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AB INITIO STUDY OF STRUCTURAL, ELECTRONIC, MECHANICAL AND THERMAL PROPERTIES OF B2 TYPE LAIN INTERMETALLIC COMPOUND

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Abstract

An investigation on structural, electronic, mechanical and thermal properties of lanthanum indium LaIn intermetallic compound under ambient pressure is performed using ab-initio calculations based on density functional theory (DFT) within generalized gradient approximation (GGA) and local density approximation (LDA). The calculated lattice parameter (a0 = 3.965 Å) agrees well with the experimental results. Electronic properties have been investigated in terms of band structure and density of states. Electronic behavior of LaIn shows that studied material is metallic and non-magnetic in which La-d and In-p states have dominant character towards metallicity. Three independent second order elastic constants (C11 = 119.36 GPa, C12 = 17.76 GPa and C44 = 47.13 GPa) have been calculated by using the method developed by Thomas Charpin and integrated it in the WIEN2k package. In this paper, we have also presented theoretical results of the mechanical properties of LaIn i.e. Bulk Modulus, Young's Modulus, Anisotropic ratio, Poisson's ratio, sound velocities for shear and longitudinal waves and Debye temperature. Cauchy Pressure and B/GH ratio have also been investigated to explore the ductile and brittle behavior of the compound.

Keywords – Ab-initio, Mechanical Properties, Debye temperature.

1. Introduction

Indium possesses unique physical and chemical properties and has been widely used in the fields of medicine and health, solar battery, national defense and military, aerospace, and modern information industry. The fundamental investigation on indium-related materials is still a challenge. Compounds of the systems of rare earths with indium have attracted significant interest during the last decades due to their crystal chemistry and physical properties [1]. The investigations of these systems *RE*In (*RE* = rare earths) [2-3] started with the studies of the crystal structure and magnetic properties of the solid solutions. The CsC1- type structure has been reported for the YIn, LaIn[4], PrIn, TmIn and YbIn [5], GdIn and DyIn [6] and ErIn [7] rare earth indium compounds. Guo et al. made a study on the phase stability, mechanical, electronic, and thermodynamic properties of In-Zr compounds [8]. Plessis et al. examined the temperature dependence of the electrical resistivity of polycrystalline RIn samples (R = Tb, Dy, Ho,Er, La, Ce) [9]. The crystal structure of LaIn compound was determined by X-ray powder diffraction, and it is found to exist in B_2 type structure [4]. To the best of our knowledge, there is not enough experimental and theoretical research about basic structural, electronic, elastic, mechanical and thermal properties related to LaIn compound was done so far. In order to take advantage of the properties of this compound for eventual technological applications, a theoretical investigation of the structural, electronic, elastic, mechanical and thermal properties is necessary. In the present paper we have theoretically investigated the structural, electronic, elastic, mechanical and thermal properties of the cubic LaIn compound, by

using the FP-LAPW method with the generalized gradient approximation (GGA).

The paper is organized in four sections. Section 2 is devoted to the method of calculation; Section 3 deals with the results and discussion and in Section 4, we present the conclusion.

2. Computational Method

The calculations have been performed using full potential linearized augmented plane wave (FP-LAPW) method [10] based on density functional theory [11,12], as implemented in WIEN2k code [13]. The generalized gradient approximation [14] in the schemes of Perdew, Burke and Ernzrhof (PBE) is applied for the exchange and correlation effects. In this code, the unit cell is divided into no overlapping muffin-tin spheres of radius RMT and an interstitial region, where the Kohn-Sham wave functions are expressed in spherical harmonics within spheres and in plan waves in the remaining space of the unit cell The basis function has been expanded up to $R_{MT}*K_{max}$ = 7.0 in order to achieve convergence, where R_{MT} is the minimum sphere radius and K_{max} is the maximal value of the reciprocal lattice vector used in the plane wave expansion. The spherical harmonics inside the muffin-tin are taken with an angular momentum l_{max} = 10 while the charge density is Fourier expanded up to G_{max} = 12 $(Ryd)^{1/2}$. The self-consistent calculations are converged when the total energy of the system is stable within
10^{-4} Ry. A dense mesh of 10x10x10 k points and the tetrahedral method [14] have been employed for the Brillouin zone integration. The total energies are fitted to a third order Birch-Murnaghan's equation of state (EOS) equation [15] to obtain the ground state properties.

$$P = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left[1 + \frac{3}{4}\left(B_0^{'} - 4\right)\left\{\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right\}\right] \quad (1)$$

where P is the pressure, V is the volume at pressure P, V_0 is the volume at ambient pressure, B_0 is the bulk modulus at ambient pressure and B_0' is the pressure derivative of bulk modulus B_0.

