

# Full Potential Study of Electronic and Optical Properties of NdF<sub>3</sub>

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**Abstract**—We report the electronic structure and optical properties of NdF<sub>3</sub> compound. Our calculations are based on density functional theory (DFT) using the full potential linearized augmented plane wave (FPLAPW) method with the inclusion of spin orbit coupling. We employed the local spin density approximation (LSDA) and Coulomb-corrected local spin density approximation, known for treating the highly correlated 4f electrons properly, is able to reproduce the correct insulating ground state. We find that the standard LSDA approach is incapable of correctly describing the electronic properties of such materials since it positions the f-bands incorrectly resulting in an incorrect metallic ground state. On the other hand, LSDA + U approximation, known for treating the highly correlated 4f electrons properly, is able to reproduce the correct insulating ground state. Interestingly, however, we do not find any significant differences in the optical properties calculated using LSDA, and LSDA + U suggesting that the 4f electrons do not play a decisive role in the optical properties of these compounds. The reflectivity for NdF<sub>3</sub> compound stays low till ~7 eV which is consistent with their large energy gaps. The calculated energy gaps are in good agreement with experiments. Our calculated reflectivity compares well with the experimental data and the results are analyzed in the light of band to band transitions.

**Keywords**—FPLAPW Method, optical properties, rare earth trifluorides LSDA+U

## I. INTRODUCTION

RARE-earth compounds have been studied intensively [1] because of their unique magnetic properties and useful technological applications as magneto-optical (MO) recording media. Among them fluoride crystalline materials have been studied due to their applications in the fields of solid state lasers and scintillators. Industrially, the fluorides are used for the manufacture of arc carbons with well balanced light emission. Particularly, lanthanum trifluoride is used in fibre optics, fluorescent lamps and radiation applications [2]. It is also used as an ion-specific fluoride detecting electrode in solutions, where it is doped with europium at the level of approximately 1% [3]. The rare earth trifluorides (RF<sub>3</sub>) are wide band gap insulators and are transparent in the visible region. Good optical properties of RF<sub>3</sub> compounds, coupled with low non-radiative emissions (mainly because of the low cut-off phonon frequencies) make these materials good host matrices for visible or infrared light emission and for other optical applications [4]. Greis and Haschke [5] have reviewed the structures and the chemistry of rare earth fluorides. The light CeF<sub>3</sub> compound exhibits a structural phase transition [5, 6] with orthorhombic YF<sub>3</sub> structure at lower temperatures and the less symmetric hexagonal structure at higher temperatures. The heavy GdF<sub>3</sub> compound has the orthorhombic YF<sub>3</sub> structure.

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Xu and Duan [7] present a theoretical investigation on the magnetic and magneto-optical properties of light rare-earth trifluorides CeF<sub>3</sub>, PrF<sub>3</sub>, and NdF<sub>3</sub>. The result shows that in the visible region the Faraday rotation is mainly caused by the intra-ionic electric-dipole transitions between the 4f<sup>n</sup> and 4f<sup>n-1</sup>5d configurations of the rare-earth ions. Recently Burian *et al.* [8] investigated the photoemission from Eu, Gd, Tb, and their trifluorides with respect to exchange splitting of core-levels. The major part of the observed splitting was reproduced by the density-functional theory (DFT) based calculations.

On the other hand measurements on the lanthanide trifluorides have focused on their optical properties [9-11] and optical applications [2]. Stephan *et al.* [9, 10] measured the reflectance of thin film sample of RF<sub>3</sub> while reflectance of single crystal of some RF<sub>3</sub> compounds were measured by Olson *et al.* [11] in the energy range 10 - 34 eV region. The principal difference between the experimental data for the two kinds of samples is that the film reflectance has sharp structure with low magnitude in the 10-15 eV region as compared to that in the single crystalline data.

The aim of this work is to perform the electronic band structure calculations and to exploit these to study the optical properties of NdF<sub>3</sub> representing light RF<sub>3</sub> compounds and also to discuss the role of f – states on these properties. Our calculations thus demonstrate the effect of occupancy of f-electron states since Nd has less than half filled f- states.

