

Electronic, elastic, thermodynamical, and dynamical properties of the rock-salt compounds
LaAs and LaP

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 436204

(<http://iopscience.iop.org/0953-8984/19/43/436204>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 06:19

Please note that [terms and conditions apply](#).

Electronic, elastic, thermodynamical, and dynamical properties of the rock-salt compounds LaAs and LaP

E Deligöz, K Çolakoğlu, Y Ö Çiftçi and H Özışık

Department of Physics, Gazi University, Teknikokullar, 06500, Ankara, Turkey

Received 16 June 2007, in final form 17 August 2007

Published 26 September 2007

Online at stacks.iop.org/JPhysCM/19/436204

Abstract

We have studied the structural, elastic, electronic, thermodynamical and vibrational properties of LaAs and LaP in the rock-salt (B1) structure by performing *ab initio* calculations within the local-density approximation (LDA). Some basic physical properties, such as the lattice constant, bulk modulus, cohesive energy, second-order elastic constants (C_{ij}), the electronic band structures, and phonon frequencies, are calculated and compared with the available experimental and other theoretical values. In order to gain further information, we have, also, predicted the Young's modulus, Poisson's ratio (ν), anisotropy factor (A), sound velocities, and Debye temperature (θ_D), and reasonable values have been found. We also present the temperature-dependent behaviour of some thermodynamical properties such as entropy and heat capacity for these compounds in the B1 phase.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, the lanthanum monpnictides have been extensively investigated as a proper reference material for understanding the various unusual structural, electronic, and magnetic properties of other rare-earth pnictides [1–12]. The nature of the f electrons in these compounds, which are responsible for some magnetic and electrical properties, can be changed from localized to itinerant, leading to significant changes in the structural, physical and chemical properties of the compounds [1]. The rare-earth pnictides, generally, have low carrier, strongly correlated systems [2], and they show dense Kondo behaviour and heavy fermion states [4, 5].

The structural properties of LaX ($X = \text{As, P}$) have recently been studied experimentally using x-ray diffraction with synchrotron radiation at room temperature and high pressures, and first-order phase transitions were found from the NaCl-type (rock-salt) structure to the tetragonal structure (distorted CsCl-type) at around 24 GPa for LaP [6], and 20 GPa for LaAs [7]. On the theoretical side, the electronic and structural properties of lanthanum pnictides have been investigated by Vaitheeswaran *et al* [8, 9] by using the self-consistent tight-binding

linear muffin-tin orbital (TB-LMTO) method. The one-electron energy band structures of the same pnictides (LaN, LaP, LaAs, LaSb, and YSb) have been calculated by Hasegawa [10] using the *ab initio* LDA method. According to these authors, the narrow 4f band lies a few electron volts above the Fermi energy and it distorts the valence band appreciably [9–11]. Tütüncü *et al* [12] have performed some *ab initio* calculations on the elastic, electronic and phonon properties of YSb and LaSb compounds in the same family.

But until now, to our best knowledge, no systematic research on the elastic, mechanical, vibrational, and thermodynamical properties of LaP and LaAs in the B1 (rock-salt) phase have been reported, although these compounds are ‘the reference materials’ of other rare-earth pnictides. Therefore, we have aimed at providing some additional information to the existing data on the physical properties of LaP and LaAs by using *ab initio* total-energy calculations. In particular, we focus our attention on the mechanical, thermodynamical, and the lattice dynamical behaviours, which are the important bulk properties of solids. The band structures and the related density of states (DOS) are also presented for the rock-salt (B1) structures for the LaAs and LaP. The calculated properties are compared with those reported in previous works. The method of calculation is given in section 2. The results and overall conclusion are presented and discussed in sections 3 and 4, respectively.

