

Theoretical studies on the high pressure phases of Lanthanum monochalcogenides

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Abstract

We report total energy and electronic structure calculations for lanthanum monochalcogenides in B1 (NaCl) and B2 (CsCl) crystal structures over a range of unit cell volumes. We employed the tight binding linear muffin-tin orbital approach to density functional theory within the local density approximation to expand the crystal orbitals and periodic electron density. In agreement with the experiment we find that B1 phase is lower in energy than B2 phase, and that the compounds transforms to B2 structure under applied pressure. This is the first qualitative prediction of the transition in La monochalcogenides and should be testable with diamond-anvil technique.

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1. Introduction

Rare earth monochalcogenides including monoxides crystallize in a face centered cubic structure of NaCl type [1,2]. The chalcogenides of rare earth metals are one such group, which possess a wide range of electrical [3], magnetic [4] and other physio chemical properties [5]. Some of the rare earth monochalcogenides exhibit insulator to metal transition induced either by doping or by high pressure [6]. When the rare earth element is trivalent, the volumes of the corresponding monochalcogenides show the usual lanthanide contraction and the compounds have metallic properties, for e.g. LaS, LaSe and LaTe have electrical resistivities at room temperature of the order of $250 \mu\Omega \text{ cm}$ [2,7]. When the rare earth element is divalent, (Sm, Eu, Yb and Tm), the volumes are larger by about 15% and are found to be semiconducting. Under pressure these divalent rare earth monochalcogenides undergoes a semiconductor to metal transition [2].

The trivalent lanthanum monochalcogenides (LaS, LaSe, LaTe) are found to be superconductors having transition temperatures in the range of 0.8–1.5 K [3]. The supercon-

ducting transition temperature T_c as well as the electronic specific heat coefficient γ increases from sulphide to telluride. Sankaralingam et al. [8] have reported a theoretical calculation of superconducting transition temperature at ambient pressures for these compounds. A few experimental studies like point contact spectroscopy [9], reflectivity measurement [10], dielectric constant and X-ray absorption [11] for LaS are available in the literature. In addition, there are reports about the phonon spectrum by Steiver et al. [12] and electronic structure calculation by Lu et al. [6]. Adequate literatures are not available for LaSe and LaTe.

All these systems possess metallic character having a carrier density in the range of $1.5\text{--}2 \times 10^{22} \text{ cm}^{-3}$ [13]. The magnetic susceptibility measurements indicate paramagnetism in these compounds [14]. The paramagnetic susceptibility χ_p of the conduction electrons has been found to increase from LaS to LaTe suggesting that the density of states at the Fermi energy $N(E_F)$ should also increase from LaS to LaTe [8]. The measured electronic specific heat coefficient γ [3] also shows the same trend and these aspects are to be discussed from the point of view of the electronic structure calculation. The Debye temperature θ_D of these compounds is found to decrease from LaS to LaTe [3].

The high pressure structural studies for all the three lanthanum monochalcogenides are lacking. Hence, an attempt has been made in the present work to investigate

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Table 1
Calculated transition pressures and volume collapse of lanthanum chalcogenides

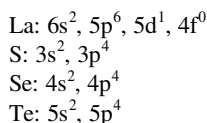
Compound	Transition pressure (GPa) (Present)	Volume collapse (%) (Present)
LaS B1 → B2	24.9	8.4
LaSe B1 → B2	12.7	11.0
LaTe B1 → B2	16.5	8.2

the high pressure structural phase transition of these compounds by means of tight binding linear muffin tin orbital method (TB-LMTO). The rest of the paper is organized as follows. Section 2 deals with the computational details. Section 3 is devoted for the results. Finally, Section 4 gives the conclusion.

2. Computational details

All the three chalcogenides namely LaS, LaSe and LaTe considered in the present work crystallize in the NaCl type structure (B1) with space group symmetry $Fm\bar{3}m$. The lanthanum atom is positioned at (0,0,0) and chalcogen at (1/2,1/2,1/2). The high pressure phase predicted in these compounds is of CsCl structure (B2 type) with the space group symmetry $Pm\bar{3}m$ in which the chalcogen atom is positioned at (1/2,1/2,1/2).

The electronic band structure was obtained using the self-consistent TB-LMTO [15,16]. von Barth and Hedin parameterization scheme has been used for the exchange correlation potential [17] within the local density approximation (LDA). Combined correction terms which account for the non-spherical shape of the atomic spheres and the truncation of the higher partial waves inside the sphere so as to minimize the errors in the LMTO method are included. The Wigner–Seitz sphere radii are chosen in such a way that the sphere boundary potential is minimum and the charge flow between the atoms are according to the electronegativity criteria. The s, p, d, and f partial waves are included. The tetrahedron method [18] of the Brillouin zone integration is used to obtain the total and partial density of states. \mathbf{E} and \mathbf{K} convergence is also checked. For loosely packed structures, empty spheres are introduced in the appropriate interstices in B1 phase without breaking the crystal symmetry. The basis orbitals used in these compounds are as follows



To study the phase stability of lanthanum monochalcogenides the electronic structure and the total energies are calculated at different cell volumes ranging from $1.05V_0$ to $0.65V_0$

in a manner similar to our earlier works [19,20] where V_0 is the equilibrium cell volume. The calculated total energies are fitted to the Birch equation of state [21] to obtain the ground state properties. The graph connecting the pressure and relative volume are shown in Fig. 1.

