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High-pressure elasticity and lattice dynamics of Mg_2La from first principles

Savaş Ağduk, Gökhan Gökoğlu*

Department of Physics, Karabük University, 78050 Karabük, Turkey

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ABSTRACT

In this study, we present the results of first principles calculations of elastic constants and structural properties of the Mg_2La cubic Laves phase (C15) up to ≈150 GPa pressure together with vibrational properties at equilibrium geometry. projector augmented wave (PAW) potentials are used with generalized gradient approximation (GGA) scheme of the density functional theory. The linear response technique of the density functional perturbation theory is applied in investigation of the phonon dispersion spectra. The static equation of states of the system has been studied with Vinet formulation. The values of applied pressure have also been obtained from the Vinet formulation of equation of states. The cubic phase of the system remains stable within the studied pressure range. The elastic anisotropy ratio indicates an electronic topological transition (ETT) around ≈100 GPa. This situation is also confirmed by electronic band structures.

1. Introduction

Magnesium based pseudo-binary alloy systems with a general formula Mg_2(RE) (RE: rare-earth element) have been taking place at the center of several theoretical [1,2] and experimental [3] studies due to the interesting electronic and mechanical properties. Magnesium alloys are exceedingly important with applications in the automobile and aircraft industry [1]. The utilization of magnesium alloys in automobile industry has a growing trend indicating 15% annual increase over the last decade [4,5]. These compounds can be stabilized in hexagonal C14 ($MgZn_2$ type) and C36 ($MgNi_2$ type), and cubic C15 ($MgCu_2$ type) structures according to the relation between the atomic radii of the constituent elements [6]. The only structural difference between cubic $MgCu_2$ and hexagonal $MgZn_2$ is the particular stacking of same four-layer structural units [7]. The close structural relationship between these types of phases has been first emphasized by Laves and Mitte [8], so these crystal structures are called “Laves phases”. In a previous experimental study [9], it has been reported that (RE)Mg_2 compounds are able to form Laves phases.

The electronic structure of various Laves phases have been discussed and summarized in a recent review article [10]. The thermodynamic properties of several Mg–La binary alloy systems have been reported in a very recent comprehensive study using DFT scheme with GGA functionals [11]. There is a substantial progress in the high-temperature forming of Mg vehicle closure components [12]. This progress also leads to the implementation of Mg sheet alloys in vehicles. In another study, the solid-solution strengthening of magnesium has been studied from first principles [13]. In that work, the solubilities of several metals in magnesium have been computed using size and chemical misfits. The rare-earth addition to magnesium based Laves structures improves considerably the mechanical strength of the material [14] which is important particularly for technological applications. It was reported that the alloying abilities of MgLa, Mg_2La, and Mg_3La should be much stronger than the other known Mg–La systems such as $Mg_{17}La_2$ and $Mg_{12}La$ [15]. The recent works focus particularly on the formation enthalpies, zero pressure electronic and elastic properties [15–18] as well as high temperature thermodynamic properties of these systems [11]. In the work of Wróbel et al. [11], the phonon dispersion spectra have been computed for several Mg–La binary systems. However, the studies on mechanical properties and pressure-dependent elastic stiffness of these compounds are very rare. Naturally, the technological applications mentioned above involve the mechanical resistance of the material against pressure. The vibrational properties of C15 Laves structure of Mg_2La system have also been studied in the present study, since the microscopic mechanisms of elastic behavior is directly governed by the phonon properties. Therefore, the major aim of the present study is to clarify the pressure dependent elastic properties and vibrational dynamics of Mg_2La Laves phase using an accurate all-electron method, projector augmented wave, within density functional theory.

The rest of the paper is organized as follows: the details of calculations performed are presented in Section 2. We present the

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* Corresponding author. Tel.: +90 370 433 8374; fax: +90 370 433 8334.
E-mail address: ggokoglu@gmail.com (G. Gökoğlu).

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results of the first-principles calculations of elastic constants at various pressures and phonon dispersion spectra in Section 3. Finally, a conclusion is presented in Section 4.

2. Computational method

The Mg_2La compound crystallizes in the face-centered cubic C15 Laves phase which conforms to $Fd\overline{3}m$ space group (#227) containing 6 atoms per primitive cell. La atoms are located on the site of diamond structure (8a positions), while Mg atoms occupy 16d positions. All the calculations presented in this study have been performed using the PWscf code, distributed with the Quantum ESPRESSO package [19,20].

Generalized gradient approximation of the density functional theory is used to approximate exchange-correlation potential with Perdew–Burke–Ernzerhof parametrization [21]. The ions are described using projector augmented waves (PAW) potentials. PAW is an all-electron method which generalizes the pseudopotential method and linear augmented plane wave (LAPW) method by taking into account the core electrons. In that sense, it presents an advantage over the usual pseudopotential method. We have produced the PAW potentials of Mg and La atoms using the ATOMPAW code developed by Holzwarth et al. [22]. In the generation of the lanthanum PAW data, a scalar relativistic scheme is followed. The non-linear core correction is applied to compensate the overlap of the core and valence charge densities giving an improved transferability. In order to generate smooth pseudo partial-waves, we use an eight-degree polynomial for lanthanum and RRKJ scheme [23] for magnesium as implemented in ATOMPAW code. The Vanderbilt procedure [24] is used as an orthogonalization scheme for projectors and partial-waves. The analytical form of the shape function is governed by the spherical Bessel functions [25]. Both of the PAW potentials produced by ourselves are now available at the pseudopotential database of the PWscf code [19]. The detailed convergence tests for these pseudopotentials are also included in the same database. As a preliminary remark, our PAW potentials converge to better than 0.1 meV per atom at a 70 Ry kinetic energy cut-off and $14 \times 14 \times 14$ k-point mesh in their respective crystal forms. We have computed the structural parameters of elemental solids of lanthanum and magnesium in order to prove the reliability of generated potentials. The calculated lattice parameters using these potentials are: $a = 3.76$ Å, $c/a = 3.220$ for alpha phase (hcp) of lanthanum and $a = 3.20$ Å, $c/a = 1.623$ for hcp structure of magnesium. These values are in great agreement with PBE and PBEsol calculations of Ref. [11].

