

**Structural, electronic, elastic, thermodynamic and phonon
properties of LaX ($X = \text{Cd}$, Hg and Zn)
compounds in the B2 phase**

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The *ab initio* computations have been performed to examine the structural, elastic, electronic and phonon properties of cubic LaX ($X = \text{Cd}$, Hg and Zn) compounds in the B2 phase. The optimized lattice constants, bulk modulus, and its pressure derivative and elastic constants are evaluated and compared with available data. Electronic band structures and total and partial densities of states (DOS) have been derived for LaX ($X = \text{Cd}$, Hg and Zn) compounds. The electronic band structures show metallic character; the conductivity is mostly governed by La-5d states for three compounds. Phonon-dispersion curves have been obtained using the first-principle linear-response approach of the density-functional perturbation theory. The specific heat capacity at a constant volume C_V of LaX ($X = \text{Cd}$, Hg and Zn) compounds are calculated and discussed.

Keywords: Elastic properties; *ab initio* calculations; density of states; phonon; ductility.

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1. Introduction

Lanthanide compounds have been widely investigated due to promising applications by many researchers in the last few decades. LaX ($X = \text{Cd}$, Hg and Zn) compounds are of considerable technological and scientific interest because of their physical and mechanical properties. These compounds have binary intermetallics

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in the CsCl (*B2*) phase at room temperature. Over the past decade, various studies^{1–16} on structural, electronic, elastic, mechanical and phase diagrams of these compounds in *B2* (CsCl) structure have been carried out. The crystal structures of LaCd and LaHg compounds have been measured by Indelli *et al.*¹ They predicted that both compounds were stable in the *B2* phase. Hasegawa *et al.*² reported the band structure of LaCd by both a nonrelativistic augmented plane-wave (APW) and a relativistic Korringa–Kohn–Rostoker (KKR) method. The study of elastic, electronic and mechanical properties of CsCl-type LaCd and LaHg compounds have been performed using full-potential linearized augmented plane-wave method (FP-LAPW), within three different forms of generalized gradient approximations (GGAs) (Perdew, Burke and Ernzerhof (PBE-GGA), Wu and Cohen (WC-GGA) and PBEsol-GGA) as the exchange correlation energy.^{4,5} The electronic band structure, the density of states (DOS), the heat of formation, electronic specific heat coefficient, cohesive energy, Debye temperature and Grüneisen constants for LaCd compound in the *B2* phase have been performed by Sirivastava *et al.*,⁶ using tight-binding linear muffin-tin orbital (TB-LMTO) method. The band structure of LaCd has been calculated by Asano and Ishida⁷ using the KKR method and local spin density approximation in both the CsCl and the tetragonal structure. They found that the Jahn–Teller effect can cause the cubic to tetragonal lattice transformation. For LaCd, the structural properties have been determined by Kadomatsu *et al.*⁸ Long⁹ has studied theoretically the crystal structural, electronic, elastic, thermodynamic and optical properties of LaCd by using CASTEP code. For LaZn in *B2* phase, Sekkal *et al.*¹¹ have calculated some ground state properties by using FP-LAPW method. They found that LaZn compound shows ductile feature because of showing *B/G* ratio more than 1.75 value. In the other work for LaZn, La knight shift and resistance measurements and the temperature dependency of susceptibility have been studied both theoretically and experimentally by Goebel *et al.*¹² LaX (*X* = Cd, Hg and Zn) compounds show similar trends, with different physical properties on the some family compounds.^{17–19}

The full phonon-dispersion curves are necessary for a microscopic understanding of the lattice dynamics. Knowledge of the phonon spectrum plays a significant role in determining various material properties such as phase transition, thermodynamic stability, transport and thermal properties. To the best of our knowledge, there are no reports on the study of vibrational properties of these compounds.

In this work, an *ab initio* investigation of the physical properties of LaX (*X* = Cd, Hg and Zn) compounds such as elastic constants, band structures and vibrational properties in the *B2* structure has been reported by the plane-wave pseudopotential density functional theory through the Quantum-ESPRESSO code²⁰ and by the quasi-harmonic approximation (QHA).²¹ The present article is organized as follow: in the following section, we describe briefly the method of calculation; the next section contains our results and discussion, involving structural, electronic, elastic, phonon and the thermal properties for the LaCd, LaHg and LaZn. A summary is provided in the end.