3. Results and discussion

3.1. High pressure structural phase transformations

The graph connecting the total energy and relative volume are as shown in Fig. 2. From the graph, one can see that B1 is the stable phase for all these compounds. The total energies obtained within DFT are used to predict the structural phase transformations, which are in agreement with the experimental studies [22].

In lanthanum monosulphide a crystallographic transition from B1 to B2 occurs around 24.9 GPa with a volume collapse of 8.4% Fig. 1. The theoretically calculated lattice parameter in the B1 phase (5.727 Å) underestimates the experimental value by 1.9%. The theoretically calculated cell parameter in the B2 phase is 3.301 Å, which cannot be compared for want of experimental studies. In lanthanum monoselenide, the B1 → B2 transition occurs around 12.7 GPa with a volume collapse of 11% Fig. 1. The lattice parameter in the B1 phase (5.957 Å) is lower than the experimental value by 1.68% and in the B2 structure the lattice parameter is 3.471 Å, which cannot be compared for want of experimental data. Lanthanum monotelluride undergoes a transition from B1 → B2 around 16.5 GPa with a volume collapse of 8.2% Fig. 1. The cell parameter in the B1 phase (6.256 Å) underestimates the experimental value by 2.3% and the cell parameter in the B2 phase is 3.621 Å. It is interesting to note that the transition pressure increases from LaSe to LaTe. Similar calculations were performed for lanthanum mononictides [23,24]. Here also we find that the transition pressure initially decreases while going from LaP to LaSb and then increases for LaBi. The calculated transition pressures for LaP and LaSb are in agreement with the experimental values. A similar trend is noticed in lanthanum monochalcogenides also. The transition pressure and the volume collapse of these compounds are tabulated in Table 1.

The bulk modulus is 107, 97 and 74 GPa, respectively, for LaS, LaSe and LaTe and is compared with available experimental results [25,26], which is given in Tables 2–4. The calculated bulk modulus is overestimated when compared to the experimental value. This may be due to inherent limitation of LDA. The bulk modulus in the B2 phase is almost twice when compared with the value in the B1 phase, which may be due to the increased covalent nature in this phase [26].

3.2. Band structure and density of states

The self-consistent band structure for these compounds is calculated in B1 and B2 phases. The band structures at

