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Theoretical study of LaP and LaAs at high pressures

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Abstract

The present work employs the self-consistent tight binding linear muffin-tin orbital method to calculate the electronic structure and the relative stabilities of LaP and LaAs at high pressures in the rocksalt, primitive tetragonal and CsCl structures. At compressed volumes, these compounds favour the tetragonal phase over the CsCl phase, which can be seen from the total energy curves. The transition from rocksalt to tetragonal occurs around 18, 11.2 GPa in the case of LaP and LaAs, respectively. The ground state properties of these systems such as bulk modulus and lattice constant are in good agreement with the experimental results. The band structure and density of states are plotted for both B1 and tetragonal phase and are compared with the available literature. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The monopnictides of rare earths, with N, P, As, Sb and Bi, crystallize in the NaCl type structure [1] and the rare-earth ion is normally in the trivalent state. Rare-earth pnictides are typically low carrier, strongly correlated systems [2]. In addition, they also show dense kondo behavior, heavy fermion state [3–7]. The term heavy fermions has been coined to describe kondo lattices which have specific heat coefficients greater than 400 mJ/mol-K^2. The presence of 4f electrons in these compounds are mainly responsible for the various magnetic and electrical properties.

The La monopnictides with the NaCl structure belong to a large group of rare-earth pnictides [3] and have recently attracted particular interest as a proper reference material for the study of various anomalous physical properties of the Ce monopnictides [8–10]. A step towards a better understanding of the physics of the La pnictides and of various anomalies of the Ce pnictides may be to investigate the one-electron energy band structure for the La

pnictides. With such a motive, this paper reports the results of the band structure and high-pressure structural phase transition of La pnictides namely LaP and LaAs.

Already a few band structure calculations are available for Ce pnictides [11,12], Sc pnictides [13–15] and Gd pnictides [16]. The high-pressure behavior of CeP has been studied experimentally by Jayaraman et al. in which a pressure-induced valence transition from Ce^{3+} state towards Ce^{4+} state occurs. Moreover, an isostructural transition accompanied by a volume collapse of around 8% at about 10 GPa occurs in CeP [17]. This transition involves change in the valence state of Ce from 3^+ to 4^+ state. Although a number of experimental and theoretical works have been carried out for rare-earth compounds, only a few data are found in the literature in explaining the electronic structure and some of the physical properties of La monopnictides. Hasegawa [18] has investigated the electronic structure of LaN, LaP, LaAs and LaSb by using self-consistent APW method. Similarly, Hasegawa [19] has calculated the electronic band structure and Fermi surface of LaSb and LaBi by relativistic APW method. So far, there is no theoretical study on the high-pressure structural phase transformation for these lanthanum monopnictides to our knowledge. Hence, an attempt has been made in the present work to compute the electronic structure, ground state properties and high-pressure structural phase transformation for these lanthanum monopnictides using self-

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consistent tight binding linear muffin-tin orbital method (TB-LMTO).

It is evident from the work of Adachi et al. [20] that lanthanum monophosphide undergoes a crystallographic transition from B1 (NaCl type) structure to a tetragonal structure, which can be viewed as a distorted CsCl structure. The transition pressure was found to be 24 GPa with a volume collapse of 16.3%. The c/a ratio was reported to be 0.87.

As far as LaAs is concerned, only optical conductivity studies has been performed by Kimura et al. [21] in which the electronic structure of LaAs is explained experimentally. In addition, dHvA study on LaAs has been performed by Morita et al. [22].

In the present work, the band structure, density of states and high pressure structural phase stability of LaP and LaAs are computed and compared with the available experimental and other theoretical results and the values obtained in the present study are in good agreement with those of others [17,23,24]. The rest of the paper is organized as follows. In Section 2, the crystallographic data and computational details of these lanthanum pnictides are given. The results are given in Section 3. The final section contains the conclusion.

2. Crystallographic aspects and computational details of lanthanum monopnictides

The lanthanum monopnictides crystallize in the simple rocksalt structure (B1type) with the space group symmetry *Fm3m*. The La atom is positioned at (0,0,0) and the pnictogen at (1/2,1/2,1/2). The structure of the high-pressure phase of LaP is tetragonal which can be viewed as a distorted CsCl structure [20] with La at (0,0,0) and pnictogen at (1/2,1/2,1/2) and the space group symmetry is *P4/mmm*.

To obtain the electronic structure and ground state properties of lanthanum monopnictides TB-LMTO method has been used [25,26]. von-Barth and Hedin parameterization has been used for the exchange correlation potential [27] within the local density approximation (LDA). The accuracy of total energies obtained within the density-functional theory, often even using the LDA, is in many cases sufficient to predict which structure at a given pressure has the lowest free energy [28]. Atomic sphere approximation (ASA) [29] has been used in the present work. In this approximation, the crystal is divided into space filling spheres centered on each of the atomic site. Combined corrections are also included, which account for the non-spherical shape of the atomic spheres and the truncation of the higher partial waves inside the sphere to minimize the errors in the LMTO method. The Wigner-Seitz sphere is chosen in such a way that the sphere boundary potential is minimum and the charge flow between the atom is in accordance with the electro-

negativity criteria. s, p, d and f partial waves are included. The tetrahedron method [30] of the Brillouin zone (K space) integration has been used to calculate partial and total density of states with 1543 **K** points in the irreducible part of the Brillouin zone for B1, and 4630 **K** points in PT and 443 **K** points in B2 phases. **E** and **K** convergence is also checked. For all these compounds the following basis orbitals are used, namely