2. Method and Materials

The *ab initio* calculations were performed using the density functional theory in the GGA in the scheme of PBE²² parameterization for exchange correlation potential and Quantum-ESPRESSO package.²⁰ The electron-ion interaction was described using the ultra-soft Vanderbilt pseudopotential,²³ in which the orbitals of La ($5d^16s^2$), Cd ($4d^{10}5s^2$), Co ($3d^74s^2$) and Hg ($4f^{14}5d^{10}6s^2$), were treated as valance electrons. The kinetic cutoff energy for a plane-wave basis set was chosen as 40 Ry. The electronic charge density was evaluated up to the kinetic energy cutoff 400 Ry. For Brillouin-zone integrations, we have selected a $10 \times 10 \times 10$ k -points mesh. The Methfessel-Paxton scheme²⁴ with a smearing parameter of $\sigma = 0.02$ Ry was used for integration up to the Fermi surface. Lattice dynamic properties were obtained using density-functional perturbation theory (DFPT) or linear response.^{25,26} The phonon frequencies were calculated on a $4 \times 4 \times 4$ q -point mesh to obtain eight dynamic matrices. Specific heats at constant volume versus temperature were calculated using the QHA.²¹

The elastic constants can be obtained by calculating the total energy as a function of volume-conserving strains that break the cubic symmetry. The bulk modulus B , C_{44} , and shear modulus $C' = (C_{11} - C_{12})/2$ are calculated from hydrostatic pressure $e = (\delta, \delta, \delta, 0, 0, 0)$, triaxial shear strain $e = (0, 0, 0, \delta, \delta, \delta)$ and volume-conserving orthorhombic strain $e = (\delta, \delta, (1+\delta)^{-2} - 1, 0, 0, 0)$, respectively.²⁷ Hence, B can be obtained from

$$\frac{\Delta E}{V} = \frac{9}{2}B\delta^2, \quad (1)$$

where V is the volume of unstrained lattice cell, and ΔE is the energy variation as a result of an applied strain with vector $e = (e_1, e_2, e_3, e_4, e_5, e_6)$. C' can be calculated from

$$\frac{\Delta E}{V} = 6C'\delta^2 + 0\delta^3. \quad (2)$$

The two expressions above yield $C_{11} = (3B + 4C')/3$ and $C_{12} = (3B - 2C')/3$, and C_{44} is given by

$$\frac{\Delta E}{V} = \frac{3}{2}C_{44}\delta^2. \quad (3)$$

General hardness is known to be a material parameter that indicates resistance to elastic or plastic deformation, this parameter is the bulk modulus B or the shear modulus G .

The shear modulus G of a cubic structure is given by:

$$G = \frac{C_{11} - C_{12} + 3C_{44}}{5}. \quad (4)$$

3. Results

First, the lattice parameters of the CsCl structure of LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds have been determined. The total energy of LaX ($X = \text{Cd}, \text{Hg}$ and Zn)

compounds are determined for different lattice constants, and equilibrium corresponded to the lowest value of total energy. Second, to obtain the lattice constants, bulk modulus and its pressure derivative of the bulk modulus, computed total energy data were fitted to Murnaghan equation of state.²⁸ The calculated lattice constants of *B2* phase have been found higher than experimental data in 1% difference. This finding is generated from GGA implementation. Third, the elastic constants are important parameters due to their close relations with various physical fundamental properties. For a single cubic crystal, there are three independent elastic constants namely C_{11} , C_{12} and C_{44} . These elastic constants and bulk modulus are obtained by calculating the total energy as a function of volume-conserving strains that break the cubic symmetry. The calculated values for a , B , dB/dP , C_{11} , C_{12} , C_{44} , for $\text{La}X$ ($X = \text{Cd, Hg and Zn}$) compounds are listed in Table 1. The calculated results have been compared with the available literature in Table 1. The calculated lattice parameters fairly agree with earlier theoretical and experimental data for $\text{La}X$ ($X = \text{Cd, Hg and Zn}$) compounds. The mechanical stability of cubic crystals requires the elastic constants to meet the well-known Born elastic stability criteria²⁹:

$$C_{11} - C_{12} > 0, \quad C_{44} > 0, \quad C_{11} + C_{12} > 0, \quad B > 0.$$

We have used the procedure and formula described in a previous study³⁰ to calculate the elastic constants and the bulk modulus for these materials. The elastic constants for three materials are in good agreement with earlier theoretical results.^{5,11} The elastic constants indicate that $\text{La}X$ ($X = \text{Cd, Hg and Zn}$) compounds are mechanically stable in the *B2* phase.

