STRUCTURAL, ELASTIC AND ELECTRONIC PROPERTIES OF NEODYMIUM CHALCOGENIDES (NdX, X=S, Se, Te): FIRST PRINCIPLES STUDY

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First principle calculations on structural, elastic and electronic properties of neodymium chalcogenides (viz. NdX, X= S, Se, Te) have been made using the full-potential augmented plane-waves plus local orbitals (APW + lo) within density-functional theory (DFT) using generalized gradient approximation (GGA) for exchange correlation potentials. The ground state lattice parameter, bulk modulus and its pressure derivative have been obtained using optimization method. Young's modulus, shear modulus, Poisson ratio, sound velocities for longitudinal and shear waves, Debye average velocity, Debye temperature and Grüneisen parameter have also been calculated for these compounds. Calculated structural, elastic and other parameters are in good agreement with available data. From electronic calculations, it has been found that electronic conductivity in neodymium chalcogenides is mainly caused by the Nd p-orbital electrons and S (Se or Se) s-orbital electrons.

1. Introduction

Due to complexity of synthesis and characterization procedure of the materials, computer modeling investigations have become very important tool to determine and to predict the material properties such as elastic, electronic, optical, magnetic, mechanical etc. The theoretical investigations provide the possibility not only to explain the already known properties of a given material but also to predict what property will be expected for a hypothetical material.

In recent years, there is growing interest in the study of the structural, elastic and electronic properties of rare earth chalcogenides (REC) due to their promising applications in spintronics and spin filtering devices [1]. Rare earth chalcogenides are trivalent at room temperature except Er and Yb chalcogenides. It is expected that REC will play a key role in electronics and photonics technology due to trivalent electronic properties relative to the highly correlated f-electrons [2].Therefore, in the present article, neodymium chalcogenides belonging to REC category have been chosen for the structural, elastic and electronic study.

Neodymium chalcogenides belong to the class of binary rare-earth chalcogenides with space group Fm3m (number 225) having (B1) NaCl-type structure. These are typical members of rare earth chalcogenides having Wyckoff's position Nd (0, 0, 0) and X (1/2, 1/2, 1/2), where X= S, Se and Te. Several studies have been made on neodymium chalcogenides e.g. Fumer et al [3] measured the energies and width of the crystal field by neutron inelastic scattering method. Papmentallo et al [4] have studied the magnetic properties of these chalcogenides. In addition to theoretical study, electronic properties of neodymium chalcogenides have been studied using LSDA+U method by Antonov et al [5].

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The knowledge of structural stability with elastic properties plays an important role in determining the strength of the compounds and provides the valuable information about the bonding between atomic planes, anisotropic character of bonding, structural stability and sound velocities. Furthermore, these are associated with specific heat, thermal expansion and Debye temperature [6]. Electronic properties provide the valuable information about bonding character, degree of ionicity, valance charge symmetry and band structure properties [7, 8]. Therefore, in the present article, we report the first principles investigations on structural, elastic and electronic properties of neodymium chalcogenides, NdX (X= S, Se, Te) in rock salt structure using full potential (linear) augmented plane wave plus local orbital (FP-APW + lo) method within the density functional theory based on Perdew-Burke- Ernzerhof (PBE) functional.

2. Computational Approach

2.1 Methodology

In the present paper, full-potential (linear) augmented plane wave plus local orbital (FP-APW + lo) method within the density functional theory, implemented in the WIEN2k code [9] has been applied for the study of structural, elastic and electronic properties of B1 type structured neodymium chalcogenides viz. NdS, NdSe and NdTe. Generalized Gradient Approximation based on Perdew-Burke- Ernzerhof (PBE-GGA) functional [10, 11] has been used to determine the optimized structure of these compounds. In this method the unit cell is divided into non-overlapping spheres centered at atomic sites of radius and an interstitial region. APW + lo method expands the Kohn–Sham orbitals in atom like Muffin–tin spheres and plane waves in interstitial region. The basis set inside each Muffin-tin sphere is split into core and valence subsets. The core states are treated within the spherical part of the potential only and are assumed to have a spherically symmetric charge density totally confined inside the Muffin–tin spheres [12-14]. The valence part is treated within a potential expanded into spherical harmonics upto l=4. The valence wave functions inside the spheres are expanded up to $l_{max} = 8$. A plane-wave expansion with $R_{mt} \cdot K_{max} = 8$, and k sampling with a 4 x 4 x 4 k-points mesh in the full Brillouin zone turns out to be satisfactory. The k integration over the Brillouin zone is performed using the Monkhorst and Pack mesh [15]. The energy that separates the valance state from the core state has been chosen to be -6.0 Ryd. The leakage electrons from the Muffin-tin radius are found to be less than 0.0001. The electronic configuration of Nd, S and Se are [Nd] $1s^2 2s^2p^6 3s^2p^6d^{10} 4s^2p^6d^{10}f^4 5s^2p^6 6s^2$, [S] $1s^2 2s^2p^6 3s^2p^4$, [Se] $1s^2 2s^2p^6 3s^2p^6d^{10} 4s^2p^4$ and [Te] $1s^2 2s^2p^6 3s^2p^6d^{10} 4s^2p^6d^{10}f^4 5s^2p^6 6s^2$ respectively. Thus, [Nd]:$4f^46s^2$, [S]:$3s^23p^4$ and [Se]:$3d^{10}4s^24p^4$ and [Te]: $4d^{10} 5s^2 5p^4$ states are treated as valance electrons.

