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Structural, electronic, magnetic and optical properties of neodymium chalcogenides using LSDA+U method

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Abstract: We have studied the electronic, magnetic and optical properties of neodymium chalcogenides by performing LSDA+U and full potential linearized augmented plane wave (FP-LAPW) method. The electronic structure calculation shows that the electronic states in Nd-chalcogenides were mainly contributed by Nd-4f electrons near Fermi energy and 3p, 4p and 5p state electrons of X (S, Se and Te), respectively. We have also studied the absorption of light via the imaginary parts of the dielectric function of Nd-chalcogenides.

Key words: DFT; DOS; magnetic moment; U

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1. Introduction

In the last few years Nd-chalcogenides have been widely investigated due to their trivalent electronic properties at room temperature. They have many applications in spintronics and filtering devices[1], non-linear optics, electro-optical components and electronics[2]. All three Nd-chalcogenides are stable in the rock salt structure at ambient temperature and pressure with lattice parameters of 5.743 Å, 5.975 Å and 6.387 Å for NdS, NdSe and NdTe, respectively. These are the typical members of binary rare-earth chalcogenides with space group Fm3m. Several studies have been made on Nd-chalcogenides. Papamantellos *et al.*[3] have studied the magnetic structures and ordered moments of these chalcogenides at 4.2 K by using the neutron diffraction method. Antonov *et al.*[4] have studied the electronic, optical and magneto optical properties of these materials using the LSDA+U method. Furrer *et al.*[5] measured the width of the crystal field by using the neutron inelastic scattering method. Verma[6] studied the electronic and optical properties of rare-earth chalcogenides and pnictides. Singh *et al.*[7] have studied the structural, elastic and electronic properties of Nd-chalcogenides using the GGA method, respectively.

In this paper we have studied the electronic structure, magnetic properties and optical properties of Nd-chalcogenides in the rock salt structure using an FP-LAPW based LSDA+U method within the formalism of the density functional theory (DFT)[8]. The local spin density approximation (LSDA) method is used for the calculation of Coulomb repulsion (U).

2. Computational details

The full potential linearized augmented plane wave (FP-LAPW) method[9] within the DFT, implemented in the WIEN2k code[10] has been applied for the study of structural, electronic, magnetic and optical properties of NaCl type structured neodymium chalcogenides, viz. NdS, NdSe and NdTe. The total energy is calculated by using the parametrization of LSDA+U[11] and the FP-LAPW method. The sets of 5p, 6s, 4f orbitals for Nd atoms, 3s, 3p orbitals for S atoms, 3s, 3p, 4s, 3d, 4p orbitals for Se atoms and 4p, 5s, 4d, 5p for Te atoms were selected as valence states whereas other lower states were treated as core states in the calculations. The plane-wave cut-off for the basis functions was set to $R_{\mathrm{MT}}K_{\max} = 7$ where $K_{\max}$ is the maximum value of the wave vector $\boldsymbol{K} = \boldsymbol{k} + \boldsymbol{G}$. The potential and charge density were expanded up to a cut-off $G_{\max} = 12\ \text{a.u.}^{-1}$. The muffin-tin radii is set to $R_{\mathrm{MT}} = 2.5$ a.u. The expansion of wave functions, as well as the density along with the potentials inside the muffin-tin spheres, were upto $l_{\max} = 10$. LSDA+U calculations were carried out using the parameters $U = 0.47$ Ry and $J = 0$ eV for Nd atoms. We have calculated U for Nd in NdX, based on the Hubbard model[12]. The on-site energies are taken to be zero. Considering that the atoms are embedded in a polarizable surrounding, U is the energy required to move an electron from one atom to another far away one. In that case U is equal to the difference of the ionization potential (E_{I}) and the electron affinity (E_{A}) of the solid. Removing an electron from a site will polarize its surroundings, thereby lowering the ground state energy of the $N - 1$ electron system[13, 14]. Thus