2. Method of calculation

The SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code [13, 14] was utilized in this study to calculate the energies and atomic forces. It solves the quantum-mechanical equation for the electrons with the density-functional approach in the local density approximation (LDA) parameterized by Ceperley and Alder [15] for the electronic exchange and correlation potential. The interactions between electrons and core ions are simulated with separable Troullier–Martins [16] norm-conserving pseudopotentials. The basis set is based on the finite-range pseudoatomic orbitals (PAOs) of the Sankey–Niklewski type [17], generalized to include multiple-zeta decays. We have generated atomic pseudopotentials separately for atoms, La, P and As by using the $5s^25p^65d4f$, $3s^23p^33d4f$, and $4s^24p^34d4f$ atomic configurations, respectively. The basis set for La is 5s and 5p as semicore (simple zeta). The 6s and 5d orbitals are described with double-zeta, and a simple-zeta 6p is used as polarization for La. The cut-off radii for the present atomic pseudopotentials are taken as s: 1.85, p: 2.20, d: 3.10, f: 1.40 au for La, and 1.85 au and 2.25 au for the s, p, d and f channels for P and As respectively. The relativistic effects are taken into account for La due to its heavy mass in pseudopotential calculations.

SIESTA calculates the self-consistent potential on a grid in real space. The fineness of this grid is determined in terms of an energy cutoff E_c in analogy to the energy cutoff when the basis set involves plane waves. By using the cut-off energies between 100 and 450 Ryd with various basis sets, we found its optimal values around of 350 Ryd. Atoms were allowed to relax until the atomic forces were less than $0.04 \text{ eV } \text{Å}^{-1}$. For final convergence, 196 *k*-points were enough to obtain the converged total energies ΔE to about 1 meV/atom for the present compounds.

3. Results and discussion

3.1. Structural and electronic properties

First, the equilibrium lattice parameter was computed by minimizing the crystal total energy calculated for the different values of lattice constant by means of Murnaghan’s equation of state [18]. The bulk modulus and its pressure derivative have also been estimated, based on

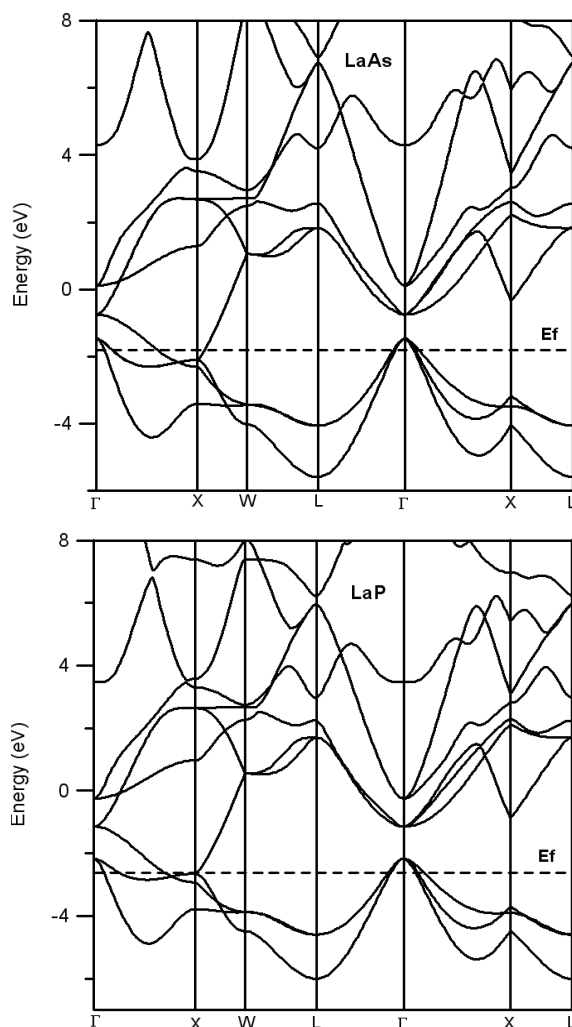


Figure 1. Calculated band structures for LaAs and LaP in the rock-salt structure.

the same Murnaghan equation of state, and the results are given in table 1 along with the experimental and theoretical values. Our calculated lattice constant (a_0) and bulk modulus (B) by using LDA, for both compounds, are in excellent agreement with the experimental [3, 7] and other theoretical values [9, 11]. The present value of bulk modulus is very close to other theoretical values and about 8% lower than the experimental value of Shirovani *et al* [7] for LaAs. For LaP, the same quantity is about higher 20% than the experimental value of Leger *et al* [3]. But, when we compare with the other theoretical values, it is 10% higher than in [11] and 10% lower than in [9]. The present values of cohesive energies for LaAs and LaP are predicted to be $-3721.78 \text{ kJ mol}^{-1}$ and $-3982.14 \text{ kJ mol}^{-1}$, respectively. Our values for cohesive energies for both compounds are much higher than those given by Pagare in [11].

