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Ab Initio Study of The Structural, Magnetic, Electronic and Thermodynamic Properties of Li2mnge Heusler Alloy

Sameer Ahmad Pala[1] , Malik Irem Rashid[2] , Dr. Veeresh Kumar[3]

[1]PHD Research Scholar at Sunrise University Alwar Rajasthan.
[2]PHD Research Scholar at Jiwaji University Gwalior.
[3]Assistant Professor at Sunrise University Alwar Rajasthan.
Email: samipala770@gmail.com

In the present work, the structural, elastic, electronic, magnetic, and thermodynamic characteristics of the Li_2MnGe alloy, crystallizing in the XA-type inverse Heusler structure, were systematically investigated using first-principles density functional theory (DFT) calculations. The crystal structure was modeled in the $F\bar{4}3m$ space group. Of the three phases reported previously in the literature, the mechanically stable phase satisfying the Born stability criteria was selected for further analysis. All calculations were performed using the Quantum ESPRESSO package within the generalized gradient approximation (GGA) framework. The atomic sites in the unit cell were occupied by a-Li (0, 0, 0), b-Li (1/4, 1/4, 1/4), Ge (1/2, 1/2, 1/2), and Mn (3/4, 3/4, 3/4). Structural optimization demonstrated the mechanical stability of the compound and yielded an equilibrium lattice parameter of 6.0443 Å. The calculated elastic constants were C_{11} = 61.96 GPa, C_{12} = 21.96 GPa, and C_{44} = 58.95 GPa, which satisfy the required Born mechanical stability conditions. The negative value of $C_{12} - C_{44}$ indicates a pronounced covalent character of bonding. The corresponding bulk modulus, shear modulus, and Young's modulus were found to be 35.29, 38.26, and 84.02 GPa, respectively, while the B/G ratio was calculated to be 0.922. A Poisson's ratio of 0.098 further indicates the predominantly covalent nature of the bonding. The calculated electronic band structure and density of states indicate metallic behaviour accompanied by strong spin polarization, with a narrow pseudo gap-like feature appearing close to the Fermi level in the spin-down channel. The electronic states around the Fermi energy are mainly derived from the Mn-3d orbitals. The calculated total magnetic moment is 3.96 μB, consistent with the Slater–Pauling rule. In addition, thermodynamic properties evaluated using the Debye model produced a Debye temperature of 409.889 K. The overall results indicate that Li_2MnGe possesses several desirable properties that make it a potential material for further investigation in spintronic applications.

Keywords: Density functional theory, Spintronic devices, XA inverse Heusler alloy.

1. INTRODUCTION

The discovery of intermetallic compounds with the X_2YZ stoichiometry during research in the early twentieth century led to the development of a class of materials that became known as Heusler alloys. These materials have attracted considerable scientific interest because they can exhibit magnetic properties even when their constituent elements do not possess ferromagnetic

characteristics individually. Depending on their chemical composition and atomic arrangement, Heusler alloys have demonstrated considerable potential for a variety of advanced technological applications, particularly in spintronics and magnetoelectronics [1–6]. Based on their composition and crystal structure, Heusler compounds are commonly divided into full-Heusler, half-Heusler, and inverse-Heusler families. Full-Heusler compounds generally possess the X_2YZ composition and contain two X atoms within the unit cell. When one of the X atoms is removed, the resulting XYZ compound is referred to as a half-Heusler alloy. In contrast, inverse Heusler compounds, also having an X_2YZ stoichiometry, exhibit a different atomic ordering from conventional full-Heusler structures and are commonly referred to as XA-type Heusler alloys [7,8]. Certain Heusler compounds can exhibit spin polarization approaching 100% at the Fermi level, making them particularly attractive for spintronic applications [9].

The present study focuses on the theoretical investigation of Li_2MnGe, an inverse Heusler alloy in which the constituent atoms are arranged according to the $F\bar{4}3m$ space group. Lithium (Li) and manganese (Mn) are technologically important elements that are widely associated with energy-storage materials, particularly lithium-ion battery systems [10]. Germanium (Ge), owing to its semiconducting and electronic characteristics, is also of significant interest in electronic and energy-related technologies [11]. The combination of these elements in Li_2MnGe therefore provides motivation for examining its fundamental physical properties and possible technological relevance.

In this work, the structural, elastic, electronic, magnetic, and thermodynamic properties of Li_2MnGe were systematically examined using first-principles calculations. Particular attention was given to identifying the mechanically stable phase of the alloy, after which the subsequent calculations were carried out using the optimized stable configuration. The theoretical investigations were performed using the Quantum ESPRESSO package within the framework of density functional theory (DFT), employing the generalized gradient approximation with the Perdew–Burke–Ernzerhof (GGA-PBE) functional [12]. In addition, temperature-dependent thermodynamic properties were evaluated using the Thermo_pw software based on the Debye model. The obtained results provide a comprehensive understanding of the fundamental properties of Li_2MnGe and its possible suitability for future spintronic applications.

