*s* states. The strong hybridization may led to form a strong covalent bonding between these atoms. For more detail and to get deep insight into the electronic structures, the optical properties were investigated. The uniaxial anisotropy and the birefringence values confirm the existence of the considerable anisotropy between the two components of the optical properties. The calculation confirm that these compounds are promising candidates for optoelectronics devices. Benjamin and Michael [21] used *ab initio* calculations to examine the structural, mechanical, electronic, magnetic, and thermodynamic properties of the half-Heusler ternary alloys XCrSb (X = Hf, Ti, Zr). In this study, the spin-polarized DFT method that is spin-polarized with generalized gradient approximation are used to perform *ab initio* calculations to investigate the physical properties of a novel half-Heusler ternary alloys XCrSb (X = Hf, Ti, Zr). It was confirmed that the alloys are stable mechanically and exhibit ferromagnetic states. The study reveals that the alloys portray half-metallic character with narrow energy gaps. And it also shows that they have a total magnetic moment of approximately 3ub. From the formation energy calculation, it shows that the alloys can be synthesized experimentally. Also, it was observed that they are mechanically stable. The heat capacities and Debye temperatures were also computed and they show high thermodynamic stability.

While these previous studies have provided valuable insights into the properties of specific compositions within the LiZnX (X = As, P, and Sb) half-Heusler alloy system, a comprehensive investigation encompassing all three compositions is still lacking. This research aims to bridge this gap by employing DFT calculations to investigate the structural properties of LiZnX (X = As, P, and Sb) comprehensively. By considering the three compositions together, a deeper understanding of the alloy's electronic structure, mechanical stability, and potential applications can be gained. The findings of this study will build upon the existing knowledge base and contribute to the ongoing exploration and utilization of half-Heusler alloys for various technological applications.

In this work, the Vienna *ab initio* simulation package is utilized to perform electronic structure calculations. The generalized gradient approximation within the Perdew–Burke–Ernzerhof functional is employed to describe the exchange-correlation effects. The Brillouin zone integration is performed using Monkhorst–Pack *k*-point mesh. The convergence criteria for energy calculations are set to ensure accuracy and reliability as implemented in the Quantum Espresso simulation software package.

3. Results and discussion

The investigation focuses on several key aspects of the half-Heusler alloy LiZnX (X = As, P, and Sb). Firstly, the

lattice parameters and crystal structure of the alloy are determined, providing insights into the arrangement of atoms and the stability of the material. Furthermore, the electronic band structure, density of states, and Fermi surface analysis are performed to understand the electronic behavior, bandgaps, and transport properties of the alloy. Additionally, the mechanical properties, including elastic constants, shear modulus, and bulk modulus, are calculated to assess the mechanical stability and strength of the material.

We performed series of self-consistent calculations to optimize the structure of LiZnX (X = As, P, and Sb). The data sets generated from the self-consistent total energy calculations were fitted to the third-order Birch–Murnaghan equation of state and the equilibrium lattice constant (a_0), bulk modulus (B), pressure derivative (B') and bandgap (E_g) were obtained (Table 1). The bulk modulus determines strength of material, and its pressure derivative measures its response to slight increase in pressure. In Fig. 1 plots of energy against volume of LiZnX (X = As, P, and Sb) show that the higher the structural volume of the material, the smaller the energy with respect to the bulk and pressure derivatives. From our calculated values, it is seen that LiZnX (X = As, P, and Sb) will be easily compressed due to the small value of its bulk modulus (Table 2).

Table 1. Calculated lattice constant (a_0), bulk modulus (B), and pressure derivative (B') of LiZnX (X = As, P, and Sb) half-Heusler alloys under study

Compound	a_0, Å	B, GPa	B', GPa	E_g, eV
LiZnAs	5.940	54.786	1.45	0.625
LiZnP	5.727	52.895	7.11	0.937
LiZnSb	6.335	40.383	3.41	0.313

4. Thermodynamic properties

The Debye vibrational energy evolution with temperature for the considered series of LiZnX alloys is demonstrated in Fig. 2.