La: $6s^2$, $5p^6$, $5d^1$, $4f^0$
P: $3s^2$, $3p^3$, $3d^0$
As: $4s^2$, $4p^3$, $4d^0$

It is well known that the LMTO method gives accurate results for densely packed structures and since the NaCl structure is a loosely packed structure, it becomes necessary to include empty spheres [31,32]. Two empty spheres are included in this structure without breaking the crystal symmetry at (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75).

3. Results and discussion

3.1. Total energy calculation and high pressure structural transformation

In order to study the structural phase stability for each of these compounds the total energies are calculated in a manner similar to our earlier works [33,34] for B1, PT and B2 structures by reducing the volume from 1.05 V_o to 0.6 V_o where 'V_o' is the equilibrium volume. The variations of the total energies with relative volume for all these compounds are given in Fig. 1. From the graphs, it can be clearly seen that B1 phase is stable in all these pnictides at ambient pressure. PT is positioned above B1 and B2 phase lies above the primitive tetragonal phase. The experimental work of Adachi et al. [20] reports a crystallographic transition in LaP from B1 to Primitive tetragonal phase, which can be viewed as a distorted CsCl structure. In the present work, calculations were performed for both primitive tetragonal and CsCl structures to determine which of these two structures is favoured more under pressure. The c/a ratio in the tetragonal phase is optimized by total energy minimization and it is found to be 0.87 for both LaP and LaAs, which is in good agreement with the experimental value [20]. The c/a minimization for LaP is shown in Fig. 2.

The calculated total energies are fitted to the Birch equation of state [35] to obtain the pressure volume relation. The graph connecting the pressure and relative volume in B1 and PT phases are shown in Fig. 3. The pressure is obtained by taking the volume derivative of the total energy. The bulk modulus

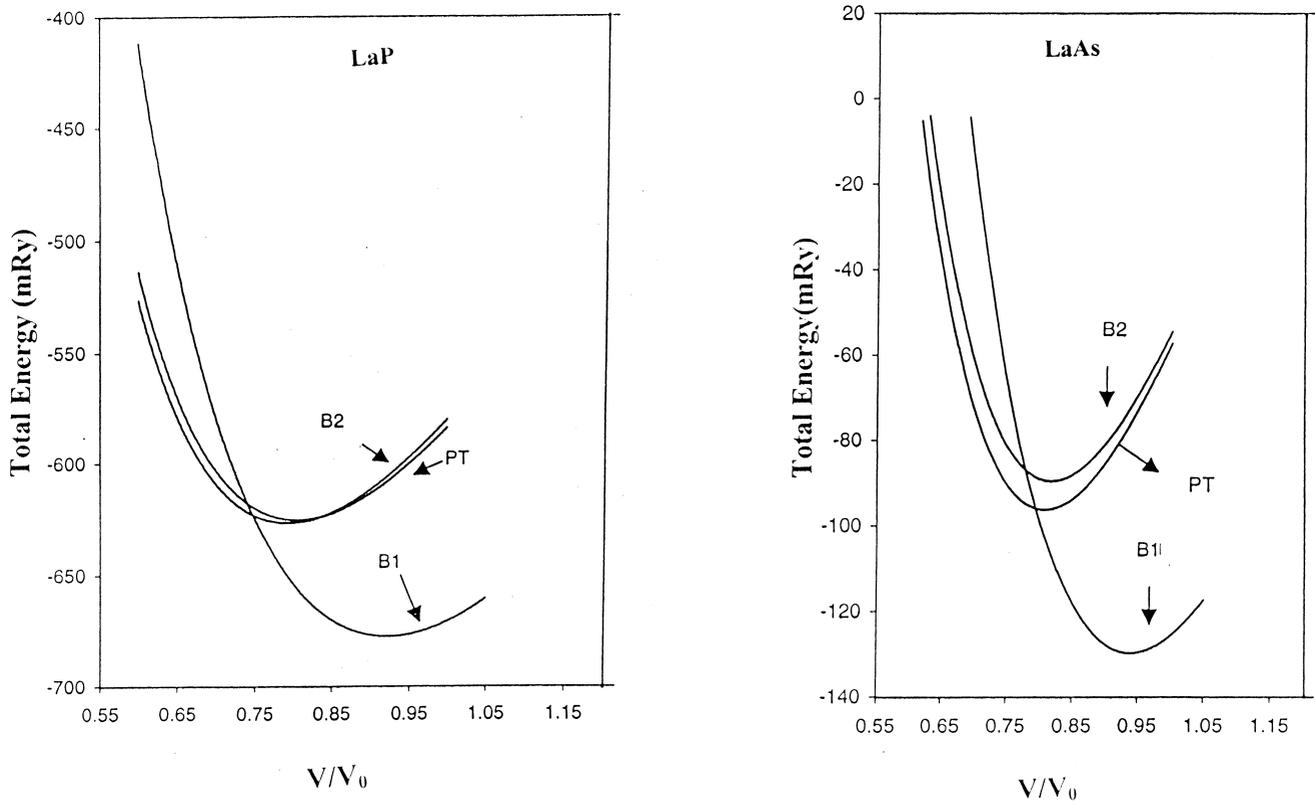$$B = -V_o \, dP/dV \tag{1}$$

is also calculated from the $P-V$ relation.