2.2 Theory of elastic moduli and related parameters

The elastic constants determine the response of the crystal to external forces, as characterized by bulk modulus, shear modulus, Young's modulus, and Poisson's ratio, and obviously play an important role in determining the strength and stability of materials. The theory of obtaining the structural and elastic moduli is described as follows [16]

The total energy of a crystal in strained state is given by

$$E_{total} = E^0{}_{total} + P(V - V_0) + \phi_{elastic} \qquad (1)$$

Where $E^0{}_{total}$ is the total energy of unstrained crystal, V_0 is volume of crystal in initial state, V is volume of the strained lattice, P and $\phi_{elastic}$ are the pressure and elastic energy respectively defined by

$$P = -\left(\frac{\partial E^{o}_{total}}{\partial V} \right)_{V=V_{o}} \tag{2}$$

and

$$\phi_{elastic} = \frac{V}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \tag{3}$$

(Here i, j, k, l = 1, 2, 3)

In Voigt two suffix notations, $\phi_{elastic}$ is given by

$$\phi_{elastic} = \frac{V}{2} . C_{ij} \varepsilon_{i} \varepsilon_{j}$$

Where C_{ij} are elastic moduli derived from second order derivative of E_{total} and are given by;

$$C_{ij} = \left(\frac{1}{V_{o}} \frac{\partial^2 E_{total}}{\partial \varepsilon_{i} \partial \varepsilon_{j}} \right)_{\varepsilon=0} \tag{4}$$

A cubic crystal has only three independent elastic constants, namely, C_{11}, C_{12} and C_{44}. As a result, a set of three equations is needed to determine all the constants. Hence, three types of strains must be applied to the starting crystal [16 - 18]

(i) The first type strain involves calculating the bulk modulus, given by the formula

$$B_{o} = (C_{11} + 2C_{12}) / 3 \tag{5}$$

(ii) Second type strain involves performing volume conservative tetragonal strain given by the following tensor

$$\begin{bmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & \frac{1}{(1+\varepsilon)^2} - 1 \end{bmatrix} \tag{6}$$

This strain has an effect on the total energy from its unstrained state given by following equation

$$E(\varepsilon) = E(0) + 3(C_{11} - C_{12})V_{o}\varepsilon^2 + o(\varepsilon^3) \tag{7}$$

(iii) Lastly, for the third type of deformation, we use the volume conserving rhombohedral strain tensor given by

$$\frac{\varepsilon}{3}\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \tag{8}$$

This volume conserving rhombohedral strain transforms the total energy to

$$E(\varepsilon) = E(0) + \frac{1}{6}(C_{11} + 2C_{12} + 4C_{44})V_0\varepsilon^2 + o(\varepsilon^3) \quad (9)$$

Where $O(\varepsilon^3)$ indicates that the neglected terms in the polynomial expansion are cubic

Once we have calculated three elastic constants namely C_{11}, C_{12} and C_{44}, bulk modulus, B, isotropic shear modulus, G, Young's modulus, Y, and Poisson ratio, ν can be calculated easily using the following explicit expressions [19]:

$$B = (C_{11} + 2C_{12})/3 \quad (10)$$

$$G = (G_V + G_R)/2 \quad (11)$$

Here G_V is Voigt's shear modulus corresponding to the upper bound of G values, and G_R is Reuss's shear modulus for cubic crystals corresponding to the lower bound values, expressed as:

$$G_V = (C_{11} - C_{12} + 2C_{44})/4$$

and

$$G_R = 5[(C_{11} - C_{12})C_{44}]/[4C_{44} + 3(C_{11} - C_{12})]$$

$$Y = \frac{9GB}{G + 3B} \quad (12)$$

$$\nu = (3B - 2G)/(6B + 2G) \quad (13)$$

2.3 Theory of sound velocity, Debye temperature and Gruneisen parameter

Sound velocity for longitudinal and shear waves (V_L and V_S) and Debye average velocity (V_m) can be obtained using bulk modulus, isotropic shear modulus and mass density. The explicit expressions are as follows [20]

$$V_L = \sqrt{\frac{3B + 2G}{3\rho}} \quad (14)$$

$$V_S = \sqrt{\frac{G}{\rho}} \quad (15)$$

and

$$V_m = \left[\frac{1}{3}\left(\frac{1}{V_L{}^3} + \frac{2}{V_S{}^3}\right)\right]^{-1/3} \quad (16)$$

The Debye temperature, θ_D and Grüneisen parameter, ς are two useful parameters in solid-state problems because of their inherent relationship to lattice vibrations. The Debye temperature θ_D can be used in characterizing the excitation of phonons and to describe various lattice thermal phenomena and Grüneisen parameter describes the phonons contribution to specific heat.

Debye temperature, θ_D [20] and Grüneisen parameter, ς [21] are sound velocity and mass density dependent, which are calculated using the expressions given by

$$\theta_D = \left(\frac{\hbar}{k_B}\right)\left[\frac{3n}{4\pi}\left(\frac{N_a\rho}{M}\right)\right]^{1/3}V_m \quad (17)$$

$$\varsigma = \frac{9(V_L{}^2 - 4V_S{}^2 / 3)}{2(V_L{}^2 + 2V_S{}^2)} \tag{18}$$

Here, in equation (17), $(\hbar = h / 2\pi)$ h being the Plank Constant and n, N_a, ρ and M, κ_B are the number of atoms in the molecule, Avogadro's number, mass density, molecular weight and Boltzmann constant respectively.

