

半休氏勒合金 LiMgAs 结构和热力学性质的第一性原理计算

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摘要: 本文利用基于密度泛函理论的第一原理方法研究了 Half-Heusler 合金 LiMgAs 的结构性质以及热力学性质. 所计算的晶格常数、弹性模量以及弹性模量对压强的导数均与实验及其他理论值相吻合. 本文还计算了 α 、 β 和 γ 三种相的 LiMgAs 声子频率, 发现没有虚频的 α -LiMgAs 热力学结构稳定, 其他两相均有虚频, 不稳定. 本文通过准谐德拜模型, 研究并获得了不同温度 0~1500 K 和不同压强 0~70 GPa 下的热膨胀系数、热容、熵、德拜温度和 Grüneisen 参数. 我们发现, 热膨胀系数、热容、熵和 Grüneisen 参数随温度的增加而增加, 随压强的增加而减小; 而温度和压强对德拜温度和弹性模量的影响和对上面其他物理量的影响恰好相反. 另外, 当温度高于 1000 K 时, 热容值变化很小, 遵循 Dulong-Petit 定律.

关键词: 第一性原理; 结构和热力学性质; 高温和高压; half-Heusler 合金

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First-principles calculations of structural and thermodynamic properties of half-Heusler alloy LiMgAs

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Abstract: The crystal structure and thermodynamic properties of half-Heusler alloy LiMgAs are investigated using first-principles calculations. The calculated ground-state quantities such as lattice parameter, bulk modulus and its pressure derivative are in agreement with previous works and the existing experimental data. Phonon spectra are calculated for LiMgAs in α , β and γ phases, it is found that the LiMgAs in α phase is dynamically stable due to no imaginary frequencies, the LiMgAs is dynamically unstable for β and γ phases with imaginary frequencies. Using the quasi-harmonic Debye model considering the phonon effects, the temperature and pressure dependencies of bulk modulus, heat capacity, entropy, Debye temperature, Grüneisen parameter and thermal expansion coefficient are investigated systematically in the ranges of 0~70 GPa and 0~1500 K. It is found that heat capacity, entropy, thermal expansion coefficient and Grüneisen parameter increase with the increasing temperature at a given pressure, and decrease with increasing temperature at a given temperature. However, the Debye temperature bulk

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modulus are contrary to the above laws of physical quantities. When temperature is higher than 1000 K, the heat capacity change a little, which obeys Dulong and Petit's rule.

Keywords: First-principles; Structural and thermodynamic properties; High pressure and high temperature; Half-Heusler alloy

1 Introduction

The world at present is facing two major problems relating to energy. One is the energy crisis and another is its environmental impact arising from conventional ways of utilizing energy resources. The first problem is driving research for alternative energy resources and the second problem concerns better ways of utilizing the energy resources. Thermoelectricity is considered to be one of the potential ways towards addressing both these problems^[1-3]. Half-Heusler materials are considered to be potential thermoelectric materials^[4-6] because of their consistent temperature stability. Furthermore, they offer the possibility of alloying, which can reduce thermal conductivity due to mass fluctuation^[2]. LiMgAs is a typical Half-Heusler materials, and there are lots of studies on the material, including experimental and theoretical research^[7-15].

The optical properties of LiMgAs have been measured using a photoluminescence method^[7] and a scanning spectrophotometer^[8]. Raman-scattering experiment has been used to measure the zone-center phonon modes of LiMgAs^[9]. The structural, elastic, electronic and phonon properties of LiMgP and LiMgAs in different phases were studied by employing the plane wave pseudopotential method based on density functional theory, within the local density approximation^[10]. Vibrational properties of LiMgAs in α -phase have been calculated^[11] by using the density functional perturbation theory as implemented in the ABINIT code. The electronic and optical properties of the filled tetrahedral compounds LiMgN, LiMgP and LiMgAs were carried out which based on the First principles calculations by means of the full-potential linearized augmented plane wave method within the local density ap-

proximation^[12]. Covalent bonding and the nature of band gaps in some half-Heusler compounds were investigated using LAPW and LMTO calculations^[13]. The half-Heusler ternary LiMgZ ($Z = \text{P, As, Bi}$) compositions were discussed using the first principles study in the density functional theory and FP-LAPW method to study thermoelectric behaviors, electronic structure and structural properties^[14]. First-principles calculations were performed to study electronic structures and magnetic properties of Mn doped LiMgAs system^[15]. Despite much work on the structural and electronic properties of LiMgAs, however, few people have investigated the thermodynamic properties under pressure and temperature. In this work, the structural and thermodynamic properties for LiMgAs are researched using first principle within a generalized gradient approximation (GGA).