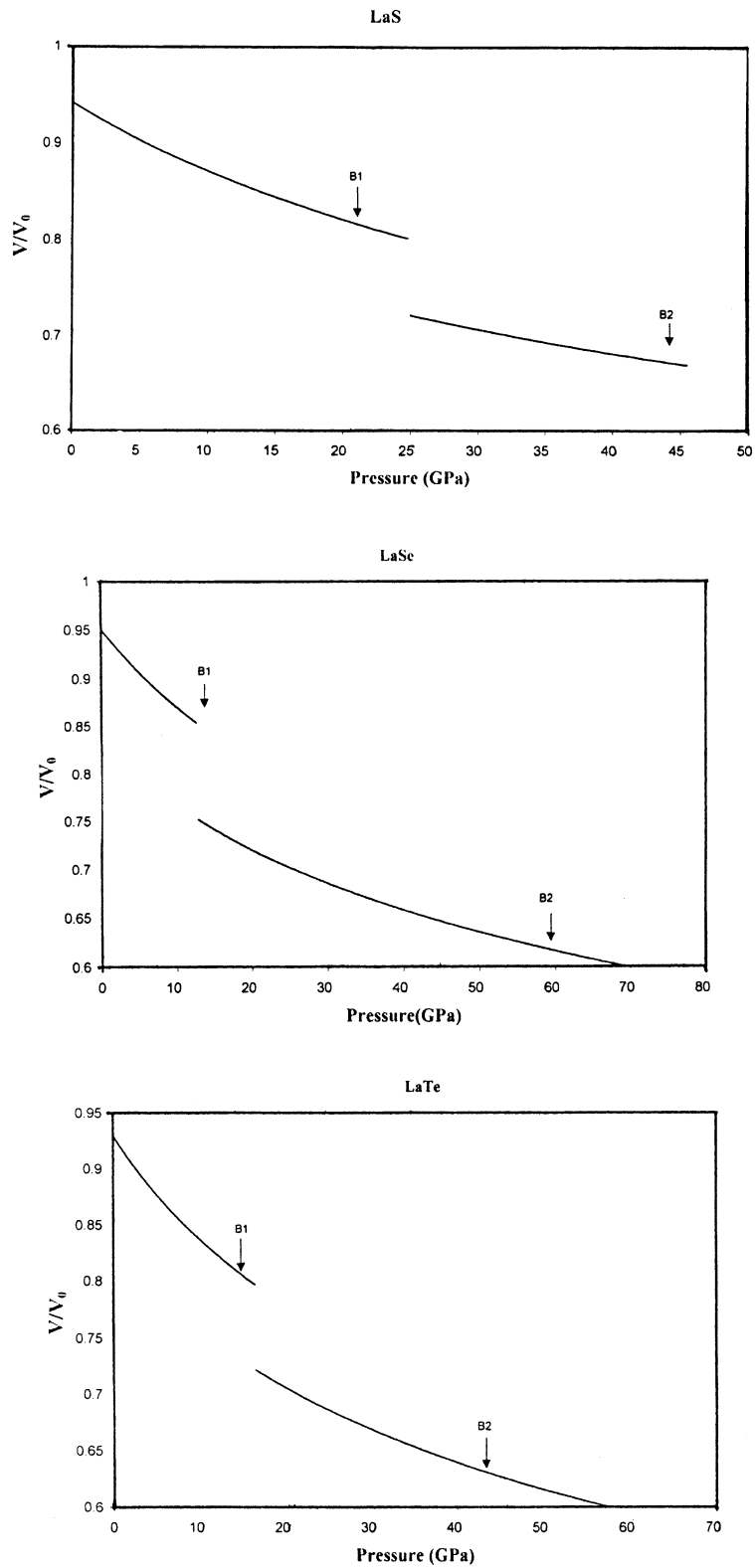


Fig. 1. Calculated pressure volume relation in the B1 and B2 structures for (a) LaS, (b) LaSe, and (c) LaTe.

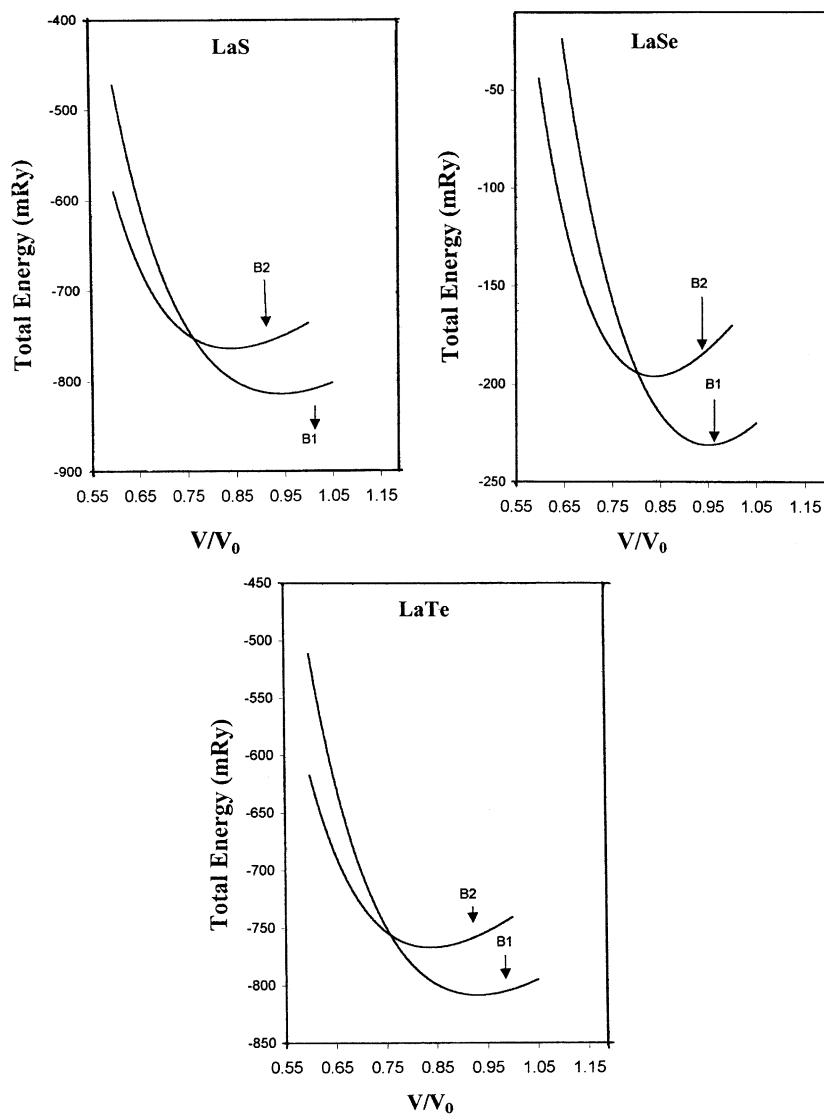


Fig. 2. (a) Calculated total energy ($-17772.00 +$) Ry vs relative volume for LaS; (b) calculated total energy ($-21831.00 +$) Ry vs relative volume for LaSe; (c) calculated total energy ($-30555.00 +$) Ry vs relative volume for LaTe.

Table 2

Structural and cohesive properties of LaS

LaS	B1			B2
	Present	Experiment	Earlier work	Present
Lattice parameter (\AA)	5.727	5.842	5.851 ^a	3.301
$N(E_F)$ (States/Ry/cell)	16.15	–	15.15 ^a	16.63
Bulk modulus (GPa)	107	86 ^b	–	228
γ (mJ/mol K ²)	2.97	3.28 ^c	2.63 ^a	–
θ_D (K)	235.4	276 ^c	–	–

^a Ref. [8].