$$\begin{cases} E_{\mathrm{I}} = E^{N-1} - E^{N}, \\ E_{\mathrm{A}} = E^{N} - E^{N+1}, \\ U = E_{\mathrm{I}} - E_{\mathrm{A}}, \end{cases} \tag{1}$$

where $E^{N(\pm 1)}$ are the ground state energy of the $N \pm 1$ electron system. A mesh of 12000 k-points for NdS and NdSe and 10000 k-points for NdTe were used to obtain 111 special k-points in the irreducible wedge of the Brillouin zone. For each calculation, the energy convergence criteria were set to be 0.0001 Ry and charge 0.0001e. The optical calculation was performed by using the dipole approximation[15].

3. Results and discussions

We observed how the total energy of the system changes with the variation of volume, which we have summarized in Fig. 1. The curve is obtained by fitting the calculated values of

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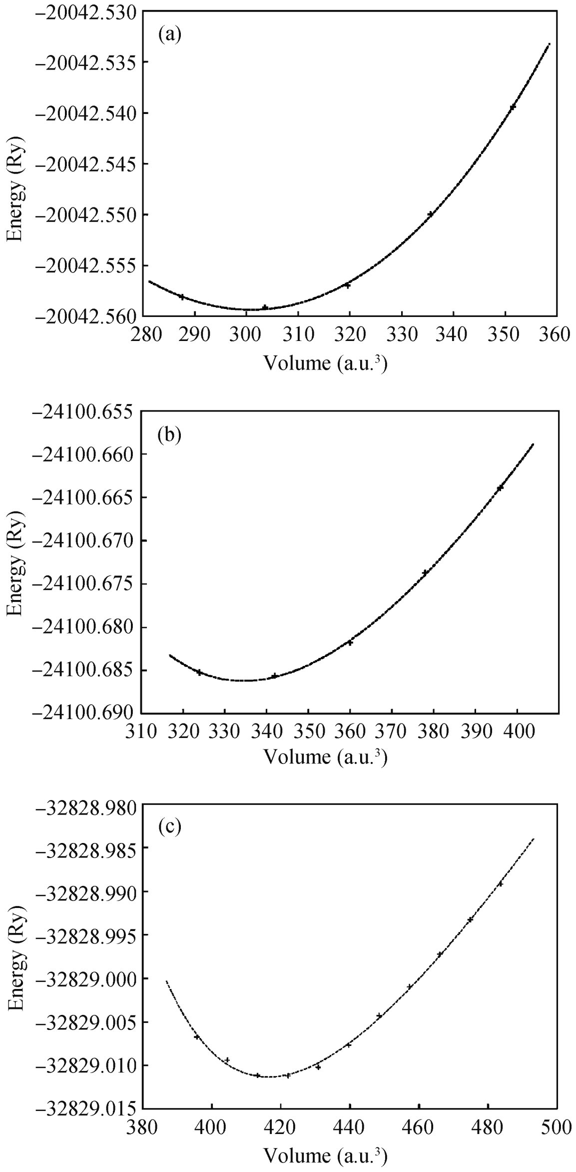

Fig. 1. Plots of energy versus volume of (a) NdS, (b) NdSe and (c) NdTe.

energies to the Murnaghan equation of state[16]. The theoretical equilibrium lattice parameters and bulk modulus were deduced from the volume corresponding to the minimum energy value. We have tabulated the equilibrium lattice parameters, bulk modulus and the equilibrium energy for NdX (X = S, Se and Te) in Table 1. From Table 1 it is clear that the calculated lattice parameters are in between the experimental and previous theoretical values. We can conclude that they are in qualitative agreement with the previous results. We have also compared the calculated value of the bulk modulus with the previously presented value. The optimized lattice parameters so obtained were used to calculate the electronic, magnetic and optical properties, the results of which are given in the next sections.

