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Structural phase stability and superconductivity of LaN

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Abstract

Results of a theoretical investigation on the structural phase stability of lanthanum nitride (LaN) is reported. We predict that LaN, which crystallizes in NaCl structure, undergoes a transition from NaCl to CsCl type structure at around 26.9 GPa with a volume collapse of 12.5%. In addition, the superconducting transition temperature (T_c) is also calculated theoretically for the first time. The high-pressure phase of LaN is CsCl structure and not the tetragonal structure as observed in other lanthanum pnictides, which has been predicted by the total energy minimization. In addition, the basic ground state properties such as the equilibrium lattice parameter, bulk modulus, cohesive energy, heat of formation, electronic specific heat coefficient are computed and compared with the available experimental and other theoretical results. The band structure and density of states are plotted for ambient and high-pressure structures. The possible reasons for the occurrence of superconductivity and the structural phase transition are also discussed. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Transition metal mononitrides, which generally crystallize in the rock salt structure, are known as refractory compounds. They exhibit extreme and unique physical properties such as relatively high hardness, brittleness, and melting point. Several of these compounds are superconductors with relatively high superconducting transition temperature (e.g. TiN, VN [1], NbN [2,3] and TaN [4]).

Lanthanum nitride (LaN), which belongs to the 5d transition metal group, encounters many problems, which are primarily related to stoichiometry [5]. Part of the measured data indicates a semi-metallic behavior while other data show that the compound is a semiconductor [6]. A previous self-consistent augmented plane wave (APW) band structure calculation by Hasegawa [7] shows a band overlap

of 9 mRy. Norman et al. [8] found that LaN has a band overlap of approximately 40 mRy making it a semi-metal. Since LaN is taken as a reference material for understanding the mixed valent CeN system, it becomes necessary to find out whether LaN is a metal, semi-metal or a semiconductor. Veyssie et al. [9] have reported the electronic specific heat coefficient of LaN to be around 3.5 mJ/mol K², which is comparable with the specific heat of lanthanum monochalcogenides.

To our knowledge no high-pressure studies either, experimental or theoretical have been reported to investigate the structural phase stability in this compound. Hence, an attempt has been made in the present work to explain the high-pressure behavior. It is observed that LaN undergoes a crystallographic transition from NaCl type to CsCl type structure, which is similar to that of lanthanum monochalcogenides [10]. The rest of the paper is organized as follows. Section 2 deals with the computational details. Section 3 explains the structural phase stability. Section 4 is purely devoted to results and discussions and Section 5 gives the conclusion.

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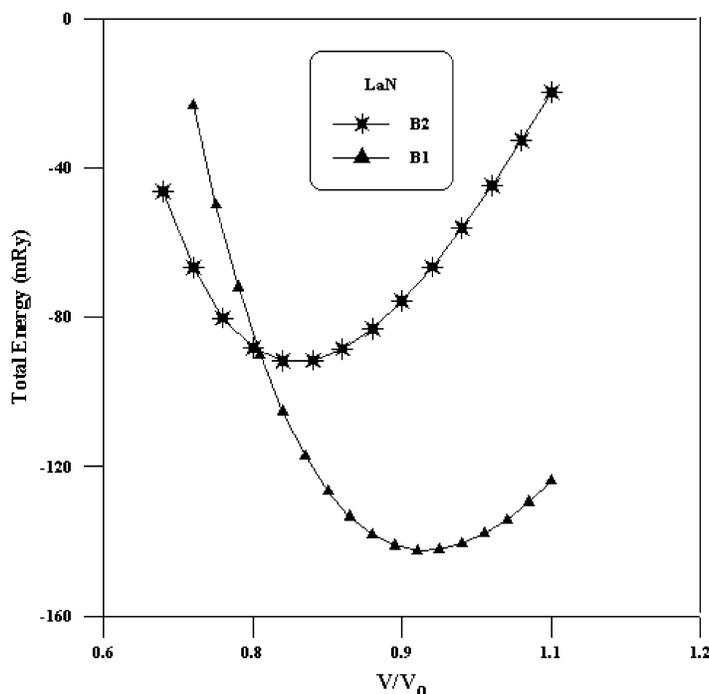


Fig. 1. Calculated total energy ($-17085.00 +$) Ry vs. relative volume for LaN.

