Pressure-induced structural phase transition and elastic properties in rare earth CeBi and LaBi

V Mankad¹, S K Gupta¹, I Lukacević² and P K Jha¹*
¹Department of Physics, Bhavnagar University, Bhavnagar-364022, India
²Department of Physics, University J. J. Strossmayer, Osijek, Croatia
E-mail: prafullaj@yahoo.com

Abstract. A comprehensive first principles study of structural, elastic, electronic and phonon properties of rare-earth CeBi and LaBi is reported within the density functional theory scheme. The ground state properties such as lattice constant, elastic constants, bulk modulus, and finally the phase transition and lattice dynamical properties of rare-earth CeBi and LaBi of rocksalt (B1) and CsCl (B2) structures are determined. The electron band structures for the two phases of both rare-earth crystals are presented. We have calculated phonon dispersion curve, showing that all phonon modes in phonon dispersion curves of B1 phase in CeBi and LaBi are positive, which indicates a stable phase for this structure.

1. Introduction
Pressure is one of the external parameters by which the interplay of the f-electrons with the normal conduction electrons may be varied. At ambient conditions, the rare-earth compounds are characterized by a fixed fⁿ configuration of atomic-like f-electrons, but the decreased lattice spacing, resulting from the application of pressure, eventually leads to the destabilization of the f-shell [1-4]. A theoretical description of this electronic transition remains a challenge. They are considered to be part of the green technology industry, helping to improve energy efficiency in magnets, batteries, non-linear opto-electronics and computers. The volume change at the crystallographic transition is attributed to a decrease of the cerium valence or a lowering of the p-f hybridization due to the larger interatomic distances in both high pressure phases [4].

Leger et al [1] performed experiment of CeBi under high pressure and they showed that cubic and tetragonal phases coexist above the transition, with quite close volumes over the whole pressure range. These experiments give accurate structural information for pressures up to 100 GPa. On the other hand, enormous improvement in computational power and an existence of a number of new, efficient and easily accessible program packages [5], considerably expand the possibility to predict the physical properties of new phases at high pressures, as well as open an insight into the actual processes at extreme conditions. It is revealed from the literature, that role of f-electrons in Ce-ion, due to trivalent to tetravalent transition at high pressure on the electronic properties and other bulk properties, such as elastic constants and phonon spectra etc. is yet to be explored in details. In the present paper, we report structural, electronic and elastic properties of CeBi and LaBi rare earth compounds using first principles calculation. The present study reports a comprehensive study on structural, electronic band structures, elastic and lattice dynamical properties of rare earth monopnictides CeBi and LaBi,

¹To whom any correspondence should be addressed.

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using first-principles density functional calculations within the pseudopotential approximation. Both compounds possess NaCl (B1) structure at ambient pressure and transform either to CsCl or body centered tetragonal (BCT) structure at higher pressures [3-4]. Our results, concerning equilibrium lattice parameter and bulk modulus, agree well with the available experimental and previous theoretical data.

2. Computational Details
All calculations in the present study are based on the implementation of plane wave density functional theory (DFT) in the Kohn-Sham framework using ABINIT simulation package [5]. The wave functions describe only the valence and the conduction electrons, while the core electrons are taken into account for pseudopotentials. For the exchange-correlation functional, we have employed the local density approximation (LDA) and generalized-gradient approximation (GGA) functional developed by Perdew, Burke and Ernzerhof (PBE) [6]. The electron-ion interactions are described through the use of Troullier and Martins type pseudo-potentials [7]. A set of convergence tests have been performed in order to choose correctly the mesh of k-points and the cut-off kinetic energy for the plane wave basis, to start the ground state and linear response calculations. The kinetic energy cut-off is set to 50 Ha for both B1 and B2 structures of both compounds. The Brillouin zone is sampled by Monkhorst-Pack mesh of k-points for B1 and B2 phases for CeBi and LaBi. Convergence tests prove that the Brillouin zone (BZ) sampling and the kinetic energy cut-off are sufficient to guarantee an excellent convergence. The convergence is ensured to the total energy around 0.001 Ha, the phonon frequencies by 1-2 cm$^{-1}$ and the transition pressure by about 1 GPa. Phonon frequencies are subsequently obtained using the linear response approach [8] based on the density functional perturbation theory (DFPT). The expression is obtained from the second derivatives of the total energy with respect to the phonon displacement of atoms or an external electric field.