3.1. Density of states

The total density of states (DOS) and partial DOS for NdX (X = S, Se, and Te) are shown in Fig. 2 for both spin channels. As seen from the figure, the total and partial DOS are quite similar for all three compounds. From the total DOS plot in Figs. 2(a), 2(e) and 2(i), we observed a sharp peak for the spin up channel centred at around 0 eV, which is taken as the Fermi level (E_{F}). Now if we examine the core region, a small peak is observed almost at –12.86 eV for both spin channels, which are mainly due to the contribution of the 3s, 4s and 5s state electrons of S, Se and Te, respectively, as can be seen from the partial DOS plot in Figs. 2(b), 2(f), and 2(j). Similarly, in the valence region, a small sharp peak is observed almost at –3.6 eV for both channels, which are mainly due to the contribution of the 3p, 4p and 5p state electrons of S, Se and Te, respectively, and the 4d state electrons of Nd, as can be seen from Figs. 2(b), 2(f), 2(j) and 2(c), 2(g), 2(k). In the conduction region a sharp peak is observed almost at 2.14 eV for spin-down channels, which is mainly due to the contribution of the 4f state electrons of Nd. In addition, the 4f state of Nd also dominates at E_{F} for the spin-up channel as can be seen from the partial DOS plot in Figs. 2(d), 2(h), 2(l). From the total and partial DOS plot we can say that the contribution due to chalcogen is higher in the core and valence region and, due to Nd electrons, is higher in the conduction and in the Fermi level. As can be seen from the total DOS plot, there is an exchange splitting of the order of 2.14 eV in the two spin channels. From the partial DOS plot in Figs. 2(b, c, f, g, j, k) we can say that there is small hybridization between the p-state electrons of chalcogenides and the d and d-eg state electrons of Nd, and that they degenerate over large part of their extension. This gives rise to the covalent bond in between the Nd and chalcogenides. But the relative amount of chalcogenides and Nd is different above and below the Fermi level. At and above the E_{F}, Nd DOS dominates the chalcogenides DOS and below the E_{F} vice versa. So, from this argument we can say that an electrovalent bond also exists in between the chalcogenides and Nd. According to Pauling, Nd has an electronegativity of 1.1 and S, Se and Te have electronegativities of 2.5, 2.4 and 2.1, respectively. From these electronegativity values, we simply expect that NdS to be the most ionic and NdTe the most covalent of the three systems. In the present calculation we have taken equal sized muffin-tin spheres for Nd and its chalcogenides, which are touching each other. The lattice parameters are also increasing for S, Se and Te, respectively. Thus absolute size of the sphere in NdTe is larger than NdS since the lattice parameter is larger in the case of NdTe, and the sphere size also does not correspond to the atomic radii of the element.

3.2. Band structure

The electronic band structure plots for NdX are shown in Figs. 3, 4 and 5. We find that the observed core level bands were due to X-s state electrons followed by X-p state electrons in the valence region in both the spin channels, as shown in Figs. 2(b, f, j). At the E_{F}, Nd-4f state, electrons were found to be contributing, which is observed in terms of flat bands in the spin-up channels for NdX, which are shown in Figs. 2(d, h, l). In the spin-down channels, bands due to Nd-4f state electrons were observed in the conduction region at about 2.14 eV, as shown in Figs. 3, 4 and 5. From the plot of the total DOS we find that exchange splitting is observed, which is due to the inclusion of U. This contradicts the result obtained by Singh