3. Results and discussion

3.1 Structural and elastic properties

Ground state properties of neodymium chalcogenides have been obtained using the calculation of total energy for a set of unit cell volume and fitted in Murnaghan's equation of state [22], which gives energy vs. volume curve equation of state. The total energy vs. volume curve for neodymium chalcogenides (viz. NdX, X=S, Se and Te) are shown in Figures 1-3. Calculated ground state lattice parameter (a_o), bulk modulus (B_o) and its first order pressure derivative (B_0'), obtained using GGA approximation are shown in Table 1. No values of ground state bulk modulus and its first order derivative for NdX (X=S, Se, Te) are available in literature. Thus, only the comparison has been made for lattice parameter [1, 4] which shows good agreement with available values.
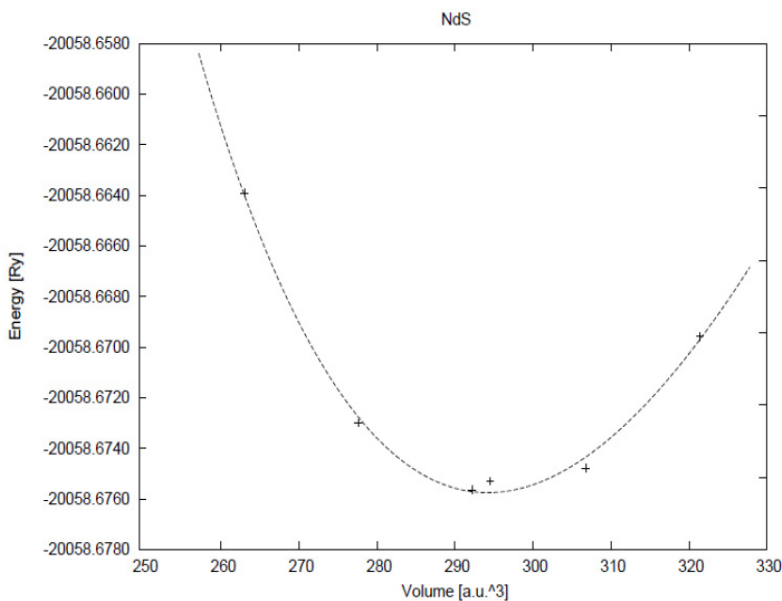

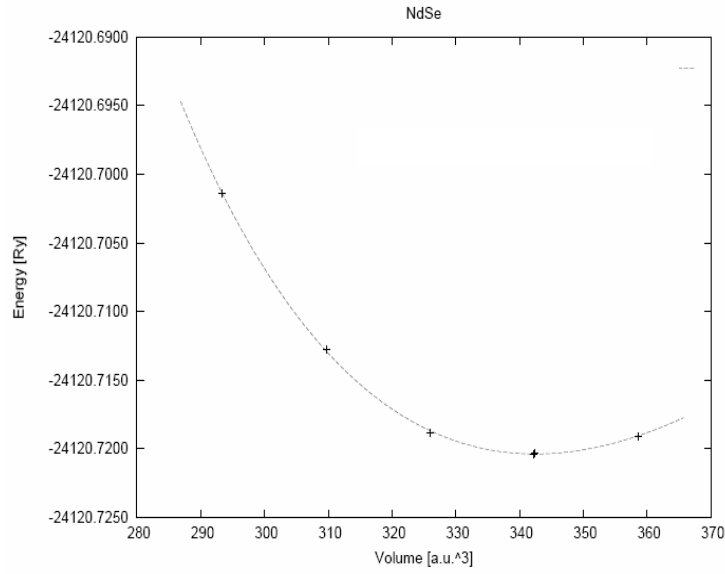*Fig. 1. Total energy as a function of volume for NdS with GGA calculation*

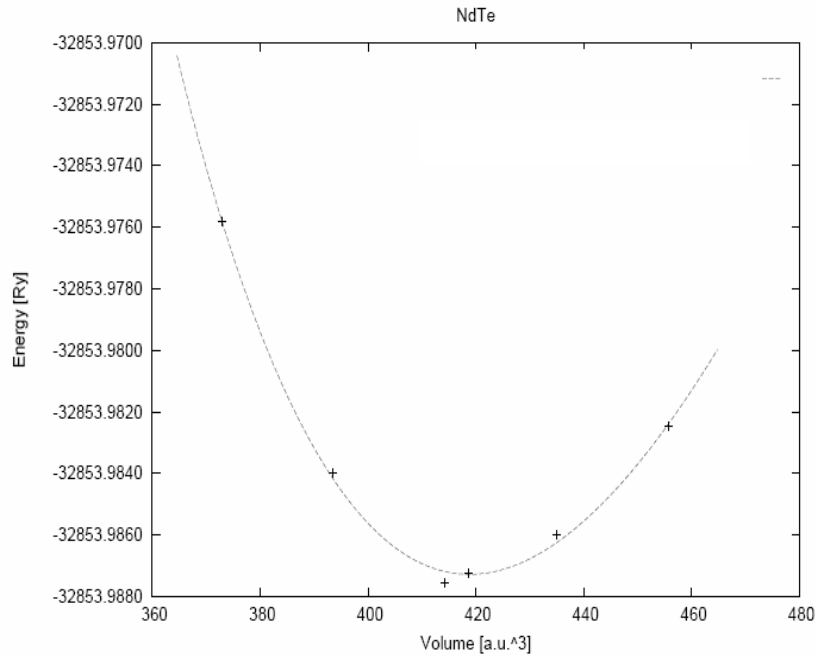*Fig. 2. Total energy as a function of volume for NdSe with GGA calculation*

Fig. 3. Total energy as a function of volume for NdTe with GGA calculation.