Although it is not our main intention here to make detailed band-structure calculations, we have predicted the band structures for LaAs and LaP along the high-symmetry directions from the calculated equilibrium lattice constant (see figure 1). The overall bands profiles are found

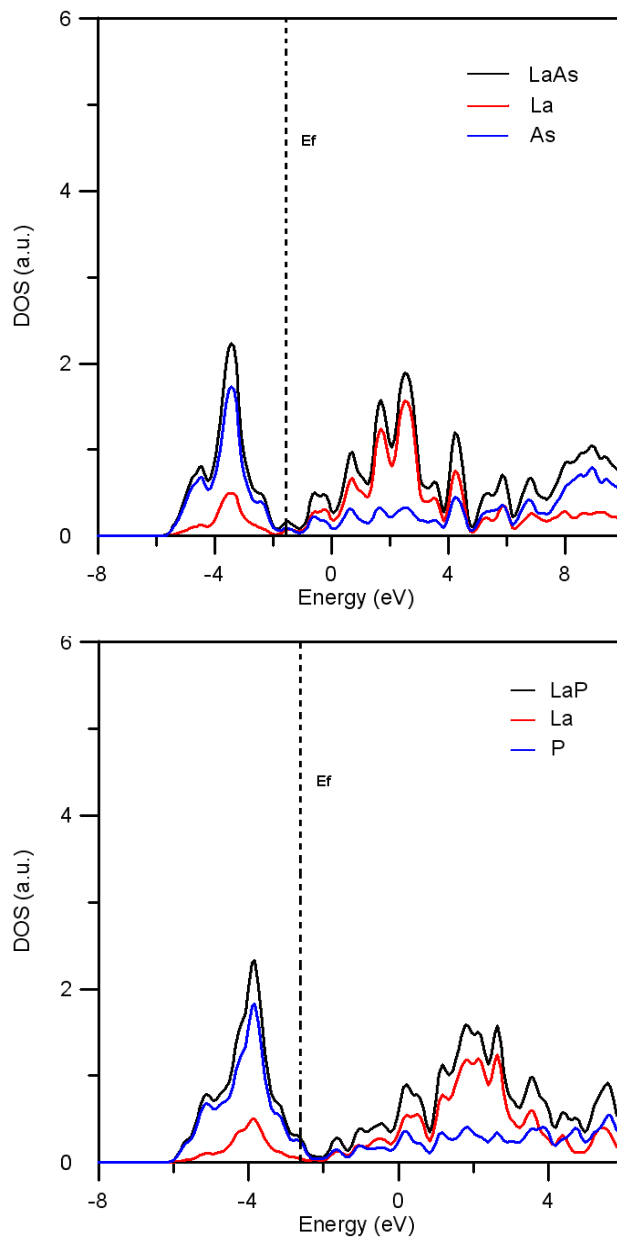


Figure 2. The calculated total DOS and atomic projected PDOS for LaAs and LaP in the rock-salt structure.

to be similar, and both compounds exhibit a metallic character. The band profiles are in good agreement with those of earlier works [9, 10].

The total and partial density of states (DOS and PDOS) corresponding to the band structures shown in figure 1 are, also, indicated in figure 2. For LaAs, the lowest valence bands are essentially dominated by La 5s states, and they occur between about -35 and -33 eV. The other valence bands that lie between -20 and -17 eV are essentially dominated by La 5p

Table 1. Calculated equilibrium lattice constant (a_0), bulk modulus (B), and the pressure derivative of bulk modulus (B'), together with the experimental values, for LaAs and LaP.