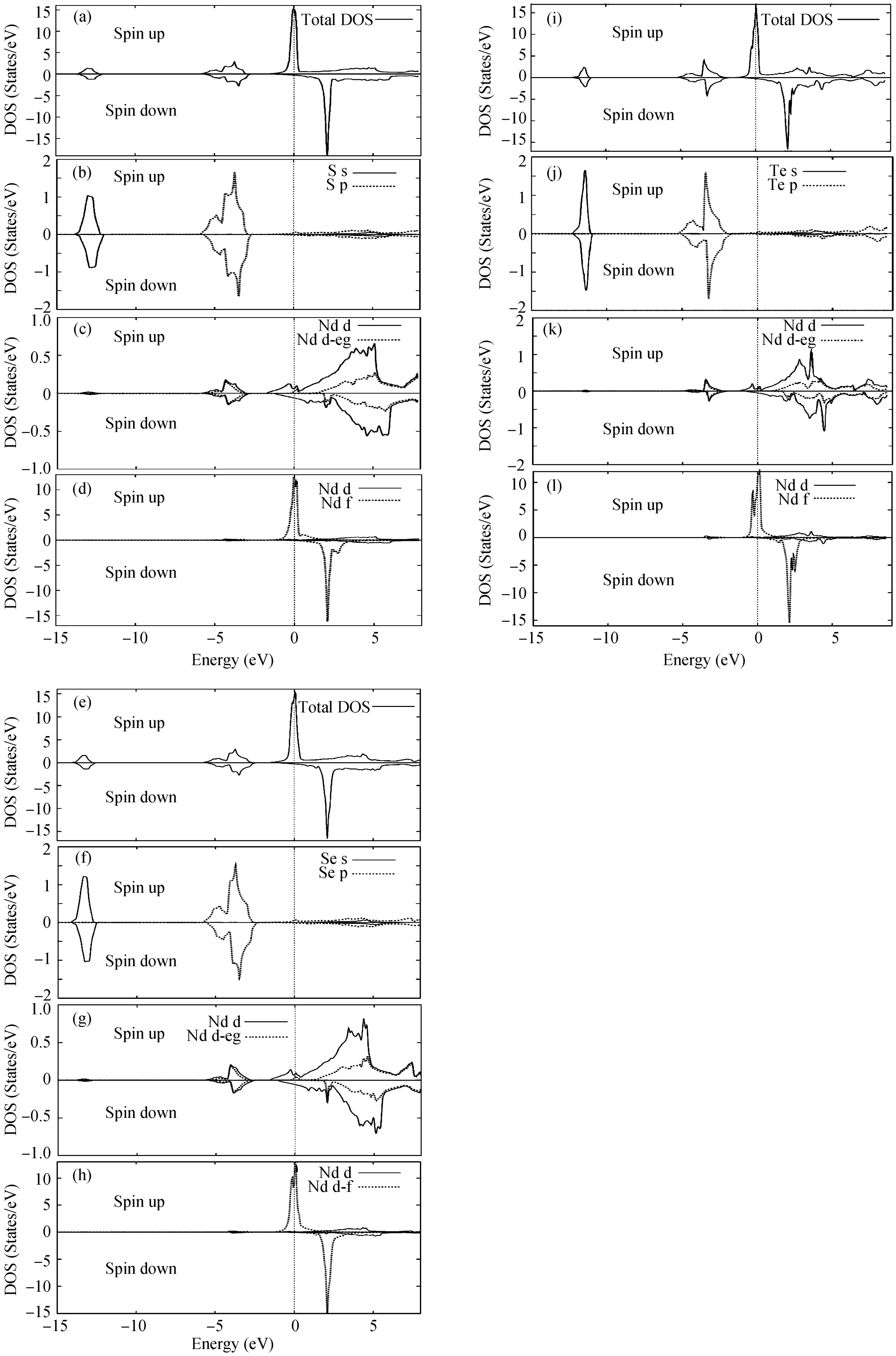

Fig. 2. Total and partial DOS for (a, b, c, d) NdS, (e, f, g, h) NdSe and (i, j, k, l) NdTe.

Table 1. The calculated equilibrium lattice parameter, bulk modulus and the energy E at the equilibrium lattice constant.