^b Ref. [24].

^c Ref. [3].

Table 3
Structural and cohesive properties of LaSe

LaSe	B1			B2
	Present	Experiment	Earlier work	Present
Lattice parameter (\AA)	5.957	6.059	6.063 ^a	3.471
$N(E_F)$ (States/Ry/cell)	17.78	–	16.93 ^a	20.84
Bulk modulus (GPa)	97.74	–	–	151.08
γ (mJ/mol K ²)	3.07	3.77 ^b	2.94 ^a	–
θ_D (K)	233.4	231 ^b	–	–

^a Ref. [8].

^b Ref. [3].

ambient conditions and at high pressure are given in Figs. 3 and 4. The overall band profile is found to be the same for all the compounds and is in good agreement with the earlier works [8,27].

From the band structure of LaS, it is evident that the lowest lying bands are mainly due to S-'s' like states, which lies around -0.90 Ry. The band, which lies around -0.42 Ry arises mainly from La-s like state, which hybridizes with La-'d' like state and S-'p' like state at the Γ point. The La-'f' like states are not completely localized and drops down below the Fermi level to an extent of -0.2 Ry along the Γ -X direction.

In the case of LaSe and LaTe, the chalcogen s like states is positioned around -0.97 and -0.82 Ry, respectively. The larger value of lattice parameter in the case of LaSe and the smaller electronegativity of Se than that of S will reduce the extent of hybridization of La-5d Se-4p states along the X-W direction. The larger lattice parameter and lesser electronegativity of Tellurium when compared with Selenium leads to a similar behavior in LaTe. In both of these compounds, the La-f bands are not completely localized and drops down below the Fermi level.

In the high pressure phase of LaS, the La-s, chalcogen p and La-d like bands hybridize with the lanthanum f like states and lie together at the Γ point. A similar case is observed in LaSe also at the Γ point, whereas at the sym-

metry point M the La-d like bands moves up towards the Fermi level. In LaTe, the La-d like bands are completely separated from the La-s like and chalcogen p like band at the Γ point. Along the Γ -X direction, the La-d like band shifts towards the Fermi level and lies close to it.

The band structure for these three compounds in the B1 phase at the same compression as that of B2 phase has been given in Fig. 5. In the B1 phase we find that the bands are shifted towards higher energy region when pressure increases.

The total and partial density of states of these chalcogenides in both the phases are shown in Figs. 6 and 7. From the DOS histogram, one observes a peak present around -0.4 Ry, which is due to La-f, La-d, and X-p like states. The La-f like states are not completely localized and drops down below the Fermi level considerably. The density of states is found to be around 16.10, 17.78, 21.80 States/Ry/cell in the case of LaS, LaSe and LaTe, respectively. This is in good agreement with the earlier work [8]. The higher density of states in this chalcogenides when compared with lanthanum pnictides [23,24] may be due to the increased metallic nature of these compounds at ambient conditions. In these systems, the La-X bonding can be expected to be metallic as the configuration of the constituent atoms are $6s^2, 5p^6, 5d^1, 4f^0$ and $3s^2, 3p^4$ for La and X, respectively, which means, that even if the filled shell

Table 4
Structural and cohesive properties of LaTe

LaTe	B1			B2
	Present	Experiment	Earlier work	Present
Lattice parameter (\AA)	6.255	6.408	5.851 ^a	3.621
$N(E_F)$ (States/Ry/cell)	21.80	–	19.03 ^a	24.50
Bulk modulus (GPa)	74.02	55 ^b	–	150.43
γ (mJ/mol K ²)	3.77	4.65 ^c	3.30 ^a	–
θ_D (K)	209	175 ^c	–	–

^a Ref. [8].

^b Ref. [23].

^c Ref. [3].