Material	Reference	a_0 (Å)	B (GPa)	B'	E_{coh} (kJ mol ⁻¹)
LaAs	Present	6.10	86.81	2.75	-3721.78
	Theory ^a	5.99	86.40		
	Theory ^b		84.54		-2670.5
	Experimental ^c	6.137	92 ± 6		
LaP	Present	6.00	80.76	3.12	-3982.14
	Theory ^a	5.85	95.22		
	Theory ^b		71.65		-2705.5
	Experimental ^d	6.02	67 ± 6		

^a Reference [9].^b Reference [11].^c Reference [7].^d Reference [3].**Table 2.** Elastic constants (in GPa) for LaAs and LaP.

Material	Reference	C_{11}	C_{12}	C_{44}
LaAs	Present	164.90	47.71	44.52
	Theory ^a	184.39	34.62	
LaP	Present	153.00	44.63	42.15
	Theory ^a	137.21	38.80	

^a Reference [11].

states. The 4p state of As atoms is also a minor contributor to these valence bands. The valence bands between -12 and -10 eV are essentially dominated by As 4s states. The 5d state of La atoms is also a minor contributor to these valence bands. In figure 2 these bands are not shown, in order to see the details of density of states that lie between -8 and 10 eV. The last valence bands are essentially dominated by As 4p states; the 5d state of La atoms also contributes to these valence bands. The conduction band consists essentially of La 5d and As 4d states. Similar situations can be observed for LaP in the DOS profile, with As 4s, As 4p, and As 4d states replaced with P 3s, P 3p, and P 3d states, respectively.

3.2. Elastic properties

The elastic constants of solids provide a link between the mechanical and dynamical behaviour of crystals, and give important information concerning the nature of the forces operating in solids. In particular, they provide information on the stability and stiffness of materials, and their *ab initio* calculation requires precise methods. Since the forces and the elastic constants are functions of the first-order and second-order derivatives of the potentials, their calculation will provide a further check on the accuracy of the calculation of forces in solids. The effect of pressure on the elastic constants is essential, especially, for understanding interatomic interactions, mechanical stability, and phase-transition mechanisms. The second-order elastic constants (C_{ij}) are calculated by using the 'volume-conserving' technique [19–21] in a manner similar to our recent works [22–25]. The present elastic constant values for LaAs and LaP are given in table 2. It can be seen from this table that the present values of C_{11} are lower by about 10% and that the values of C_{12} are higher by about 15% than the values reported in [11] for both compounds.

Table 3. The calculated Zener anisotropy factor (A), Poisson's ratio (ν), Young's modulus (Y), and shear modulus for LaAs and LaP.

Material	Reference	A	ν	Y (GPa)	C' (GPa)
LaAs	Present	0.76	0.259	125.20	51.55
LaP	Present	0.77	0.257	117.27	48.18

The traditional mechanical stability conditions on the elastic constants in cubic crystals are known to be $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, and $C_{12} < B < C_{11}$. Our results for the elastic constants in table 2 obey these stability conditions.

The Zener anisotropy factor A , Poisson's ratio ν , and Young's modulus Y , which are the most interesting elastic properties for applications, are often measured for polycrystalline materials when investigating their hardness. These quantities are calculated in terms of the computed data using the following relations [26]:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}, \quad (1)$$

$$\nu = \frac{1}{2} \left[\frac{(B - \frac{2}{3}G)}{(B + \frac{1}{3}G)} \right], \quad (2)$$

and

$$Y = \frac{9GB}{G + 3B} \quad (3)$$

where $G = (G_V + G_R)/2$ is the isotropic shear modulus, G_V is Voigt's shear modulus corresponding to the upper bound of G values, and G_R is Reuss's shear modulus corresponding to the lower bound of G values; they can be written as $G_V = (C_{11} - C_{12} + 3C_{44})/5$, and $5/G_R = 4/(C_{11} - C_{12}) + 3/C_{44}$. The calculated Zener anisotropy factor (A), Poisson's ratio (ν), Young's modulus (Y), and shear modulus ($C' = (C_{11} - C_{12} + 2C_{44})/4$) for LaAs and LaP are given in table 3.