Compound	Lattice parameter (Å)			Bulk modulus (GPa)		Equilibrium energy (Ry)
	Experimental	Theoretical (previous)	Our result	Previous	Present	
NdS	5.69[17]	5.59[7]	5.629	94.88[7]	65.266	−20042.56
NdSe	5.789[18]	5.87[7]	5.83	64.81[7]	83.195	−24100.686
NdTe	6.249[18]	6.28[7]	6.273	52.95[7]	109.347	−32829.011

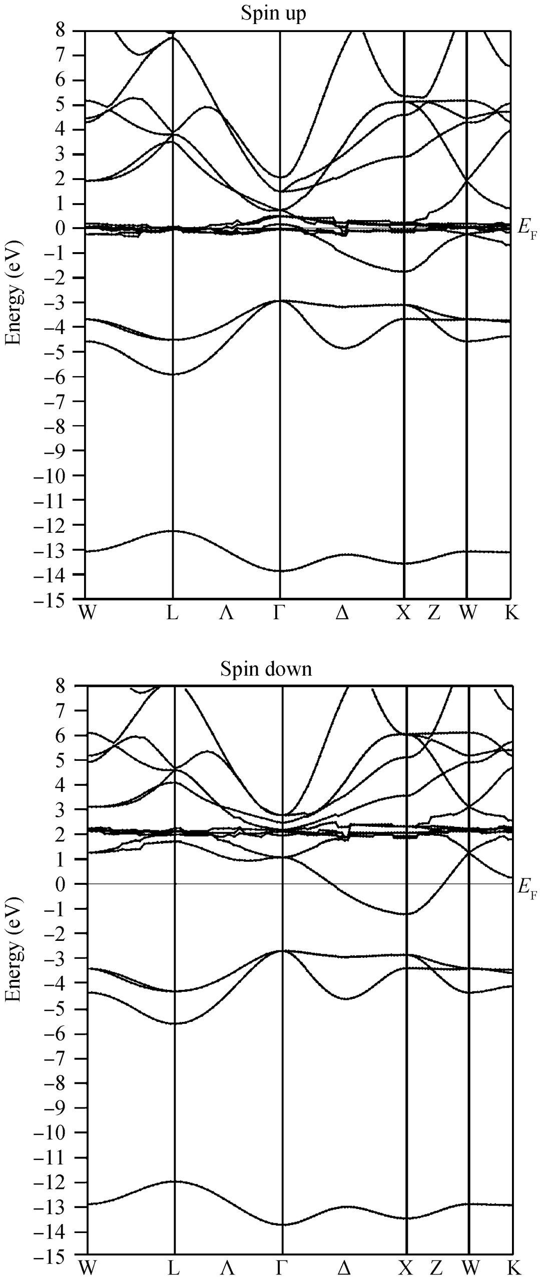

Fig. 3. Plot of band structure of NdS.