2. Computational details

The electronic structure and the total energies within the atomic sphere approximation (ASA) are obtained by means of tight-binding linear muffin-tin orbital method (TB-LMTO) [11,12]. The exchange correlation potential within the local density approximation (LDA) is calculated using the parameterization scheme of von-Barth and Hedin [13]. Combined correction terms are also included which accounts for the non-spherical shape of the atomic spheres and truncation of the higher partial waves inside the spheres to minimize the errors in the LMTO method. The density of states was calculated by the method of tetrahedron [14]. The Wigner–Seitz sphere is chosen in such way that the sphere boundary potential is minimum and the charge flow is in accordance with the electro negativity criteria. The E and K convergence were also checked.

3. Structural phase stability

In order to study the structural phase stability of LaN, the total energies were calculated in a manner similar to our earlier works [15,16] for both NaCl (B1 type) and CsCl (B2 type) structures for various volumes ranging from $1.05V_0$ to $0.65V_0$, where V_0 is the experimental equilibrium volume. The reason for choosing CsCl structure as the other phase is as follows. LaN belongs to the family of lanthanum pnictides. Since no experimental X-ray diffraction studies for LaN is available, and also the other member namely LaP

is reported to undergo a structural phase transition from NaCl type to primitive tetragonal by X-ray studies [17] we thought that LaN will also follow the path of LaP. So, we decided to minimize the total energy as a function of c/a and we find that the total energy showed a minimum for $c/a = 1$. In the case of LaP it is pointed out that the primitive tetragonal structure is a distorted CsCl type structure with less distortion and the distortion increases as one move from LaP to LaBi. When one moves to LaN the distortion may not be there and it goes to CsCl (B2 type) structure. The variation of the total energies with relative volume is given in Fig. 1. The calculated total energies are fitted to the Birch equation of state [18] to obtain the pressure–volume relation. The pressure is obtained by taking the volume derivative of the total energy ($P = -dE/dV$). The bulk modulus $B = -V_0 dP/dV$ is calculated from the pressure–volume relation. At a given pressure a stable structure is one for which the enthalpy has its lowest value and the transition pressures are calculated at which the enthalpies of the two phases are equal. The transition pressure from B1 to B2 is predicted to be around 26.9 GPa with a volume reduction of 12.5%. The self-consistent band structures are obtained in both NaCl and CsCl structures. The calculated ground state properties in B1 and B2 phases are given in Table 1.

4. Results and discussion

The electronic properties of LaN have been studied by means of the TB-LMTO method. Using the total energy

Table 1
Calculated ground state properties of LaN in NaCl and CsCl phases

Parameters	NaCl		CsCl
	Present	Experiment	Present
Lattice constant (a.u.)	9.756	10.021 ^a	5.613
Bulk modulus (GPa)	152	–	282
$N(E_F)$ (states/Ry/f.u.)	11.59	–	3.07
γ (mJ/mol K ²)	2.0	3.5 ^b	0.5
E_c (Ry)	1.22	–	1.15
$-\Delta H$ (kcal/mol)	87.0	72.0 ^c	78.8
W_c (Ry)	0.89	–	0.93
λ	0.42	–	–
T_c (K)	0.65	0.75 ^d	–
Transition pressure (GPa)	26.9	–	–
Volume collapse (%)	12.5	–	–
La–La (a.u.)	6.841	–	5.613
La–N (a.u.)	4.837	–	4.861

^a From Ref. [31].

^b From Ref. [20].

^c From Ref. [6].

^d From Ref. [9].

calculations, the structural stability has been studied. From the present study we find that LaN is stable in B1 phase, which is in agreement with the experimental result. The calculated equilibrium lattice parameter and bulk modulus in the B1 phase are in good agreement with the earlier experimental and theoretical results.