Fig. 1. (a) Calculated total energy (−17658.00+) Ry versus relative volume for LaP. (b) Calculated total energy (−21493.00+) Ry versus relative volume for LaAs.

The theoretically calculated equilibrium lattice constant and the Bulk modulus for B1 and PT structures are given in Tables 1 and 2 and are compared with the available experimental works. The structural phase stability is determined by calculating Gibb's-free energy (G) [36] for B1 and PT structures, which is
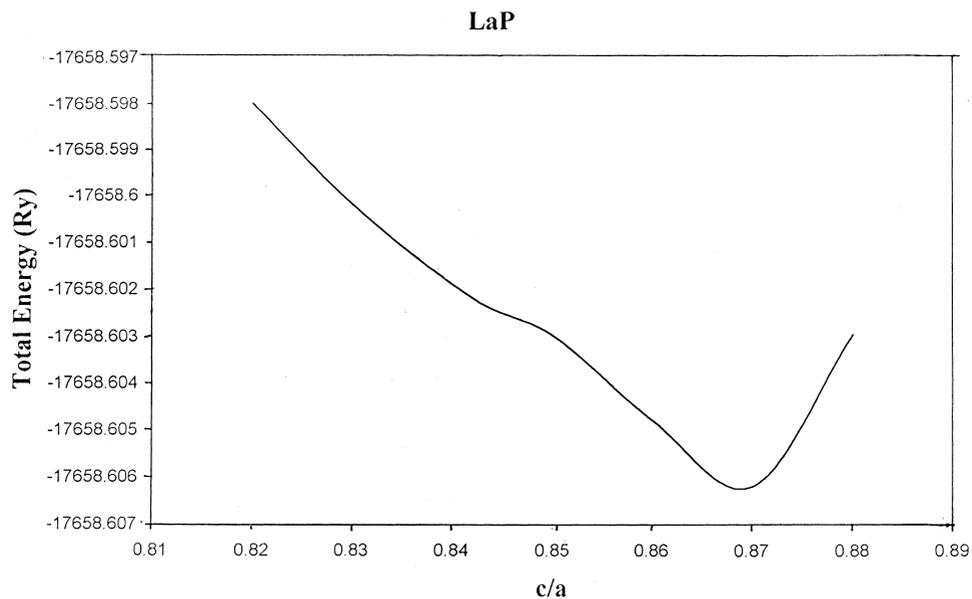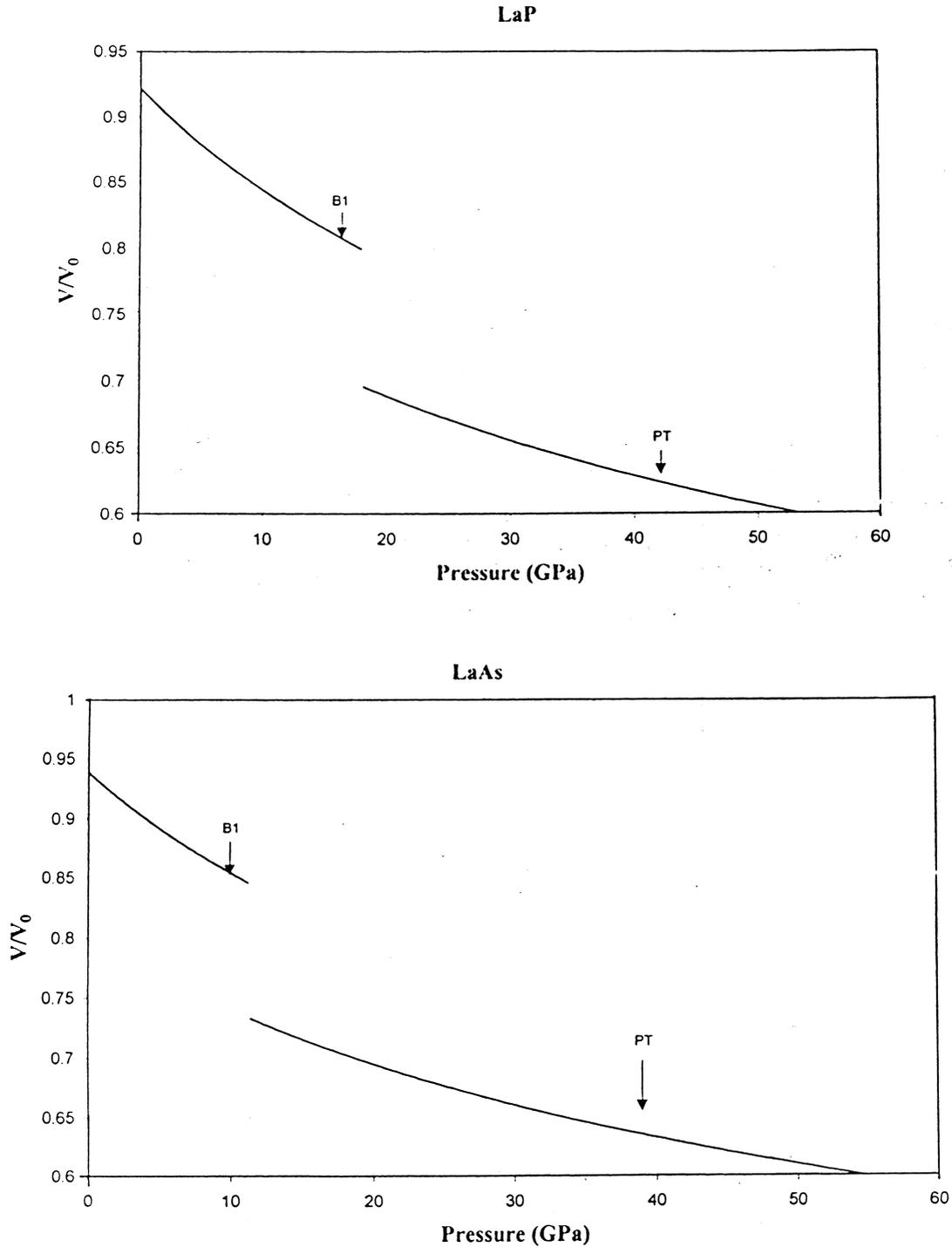