The Debye temperature (θ_D) is a fundamental physical property, and it is used to distinguish between high- and low-temperature regions for a solid. If $T > \theta_D$ we expect all modes to have energy $k_B T$, and if $T < \theta_D$ one expects high-frequency modes to be frozen [27]. In the present case, the Debye temperature (θ_D) is estimated, for $T < \theta_D$ by using the calculated elastic constant data, in terms of the following well-known relations [28]:

$$\theta_D = \frac{h}{k} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} v_m \quad (4)$$

where v_m is the average wave velocity, and is approximately given by

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-1/3} \quad (5)$$

where v_l and v_t are the longitudinal and transverse elastic wave velocities, respectively, which are obtained from Navier's equation [29],

$$v_l = \sqrt{\frac{3B + 4G}{3\rho}}, \quad (6)$$

and

$$v_t = \sqrt{\frac{G}{\rho}}. \quad (7)$$

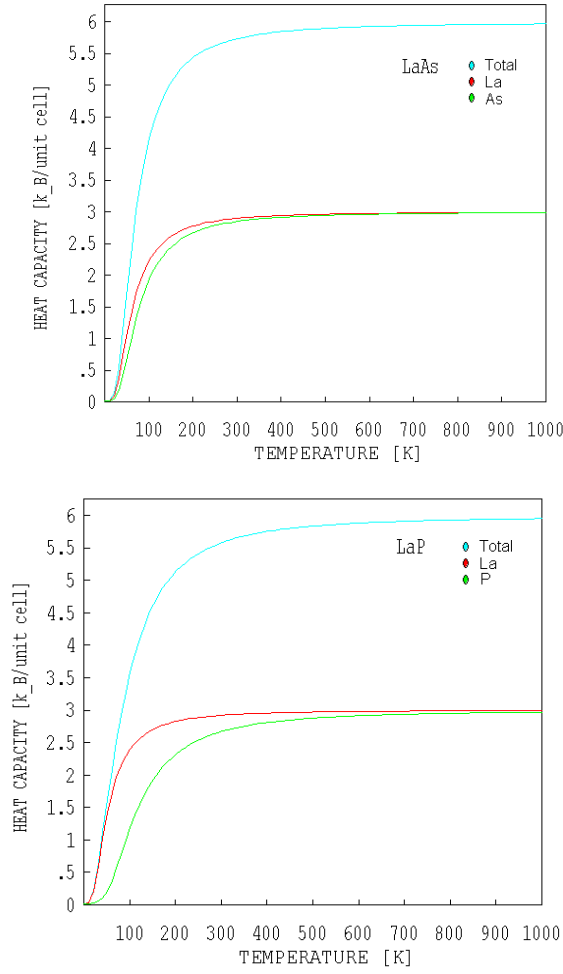


Figure 3. Temperature dependence of heat capacity for LaAs and LaP in the rock-salt structure.

Table 4. The longitudinal, transverse, and average elastic wave velocities, together with the Debye temperature, for LaP and LaAs.

Material	Reference	v_l (m s ⁻¹)	v_t (m s ⁻¹)	v_m (m s ⁻¹)	θ_D (K)
LaAs	Present	4886.82	2784.52	3094.86	301.75
LaP	Present	5231.89	2988.08	3320.45	329.46

The calculated longitudinal, transverse, and average elastic wave velocities for LaAs and LaP are given in table 4. The present values of Debye temperature for LaAs and LaP are predicted to be 301.75 K and 329.46 K, respectively. These values are much higher than that for the constituent atom La (142 K) in the β phase.

3.3. Temperature dependence of entropy and heat capacity

We have also plotted the temperature-dependent variations of the entropy and heat capacity (C_v), at constant volume in the B1 structure for each compound and their constituent atoms, by using the data obtained from SIESTA and PHONON codes [30] in figures 3 and 4.