Elastic moduli are the important parameters of a material, which provide the valuable information about the structural stability of the material. Second-order elastic constants and their pressure derivatives provide insight into the nature of binding forces between atoms since they are represented by the derivatives of free energy of the crystal. Further, the response of a material to an applied stress is determined by the elastic constants.

Elastic moduli of neodymium chalcogenides obtained from energy variations due to application of small strain to equilibrium lattice configuration, have been given in Table 2. Bulk modulus, B Young's modulus, Y isotropic shear modulus, G and Poisson ratio, ν have also been listed in Table 2. To the best of our knowledge, no experimental or theoretical values of elastic moduli for the studied compounds are available in literature. The mechanical stability conditions

[23, 24] ($C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$) can lead for the validity of elastic moduli. The calculated elastic constant values satisfy all these stability conditions, including the fact that $C_{12} < C_{11}$. Furthermore, calculated elastic moduli also satisfy the cubic stability condition i.e. $C_{12} < B < C_{11}$. Thus our calculated values of elastic moduli are justified.

Table 1. Calculated lattice constant, a_0 ($\overset{0}{A}$), bulk modulus, B_0 (GPa), its pressure derivative, B_0' for NdS and NdSe using GGA functional.

		NdS	NdSe	NdTe
a_0	Present	5.59	5.87	6.28
	Other	5.69[a]	5.90[a]	6.26[a]
		5.64[b]	5.90[b]	6.24[b]
		5.695[b]	5.904[b]	6.247[b]
B_0	Present	94.88	64.81	52.95
	Other	----	----	----
B_0'	Present	5.55	5.32	5.17
	Other	----	----	----

[a]Ref.[1], [b]Ref.[4]

Table 2. Calculated elastic moduli, C_{ij} (GPa), Bulk modulus, B (GPa), Young's modulus, Y (GPa), Isotropic shear modulus, G (GPa), Poisson ratio, V using GGA

	NdS	NdSe	NdTe
C_{11}	220.51	149.52	123.52
C_{12}	33.58	26.06	21.67
C_{44}	18.11	15.63	13.51
Y	99.35	74.17	62.49
B	95.72	67.21	55.62
G	37.43	28.17	23.80
B/G	2.55	2.38	2.33
V	0.312	0.316	0.327

Higher values of Young's modulus in comparison to the bulk modulus (see Table 2) indicate that these materials are hard to be broken [25]. The *B/G* value is an index of ductility/brittleness of a material, proposed by Pugh [26]. If $B / G > 1.75$, then ductile behavior is predicted, Otherwise, the material behavior in brittle manner. The *B/G* ratio for three neodymium chalcogenides is found to be greater than 1.75 (Table 2). Therefore, all the three compounds are

ductile. The B/G ratio is larger for NdS and smaller for NdTe, reflecting NdS is most ductile, while NdTe is least ductile. Furthermore, the ratio B/G depends upon isotropic shear modulus, G and bulk modulus, B via elastic constants (see equation (10), (11) and (12)). Values of elastic moduli (C_{11}, C_{12} and C_{44}) are maximum for NdS and minimum for NdTe, indicating, greater the values of C_{11}, C_{12} and C_{44} greater will be ductile behaviour of the compounds in these Nd chalcogenides. The Poisson ratio, ν gives the information about the covalent/ionic behaviour of the materials. The value of the Poisson ratio, ν for covalent materials is of order of 0.1, whereas for ionic materials a typical value of ν is 0.25 [23]. In our case $\nu \sim 0.31$, i. e. a higher covalent contribution in interatomic bonding is found in these chalcogenides.

Table 3. Calculated, Mass density, ρ (gm/cm^3), sound velocities (10^3 m/sec) for longitudinal and shear wave (V_L and V_S), average Debye velocity, V_m (10^3 m/sec), Debye temperature, θ_D (K) and Grüneisen parameter for NdS, NdSe and NdTe

	NdS	NdSe	NdTe
ρ	6.70	7.23	7.26
V_L	4.66	3.79	3.47
V_S	2.36	1.96	1.81
V_m	2.65	2.20	2.02
θ_D	584	463	398
ζ	1.95	1.87	1.85

The sound velocity for longitudinal and shear waves (V_L and V_S) and Debye average velocity, V_m have been calculated using equations (14), (15) and (16) respectively and are presented in Table 3. It is clear from sound velocity data that sound velocity decrease from NdS to NdTe due to increasing the anion weight. Debye temperature, θ_D and Grüneisen parameter, ς have been calculated from equations (17) and (18) and also given in Table 2. Debye temperature is directly related to the Debye average velocity (see equation (17)). Thus greater the Debye average velocity, greater is the Debye temperature. Furthermore, Debye temperature decreases from NdS to NdTe due to decrease in Debye average velocity, which is an effect of increasing in the atomic weight. Grüneisen parameter is the measure of anharmonicity. Greater the Grüneisen parameter, greater will be anharmonicity. Grüneisen parameter is large for NdTe, thus, anharmonicity is larger in NdTe. These findings are in general trends of the similar NaCl structured compounds [1, 19, 23 and 28].