Fig. 2. c/a minimization for LaP.

LaP

LaAs

Fig. 3. Calculated pressure volume relation in the B1 and PT structures for (a) LaP and (b) LaAs.

$$G = E_{tot} + PV - TS \qquad (2)$$

Since the theoretical calculations are performed at 0 K Gibb's-free energy becomes equal to the enthalpy (H)

$$H = E_{tot} + PV \qquad (3)$$

At a given pressure a stable structure is one for which

enthalpy has its lowest value and the transition pressures are calculated at which the enthalpies for the two phases are equal. The transition pressure from B1 to PT structure, volume reductions are given in Table 3 and are compared with the earlier literature [20].

From the graph connecting the total energy and relative volume one can clearly see the relative stabilities of the high-pressure phases of LaP and LaAs. As the Primitive

Table 1
Structural and cohesive properties of LaP

LaP	B1		PT	
	Present	Expt.	Present	Expt.
Lattice parameter (Å)	$a = 5.851$	6.012	$a = 3.530$ $c = 3.059$ $c/a = 0.87$	3.460[a] 3.007 0.869
$N(E_F)$ (states/Ry/cell)	2.20	–	9.66	–
Bulk modulus (GPa)	95.22	112[b]	177	–
				–
γ (mJ/mol-K^2)	0.38	0.8	–	

[a] Ref. [20].
[b] Ref. [37].

Table 2
Structural and cohesive properties of LaAs

LaAs	B1		PT	
	Present	Expt.	Present	Expt.
Lattice parameter (Å)	$a = 5.997$	6.124	$a = 3.645$ $c = 3.171$ $c/a = 0.86$	– – –
$N(E_F)$ (states/Ry/cell)	1.86	–	10.85	–
Bulk modulus (GPa)	86.40	–	142.22	–
				–
γ (mJ/mol-K^2)	0.32	1.0	–	

tetragonal phase can be viewed as a distorted CsCl structure, one may think of a transition from B1 to PT as well as from B1 to B2. Hence, total energies were computed for B1, PT and B2 structures. In both the compounds, B1 phase is stable at ambient conditions. Between the two high-pressure phases B2 and PT it is found that the tetragonal phase is energetically lower than B2. It is a well-known that for a phase to be stable, its energy should be minimum. The B2 phase lies above the tetragonal phase in both LaP and LaAs and the energy difference between the two phases is around 1 mRy in the case of LaP and 7 mRy in LaAs. Hence the B2 phase does not compete as a high-pressure phase in these range of volumes and a transition from B1 to PT is only possible in both the compounds.

Lanthanum monophosphide undergoes a crystallographic transition from B1 to PT around 18 GPa and the volume collapse is found to be 11.7%. The theoretically

Table 3
Calculated transition pressures and volume collapse

Compound	Transition pressure (GPa)		Volume collapse (%)	
	Present	Expt.	Present	Expt.
LaP	18	24	11.7	16.3
LaAs	11.2	–	11.9	–

calculated lattice parameter in B1 phase (5.851 Å) underestimates the experimental value by 2.6%. Similarly the lattice parameters in the PT phase are $a = 3.516$ Å, $c = 3.059$ Å and has a deviation of 1.6% from the experimental value [20].

The high-pressure behaviour of LaAs is as follows: the transition from B1 to PT occurs around 11.2 GPa with a volume collapse of 11.9%. No experimental results are available to compare the above transition. The theoretically calculated lattice parameter in the B1 phase is 5.998 Å, which deviates from the experimental value by 2%. In the PT structure the cell parameters are $a = 3.645$ Å and $c = 3.171$ Å, which finds no experimental results for comparison.