Table 1. Calculated lattice constant a (in Å), bulk modulus B (in GPa) and elastic constants C_{ij} (GPa) for LaCd , LaHg and LaZn compounds, compared with the available experimental and theoretical data.

	Ref.	$a(\text{Å})$	B	dB/dt	C_{11}	C_{12}	C_{44}	G	B/G
LaCd	This work	3.944	44.172	4.12	58.37	37.073	42.51	29.765	1.484
	FP-LAPW ⁵	3.934	45.46	4.48	72.71	33.37	37.01	41.80	1.08
	Exp. ¹	3.905							
	APW ²	3.909							
	TB-LMTO ⁶	3.830	64.77						
	CASTEP ⁷	3.904	50.8		64.7	43.9	41.3		
Exp. ⁸	3.910								
LaHg	This work	3.914	50.59	3.14	68.52	41.99	22.59	24.86	2.034
	FP-LAPW ⁵	3.911	53.09	4.56	75.38	41.95	34.33	25.71	2.06
	Exp. ¹	3.864							
LaZn	This work	3.773	46.088	3.16	71.64	33.30	30.176	25.774	1.788
	FP-LAPW ¹¹	3.75	46.71	4.33	67.62	36.26	15.25	15.42	3.02
	Theory ¹³	3.752							
	Exp. ¹⁵	3.76							
	Exp. ¹⁶	3.572							

In this work, the ductile and brittle nature of LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds have been analyzed by computing Pugh's ratio (B/G).³¹ The critical value of Pugh's ratio (B/G) that separates brittleness and ductility is around to 1.75. If B/G ratio is higher than 1.75, the material is ductile, otherwise, the material is a brittle compound. Our calculated B/G values are 1.484, 2.034 and 1.788 for LaCd, LaHg and LaZn, respectively. LaHg and LaZn compounds have a ductile nature, while LaCd compound shows brittle properties. Our computed values of these materials are in good agreement with previous data.^{5,11} Thus, we need further information about experimental studies to compare with values that we calculated for LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds.

The electronic band structure of LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds are presented in the Fig. 1 along the high symmetry directions in the first Brillouin zone. LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds show metallic characters because there are no energy bandgaps and orbital have an ability to move through the Fermi level. Total and projected DOS for LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds as calculated for equilibrium geometries are presented in Fig. 2. The overall electronic band profiles are the same for all the compounds and are in good agreement with the previous work.⁵ The predominant contributions to the DOS at the Fermi level come from the La-5*d* and Cd-5*p* states for LaCd, La-5*d* and Hg-6*p* states for LaHg and La-5*d* and La-6*p* states for LaZn, respectively. The region of condition bands for these materials is due to mainly "5*d*"-like states of La atoms. The bands under Fermi level about -1 eV are caused by La-5*d* and Cd-5*d* states for LaCd, La-5*d* and Hg-6*p* states for LaHg, and La-5*d*, La-6*s* and La-6*p* states for LaZn, respectively. The lowest peaks below Fermi level for three compounds are originated from La-5*d*, La-6*s* and Cd-5*s* states for LaCd, La-6*p* and Hg-6*s* states for LaHg, and La-5*d*, La-6*p* and Zn-4*s* states for LaZn, respectively. There is one peak at 3.6, 4.7 and 3.8 eV for LaCd, LaHg and LaZn, respectively.

In the present work, we have reported for first time the dynamical properties of LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds. Lattice-dynamical properties of the LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds have been studied by using the DFPT as implemented in the Quantum-ESPRESSO package.²⁰ Figure 3 shows the calculated phonon-dispersion curves along the high symmetry directions in the first Brillouin-zone together with their corresponding total and projected phonon DOS for LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds in the *B2* phase. The unit cell of LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds in the *B2* phase contain two atoms, which give rise to six phonon branches in the full phonon-dispersion curves, out of which three are acoustical modes and three are optical modes. The absence of negative phonon frequency in the full phonon-dispersion curves for LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds confirm the dynamical stability. For these studied materials, there is no bandgap between the acoustical and the optical phonon branches. According to the projected DOS in Fig. 3 (right panel), the optical modes are almost excited by Cd atoms for LaCd and Zn atoms for LaZn. La atoms mainly contribute to