2 Calculation methods

The first-principles calculations of LiMgAs are performed by using CASTEP simulation package^[16] which is based on density functional theory. The Vanderbilt ultrasoft pseudopotential^[17] is used. Exchange-correlation effects are taken into account using the Generalized Gradient Approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)^[18]. The plane wave cut-off energy of 460 eV is employed. The valance electrons is considered in this study included $1s^2s^1$ for Li, $2p^63s^2$ for Mg and $4s^24p^3$ for As. The k -point meshes of $4 \times 4 \times 4$ are generated by using the Monkhorst-Pack scheme^[19].

The calculations of thermodynamic properties, which are carried out by using the GIBBS program, are based on the Quasi-Harmonic Debye model (QHD)^[20,21]. After the parameters of the minimum energy are calculated, the lattice parameters are obtained, the GIBBS code is input

with the energy-volume (E - V) data acquired from the first-principles calculations using the previous structure set.

3 Results and discussion

3.1 Structural properties

LiMgAs crystallizes in tetrahedral structure with a space group $F\bar{4}3m$. The structure can be assumed to be derived from the combination of a rock-salt type (NaCl) structure with a zinc-blende type structure. Mg cation sits at $(0, 0, 0)$, with As at $(0.25, 0.25, 0.25)$ and Li at $(0.5, 0.5, 0.5)$ (α phase). It is also feasible for Li to occupy either the $(0.75, 0.75, 0.75)$ site neighboring the Mg cation position (β phase) or switching with As sit in between the Mg and As (γ phase). For the α phase, β phase and γ phase of the LiMgAs, a series of the different lattice constant a are set to calculate the total energies E and corresponding volumes V , which shown in Fig. 1. It is noted that the α phase is the most stable state. The energy-volume(E - V) can be obtained by fitting the calculated E - V data to the third Birch-Murnaghan EOS^[22]. At equilibrium volume, the obtaining lattice constants, bulk modulus B_0 (GPa) and its pressure derivate B'_0 for the α phase, β phase and γ phase of the LiMgAs are listed in Tab. 1, compared with experimental data^[8] and other theoretical results^[10, 13, 15, 23]. It is seen the calculated values are in good agreement with experimental value and other calculated results.

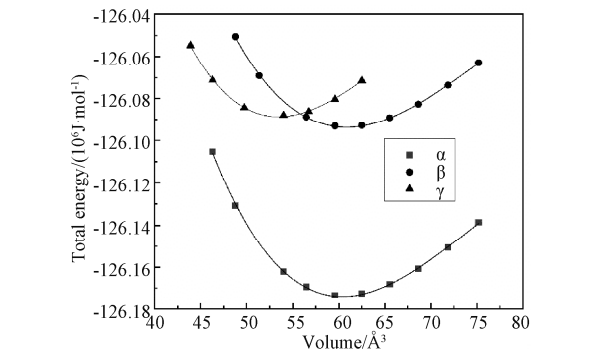


Fig. 1 Energy versus volume for α , β and γ phase of LiMgAs

In order to investigate the behaviors of the

phase transition pressure, we obtain the relation of the enthalpy and pressure using the third Birch-Murnaghan EOS^[22]. According to the isoenthalpy principle, the phase transition pressure for the α phase and the γ phase is 26.5 GPa, for the β phase and the γ phase is 2 GPa, while there is no transition pressure for the α phase and the β phase, which is shown in Fig. 2.