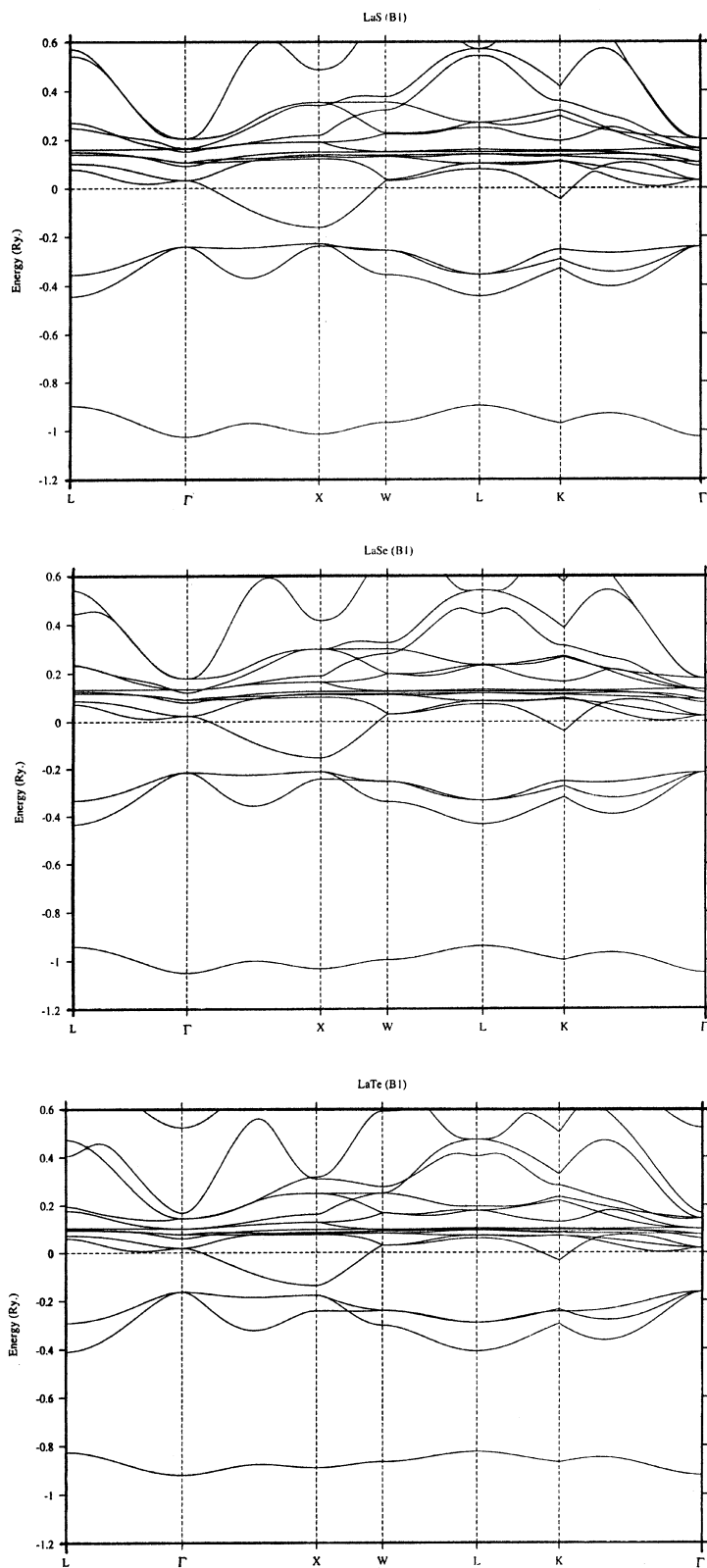


Fig. 3. Band structure in the B1 phase for (a) LaS, (b) LaSe, and (c) LaTe.