3. Results and Discussion

3.1 Crystal Structural Properties

LaIn with B_2 CsCl-type has two atoms in one unit cell with *Pm*3*m* space group. Figure 1(a) illustrates the crystal structure of LaIn. The La atoms are positioned at (0, 0, 0), In atoms at the centre of unit cell (0.5, 0.5, 0.5) [16]. For calculating the ground state properties of LaIn, the total energy is calculated as a function of volume in their B_2 (CsCl) structure. The calculated total energies are fitted to the Birch equation of state [15]. The ground state properties, such as equilibrium lattice constants (a_0), bulk modulus (B) and its pressure derivative (B′) have been calculated and presented in table1.

The calculated lattice parameter is in reasonable agreement with the experimental calculations.

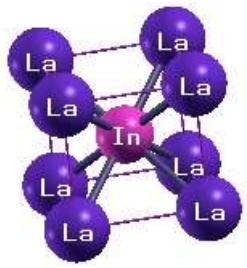

Figure1 Crystal structure of LaIn

Table1. Theoretical and experimental lattice constants a (Å), Bulk Modulus(B), its pressure derivative B' as well as unit cell volumes of LaIn in B_2 cubic phase

Method	a_0 (Å)	B (GPa)	B'	$N(E_F)$ (States/eV)	Cv/T (mJ/mol K^2)
PBE-GGA	3.965	53.42	3.53	1.05	2.48
LDA	3.857	58.63	3.69	-	-
Experimental	3.985[4]	-	-	-	-

3.2 Electronic Properties

The energy band structure and corresponding density of states are prominent quantities that determine the electronic structure of a system. The non spin polarized calculation has been performed using PBE-GGA approximation to understand the electronic behavior of LaIn intermetallic compound in terms of electronic band structure (BS) and density of states (DOS). Also, it is one among the most accurate scheme for band structure calculations. It is based on full-potential linearized augmented plane wave FP-LAPW, one of the most accurate schemes for band structure calculations. We have used an optimized geometry obtained through a self consistent process to investigate the electronic structure of the crystal lattice of the material.

The band structure at equilibrium lattice constant of LaIn in B_2 crystal structure were calculated along the high symmetry directions in the brillouin zone and shown in fig.2(a), in which Fermi energy E_f = 0 is assumed. The bands in the energy range around -3.5 and -2.0 eV are due to La '5d' states and In '5p' states . It can be seen from the band structure that two bands are crossing the Fermi level. This intersection of band with fermi level clearly revealed the metallic character of LaIn in B_2 CsCl structure.

The total DOS plot of LaIn shown in fig. 2(b), shows the total density of states of La- (La 'd' anf 'f') and In- (In 'p') in LaIn compound respectively. In LaIn DOS plot, emerges that electronic structure is characterized by In 'p' states lying in between (-3.5 eV to -2eV) below the Fermi level, while the La 'd' and 'f' states are situated above the Fermi level. The predominant contribution of the density of states at the Fermi level originates due to the contribution of 'd' like state of La and '*p*' like state of In. Rest of other states of La and In both do not contribute much at Fermi level. The metallic character of this compound is a consequence of contribution of'd' state and 'p' state of La and In respectively.

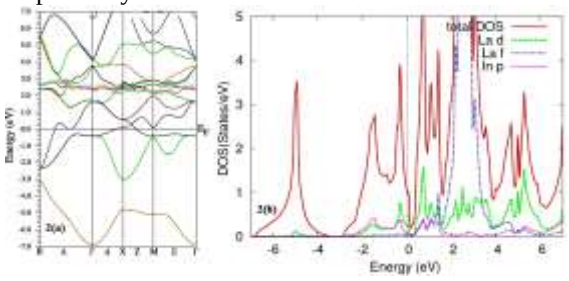

Figure2 (a) Electronic Band structure and 2(b) Density of states of LaIn

The electronic specific heat coefficient $\gamma = \frac{C_V}{T}$ which is the function of density of states is calculated for the LaIn compound and summarized in Table 1. For non-interacting electrons, the electronic specific heat coefficient is proportional to the total DOS at the Fermi level $N(E_F)$ and is given by $\gamma = \frac{\pi^2 N(E_F) K_B^2}{3}$,

where $N(E_F)$ is the DOS at Fermi level and K_B is the Boltzmann's constant. The obtained values of $N(E_F)$ enable us to calculate the bare electronic specific heat coefficient. Due to the lack of availability of any reference data it could not be compared.