3.2 Electronic properties

In order to investigate the bonding properties of neodymium chalcogenides, total valance charge density distribution has been shown in Figures 4-6 for NdS, NdSe and NdTe respectively. The charge density distribution shows spherically symmetric concentration centered on Nd and S (Se or Te) atoms. The charge density is more symmetric and dense around S (Se or Te) than that of neodymium. It is characterized by ionic bonding due to small charge transfer from Nd to S (Se or Se). The charge distribution shows the weak bonding and consequently considered as the result of semi-metallic bonding.
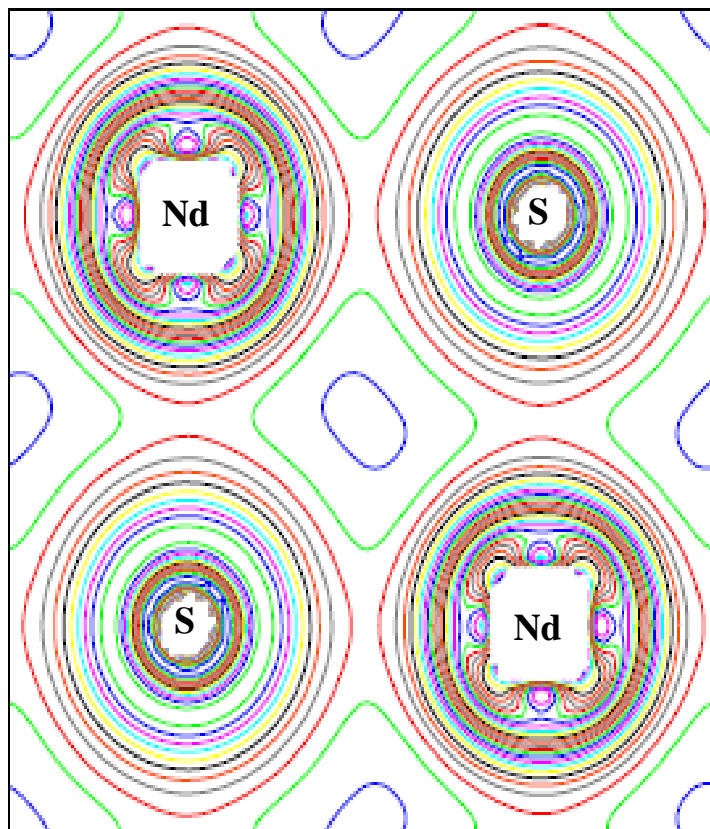
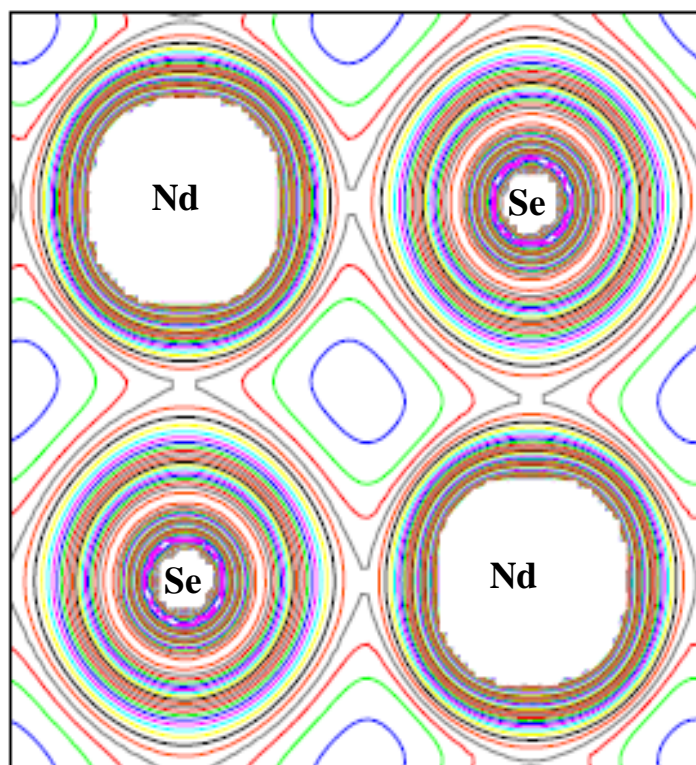*Fig. 4. Contour plot of the total valence charge density in the (100) plane of NdS*

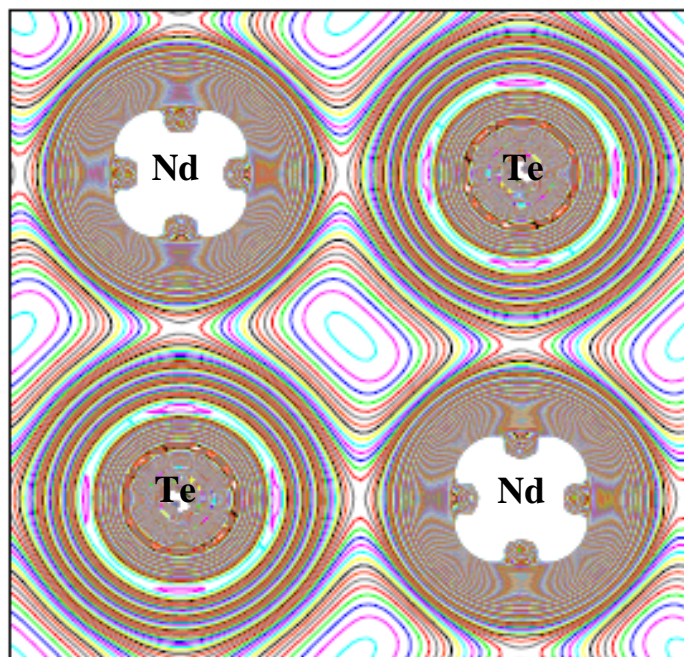*Fig. 5. Contour plot of the total valence charge density in the (100) plane of NdSe*