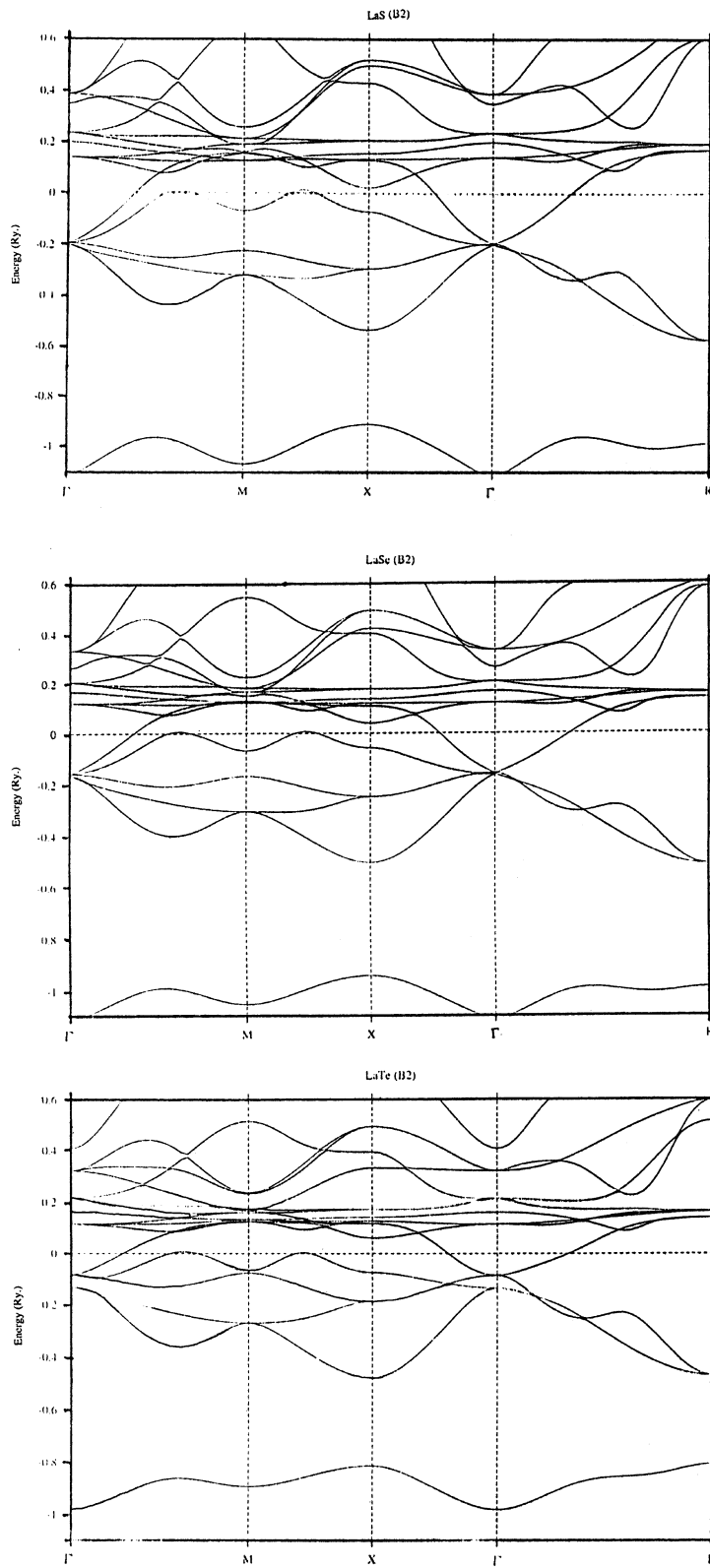


Fig. 4. Band structure in the B2 phase for (a) LaS, (b) LaSe, and (c) LaTe.

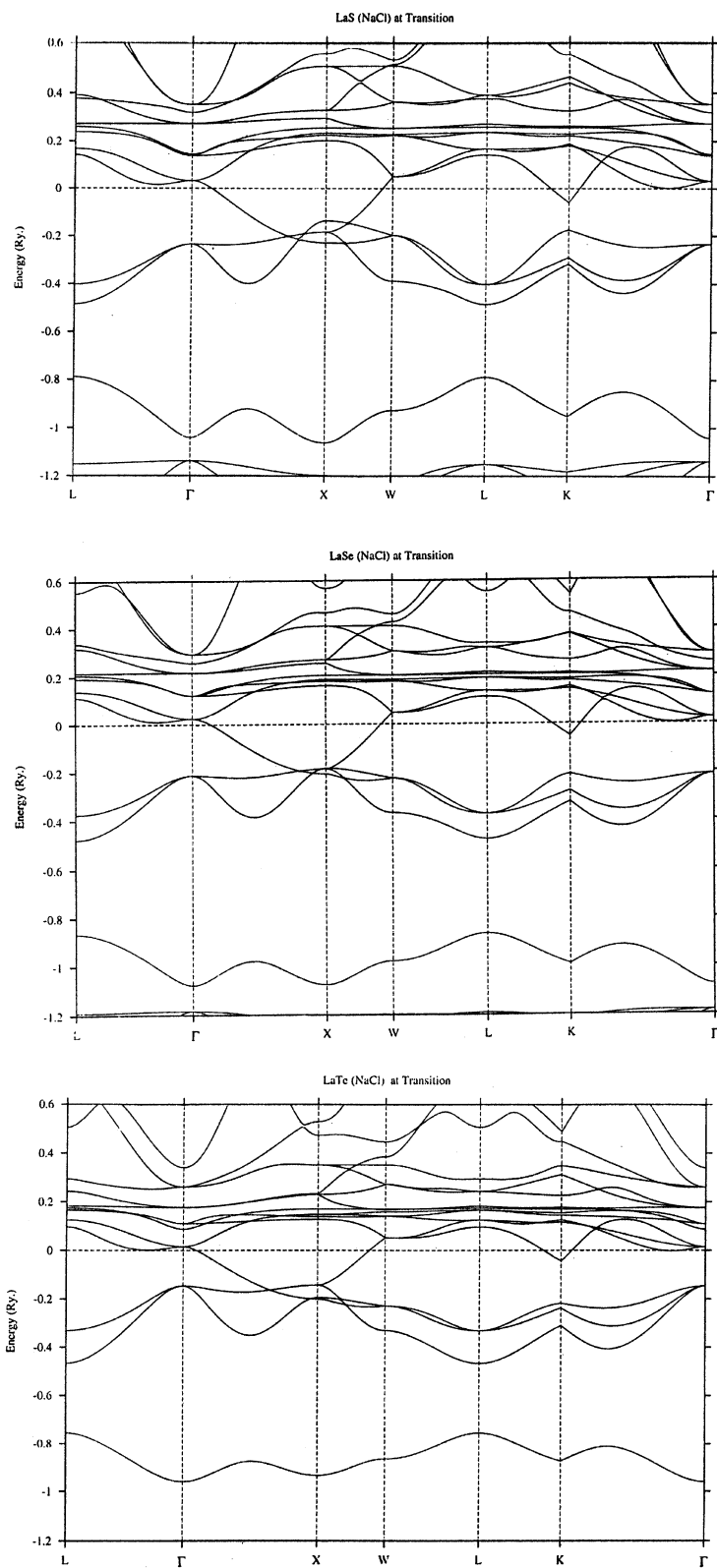


Fig. 5. Band structure in the B1 phase for the same compression as that of B2.