2. MATERIAL AND METHODS

In this study, the structural, elastic, electronic, and thermodynamic properties of a Li2MnGe alloy with an inverse Heusler (XA) crystal structure were systematically investigated via density functional theory (DFT) based on first-principles (ab initio) calculations. These calculations were performed within the generalized gradient approximation (GGA) framework, employing the Perdew–Burke–Ernzerhof (PBE) parameter as the exchange-correlation functional. The open-source electronic-structure software package Quantum ESPRESSO was selected for the calculations. The program employs a plane wavebased approach, utilizing this method to model potential distributions and atomic interactions in the crystal structure with a high degree of accuracy. During the structural modeling process, different atomic arrangement scenarios were investigated, in addition to the XA-type inverse Heusler configuration corresponding to the $F\bar{4}3m$ space group. In this context, geometry

optimization was performed for structures in which Li, Mn, and Ge atoms were placed at alternative Wyckoff positions. Each structure obtained was then tested within the framework of mechanical stability criteria. Mechanical stability, therefore, can be defined as the ability of a crystal structure to resist external deformations by satisfying the Born stability criterion given in equation (1) for its elastic constants.

$$C_{44} > 0;\ C_{11} - C_{12} > 0;\ C_{11} + 2C_{12} > 0 \quad (1)$$

In light of the comparisons conducted, it was ascertained that only the configurations situated in the Li(0,0,0), Li(¼,¼,¼), Ge(½,½,½), and Mn(¾,¾,¾) positions exhibited mechanical stability. These criteria could not be met under any other alternative arrangements, and at least one of the elastic constants was found to be negative. Consequently, the mechanically stable configuration was selected as the reference structure for the subsequent study. All calculations were conducted on the basis of this reference structure. In the structural optimization process, iterations were performed until the total energy difference within the unit cell fell below 10^{-6} eV and the maximum force value on each atom fell below 0.01 eV/Å. The Monkhorst-Pack algorithm was employed to sample the k-space, resulting in the generation of an 8×8×8 k-point grid. Methfessel–Paxton smearing method was employed to calculate the electronic density distribution in a more stable manner, with the smearing parameter fixed at 0.02 Ry. This technique is widely used, especially in metallic systems, to increase accuracy in regions close to the Fermi surface [13]. The calculation of elastic constants was performed via the Thermo Pw module, which is fully compatible with Quantum ESPRESSO. This approach was employed to reevaluate the mechanical stability criteria and obtain temperature-dependent thermodynamic variables. By utilizing parameters such as the phonon frequency and Debye temperature obtained through the utilization of the aforementioned module, the heat capacity (C_v), Debye temperature (θD), and entropy of the alloy were calculated. For these thermodynamic analyses, an approach based on the Debye model was adopted, and the effect of temperature on material behavior was evaluated in detail. The plane wave energy cutoff value employed in the Fourier transform of wave functions was evaluated prior to calculation and optimized with respect to calculation accuracy and time–cost balance. The pseudopotentials employed were selected as PBE-GGA-based and ultrasoft or Projector Augmented-Wave (PAW) potentials, enabling the calculation of magnetic properties with spin polarization taken into account.

3. RESULTS

The Li_2MnGe alloy was modeled in the XA-type inverse-Heusler structure with the $F\bar{4}3m$ (No. 216) space group. Within the crystal structure, the atomic arrangement is organized according to the following Wyckoff positions: the Li atoms are positioned at the origin (0,0,0), and at point (¼,¼,¼), the Ge atom is located at (½,½,½), and the Mn atom is placed at (¾,¾,¾). Initially, a series of configurations were tested; however, this arrangement was determined to be the only one that satisfied the system's mechanical stability criteria. Consequently, structural optimization yielded a calculated equilibrium lattice parameter of 6.0443 Å for the Li_2MnGe alloy. The Figure 1 below illustrates an example unit cell structure of the aforementioned alloy, rendered via the Vesta program.

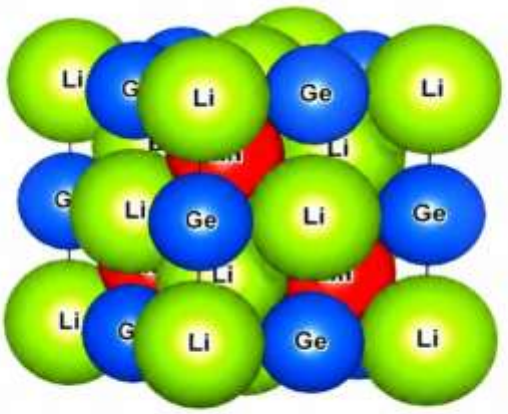

Figure 1. Representative lattice structure of the Li_2MnGe alloy.