Tab. 1 The calculated lattice constants a , bulk modulus B_0 and its pressure derivate B'_0 at equilibrium volume compared to experimental and other works of half-Heusler alloy LiMgAs

Material	$a/\text{\AA}$	B_0/GPa	B'_0
α -LiMgAs	6.228		
	6.090 ^[10]	48.00	4.09
	6.080 ^[23]	51.50 ^[10]	3.80 ^[10]
	6.218 ^[13]	51.57 ^[23]	4.12 ^[23]
	6.221 ^[15]	42.90 ^[13]	
β -LiMgAs	6.181 ^[8]		
	6.242	42.49	3.84
γ -LiMgAs	6.097 ^[10]	48.60 ^[10]	3.85 ^[10]
	5.981	48.09	3.78
	5.838 ^[10]	54.6 ^[10]	3.95 ^[10]

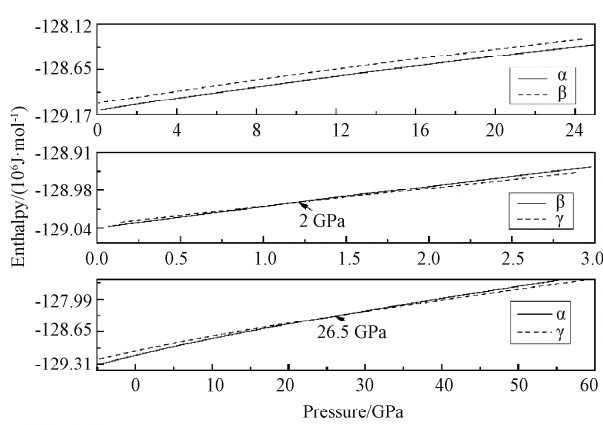


Fig. 2 Enthalpy versus pressure for α , β and γ phases of LiMgAs

3.2 Dynamical properties

The importance of the phonon interpretation of lattice dynamics is illustrated by the large number of physical properties that can be understood in terms of phonons: infrared, Raman, and neutron scattering spectra, specific heat, thermal expansion, and heat conduction, and so on. The basic theory of phonons, in crystals is well under-

stood and has been described in detail^[24,25]. In our phonon calculations, finite displacement calculations are carried out in the supercell with cut-off radius 5.0 Å, $7 \times 7 \times 7$ meshes are used in the interpolation of the phonon calculations. the phonon dispersion curves along the high symmetry directions in the Brillouin zone for LiMgAs in the α , β and γ phases are plotted in Fig. 3. There

are no imaginary frequencies in α phase in the Brillouin zone, however, the β phase and the γ phase have imaginary frequencies, which intimates the LiMgAs in α phase is dynamically stable, the LiMgAs is dynamically unstable for β and γ phases. So, the following thermodynamic properties will only focus on the the α phase of LiMgAs.

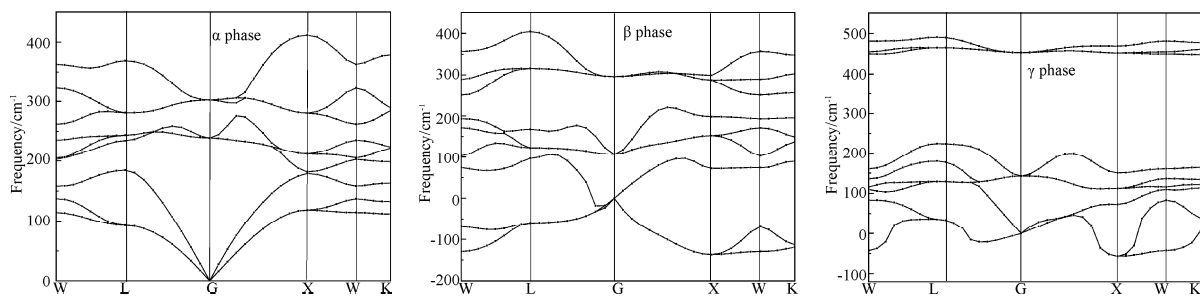


Fig. 3 The phonon dispersion curves for the α , β and γ phases of the LiMgAs

The calculated phonon frequencies of α phase at the zone center are $\text{TO}(G) = 238.82 \text{ cm}^{-1}$, $\text{LO}(G) = 302.46 \text{ cm}^{-1}$, which agree well with the previous theoretical results^[10] ($\text{TO}(G) = 253.30 \text{ cm}^{-1}$, $\text{LO}(G) = 303.70 \text{ cm}^{-1}$) and are smaller than experimental results ($\text{TO}(G) = 307 \text{ cm}^{-1}$, $\text{LO}(G) = 329 \text{ cm}^{-1}$). The discrepancies between the theoretical calculation and experimental results are similar to LiZnAs with identical structure^[26], which may result from the difference between the observed and calculated lattice constants and lattice imperfection. Our calculated value of the zone-center $\text{LO}(G)$ - $\text{TO}(G)$ splittings are 63.64 cm^{-1} for the LiMgAs in α phase.