Fig. 6. Contour plot of the total valence charge density in the (100) plane of NdTe

To explain the contribution to electronic conductivity, the electron dispersion curve along high symmetry direction in the Brillouin zone with GGA calculation for NdS, NdSe and NdTe have been shown Figures 7-9 respectively. Calculated total density of states for NdS, NdSe and NdTe with their separate atoms have been shown in Figure 10 and partial density of states spectrum for s, p, d and f states for Nd, S, Se and Te have been shown in Figures 11-14. The overall profiles of the band structure and density of states show similar features for the three compounds. The spectra are mainly composed of three groups of states at around -18.5 eV, -13 ev, -4 eV, below the Fermi level. From Figure 7-14, it can be seen that the lowest lying bands at around -18.5 eV arise from the Nd p-states with a small amount of S (or Se or Te) s-states. The states in the bands at around -13 eV are entirely derived from S (or Se or Te) s-states with a small amount of Nd p-states, while Nd s-states have negligible contribution. The states around -4 eV arise from S (or Se or Te) p states and Nd d and f states.
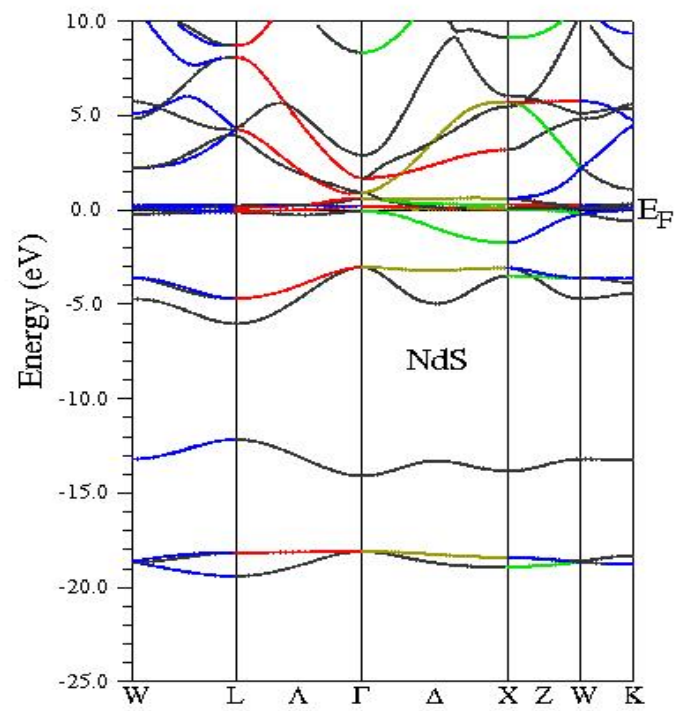
Fig. 7. The electron dispersion curve along high symmetry direction in the Brilloun zone
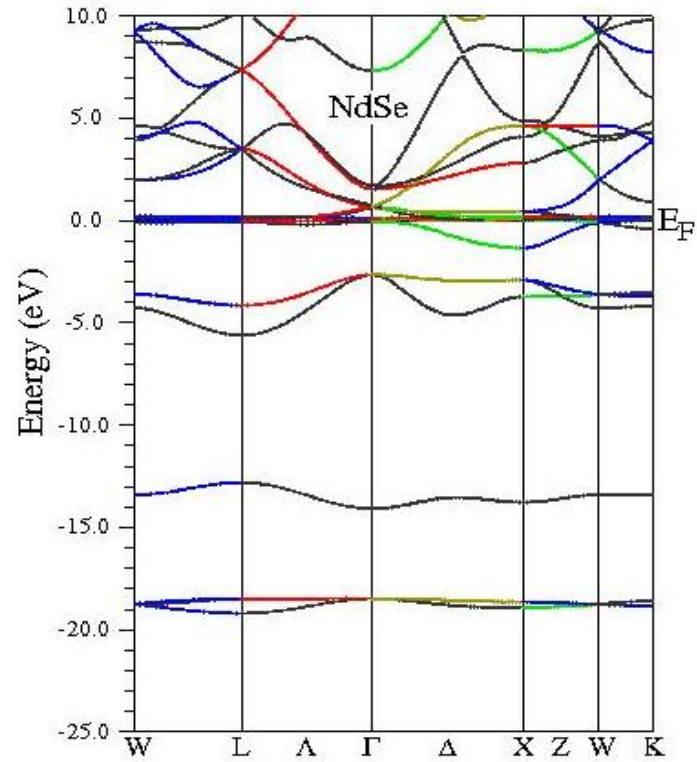*for NdS   with GGA calculation.*

Fig. 8. The electron dispersion curve along high symmetry direction in the Brilloun zone
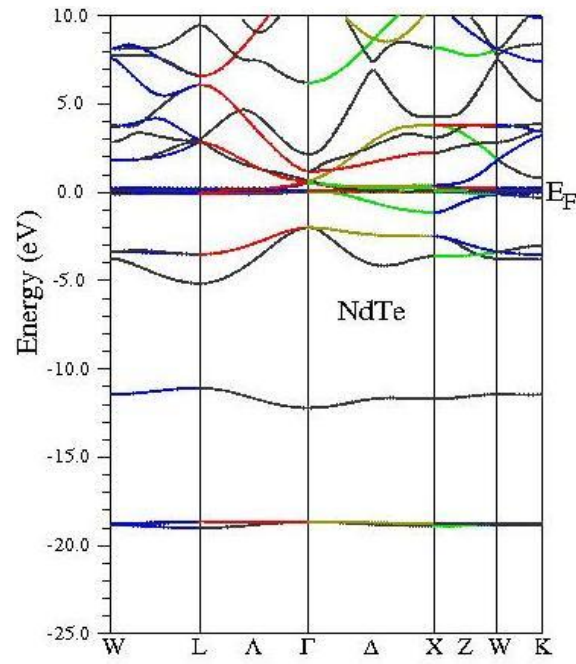*for NdSe with GGA calculation.*