The bulk modulus in the B1 phase decreases from LaP to LaAs, which is in good agreement with that of experiments. Moreover, the bulk modulus in the high-pressure phase is almost twice when compared to the value in B1 phase. This is in accordance with Leger et al. [37] who has stated that the covalently bonded compounds are well known to have high bulk moduli. This may be due to increased strength of covalent bonding under high pressure.

3.2. Band structure and density of states

The self-consistent band structures for these compounds are obtained for both B1 and PT structures and are shown in Figs. 4 and 5. The overall band profile is found to be the same for these compounds and is in good agreement with the earlier works [16,18]. From the band structure, it is seen that the lowest lying band in both LaP and LaAs is mainly due to the pnictogen 's' like state and it lies around -0.6 Ry. In both these compounds the band which is lying above the pnictogen 's' state is the La 's' like band which hybridizes with the pnictogen 'p' like band at the Γ point. These bands lie just below the Fermi energy. The narrow bands originating above the Fermi level around 0.18 Ry are mainly due to La 'f' like states. These bands are not completely localized and drop down below the Fermi level around -0.08 Ry along the Γ–X direction.

In the high pressure phase of LaP and LaAs one can clearly see the hybridization of La 's' like states with the pnictogen 'p' like states at the symmetry point M. In LaAs the pnictogen, 'p' like state hybridizes with the La 'd' like state at the Γ point. Further the La 'd' like states hybridize with the La 'f' like states along the X–Γ direction. Though the 'f' like states are delocalized the contribution from the 'd' like states is more at the Fermi level. This contribution of the 'd' like states is more in the high pressure phase when compared to the ambient conditions which may be one of the reasons for the increased density of states in the high pressure phase.