3.3 Thermodynamic properties

To investigate the thermodynamic properties of LiMgAs under high temperature and high pressure, we have applied the quasi-harmonic Debye approximation. As the first step, a set of total energy calculation versus primitive cell volume (E - V), in the static approximation, is carried out for each compound and fitted with the third Birch-Murnaghan EOS in order to determine its structural parameters at $p = 0$ and $T = 0$, and then derived the macroscopic properties as a function of p and T from standard thermodynamic relations. The thermal properties are determined in the tem-

perature range from 0 to 1000 K, the pressure range from 0 to 70 GPa.

The bulk modulus variation versus temperature at a given pressure is showed in Tab. 2. The compressibility increases with increasing temperature at a given pressure and decreases with pressure at a given temperature. These results are due to the fact that the effect of increasing pressure on the material is the same as the decreasing temperature of the material. The effect of the temperature T on the isothermal bulk modulus is less important than that of the pressure.

The variation of the thermal expansion coefficient α as a function of temperature and pressure is showed in Fig. 4. It is shown that, at a given pressure, α increases sharply with the increase of temperature up to 300 K. When $T > 300 \text{ K}$, α gradually increases linearly with enhanced temperature and the propensity of increment becomes moderate, which means that the temperature dependence of α is very small at high temperature. For a given temperature, α decreases drastically with the increase of pressure.

Knowledge of the heat capacity of a substance not only provides essential insight into its vibrational properties, but also is mandatory for many applications. The relationship between the

heat capacity C_V and temperature at different pressures ($p = 0, 20, 40, 70$ GPa) is shown in Fig. 5, and C_V is calculated by the obtained phonon dispersion, which is plotted hollow circle in Fig. 3. It is shown that the thermodynamic properties of LiMgAs based on the quasi-harmonic Debye approximation are reasonable. C_V is very small at low temperatures, and approaches a constant value at high temperatures. At low temperatures, C_V increases exponentially, which follow the Debye model ($C_V \sim T^3$), and at sufficiently high temperatures (>1000 K), the heat capacity obeys Dulong and Petit's rule, and the difference between them is very slight, which are similar to the calculational results^[27-31].

Tab. 2 The calculated bulk modulus B , Debye temperature θ_D and Grüneisen parameter γ of LiMgAs at different pressure and temperature for half-Heusler alloy LiMgAs

Pressure /GPa	Parameters	Temperature/K				
		0	300	600	900	1500
0	θ_D /K	373.64	362.68	345.15	326.97	290.00
	γ	1.918	1.921	1.927	1.935	1.946
	B /GPa	47.42	44.49	40.98	37.64	31.47
10	θ_D /K	499.45	492.04	478.26	463.78	434.08
	γ	1.886	1.888	1.891	1.896	1.902
	B /GPa	88.26	85.22	81.01	77.01	69.33
20	θ_D /K	595.3	589.66	578.02	565.50	539.78
	γ	1.867	1.869	1.871	1.874	1.878
	B /GPa	128.75	125.65	121.01	116.52	107.83
30	θ_D /K	674.95	670.39	660.12	648.91	625.78
	γ	1.854	1.855	1.856	1.859	1.862
	B /GPa	169.01	165.89	160.98	156.12	146.74
40	θ_D /K	744.29	740.46	731.19	720.89	699.58
	γ	1.844	1.844	1.846	1.848	1.85
	B /GPa	209.10	205.99	200.93	195.79	185.96
50	θ_D /K	806.49	803.19	794.69	785.07	765.12
	γ	1.835	1.836	1.837	1.838	1.841
	B /GPa	249.05	245.98	240.87	235.50	225.41
60	θ_D /K	863.32	860.5	852.55	843.59	824.65
	γ	1.828	1.828	1.829	1.831	1.833
	B /GPa	288.89	285.88	280.80	275.26	265.07
70	θ_D /K	916.1	913.71	906.16	897.74	879.64
	γ	1.822	1.822	1.823	1.824	1.826
	B /GPa	328.62	325.70	320.71	315.06	304.90