Fig. 9. The electron dispersion curve along high symmetry direction in the Brilloun zone for NdTe   with GGA calculation.
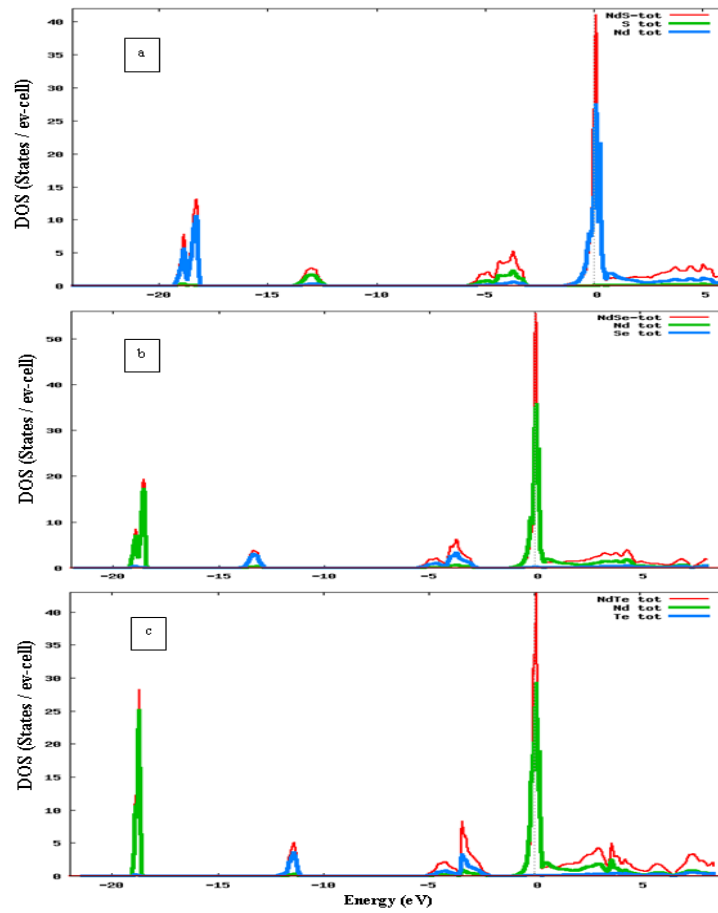

Fig. 10. Calculated total density of states for (a) NdS, Nd and S (b) NdSe, Nd and Se (c) NdTe, Nd and Te
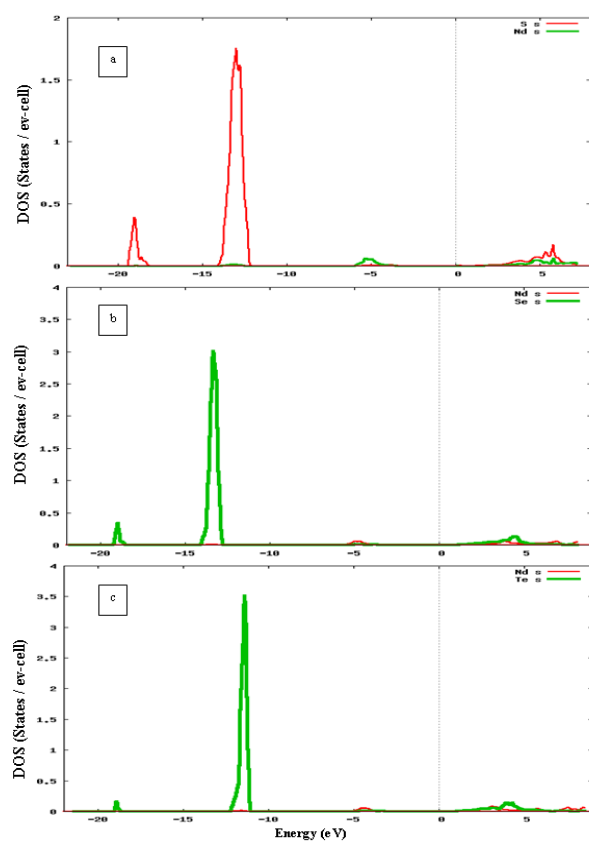
Fig. 11. Calculated partial density of states for s-states for (a) Nd and S (b) Nd and Se (c) Nd and Te
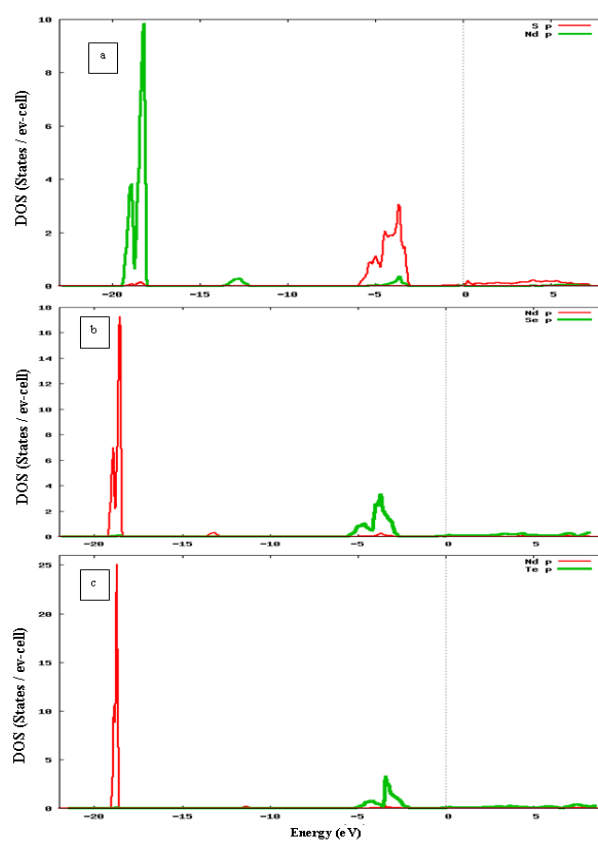