The theoretically calculated density of states $N(E_F)$ at the Fermi level at ambient pressure is 11.59 states/Ry/f.u., which is relatively high when compared with the other lanthanum pnictides [17,19]. Using the density of states, the electronic specific heat coefficient is calculated and

compared with the experimental value reported by Gambino et al. [20]. Apart from this, the $N(E_F)$ is nearly the same as that of LaS, which is a superconductor [21].

The band structure of LaN is compared with the isostructural compound LaS which is a superconductor having transition temperature of 0.8 K. Even though LaN and LaS are having similar physical properties both at ambient and at high-pressures, one can see some slight differences in their band structures.

In LaS the lowest lying bands are mainly due to the S s-like states and the bands which are close to the Fermi level are the La d-like and S p-like states. The main contribution to the density of states in the case of LaS comes from La d-like states. In LaN we find a notable hybridization between N p-like, La d-like and La s-like states near the Fermi level.

In the high-pressure CsCl structure the band which is around -0.9 Ry is due to the N s-like states. At the symmetry point Γ a hybridization between La d-like states with N p-like states are seen. Also one can find an appreciable hybridization of La d and La f-like states with N p-like states along the $X-\Gamma$ direction.

The DOS histogram of LaN in both NaCl and CsCl structure is shown in Figs. 2 and 3. From the DOS one can clearly see that the peak which is lying around -0.9 Ry is mainly due to N s-like states. The two peaks, which are present close to the Fermi level, are mainly due to the La d-like and N p-like states. The hybridization between La d-like and N p-like states is predominantly seen at the Fermi level. The peaks, which are present around 0.5 Ry, are mainly due to La f-like states and they do not contribute to the density of states at the Fermi level. The N p-like states contribute more at E_F when compared to the La d-like states and this leads to the higher density of states in LaN when compared to the other La pnictides.

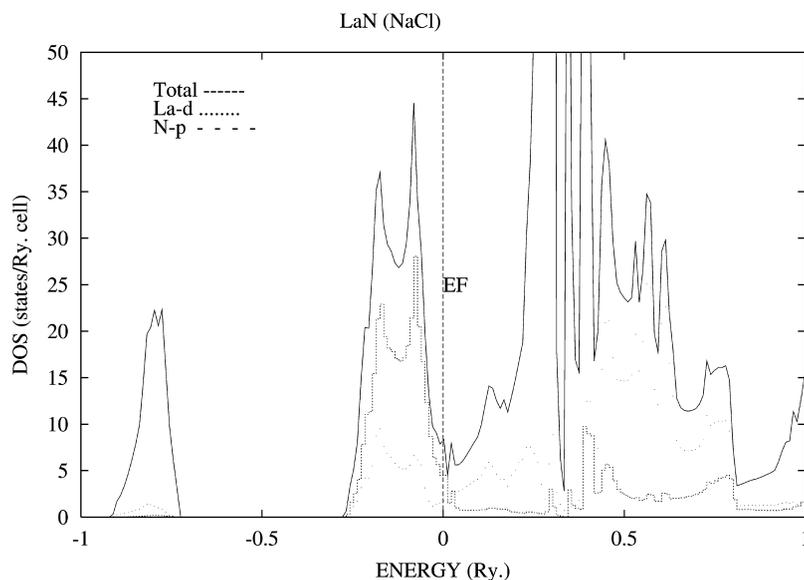


Fig. 2. Density of states in the B1 phase for LaN.