The electronic structure and magnetic character of the Li2MnGe alloy were analyzed via spin-polarized calculations within the framework of density functional theory (DFT). The obtained band structure and density of states (DOS) distributions reveal the conductivity and magnetism potential of the alloy. The electronic band and DOS graphs for the alloy are shown in Figures 2 and 3, respectively.

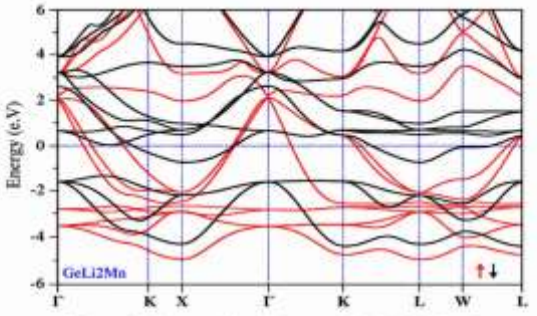

Figure 2. Electronic band diagram of the Li_2MnGe alloy.

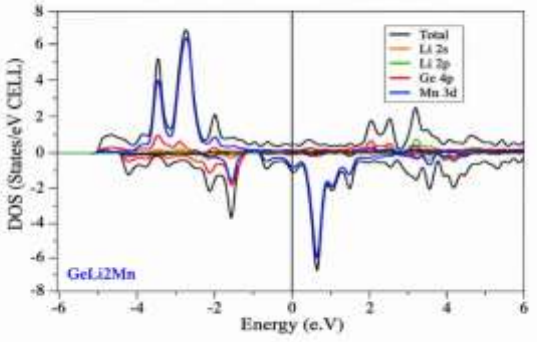

Figure 3. DOS diagram of the Li_2MnGe alloy.

Upon examination of the band structure diagrams (dissociated for spin-up and spin-down channels), the presence of bands crossing the Fermi level is observed in the spin-up channel, whereas a constricted energy gap in proximity to the Fermi level is evident in the spin-down channel. This band configuration indicates a highly spin-polarized metallic character with a narrow pseudogap-like feature near the Fermi level in the spin-down channel. Similar spin-dependent electronic structures have been reported for several Heusler alloys in the literature [14]. Total and projected DOS analyses demonstrate that the density surrounding the Fermi energy is predominantly attributable to the 3d orbitals of the Mn atom. This finding suggests that the conductivity and magnetic moment are predominantly influenced by d electrons, with the contributions of Li and Ge atoms being relatively negligible. This phenomenon can be attributed to the classical Heusler mechanism, This behavior can be mainly attributed to the Mn 3d states, which dominate the electronic states near the Fermi level and play a major role in spin polarization [15]. Pursuant to magnetic calculations, the total magnetic moment of Li_2MnGe was found to be 3.96 μB. In this context, Li_2MnGe may be considered a potential candidate for spintronic applications owing to its high spin polarization and favorable electronic transport characteristics. The second-order elastic constants (C_{11}, C_{12}, and C_{44}) were calculated to reveal the mechanical behavior of the Li_2MnGe alloy. This information provides important insights into the interatomic bond characteristics, hardness, brittleness, and anisotropy of the structure. The subsequent calculations yielded the following results: C_{11} = 61.96 GPa, C_{12} = 21.96 GPa, and C_{44} = 58.95 GPa. The C_{11} constant is indicative of the resistance of the atoms to linear compression, whereas C_{12} signifies the elastic interaction between axes. Finally, C_{44} denotes the structure's resistance to shear stresses. Specifically, the relatively high value of C_{44} indicates a pronounced resistance to shear deformation [16]. The macroscopic mechanical moduli derived from the elastic constants were calculated via the Hill approach, which is the average of the Voigt and Reuss limits. In this context, the bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio (σ), and anisotropy factor (A) are expressed by the following

$$B = (C_{11} + 2C_{12})/3 \quad (2)$$

$$G = 5(C_{11} - 2C_{12}).C_{44}/(3(C_{11} - 2C_{12}) + C_{44}) \quad (3)$$

$$E = 9.B.G/(3B + G) \quad (4)$$

$$\sigma = 1/2\ (1 - E/3B) \quad (5)$$

$$A = 2.C_{44}/(C_{11} - C_{12}) \quad (6)$$

The following values were obtained for the Li2MnGe alloy through the application of the aforementioned formulas: the values for B, G, E, and σ are 35.29 GPa, 38.26 GPa, 84.02 GPa, and 0.098, respectively. A low Poisson's ratio suggests that directional covalent bonds are the predominant bond characteristic in the material, indicating that interatomic forces are distributed in a more rigid and directional manner [17]. The calculated Young's modulus indicates a moderate elastic stiffness of the alloy. The low bulk modulus indicates that the structure is relatively compressible under external pressure. The Pugh ratio (B/G) was calculated to be 0.922. This ratio is a critical criterion employed for the classification of brittleness and ductility. The threshold value of 1.75 is generally used as a reference. Systems with values below the threshold are considered brittle, whereas those with values above the threshold are considered ductile. Consequently, the Li2MnGe alloy has a brittle structure,