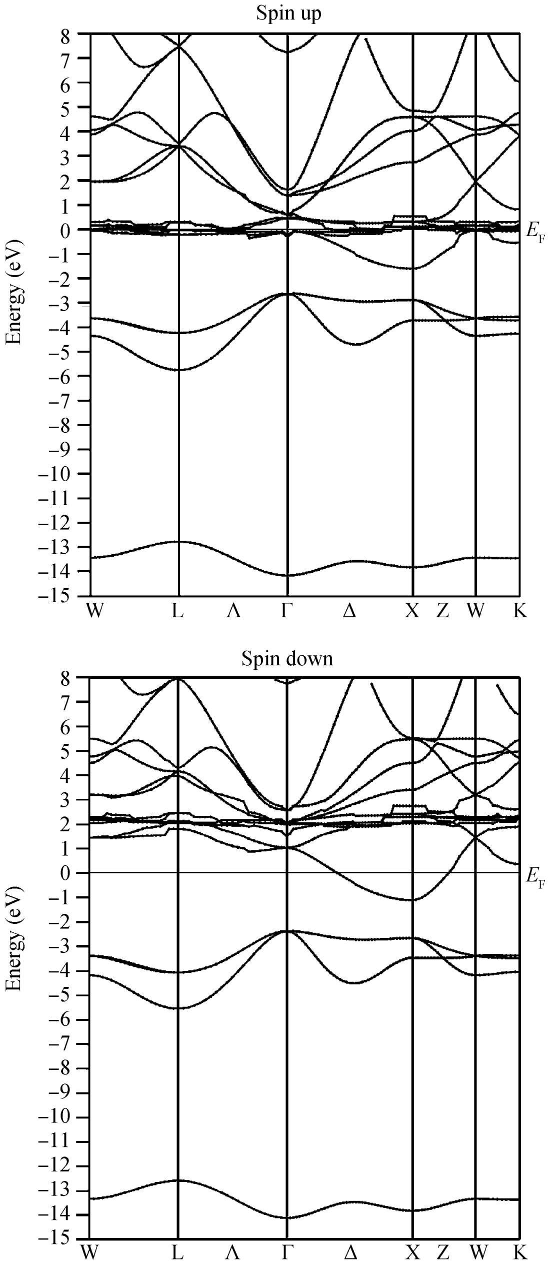

Fig. 4. Plot of band structure of NdSe.

et al.[7] where GGA was employed. The magnetic moment of Nd chalcogenides are given Table 2 along with previous theoretical data. The contribution of the Nd atom to the magnetic moment is $3.34\mu_B$, $3.38\mu_B$ and $3.35\mu_B$, for NdS, NdSe and NdTe respectively, which is evident from the exchange splitting in the DOS of Nd-f states [Figs. 2(d, h, l)].

3.3. Optical properties

The absorptive parts of the dielectric function ε_2 are shown in Fig. 6, which is plotted as a function of energy. Optical spectra have been analyzed for the energy range 0–14 eV. The main feature is a sharp peak with maximum around the Fermi level. Thus the critical points are embedded at the E_F, unlike the op-

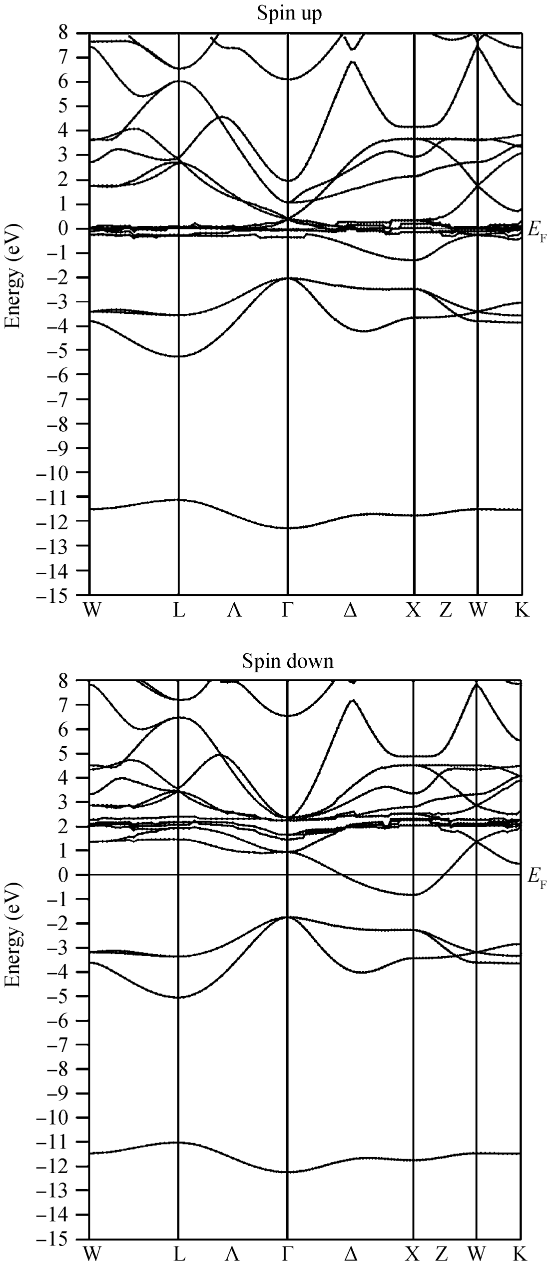

Fig. 5. Plot of the band structure of NdTe.

Table 2. The magnetic moments for Nd chalcogenides.