Table 2. Calculated specific heat (C_v), Debye temperature (K), Debye velocities (m/s) and zero points energy (eV/cell) of LiZnX (X = As, P, and Sb) half-Heusler alloys under study

Compound	C_v, J/(K·N·mol)	Debye tempera-ture, K	Debye velocities, m/s	Zero points energy, eV/cell
LiZnAs	70.5512	333.624	2905.687	0.097
LiZnP	68.436	409.983	3446.908	0.119
LiZnSb	71.378	299.807	2986.070	0.087

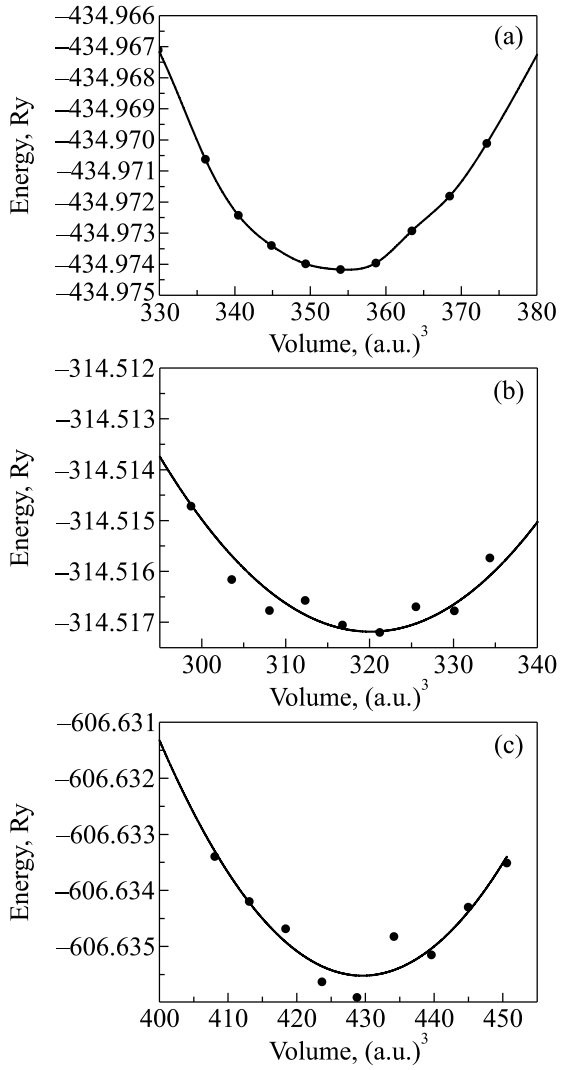

Fig. 1. Dependences of energy on the volume of the LiZnAs (a), LiZnP (b), and LiZnSb (c) compounds.

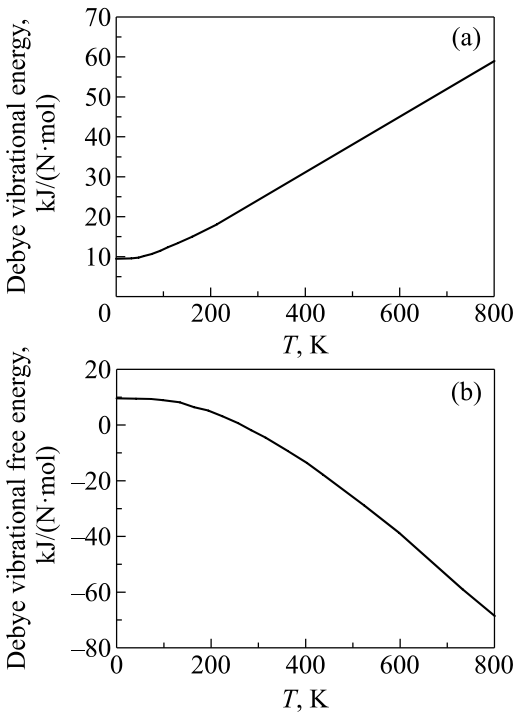

Fig. 2. Temperature dependences of the Debye vibrational energy for the LiZnAs (a) and LiZnP (b) compounds.