## II. DETAILS OF CALCULATIONS

NdF<sub>3</sub> are known to crystallize in hexagonal structure {space group  $P6_3/mmc (D_{6h}^4)$ } with two formula units in the unit cell. The rare earth atoms in the unit cell of hexagonal structure are located at 2c sites [ $\pm (1/3, 2/3, 1/4)$ ] [13]. Based on the surroundings, there are two types of F atoms in the unit cell. Two atoms of the first type are at 2b sites [ $\pm (0, 0, 1/4)$ ] and four atoms of the second type are at 4f sites [ $\pm (1/3, 2/3, u), \pm (2/3, 1/3, u + 1/2)$ ], where  $u = 0.57$  [12]. The first type of F atoms are at 4c site with  $u$  and  $v$  as 0.528a and 0.601c and the two F atoms of the other kind are at 8d sites [ $\pm (x, y, z), \pm (x, 1/2 - y, z), \pm (x + 1/2, y, 1/2 - z)$  and  $\pm (x + 1/2, 1/2 - y, 1/2 - z)$ ], where  $x, y$  and  $z$  are 0.165a, 0.060b, and 0.63c (a, b and c are the orthorhombic lattice parameters), respectively [13]. Spin-polarized calculations have been performed using the experimental lattice parameters [13]. The calculations have been performed using the full-potential linearized-augmented-plane-wave method as implemented in the WIEN2K code [14], within LSDA+U approximations. The LSDA+U method, introduced by Anisimov *et al.* [15], explicitly includes the onsite Coulomb interaction term in the conventional Hamiltonian. The intra-atomic correction energy  $U$  is taken to be 5.0 eV for CeF<sub>3</sub> [16]. We used  $R_{mt}K_{max}$  equal to 7.0, resulting in 1775 plane waves for the basis functions and the cut off energy is 7.84 Ry. Convergence with respect to energy and number of k points (5000 k points for self consistency) has been thoroughly checked. Since calculations of the optical

properties require a dense k-space mesh, we used 8000 k points in the Brillouin zone for calculation of the reflectivity and related optical properties.

### III. RESULTS AND DISCUSSIONS

The spin polarized band structure (BS) of NdF<sub>3</sub> using LSDA+U approximation is shown in Fig. 1. The BS of NdF<sub>3</sub>, with no bands intersecting the Fermi level, shows the nonmetallic nature. We note that the difference in the spin up and spin down bands is mainly due to the position of *f* states. The occupied spin up *f* states are at ~ 0.01 eV below Fermi Energy ( $E_F$ ) and unoccupied spin up *f* states are centered around 5.0 eV above  $E_F$ , while the spin down *f* states are unoccupied and lie around 6.0 eV above  $E_F$ . The splitting of ionic levels is seen to be much larger than that expected due to spin-orbit splitting alone, hence the crystal-field effects dominate, as has also been reported earlier [17] for NdF<sub>3</sub> compound. The LSDA+U approximation shifts the *f* bands in the Density of states (DOS) away from  $E_F$  yielding an insulating ground state in agreement with experiments [11]. This indicates strongly correlated behavior of *f*-electrons in these compounds.

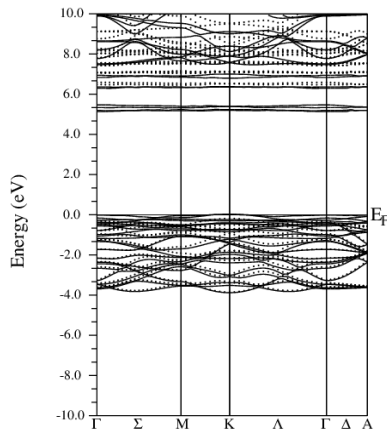


Fig. 1 Band Structure of NdF<sub>3</sub> using LSDA+U for spin up (solid lines) and spin down (dotted lines) states. The top of the valence band is at 0 eV (marked as  $E_F$ )

The total DOS for NdF<sub>3</sub>, using LSDA+U is shown in Fig. 2. The *f* states are highly localized in general and easily identified as sharp peaks in the total DOS. The occupied *f* states lie close to  $E_F$  in the NdF<sub>3</sub> while the broad valence band is constituted by F-*p* states. The broad conduction band is made up of *d* states of both Nd and F atoms. The majority Nd-*f* states are hybridized with the valence band i.e. with the F-*p* states. Due to this, spin up *f* bands are broader in NdF<sub>3</sub> compound.