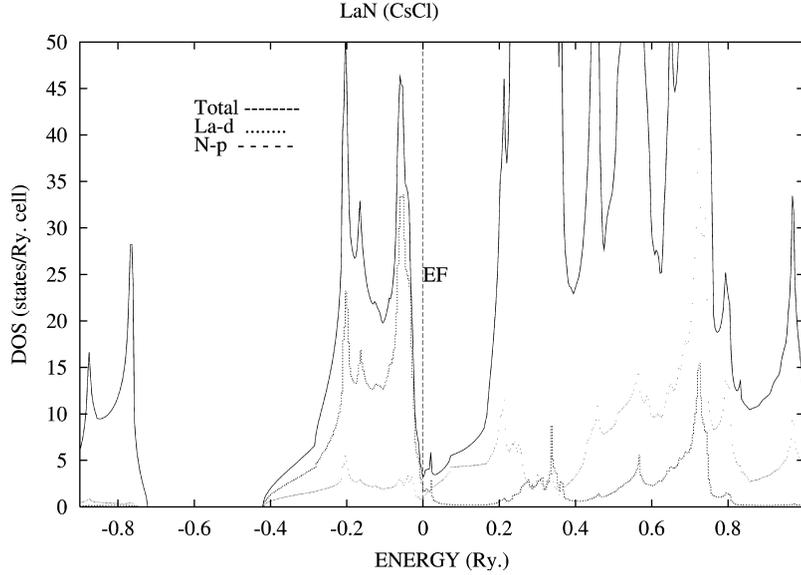


Fig. 3. Density of states in the B2 phase for LaN.

In the high-pressure phase the peaks which lie around -1 Ry is due to the N s-like states. The peaks, which are close to the Fermi level, are due to La d and N p-like states. The states, which lie around 0.5 Ry, are due to La f-like states. From the DOS one can clearly see that the N p-like contribution is more at the Fermi level. The contribution to E_F from N p-like state is less in B2 when compared to B1.

From the density of states the electronic specific heat coefficient is calculated using the expression:

$$\gamma = \pi^2/3k_B^2 N(E_F) \quad (1)$$

which comes around 2.0 mJ/mol K^2 . Gambino et al. [20] measured the specific heat co-efficient and reported a value of 3.5 mJ/mol K^2 . From the experimental and theoretical value of γ , one can estimate the electron–phonon coupling constant λ using the expression:

$$\gamma_{\text{exp}} = \gamma_{\text{the}}(1 + \lambda). \quad (2)$$

Using this expression the value of λ is found to be 0.75 .

The cohesive energy is a measure of the strength of the forces, which bind atoms together in the solid state. In this connection, the cohesive energy of LaN in the B1 and B2 structures is calculated. The cohesive energy (E_{coh}) of a given phase is defined as the difference in the total energy of the constituent atoms at infinite separation and the total energy of that particular phase.

$$E_{\text{coh}}^{\text{AB}} = [E_{\text{atom}}^{\text{A}} + E_{\text{atom}}^{\text{B}} - E_{\text{total}}^{\text{AB}}],$$

where $E_{\text{total}}^{\text{AB}}$ refers to the total energy of the compound LaN at equilibrium lattice constant and $E_{\text{atom}}^{\text{A}}$, and $E_{\text{atom}}^{\text{B}}$ are the atomic energies of the pure constituents.

The formation energy is also calculated in order to study the stability of a phase. To determine the heat of formation we first calculated the total energy of elemental La, and N

corresponding to their respective equilibrium lattice parameters. At zero temperature, there is no entropy contribution to the free energy; therefore, the heat of formation can be obtained from the following relation:

$$E_{\text{form}}^{\text{AB}} = [E_{\text{Tot}}^{\text{AB}} - (E_{\text{solid}}^{\text{A}} + E_{\text{solid}}^{\text{B}})],$$

where $E_{\text{Tot}}^{\text{AB}}$ refers to the total energy of LaN at equilibrium lattice constant and $E_{\text{solid}}^{\text{A}}$, $E_{\text{solid}}^{\text{B}}$ are the total energy of the pure elemental constituents. The calculated values of the cohesive energies and heat of formation (ΔH) are given in Table 1. The theoretically calculated value of formation energy is roughly 20% more than the experimental value. This may be due to the usage of LDA.