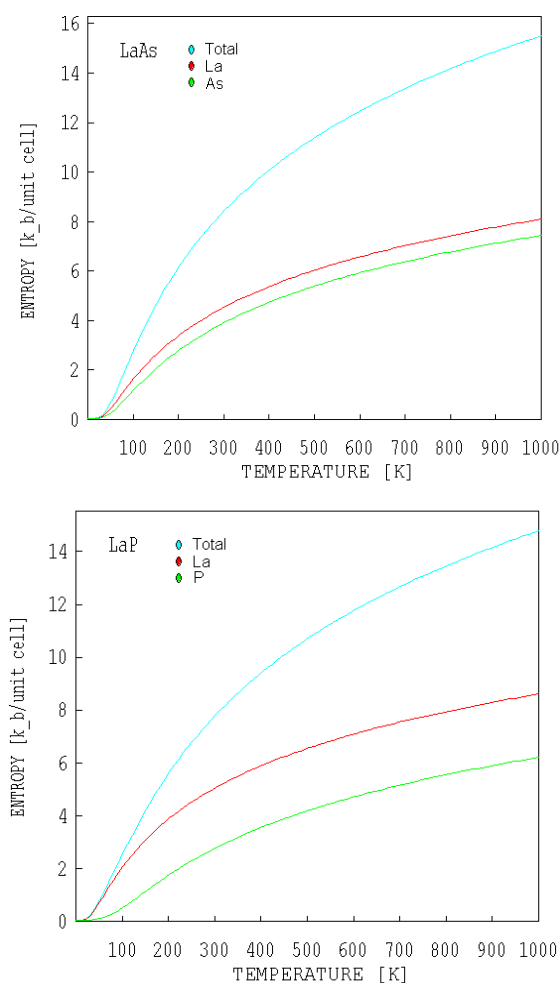


Figure 4. Temperature dependence of entropy for LaAs and LaP in the rock-salt structure.

The contributions from the lattice vibrations to the total heat capacity of LaAs and LaP are illustrated in figure 3. The temperature is limited to 1000 K to decrease the probable influence of anharmonicity. The lattice contribution to the heat capacity shown in figure 3 follows the Debye model and approaches the Dulong–Petit limit at high temperatures (about room temperature). It is interesting to note that the curvature of the pnictide atoms (As and P) in the heat capacity curves at low temperature (about 350 K) decreases, again, on going from P to As. Also, when the magnitude of the mass of the constituent atoms approaches each other, their partial heat capacity curves approach each other, even at low temperatures. At high temperature, it can be seen from these figures that the total heat capacity for each compound is approximately equal to the sum of the heat capacities of the constituent atoms.

The variations of entropy with temperature for LaAs and LaP are given in figure 4 over the same temperature range. Obviously, the total and partial entropy graphs exhibit a similar trend, and again, when the sizes of the constituent atoms are close to each other, their partial entropy–temperature graphs also approach each other.