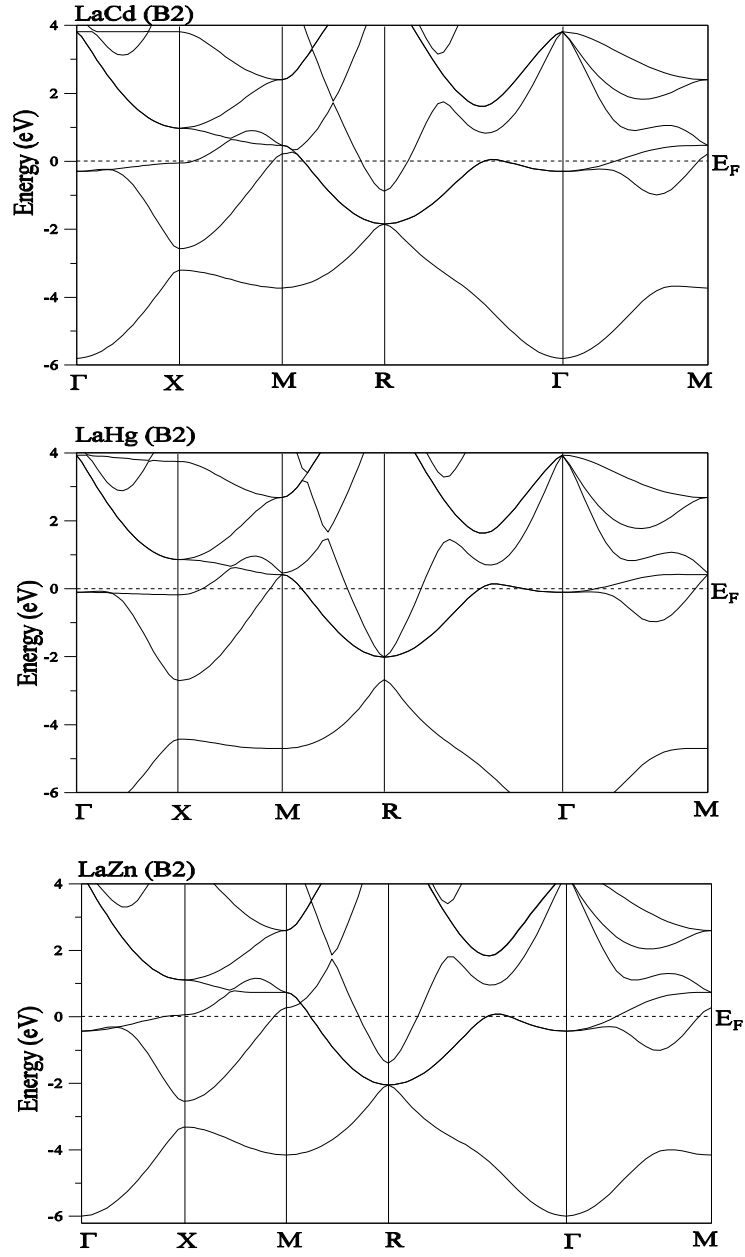


Fig. 1. The electronic band structures of LaCd, LaHg and LaZn compounds in B2 phase.

the region of the modes with lower frequency for LaCd and LaZn compounds. For LaHg compound, the predominant contributions of the projected DOS at optical branches come from the La atoms, while acoustic branches are due to the Hg atoms. This is because Hg atom is lighter than the La atom. The zone-center optic phonon