implying that the material is susceptible to fracture without undergoing plastic deformation [18,19]. The A value for the Li2MnGe alloy was found to be 2.9475. The condition $A \neq 1$ indicates that the crystal is elastically anisotropic, meaning that it exhibits different elastic behaviors in different crystal directions. This observation suggests that the material may exhibit anisotropy, with different directions possessing distinct mechanical properties. This property is particularly salient in structural engineering applications, where it must be considered to ensure the integrity and reliability of the structure. In summary, the Li2MnGe alloy has distinct covalent bonding, brittle, and anisotropic mechanical characteristics, exhibiting both a low Poisson's ratio and a high anisotropy coefficient. The results obtained are consistent with those of other Heusler and half-Heusler alloys, which exhibit similar properties [20,21]. The temperature-dependent thermodynamic behavior of the Li2MnGe alloy was evaluated within the framework of density functional theory (DFT) based on the Debye model. The Thermo Pw module was utilized in these analyses, and fundamental parameters such as heat capacity (C_v), entropy, internal energy, and Debye temperature (θD) were calculated over the 0–800 K temperature range. The calculations revealed that the alloy's Debye temperature is approximately 409.889 K. This value indicates relatively high characteristic lattice vibration frequencies and suggests comparatively stiff interatomic bonding within the crystal structure. The Debye temperature is also directly related to phonon properties and was obtained through the sound velocities and elastic moduli of the material. The calculations for the heat capacity (C_v) of the alloy demonstrated a swift rise at low temperatures, which decelerated as the temperature increased and approached the Dulong–Petit limit. This limit signifies the maximum heat capacity that solids with a crystalline structure can attain at elevated temperatures. It is expressed by the relationship $Cv \approx 3NkB$. Furthermore, entropy calculations demonstrate a direct correlation between increasing temperature and an increase in material disorder. This increase indicates that microscopic disorder increases with temperature, which is consistent with the second law of thermodynamics. Furthermore, the internal energy continuously increases with temperature. This finding suggests that the thermal energy contributions are distributed uniformly throughout the lattice system and that the crystal structure can absorb additional energy with increasing temperature. Consequently, the calculated thermodynamic properties suggest that Li_2MnGe may be of interest for future investigations in electronic, magnetic, and multifunctional material applications

4. CONCLUSIONS

In this study, the structural, elastic, electronic, magnetic, and thermodynamic properties of a Li2MnGe alloy with an XA-type inverse Heusler crystal structure were systematically investigated within the framework of density functional theory (DFT) based on first-principles calculations. A comprehensive evaluation of three distinct crystal structure configurations proposed in the literature was conducted, and only one was found to be mechanically stable. Consequently, calculations were pursued on the basis of this structure. The equilibrium lattice parameter of 6.0443 Å, obtained through lattice optimization, demonstrated the crystalline stability of the alloy. The calculated elastic constants and derived mechanical moduli revealed that the Li2MnGe alloy exhibited brittle and anisotropic mechanical behavior along with a distinct covalent bonding character. Electronic band structure and density of states analyses

demonstrated that the alloy exhibits metallic conductivity with a highly spin-polarized electronic structure and a narrow pseudogap-like feature near the Fermi level in the spin-down channel. The calculation of the total magnetic moment as 3.96 μB is consistent with the Slater–Pauling principle and confirms the ferromagnetic nature of the alloy. Additionally, the Debye temperature of approximately 409.889 K, obtained from thermodynamic analyses based on the Debye model, suggests relatively stiff interatomic bonding and characteristic lattice vibrational behavior. The calculated structural, electronic, magnetic, and thermodynamic properties suggest that Li_2MnGe may be considered a potential candidate for future investigations in spintronic devices, magnetic sensing technologies, and multifunctional material systems. In the future, it is recommended that these theoretical findings be verified through experimental studies and that the properties of Li_2MnGe in thinfilm form be investigated in greater detail. Thin-film Heusler alloys are of particular interest for spintronic devices such as magnetic tunnel junctions, spin valves, and spin-transfer torque memories. Furthermore, strain effects induced during thin-film growth may influence the electronic and magnetic properties of Li_2MnGe, providing additional opportunities for performance optimization. The electronic and magnetic behavior of the alloy may also be further tuned through doping and strain-engineering approaches. Additionally, the examination of structural changes in response to external factors such as temperature, pressure, and magnetic fields will provide more comprehensive insights into the suitability of materials for integration into multifaceted engineering applications.

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