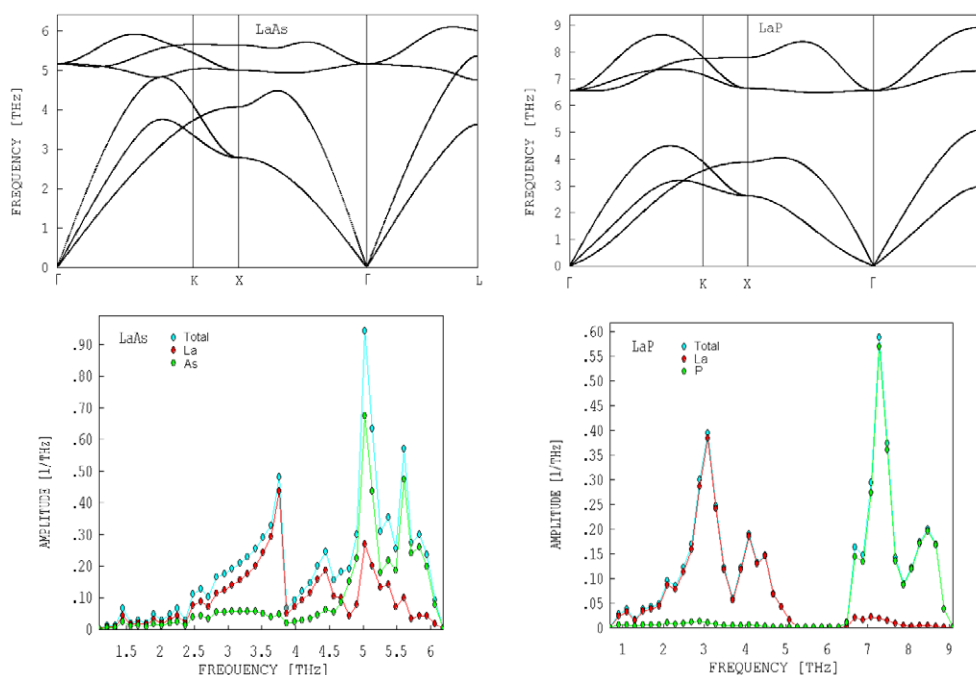


Figure 5. Calculated phonon dispersions, total and partial density of states for LaAs and LaP in the rock-salt structure.

3.4. Phonon properties

The present LDA phonon dispersion curves and density of states of LaAs and LaP along the high-symmetry directions were calculated by using the PHONON software [30]. This code, which is compatible with SIESTA, uses the ‘Direct Method’ [31] and the Hellman–Feynman forces on atoms for generating the phonon dispersion and the DOS, and its theoretical and applicational details can be found in the PHONON manual [32] and references therein. Specifically, we have calculated the phonon dispersion curves in high-symmetry directions and the DOS for a $2 \times 2 \times 2$ cubic supercell with 64 atoms. The displacement amplitudes are taken as 0.03 \AA , and the positive and negative atomic displacements along the x , y , and z directions are taken into account. The Hellmann–Feynman forces acting on the atoms in the supercell are evaluated to construct the force constants and dynamical matrix.

Many of the physical properties of solids depend on their phonon properties, such as specific heat, thermal expansion, heat conduction, and electron–phonon interaction. Although some works have performed on the structural and electronic properties of these compounds, no experimental or other theoretical works exist on the lattice dynamics for comparison with our results. The obtained phonon dispersion curves and the corresponding one-phonon density of states for LaAs and LaP along the high-symmetry directions are illustrated in figure 5.

It can be seen from the figure 5 that the mass difference between anions and cations seriously affects the shapes of the dispersion curves and the corresponding density of states. For LaAs, the clear gap between the acoustic and optic branches are not seen, and they cross in the $[111]$ symmetry direction at large wavevectors. However, for the LaP compound, the gaps (2.06 THz) between the acoustic and optical branches are very clear. The maximum values of the phonon frequencies for acoustic branches decrease on going from As to P. The lower

graphs show the related total and partial density of phonon states for each compound. One can see that the main contribution to acoustic phonons comes from the lanthanum sublattice, while the high-frequency phonons are dominated by the pnictide ions. Also, the contribution to the optical modes from La increases on going from P to As, but for acoustic modes, the contribution from the pnictide ions increases on going from P to As. Also, it can be seen from the DOS curves that the position of the sharpest peak that results from the optical phonon modes, again, decreases on going from P to As.

4. Summary and conclusion

In this work, we have presented the results of several ground-state, structural, mechanical, vibrational, and thermodynamical properties of LaAs and LaP compounds in the rock-salt (B1) structure, using first-principles calculations based on the SIESTA method within the local-density approximation. Specifically, the lattice constants, bulk moduli, the pressure derivative of bulk moduli, sound velocities, Debye temperatures, zero-pressure elastic constants and their related quantities, such as Young's modulus, anisotropy factor, and Poisson's ratio, have been calculated. The present results are, generally, in agreement with the available experimental data and the results of some other theoretical studies. The original aspects of the present calculations concern the phonon dispersion curves and thermodynamical results, which have not been considered so far. We hope that some of our results will be tested in the future both experimentally and theoretically, with different methods, to confirm their reliability.