The total and partial density of states of these pnictides is shown in Figs. 6 and 7. The DOS histogram of these
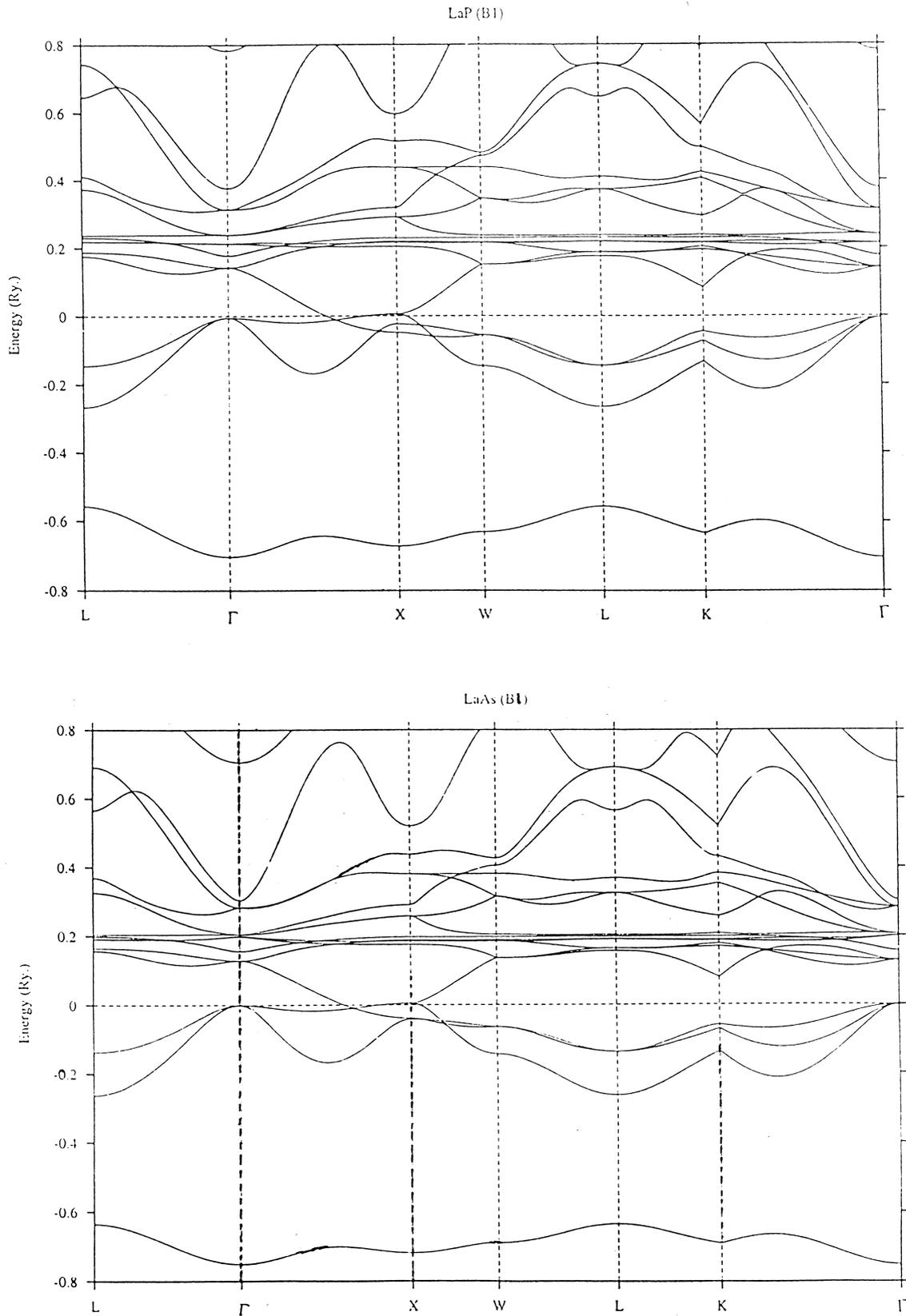
Fig. 4. Band structure in the B1 phase for (a) LaP and (b) LaAs.
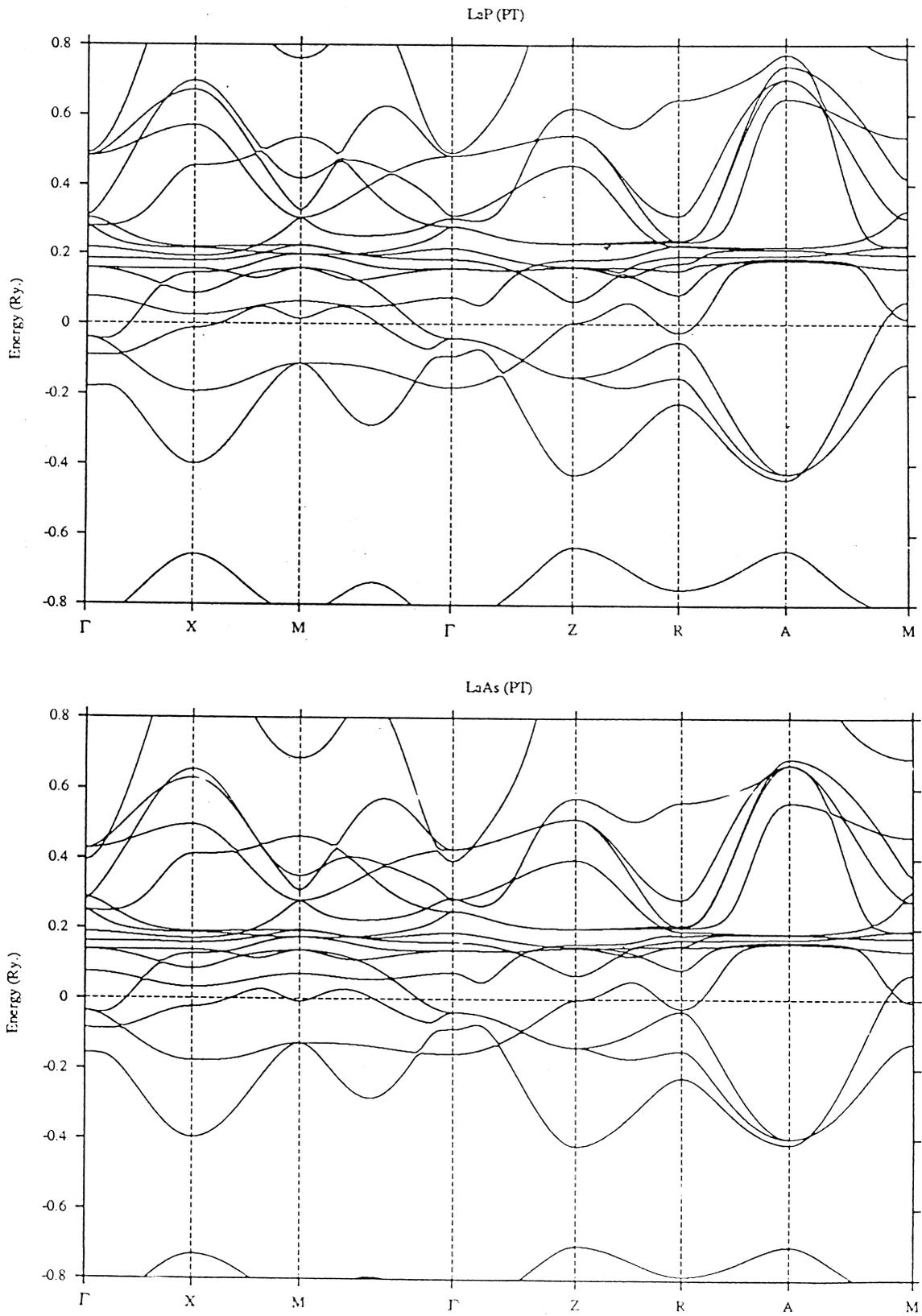
LaP (PT)

LaAs (PT)