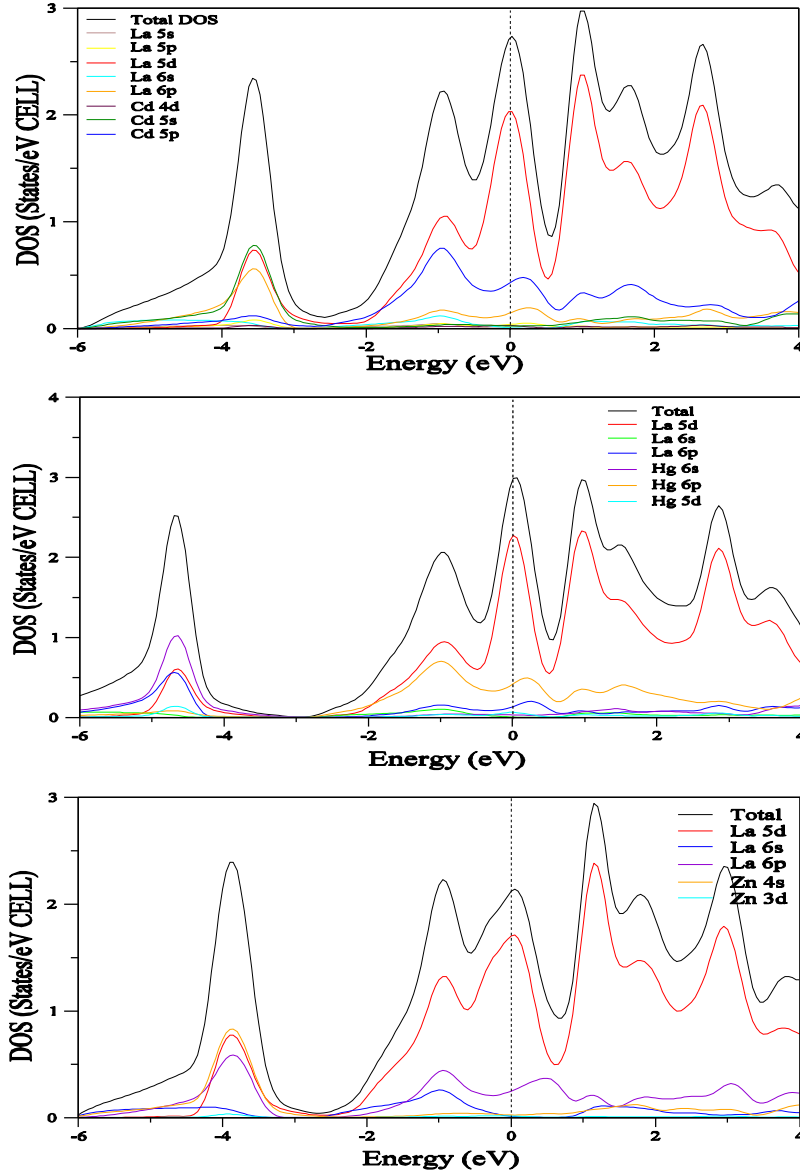


Fig. 2. The total and partial DOS of LaCd, LaHg and LaZn compounds in the B2 phase.

modes for LaCd, LaHg and LaZn compounds are computed as 2.714, 2.074 and 3.332 THz, respectively.

General trends of LaHg phonon-dispersion curves are consistent with previous works on IrGa³² and ScCu.³³

There are no available theoretical or experimental data for the phonon frequencies of these materials to be compared with our present results.