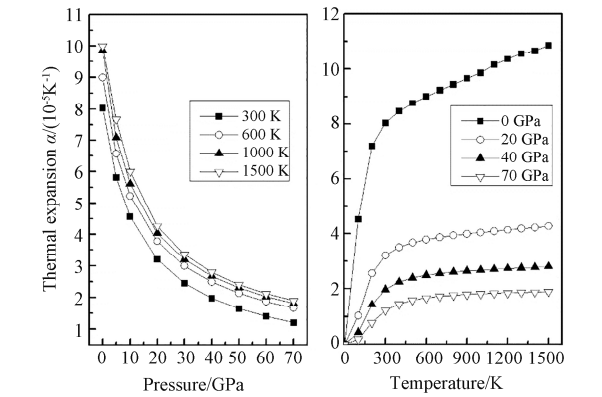


Fig. 4 Variation of thermal expansion coefficient α as a function of temperature and pressure for half-Heusler alloy LiMgAs in the α phase

Entropy is a measure of the chaos for a material system. Entropy under different pressures and temperatures is showed in Fig. 6. Under the same pressure, the entropy increases with the increase of temperature, and the increasing trend gradually slows down at high temperature. At the same temperature, entropy decreases with the increase of pressure. The rise and fall of entropy is relate to the vibration between LiMgAs atoms. Pressure reduces the vibration amplitude of Li, Mg and As atoms, so entropy decreases with increasing Pressure.

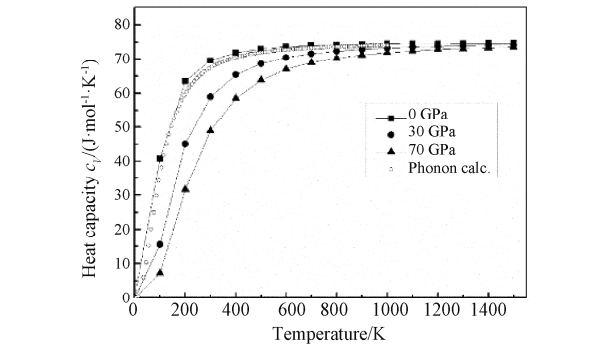


Fig. 5 Variation of the heat capacities C_V as a function of temperature at different pressure for half-Heusler alloy LiMgAs, hollow circle present the obtained value by phonon dispersion calculation in the α phase

The Debye temperature θ_D is closely related to many physical properties of solids, such as elastic properties, sound velocities, hardness and specific heat. Another important thermodynamic parameter is Grüneisen parameter γ , which describes the anharmonic effects in the crystal vi-

brations, and also, it is used to characterize the thermodynamic behavior of a material at high pressures and temperatures. the Debye temperatures and Grüneisen parameters for LiMgAs at different pressures and temperatures are listed in Tab. 2. At a constant temperature, θ_D increases with the increasing pressure, while γ decreases. However, at a constant pressure, θ_D decreases with the increasing temperature, while γ increases.

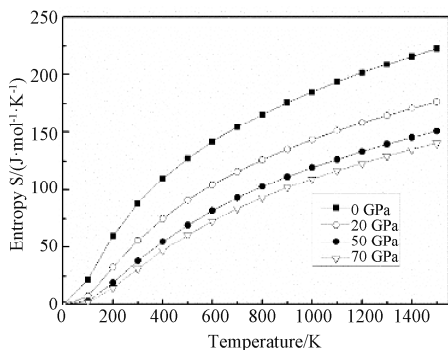


Fig. 6 Variation of the entropy S as a function of temperature at different pressure for half-Heusler alloy LiMgAs in the α phase

4 Conclusions

Using the first-principles plane-wave pseudo-potential density functional theory within GGA and the quasi-harmonic Debye model (QHD), the structural, thermodynamic properties of LiMgAs have been investigated. The calculated structural parameters at zero pressure are in agreement with the available experimental data. It is found the phase transition pressure for the α phase and the γ phase is 26.5 GPa, and for the β phase and the γ phase is 2 GPa. No phase transition occurs between α phase and β phase. There are no imaginary frequencies in the α phase, which intimates the LiMgAs is dynamically stable in α phase, and β and γ phases are unstable due to imaginary frequencies. It is found that the high temperature leads to a smaller bulk modulus, a larger heat capacity, larger entropy, larger thermal expansion coefficient and a larger Grüneisen parameter at a given pressure. However, the high-pressure results in a larger bulk modulus, a smaller heat ca-

capacity, a smaller entropy, a smaller Grüneisen parameter and a smaller thermal expansion coefficient at a given temperature. The heat capacity and the thermal expansion coefficient tend to a constant value at high temperatures and high pressure.

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