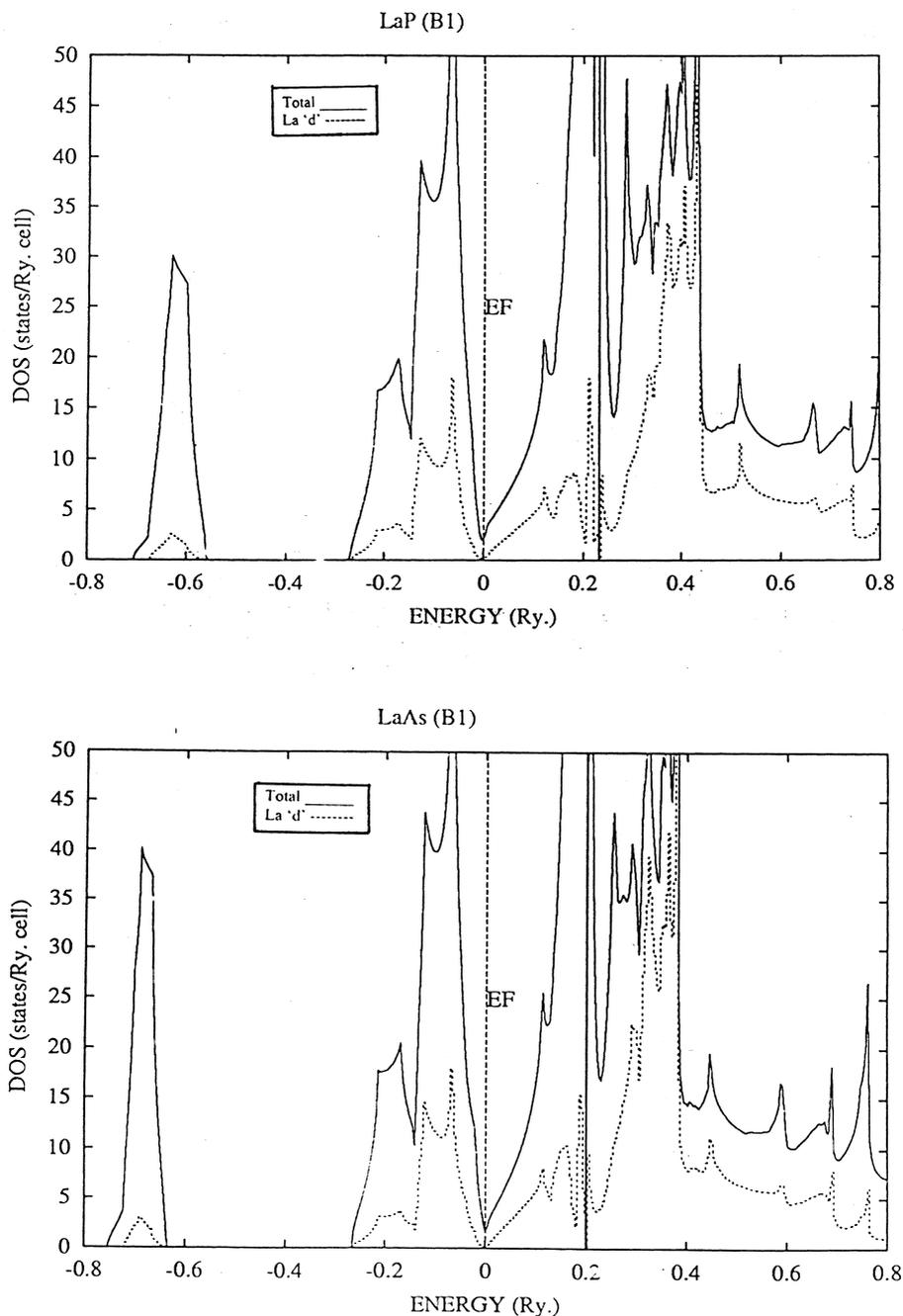Fig. 5. Band structure in the PT phase for (a) LaP and (b) LaAs.

Fig. 6. Density of states in the B1 phase for (a) LaP and (b) LaAs.

pnictides in B1 consists of a peak present in the lowest energy part of the DOS curve which is mainly due to the pnictogen 's' state. The region which lies above this is due to La 's', followed by the contribution from La 'd' like and pnictogen 'p' like states which are energetically degenerate till the Fermi level. The regions, which lie above these states has a major contribution from La 'f' like states.

In the high-pressure phase the contribution from the La, 'd' like states is more at the Fermi level when compared to the La 'f' contribution. This 'd' contribution further increases as we go from LaP to LaAs, which may be one

of the reasons for the increase in the density of states in the high-pressure phase. This can be clearly seen from the DOS histogram wherein at E_F the major contribution to the density of states is from the La 'd' like states.

The electronic-specific heat coefficient is calculated from the expression, $\gamma = \pi^2 k_B^2 N(E_F)/3$ using the calculated density of states at the Fermi energy. The calculated values are compared with the available experimental [18] and are tabulated in Tables 2 and 3.