In order to study the structural phase transition of LaN total energies calculations were performed for both the tetragonal and CsCl structures. As a first step, the c/a optimization has been carried out in the case of tetragonal phase. It was found that the total energy is minimized only for $c/a = 1$. Even though LaN belongs to Pnictides family, many of its properties are similar to that of Chalcogenides. In the case of LaS [10], there is a structural phase transition from B1 (NaCl) type to B2 (CsCl) type around 24.9 GPa with a volume collapse of 8.4% . LaN is now predicted to undergo a similar transition around 26.9 GPa. A similar transition is also predicted in the case of ScN [22]. The density of states at E_F and the electronic specific heat coefficient of LaN are comparable to that of LaS. Similar to LaS, LaN may also show superconductivity at ambient conditions.

It is well established that the bonding nature of solids can be explained through band-structure calculations [23,24]. In the case of LaN it can be clearly seen that the La d-like states and N p-like states are hybridized to a greater extent. From the electron density contours of LaN in both NaCl and CsCl

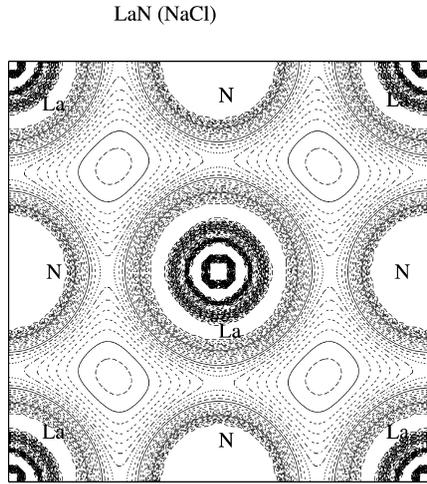


Fig. 4. Electron charge density of LaN in B1 phase for (100) plane.

structures one can clearly distinguish between the metallic and covalent nature of bonding. In order to have deeper understanding about the bonding behavior of LaN, the charge density distributions are given in (100) plane and (100) plane for NaCl and CsCl type structures, respectively, as shown in Figs. 4 and 5.

From the charge density plots in the B1 phase, one can clearly see the bonding between the La and N atoms, which depicts the metallic nature of LaN. In this plane namely (100) the distance between the La and La is around 6.841 a.u., whereas the distance between the La and N atom is 4.837 a.u. In the high-pressure CsCl structure the La–La distance (5.613 a.u.) decreases considerably when compared to the B1 phase whereas the La–N distance (4.861 a.u.) increases slightly compared with the B1 phase. Hence, there is a strong covalent bonding between the La–La atoms in the CsCl structure.

The calculated density of states at the Fermi level of LaN

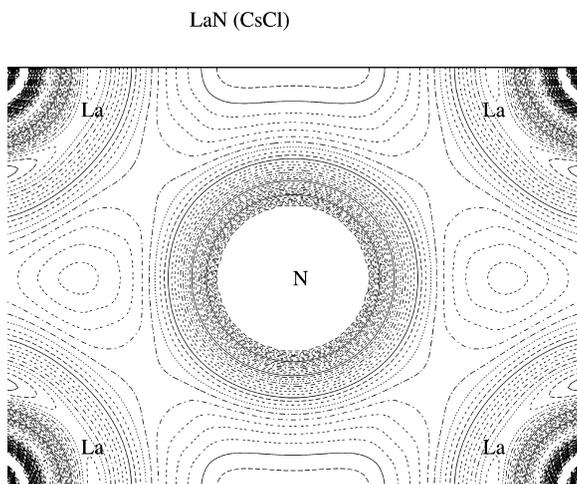


Fig. 5. Electron charge density of LaN in B2 phase for (110) plane.

is comparable with that of LaS. LaS is reported to be a superconductor with a transition temperature of 0.8 K. Hence one may think that LaN may also be a superconductor. An attempt has been made for the first time to calculate theoretically the superconducting transition temperature of LaN. The superconducting transition temperature is calculated using McMillan's formula [25]

$$T_c = \frac{\Theta_D}{1.45} \exp \left\{ \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right\}, \quad (3)$$

where Θ_D is the Debye temperature and μ^* is the electron–electron interaction parameter. The electron–phonon coupling constant for LaN is calculated using Phillip's formula [26], which is

$$\lambda = \lambda_A + \lambda_B, \quad (4)$$

$$\lambda = \frac{N_A(E_F) \langle I_A^2 \rangle}{M_A \langle \omega_A^2 \rangle} + \frac{N_B(E_F) \langle I_B^2 \rangle}{M_B \langle \omega_B^2 \rangle}, \quad (5)$$

where A and B stand for the metal and non-metal atoms in the compound, respectively. The quantities $N_A(E_F)$ and $N_B(E_F)$ are the densities of states at Fermi energy for the A and B atoms, respectively, in the compound are obtained from the band structure calculations. This kind of separation is valid when the difference in the masses is large ($M_A > M_B$).