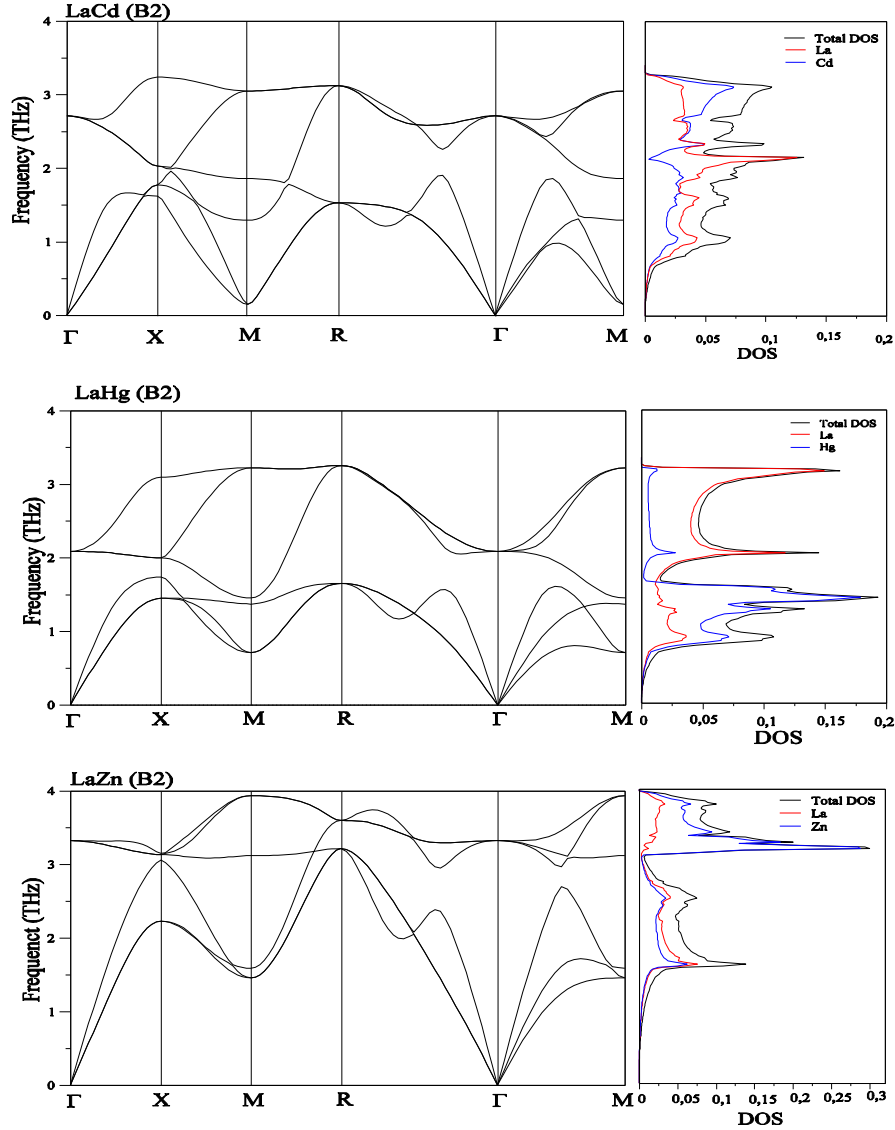


Fig. 3. Phonon-dispersion curves and projected DOS of LaCd, LaHg and LaZn compounds in the $B2$ phase.

Within the framework of QHA, the specific heat capacities C_v at constant volume as a function of temperature T for LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds are shown in Fig. 4. As the temperature increases, the calculated specific heat capacity C_v increases rapidly with temperature. At high temperatures ($T > 350$ K), the C_v increases slowly with the temperature and it almost approaches to the Dulong–Petit limit.³⁴ Unfortunately, we have no experimental data for LaX ($X = \text{Cd}, \text{Hg}$ and Zn) compounds specific heat capacity.

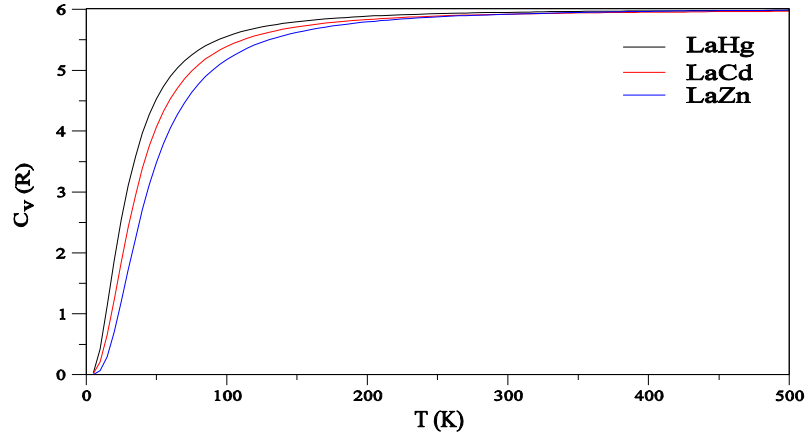


Fig. 4. The specific heats at constant pressure versus temperature for LaCd, LaHg and LaZn in the B2 phase.

4. Conclusions

In summary, we have presented a theoretical study about the structural, elastic, electronic, thermodynamic and dynamical properties of LaX ($X = \text{Cd, Hg and Zn}$) compounds in the B2 phase. The computed values for lattice constants of all compounds are in good agreement with available experimental data. The analysis of elastic constants confirms that all materials are in a mechanically stable state. The brittleness and the ductility properties of LaX ($X = \text{Cd, Hg and Zn}$) compounds have been estimated by computing Pugh's ratio (B/G). Computed LaCd compound have in a brittle manner, however the LaHg and LaZn compounds are ductile in nature. The computed electronic structure, and their corresponding total and projected DOS for LaX ($X = \text{Cd, Hg and Zn}$) compounds are in good agreement with the existing data. Phonon DOS and dispersion curves for LaX ($X = \text{Cd, Hg and Zn}$) compounds have been calculated for the first time in the framework of the DFPT. The specific heat capacities at constant volume as a function of temperature T for these materials have also been presented and discussed.

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