3.3 Mechanical Properties

The elastic constants are essential for understanding macroscopic mechanical properties of crystal as they relate to various fundamental solid state properties and thermodynamic properties. Elastic constants (Cij) represent the stresses required for the occurrence of unit strains in the crystal, which are the measure of how easily material elastically deforms. The larger is the value of Cij, the better the mechanical properties of the crystal. For the cubic crystal structure of LaIn, there are three independent elastic constants: C_{11}, C_{12} and C_{44}. C_{11} and C_{12} represent the longitudinal and transverse strain stiffness constants respectively. C_{44} is the shear strain stiffness constant. The elastic constants (Cij) of LaIn are calculated by fitting the relation curve of strain and energy difference. The calculated elastic properties (Cij, G_H and E) are listed in Table 2. Furthermore, the value of anisotropy factor *A*, Poisson ratio σ and Pugh's criterion B/ G_H is also listed. The bulk modulus *B* and Voigt-Reuss-Hill averaged shear modulus G_H [17] were obtained by using second order elastic constants of LaIn. The elastic stability is a necessary condition for a crystal to exist. The requirements of mechanical stability for a cubic crystal lead to the following restrictions on the elastic constants [18]: $C_{11}>0$, $C_{44}>0$, $C_{11}-C_{12}>0$, $C_{11}+2C_{12}>0$, $C_{11} > B > C_{12}$. Obviously, the calculated elastic constants satisfy the mechanical stability criterion, which means that LaIn is stable in B_2 structure. Pugh [19] proposed that material predicted to be in ductile behavior if the value of $B/G_H>1.75$. Obviously, our calculated value doesn't satisfy this criterion. The LaIn is predicted to be brittle. Cauchy pressure C_{12}-C_{44} is another index for determining the ductile/Brittle nature of metallic compound, where positive (negative) values of C_{12}-C_{44} correspond to ductile (Brittle) materials. The calculated Cauchy pressure for LaIn compound considered here negative, i.e. indicating a brittle nature of LaIn.

Table2. The calculated second order elastic constants (SOEC's) and Mechanical properties of LaIn.

C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	A	G_H (GPa)	E (GPa)	σ	B/ G_H	C_{12} - C_{44}
119.36	17.76	47.13	1.01	49.26	112.16	0.13	1.049	-30.40

Poisson's ratio [20] is another important parameter for deciding the ductile/ brittle nature of

solids. σ is less than 0.33 for the brittle materials. Thus from the calculated value of σ, the brittleness of LaIn is again confirmed. Another important parameter is elastic anisotropy factor A, which gives a measure of anisotropy in the crystals. For isotropic crystals, A = 1 and our calculated value is nearly equal to 1. The compound investigated here is elastically isotropic in nature.

3.4 Thermal Properties

With the calculated value of Young's modulus E, the bulk modulus B, and the shear modulus G, one may derive the Debye temperature using the equation (1).

$$\theta_D = \frac{h}{k_B}\left[\frac{3n}{4\pi V_a}\right]^{\frac{1}{3}} v_m \quad (1)$$

where h is a Planck's constant, k_B is Boltzmann's constant, V_a is the atomic volume, n is the number of atoms per formula unit cell and v_m is average sound velocity. The average sound velocity is given by

$$v_m = \left[\frac{1}{3}\left(\frac{2}{{v_t}^3} + \frac{1}{{v_l}^3}\right)\right]^{\frac{-1}{2}} \quad (2)$$

where v_l and v_t are the longitudinal and transverse sound velocities, which may be obtained from the shear modulus G_H and bulk modulus B using

$$v_l = \sqrt{\frac{\left[C_{11} + \frac{2}{5}(2C_{44} + C_{12} - C_{11})\right]}{\rho}} \quad (3)$$

And,

$$v_t = \sqrt{\frac{\left[C_{44} - \frac{1}{5}(2C_{44} + C_{12} - C_{11})\right]}{\rho}} \quad (4)$$

Where C_{11}, C_{12}, C_{44} are second order elastic constants and ρ is mass per unit volume.

At low temperature the vibrational excitations arise solely from acoustic vibrations. Hence at low temperature the Debye temperature is calculated from elastic constants. We have calculated the average sound velocities and Debye temperature as well as the density of LaIn for B2-phase by using the calculated elastic constants which are given in Table 3.

Table3. The calculated density ρ, longitudinal v_l, transverse v_t, average elastic wave velocities v_m and Debye temperature θ_D for LaIn.

ρ x 10^3 (Kg/m^3)	v_l (m/s)	v_t (m/s)	v_m (m/s)	θ_D (K)
12.492	3065.30	1985.79	2178.58	206.26

4. Conclusion

We have investigated the structural, electronic, mechanical and thermal properties of LaIn intermetallic compound. The crystal structural parameters like lattice constant, bulk modulus and its pressure derivative are derived. The obtained theoretical value for lattice constant is found to be in good agreement with the experimental result. From the electronic properties, it can be suggested that LaIn is metallic in nature and mainly '5d'like state of La atom is responsible for the metallicity of this compound. The second order elastic constants are reported which satisfy the mechanical stability criterion. It is found that LaIn possesses the brittle nature. The elastic properties, elastic modulii, sound wave velocity and Debye temperature are also investigated.

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