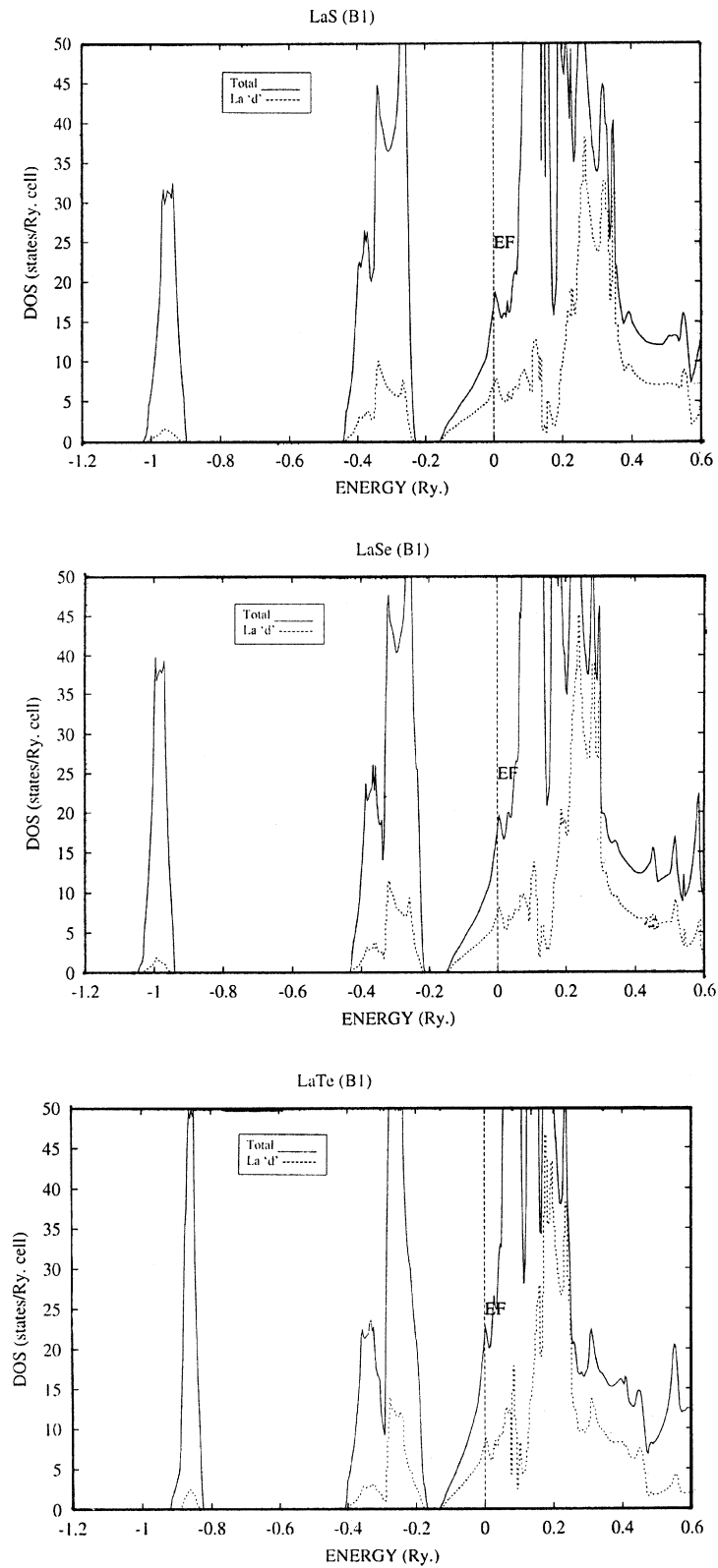


Fig. 6. Density of states in the B1 phase for (a) LaS, (b) LaSe, and (c) LaTe.