The partial number of electrons is given in Table 4. From the table it is seen that there is a continuous transfer
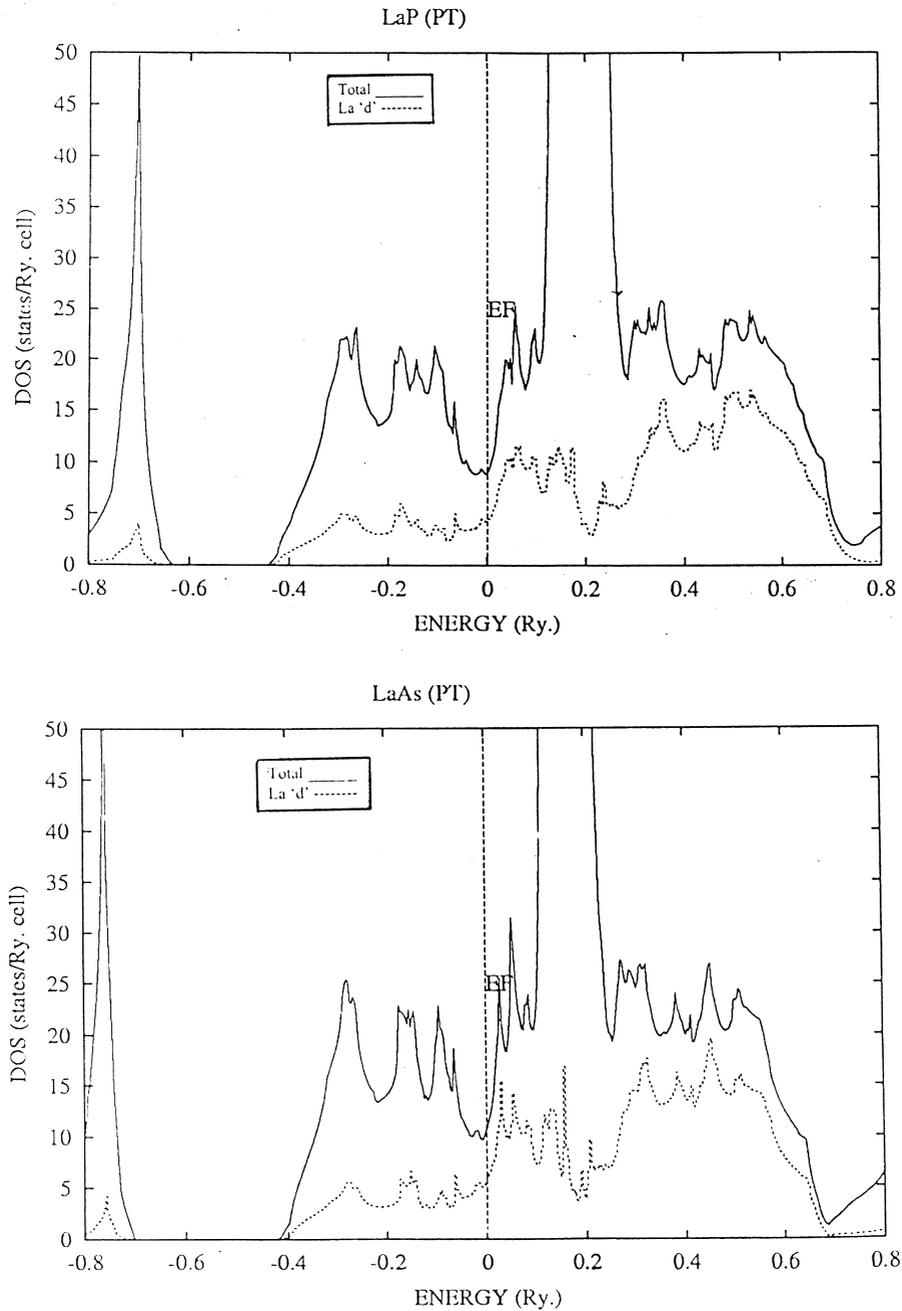
Fig. 7. Density of states in the PT phase for (a) LaP and (b) LaAs.

Table 4
Partial number of electrons as a function of V/V_o for LaP

V/V_o	La				P	
	's'	'p'	'd'	'f'	's'	'p'
1.05	0.320	6.084	1.403	0.329	1.733	3.512
1.0	0.315	6.075	1.432	3.329	1.720	3.479
0.95	0.310	6.063	1.466	0.329	1.706	3.441
0.90	0.305	6.047	1.506	0.329	1.691	3.394
0.85	0.300	6.027	1.550	0.330	1.675	3.344
0.80	0.295	6.000	1.600	0.332	1.659	3.286
0.75	0.291	5.964	1.659	0.337	1.642	3.217
0.70	0.288	5.910	1.727	0.353	1.623	3.138

of electrons from pnictogen 's' and 'p' like states to the lanthanum 'd' like states, which may be one of the reasons for the observed structural phase transformation under pressure.

4. Conclusion

Using the density functional ab initio total energy calculations, we have shown that LaP undergoes a structural transition from NaCl type structure to primitive tetragonal type structure around 18 GPa. In the case of LaAs,

we predict a transition from B1 to PT structure around 11.2 GPa. This may easily be tested using diamond anvil cell. For LaP and LaAs the ground state properties are calculated in both the phases and compared with available data. We find a good agreement between theory and experiment. The value of the bulk modulus in PT phase is almost twice that in the B1 phase. This may be due to the increased strength of the covalent bonding. The possible cause for the structural phase transformation is also discussed.

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