Acknowledgments

This work is supported by Gazi University Research-Project Unit under Project No: 05/2007-42. We gratefully acknowledge Dr Mehmet Çakmak for his valuable comments on the final form of this manuscript. Finally, we also wish to thank the referee for useful suggestions and comments.

References

- [1] Shekar N V and Sahu P Ch 2006 *J. Mater. Sci.* **41** 3207
- [2] Li D X, Haga Y, Shida H, Suzuki T and Kwon Y S 1996 *Phys. Rev. B* **54** 10483
- [3] Leger J M, Ravot D and Mignot J R 1984 *J. Phys. C: Solid State Phys.* **17** 4935
- [4] Yoshida M, Koyama K, Sakon T, Ochiai A and Motokawa M 2000 *J. Phys. Soc. Japan* **69** 3629
- [5] Suzuki T 1993 *Physica B* **347** 186
- [6] Adachi T, Shirotani I, Hayashi J and Shimomura O 1998 *Phys. Lett. A* **250** 389
- [7] Shirotani I, Yamanashi K, Hayashi J, Ishimatsu N, Shimomura O and Kikegawa T 2003 *Solid State Commun.* **127** 573
- [8] Vaitheeswaran G, Kanchana V and Rajgopalan M 2002 *Physica B* **315** 64
- [9] Vaitheeswaran G, Kanchana V and Rajgopalan M 2002 *J. Alloys Compounds* **336** 46
- [10] Hasegawa A 1980 *J. Phys. C: Solid State Phys.* **13** 6147
- [11] Pagare G, Sanyal S P and Jha P K 2005 *J. Alloys Compounds* **398** 16
- [12] Tütüncü H M, Bağcı and Srivastava G P 2007 *J. Phys.: Condens. Matter* **19** 156207
- [13] Ordejón P, Artacho E and Soler J M 1996 *Phys. Rev. B* **53** R10441 (Rapid Communication)
- [14] Soler J M, Artacho E, Gale J D, García A, Junquera J, Ordejón P and Sánchez-Portal D 2002 *J. Phys.: Condens. Matter* **14** 2745
- [15] Ceperley D M and Alder M J 1980 *Phys. Rev. Lett.* **45** 566
- [16] Troullier N and Martins J L 1991 *Phys. Rev. B* **43** 1993
- [17] Sankey O F and Niklewski D J 1989 *Phys. Rev. B* **40** 3979
- [18] Murnaghan F D 1944 *Proc. Natl Acad. Sci. USA* **30** 5390
- [19] Mehl J 1993 *Phys. Rev. B* **47** 2493

- [20] Wang S Q and Ye H Q 2003 *Phys. Status Solidi b* **240** 45
- [21] Gülseren O and Cohen R E 2002 *Phys. Rev. B* **65** 64103
- [22] Deligöz E, Çolakoğlu K and Çiftçi Y 2006 *Physica B* **373** 124
- [23] Deligöz E, Çolakoğlu K and Çiftçi Y Ö 2007 *J. Phys. Chem. Solids* **68** 482
- [24] Deligöz E, Çolakoğlu K, Çiftçi Y Ö and Özışık H 2007 *Comput. Mater. Sci.* **39** 533
- [25] Deligöz E, Çolakoğlu K and Çiftçi Y Ö 2007 *J. Alloys Compounds* **438** 66
- [26] Mayer B, Anton H, Bott E, Methfessel M, Sticht J and Schmidt P C 2003 *Intermetallics* **11** 23
- [27] Christman J R 1988 *Fundamentals of Solid State Physics* (New York: Wiley)
- [28] Johnston I, Keeler G, Rollins R and Spicklemire S 1996 *Solid State Physics Simulations, The Consortium for Upper-Level Physics Software* (New York: Wiley)
- [29] Sreiber E, Anderson O L and Soga N 1973 *Elastic Constants and their Measurements* (New York: McGraw-Hill)
- [30] Parlinski K 2003 Software PHONON and references therein
- [31] Parlinski K, Li Z Q and Kawazoe Y 1997 *Phys. Rev. Lett.* **78** 4063
- [32] <http://wolf.ifj.edu.pl/phonon>