$\langle I^2 \rangle$ is the square of the electron–phonon matrix element averaged over the Fermi surface. The parameters necessary to calculate the matrix element are taken from the self-consistent band structure results and $\langle I^2 \rangle$ are calculated both for La and N atom sites in a manner similar to our earlier works [27–29].

The value of the Debye temperature for the compound is taken as 300 K [30]. However, to calculate the values of λ_A and λ_B one needs information about the partial character of the phonon spectrum which is not available. Since the difference in masses is large the following approximation is used to calculate $\langle \omega_A^2 \rangle$ and $\langle \omega_B^2 \rangle$.

By virtue of mass inequality the metallic atoms oscillates in the acoustic frequency range and the non-metal in the optical frequency range. This approximation can be written as

$$\langle \omega_A^2 \rangle \approx 1/M_A, \quad \langle \omega_B^2 \rangle \approx 1/M_B, \quad (6)$$

$$\langle \omega_A^2 \rangle / \langle \omega_B^2 \rangle \approx M_B / M_A. \quad (7)$$

The value of Θ_D for La is taken from the literature and that of N is calculated using Eqs. (6) and (7) by setting $\langle \omega^2 \rangle = 0.5\Theta_D^2$. The calculated values of $\langle \omega_A^2 \rangle$ and $\langle \omega_B^2 \rangle$ are used to compute λ_A , λ_B and λ for the compound. Using this value of λ , T_c is calculated by McMillan's formula, which is 0.65 K, in agreement with the experimental value [9].

5. Conclusions

To summarize, a structural phase transition is predicted

Table 2
Partial number of electrons as a function of pressure

Pressure (GPa)	Lanthanum				Nitrogen	
	s	p	d	f	s	p
2	0.284	6.034	1.373	0.433	1.741	3.787
6	0.282	6.024	1.384	0.439	1.737	3.774
10	0.281	6.013	1.394	0.455	1.733	3.766
14	0.280	6.001	1.406	0.441	1.728	3.757
18	0.279	5.992	1.414	0.457	1.725	3.749
22	0.278	5.982	1.423	0.463	1.721	3.742
27	0.276	5.963	1.438	0.476	1.716	3.728

in which LaN undergoes a transition from B1 (NaCl) type to B2 (CsCl) type structure around 26.9 GPa, with a volume collapse of 12.5% which can be easily verified with a diamond anvil cell. This transition is similar to that observed in LaS.

The superconducting transition temperature is theoretically calculated for the first time using McMillan's formula and found to be around 0.65 K which compares well with the experimentally reported value of 0.75 K. In addition, the superconducting transition temperature of LaN agrees quite well with that of LaS, which is 0.8 K. Hence one may conclude that physical properties of LaN and LaS are similar at ambient pressure.

The density of histogram clearly shows that E_F falls on the peak of their respective DOS curves and this may be one of the reasons for the system to be a superconductor, which can be also seen in the case of lanthanum chalcogenides [10], whereas it is not seen in other lanthanum pnictides [17,19]. There is a continuous transfer of electrons from N s and p-like states to La d-like states under pressure, which is also seen in lanthanum chalcogenides. In LaN sp \rightarrow d electron transfer may be responsible for the predicted structural transition as shown in Table 2. In addition, the calculated ground state properties such as equilibrium lattice parameter, bulk modulus, cohesive energy (E_c), heat of formation (ΔH), and electronic specific heat coefficient (γ) and conduction band width (W_c) are tabulated and compared with available experimental and other theoretical results.

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