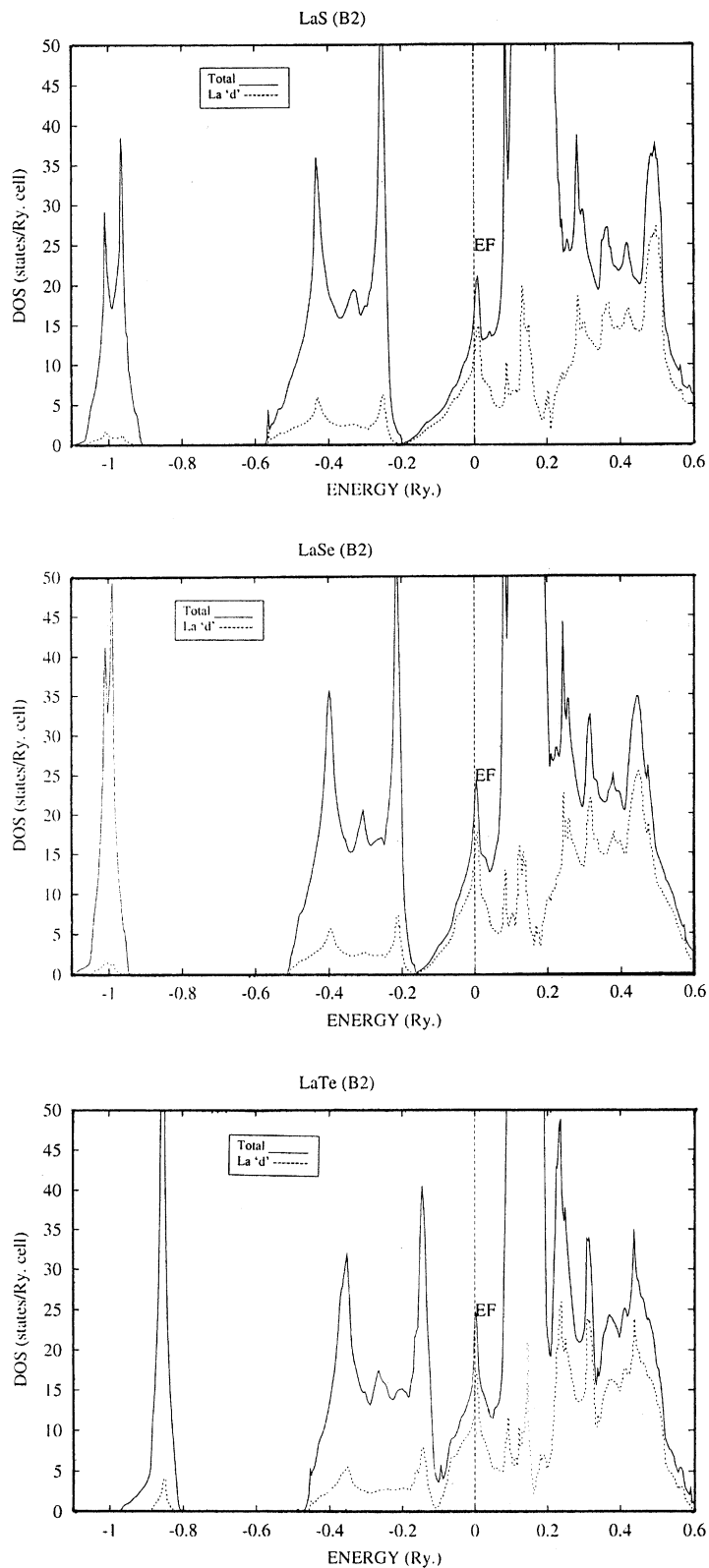


Fig. 7. Density of states in the B2 phase for (a) LaS, (b) LaSe, and (c) LaTe.

Table 5
Partial number of electrons as a function of V/V_0

V/V_0	La				S	
	s	p	d	f	s	p
1.05	0.257	6.032	1.444	0.424	1.815	4.285
1.00	0.256	6.020	1.466	0.429	1.804	4.249
0.95	0.255	6.006	1.489	0.437	1.793	4.210
0.90	0.254	5.989	1.516	0.445	1.778	4.168
0.85	0.253	5.968	1.541	0.457	1.766	4.122
0.80	0.254	5.942	1.571	0.471	1.751	4.072
0.75	0.255	5.910	1.600	0.488	1.734	4.017
0.70	0.256	5.870	1.642	0.507	1.714	3.955

configuration $3p^6$ for the chalcogen atom is achieved by the transfer of two electrons from La to X, the presence of the 5d electron in La will induce metallic character in these compounds [8].

In the high pressure phase of these compounds the La-d contribution increases from LaS to LaTe which may be the reason for the increase in the density of states as one goes from S to Te. This can be clearly seen from the DOS histogram.

The partial number of electrons for LaS in the B1 phase is given in Table 5. From the table it is seen that there is a transfer of electrons from chalcogen s and p like states to the La-d like states continuously under pressure, which may be responsible for the observed structural transformation. Similar behavior is observed in LaSe and LaTe.

3.3. Electronic specific heat coefficient and Debye temperature

Using the calculated DOS, the electronic specific heat coefficient is calculated using the expression, $\gamma = \pi^2 k_B^2 N(E_F)/3$. The values are tabulated in Tables 2–4 along with the experimental values. A good agreement is seen from the table. The Debye temperature θ_D is calculated from the relation,

$$\theta_D = 41.63(r_0 B/M)^{1/2}$$

where M is the mass of the compound, B is the bulk modulus and r_0 is the Wigner seitz sphere radius. The calculated values are compared with the available theoretical and experimental values and are given in Tables 2–4.

4. Conclusion

Our key result is the prediction that LaX compounds will transform from NaCl (B1) to CsCl (B2) structure at a pressure of 24.9, 12.7, 16.5 GPa, respectively. It should be possible to attain this transition in a diamond anvil cell, verify our prediction and to examine the electronic properties of these compounds. The transition pressures of LaS and

LaSe are compared with isostructural compounds CeS and CeSe in which a similar transition occurs around 24.3 and 12.4 GPa [28]. The bulk modulus in the B1 phase is over-estimated which may be due to the inherent limitation of LDA. In B2 phase the value of bulk modulus become doubled compared to B1 phase, which may be due to increased covalent nature. All these three compounds show metallic character, which may be due to the ionic and metallic bonding between La and X atoms. Very recently the electronic structure and physical properties of transition metal mononitrides was reported by Stampfl et al. [29] using FLAPW with GGA. They find that GGA yields 1–2% larger lattice parameter and 10–20% smaller bulk modulus. From this work using TB-LMTO we find that the lattice parameter are underestimated by 2% but the bulk modulus are over estimated by 40–50%.

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