Compound	Magnetic moment μ_B	
	Previous[3]	Our result
NdS	3.62	3.65
NdSe	3.52	3.69
NdTe	3.54	3.78

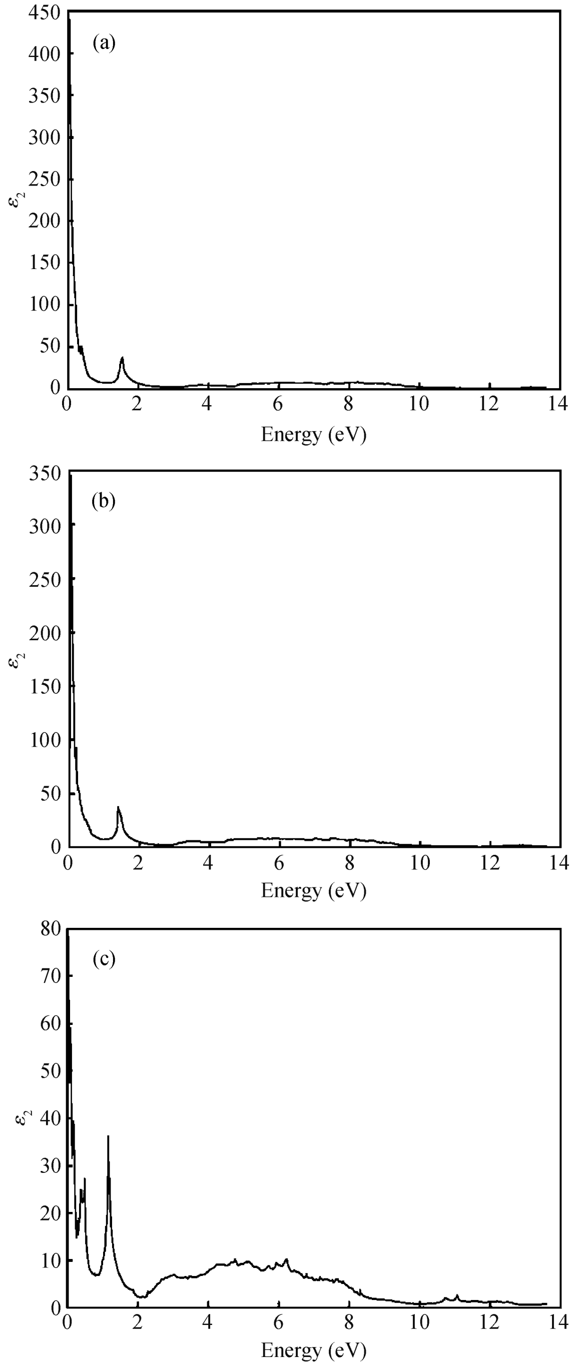

Fig. 6. Absorptive part of the optical constants for (a) NdS, (b) NdSe and (c) NdTe.

tical critical points for BeX[19]. These were followed by small structures ~1.5 eV (Fig. 6), which were observed for all three chalcogenides. The peaks reproduced in our calculation, are the general form of the spectra. The trends in ε_2 may be linked to the trends observed in the DOS and band structures. Analysis of Fig. 6 shows that the 0–0.5 eV photon-energy range is characterized by small absorption and appreciable reflectivity. The 0.6–1.4 eV photon energy range is characterized by high transparency, no absorption and small reflectivity. The photon energy ranging from 2.2 to 12.0 eV is characterized by maximum reflectivity with small absorption.

4. Conclusion

From the first principles study of the structure, DOS, band structure and optical properties of Nd-chalcogenides (S, Se and Te), we find that the DOS contributions were mainly due to Nd-4f states in the spin up configuration at E_F. The DOS and band structures suggested weak hybridization of Nd-5d and X-p state electrons. The magnetic moments were explained on the basis of exchange splittings of Nd-4f state electrons. The behavior of the imaginary part of the dielectric constant suggested that the system exhibits small absorption[13] and appreciable reflectivity just above $E_{\rm F}$, which is followed by high transparency and small reflectivity in the conduction region.

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