In calculations on Laves structure, Brillouin zone integration is performed with automatically generated $14 \times 14 \times 14$ k-point mesh, following the convention of Monkhorst and Pack [26], yielding 104 k-points centered at Γ-point. Wave-functions are expanded in plane wave basis sets up to a kinetic energy cut-off value of 70 Ry. This produces approximately ≈11300 plane waves. The convergence criteria for total energy is 1×10^{-8} Ry in self-consistent calculations. Marzari–Vanderbilt type smearing is applied on fermionic occupation function with $\sigma = 0.02$ Ry smearing parameter [27].

The three independent elastic stiffness coefficients of the cubic crystal under study, C_{11}, C_{12}, and C_{44} are calculated using volume conserving (isochoric) strains. The use of isochoric strains eliminates the first order terms in energy due to the initial hydrostatic pressure. This procedure gives accurate results, since the energy of the crystal depends more strongly on volume than distortions [28]. The shear elastic constant C_s is calculated via tetragonal distortion, while a monoclinic distortion is used to calculate C_{44}. Under these distortions, the strain energies can be expressed as

$$E(\delta) = E(0) + 6C_s V\delta^2 + O(\delta^3), \quad (1)$$

$$E(\delta) = E(0) + 2C_{44} V\delta^2 + O(\delta^4) \quad (2)$$

for tetragonal (1) and monoclinic (2) distortions, respectively [29]. $E(0)$ is the unstrained ground state energy of the system and V is its volume. C_{44} and C_s are obtained from the quadratic coefficients of Eqs. (1) and (2). Other elastic constants (C_{11} and C_{12}) are calculated using C_s and bulk modulus B. The details of the elastic constant calculation method have been explained in detail in Refs. [30,31]. The hydrostatic pressure applied on the system has been realized by changing the lattice constant. The pressure value corresponding to a definite lattice constant is determined from pressure–volume curve of Vinet equation of states [32].

The full phonon dispersion spectra along the main symmetry directions in irreducible Brillouin zone are constructed by using DFPT in the linear response approach [33–35], in which second order derivatives of the total energy are calculated to obtain dynamical matrix. DFPT allows us to examine vibrational properties of materials at a high accuracy level. Energy threshold value for convergence is 1×10^{-16} Ry in phonon calculations. The dynamical matrices are produced in a k-point grid of $6 \times 6 \times 6$ in irreducible wedge of the Brillouin zone. Then the full phonon dispersion spectra can be calculated from interatomic force constants by Fourier transform of dynamical matrices.

3. Results and discussion

The formation of cubic C15 or hexagonal C14 Laves structures is realized according to the ratio of atomic radii of the constituent elements. For the X_2A stoichiometry, the cubic phase is formed if the following condition is satisfied;

$$\frac{d_A}{d_X} > \sqrt{\frac{3}{2}}$$

where d_A and d_X are the atomic radii of A and X atoms, respectively [6]. Otherwise, the hexagonal C14 phase is energetically favored. The atomic radii of Mg and La atoms are 1.50 Å and 1.95 Å [36], respectively, indicating an energetically favored cubic phase. It can be generalized that the formation of cubic phase is more probable for Mg_2(RE) structures including a rare-earth element with less than half-filled 4f electronic orbital [3].

The structural parameters of the system (e.g., lattice constant and bulk modulus) have been studied by Vinet formulation [32] of equation of states (EOS) using energy vs. volume $E(V)$ variation which is obtained by calculation of total energies at more than 30 different volumes between the range 0.8 and 1.2 V_0, where V_0 is the equilibrium volume. The volume derivative of EOS formula gives pressure–volume $P(V)$ curve which is used to identify volume value corresponding to a given pressure. The asymptotic standard errors in EOS fit are less than 0.15% as an indication of the accuracy of performed calculations. In Fig. 1, the static equation of states of Mg_2La structure is shown as energy-lattice constant (a) and pressure–volume (b) variation. The calculated equilibrium volume is 168.819 Å^3 resulting 8.773 Å lattice constant. The calculated zero pressure bulk modulus is 36.71 GPa. The lattice constant of this C15 Laves phase was determined experimentally as 8.774 Å [37].

The second order elastic constants of the system are calculated using tetragonal and monoclinic distortions on face-centered cubic Laves structure as explained in previous section. The system is transformed into body-centered tetragonal structure under the isochoric tetragonal distortion, while a body-centered orthorhombic cell is created under the monoclinic distortion. Although the forces on the atoms are exactly zero in cubic phase, the ionic minimization is needed in order to optimize distorted structures. The minimization is performed using Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [38], until the forces on the atoms are less than