Fig. 12. Calculated partial density of states for p-states for (a) Nd and S (b) Nd and Se (c) Nd and Te
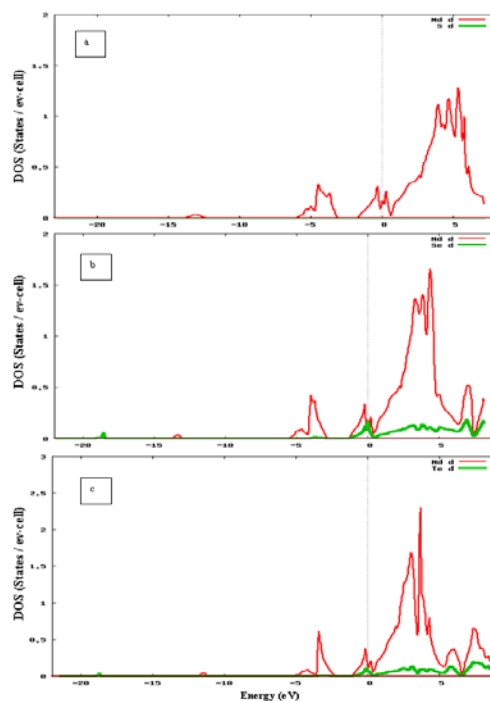
Fig. 13. Calculated partial density of states for d-states for (a) Nd and S (b) Nd and Se (c) Nd and Te
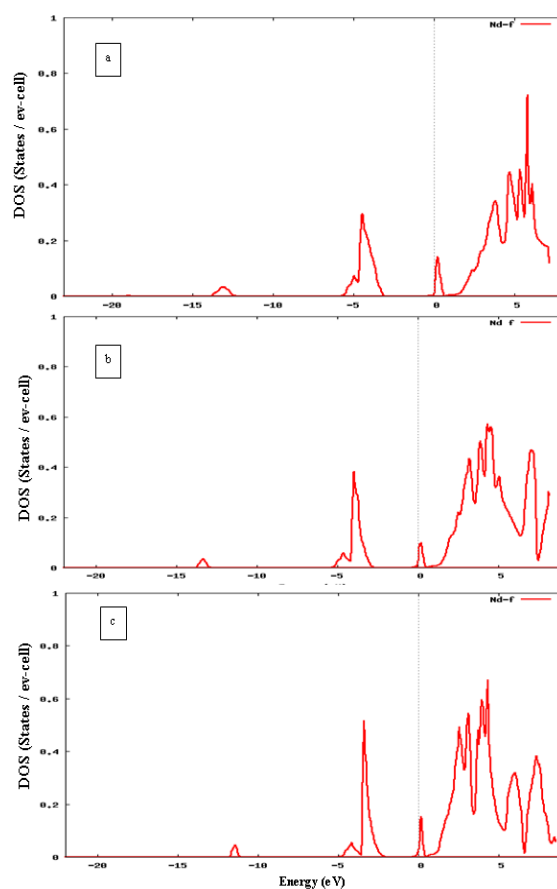

Fig. 14. Calculated partial density of states for f-states for (a) Nd and S (b) Nd and Se (c) Nd and Te

All above discussion regarding electronic properties is in good agreement with previously published theoretical results on electronic properties of neodymium chalcogenides using LSDA+U method by Antonov et al [5], justifying our predictions on electronic properties using GGA-PBE approximation.

4. Conclusion

In Conclusion, First principle method has been used to study the structural, elastic and electronic properties of NaCl type compounds, NdX, X=S, Se and Te. The following conclusions have been drawn from the calculations;

Calculations indicate that the present values of equilibrium lattice constant, a_0 and bulk moduli, B_0 are in good agreement with available literature values.

The present calculations provide reliable values of elastic moduli at absolute zero temperature and zero pressure for B1 structured neodymium monochalcogenides with the accuracy of the PBE-GGA exchange-correlation functional.

The Young's modulus, shear modulus, Poisson's ratio, Debye temperature, sound velocity, Grüneisen parameter and other elastic properties have also been calculated for these compounds at ambient pressure for the first time.

The present calculations provide reliable description of total charge densities and density of states for neodymium chalcogenides.

So for as electronic conductivity of these compounds is concerned, p-states of Nd are responsible for the electronic conductivity in the three compounds and S (or Se or Te) p-like states in NdS (or NdSe or NdTe) have small contribution to electrical conductivity.

The above facts are relevant in connection with the possibility of originating a semi-metallic behavior of studied compounds.

Acknowledgement

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