**Table 1.** Calculated values of lattice parameter, elastic constants (in GPa) and bulk modulus of rare-earth bismuthides.

| Structure  | Lattice Constant (Bohr) | C$_{11}$ | C$_{12}$ | C$_{44}$ | Bulk Modulus (GPa) |
|-----------|-------------------------|---------|---------|---------|-------------------|
| CeBi (B1) | 12.45 (LDA), 12.38 (GGA) | 109.70 | 5.97 | 9.94 | 40.54 |
| Present   |                         |         |         |         |                   |
| Others    | 12.40$^a$, 12.26$^b$    | 107.26$^a$ | 24.36$^a$ | 14.85$^a$ | 49.6 |
| Experiment|                         |         |         |         |                   |
| CeBi (B2) | 7.79 (LDA), 7.84 (GGA)  | 46.80   | 37.39   | 10.30   | 40.52 |
| Present   | 7.06                    |         |         |         |                   |
| LaBi (B1) | 12.04                   | 172.35  | 17.65   | 6.65    | 69.19 |
| Present   |                         |         |         |         |                   |
| Other     | 12.08$^c$, 12.35$^c$, 12.08$^d$, 123.14$^a$, 119.7$^b$, 58.15$^e$, 140.12$^c$, 120.63$^d$, 19.5$^a$, 17.1$^b$, 17.94$^a$, 20.52$^a$, 65.18$^c$, 62.20$^c$, 65.18$^1$, 50.03$^b$ |
| Experiment| 12.40                   |         |         |         |                   |
| LaBi (B2) | 7.80                    | 33.74   | 36.97   | 8.88    | 35.89 |
| Present   |                         |         |         |         |                   |

$^a$Ref [10], $^b$Ref [11], $^c$Ref [3], $^d$Ref [12], $^e$Ref [13], $^f$Ref [14], $^g$Ref [2], $^h$Ref [15]
3. Results and Discussion
As a first step, we have performed the structural optimization of B1 and B2 phases of CeBi and LaBi rare-earth crystals. The structural optimization has been performed under the minimum condition of the total energy. We computed the equilibrium lattice constant ($a_0$) and the bulk moduli ($B_0$) by fitting the energy-volume curves to the third order Birch-Murnaghan equation of states (EOS) [9]. The equilibrium lattice parameters for both compounds, along with available experimental and other theoretical data, are listed in Table I. It can be clearly seen that the calculated lattice parameter for the CeBi and LaBi compounds are in a satisfactory agreement with the previous calculations and available experimental data. Figure 1 presents the total energy vs lattice constant curves for CeBi using both LDA and GGA calculations. It is clear from the figure that there is a large difference between the total energies in both phases from both calculations. This may be due to the contribution of $f$- electron, which may be responsible for it.

![Figure 1](image1.png)

**Figure 1.** Total energy minimization of CeBi crystal in rocksalt and CsCl phase

Elastic constants which are associated with homogeneous strains, i.e. with macroscopic distortion of the crystals, can be calculated from the force constants. Most importantly, the knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid, load deflection, inter-atomic bonding, internal strain, sound velocities and fracture toughness. The calculated elastic constants are in the range of earlier calculations and physically significant. However, it could not be compared with experiment due to non availability of data. The elastic or mechanical stability can be checked by the whole set of elastic stiffness constant $C_{ij}$ using the Born-Huang criterion. The key criterion for mechanical stability of a crystal is that a strain energy must be positive. It is clear that both CeBi and LaBi are mechanically stable in B1 and B2 phase. We have also calculated the electronic band structure for both phases of both compounds at different pressures and presented pressure dependent band structure for CeBi and LaBi in Fig. 2. As pressure increases, the
conduction band width increases, because of the enhanced overlap of the wave function with the neighbouring atoms.

From the band structure, it is also seen that the lowest lying band in these compounds is mainly due to monopnictides ‘s’-like state and the band lying above mainly due to the monopnictides p-like state which hybridizes with Ce and La ‘s’ and ‘d’-like states at Γ-points. The narrow bands originating above the Fermi level are mainly due to Ce and La ‘f’-like states, and the major contribution is mainly from Ce and La ‘d’-like states. Localization of the f electron has taken away the occupied f-electron weight of approximately one electron, with delocalized f electrons is situated in the vicinity of the Fermi energy (not shown in the figure). A trend of increasing localization of the f electron is observed with increasing nuclear charge of the ligand, which also causes a volume increase. We note that due to the increasing localization, the f electron in CeBi and LaBi remains localized in the B2 structure.

![Band structure](image)

**Figure 2.** Calculated bandstructure of CeBi and LaBi at different pressure.

We have calculated phonon dispersion curve (presented elsewhere) gives impression that both compounds in rock salt structure are dynamically stable as the frequency of phonon modes throughout the Brillouin zone is positive.

4. Conclusion
In this study we have reported the results of *ab-initio* calculations on structural, elastic, electronic and vibrational properties for two CeBi and LaBi in their rocksalt and CsCl phase using plane wave method within GGA and LDA. There is a good agreement in the case of lattice parameters and elastic constant with previous reports. The band structure calculation shows the metallic nature. The energy difference between B1 and B2 phase of CeBi indicate that LDA and GGA are not suitable pseudopotential for the study of phase transition.

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