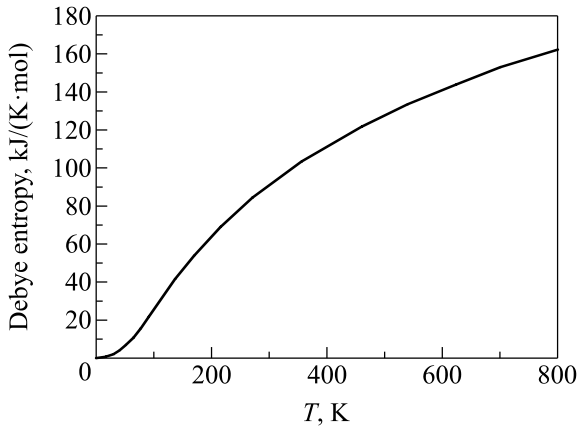

Fig. 3. Temperature dependence of the Debye entropy for the LiZnSb compound.

In Fig. 2(a), the temperature dependence of the Debye vibrational energy for LiZnAs shows that at low temperature it is constant, but increases with temperature increment. Furthermore, Fig. 2(b), as the Debye vibrational free energy decreases, the temperature increases for LiZnP, similar to Fig. 3 for LiZnSb. While in Fig. 4, the Debye model correctly predicts the low-temperature behavior of heat capacity, following the Debye T^3 law. It is shown that at higher temperatures it follows the Dulong–Petit law. But due to simplifying assumptions, its accuracy suffers at intermediate temperatures. At room temperature, the Debye specific heat C_v = 70 J / (K·N·mol).

Summary

In conclusion, the structural and thermodynamic study of LiZnX (X = As, P, and Sb) half-Heusler alloys properties using the DFT computations provides new insights into this intriguing material system. A stable structure of a half-Heusler type is manifested. However, it can be easily compressed due to the small value of its bulk modulus. The Debye model correctly predicts the low-temperature dependence of heat capacity, which is proportional to the Debye T^3 law, with a Dulong–Petit behavior at elevated temperatures.

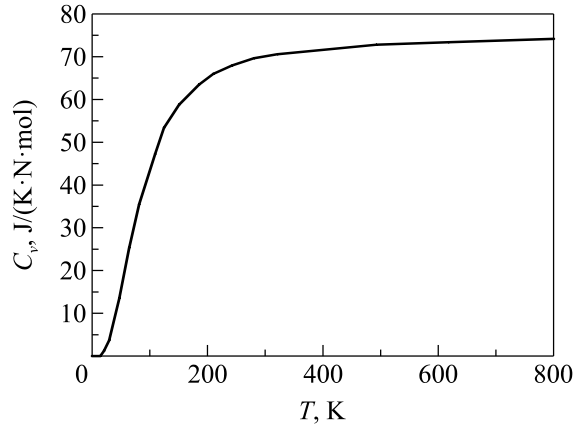

Fig. 4. Temperature dependence of the Debye heat capacity C_v.

But due to simplifying assumptions, the results accuracy suffers at intermediate temperatures. At room temperature, Debye specific heat C_v = 70 J / (K·N·mol).

Acknowledgments

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Про взаємодію термодинамічних і структурних властивостей напівгейслерівських сплавів на основі LiZn

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Напівгейслерівські сплави LiZnX (X = As, P та Sb) привернули значну увагу завдяки своїм винятковим термоелектричним і магнітним властивостям, що робить їх перспективним матеріалом для різних застосувань. У даному дослідженні використовується теорія функціонала густини, щоб дослідити дані про структурні та термодинамічні властивості напівгейслерівських сплавів LiZnX (X = As, P та Sb). Використано обчислення з перших принципів, які реалізовані в програмному забезпеченні квантового моделювання Espresso. Виявилось, що LiZnX (X = As, P та Sb) буде легко стискатися через невелике значення його об'ємного модуля. Отримано, що структура стабільна і відповідає напівкристалу Гейслера. Модель Дебая правильно передбачає низьку температурну залежність теплоємності, що спостерігається, яка пропорційна закону Дебая T^3. При кімнатній температурі теплоємність Дебая C_v = 70 Дж/(К·Н·моль).

Ключові слова: напівгейслерівські сплави LiZnAs, LiZnP, LiZnSb, структура, ширина забороненої зони, коливальна енергія Дебая, теплоємність.