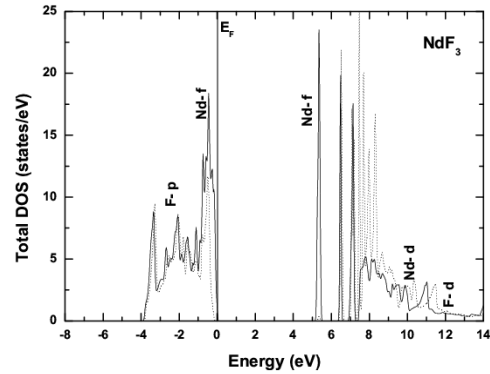


Fig. 2 Total Density of States for NdF<sub>3</sub> using LSDA+U approximation. Solid (dotted) lines represent the majority (minority) states. The top of the valence band is at 0 eV (marked as  $E_F$ )

Our calculations predict NdF<sub>3</sub> as wide band gap insulators. Our calculated energy gap for NdF<sub>3</sub> is 7.3 eV. Calculated total magnetic moment 2.99 is in agreement with the experimental value [19] of 3.6. A good agreement with the experimental value is not expected since latter have been estimated from the value reported for La<sub>x</sub>Nd<sub>1-x</sub>F<sub>3</sub> single crystal. Keeping in mind the fact that the LSDA fails to give the correct insulating ground state for rare earth compounds these LSDA+U results are quite encouraging.

Keeping these observations in mind and also because LSDA + U is able to reproduce the correct ground state, henceforth all the results on optical properties have been presented with LSDA + U approximation only, for the sake of good readability of figures. The upper panel of Fig. 3 displays the results for parallel reflectivity  $R_{||}$  (when electric field  $\vec{E} \parallel$  to c-axis) while the lower panel shows the perpendicular reflectivity  $R_{\perp}$  (when  $\vec{E} \perp$  to c-axis) for NdF<sub>3</sub> compound along with the experimental data from Olson *et al.* [11] The calculated reflectivity projects an insulating behavior at low photon energies indicating largely a transparent nature, with a reflectivity as low as 8%, in the visible and ultra violet range. The reflectivity for NdF<sub>3</sub> stays low till ~ 7 eV which is consistent with their large energy gaps. After this there is a rise in the calculated values marking the onset of interband transitions. The calculated spectra show relatively sharper features with more structures particularly in the high energy range as compared to experimental curve. Nevertheless, our calculations also show similar trends for the reflectivities e.g. likewise experimental data, there is a broad structure, consisting of two main peaks in the energy range 8 -15 eV for  $R_{||}$ . The experimental and calculated curves match well magnitude wise. Similarly  $R_{\perp}$  also has a good agreement with experimental data in this energy range, with the magnitude showing very good agreement. The drop in experimental as well as calculated reflectivity at ~ 17 eV is easily explained by the density of states curves (Fig. 2) which show this energy as the separation between the top of the conduction band and bottom of the valence band thus exhausting transitions between all the states in these bands. The low R values around 17 eV are reproduced fairly well for NdF<sub>3</sub> compound by our calculations, and so is the experimental peak around 27 eV.

Besides this, the calculations show two sharp peaks for the  $R_{\parallel}$  of the  $\text{NdF}_3$  compound around 20 eV and 23.5 eV. The two seem to be fused into a single peak around 24 eV in the experimental data. It indicates that the calculated results will show better agreement when stronger relaxation effects are taken into account.

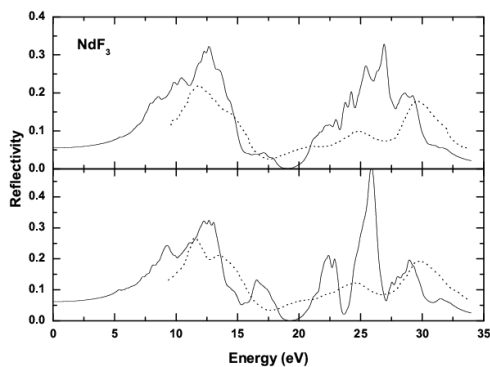


Fig. 3 Parallel component (upper panel) and perpendicular component (lower panel) of the reflectivity of  $\text{NdF}_3$  using LSDA+U approximations, along with experimental data [11]

Analyzing the origin of these structures, we find that the structures up to  $\sim 17$  eV are due to the transitions from occupied  $F-p$  states to unoccupied  $R-d$  and  $F-d$  states. Comparison of the experiment and the theory for the prominent peak in the 10 - 15 eV range suggests that calculations show slightly larger dispersion for the shallow valence bands, in the low energy region. This seems to suggest a strong impact of inter atomic interactions on the  $F-p$  states. Our results show that the peaks around 20 and 23.5 eV involve transitions from the occupied  $f$ -states and terminating at unoccupied  $f$ -states. Almost same position of the structures in the experimental spectra indicates that the relative separation of states, involved in interband transitions leading to these structures, remains almost unaltered. Our calculations bring out most of the features of the experimental data at correct energies although the calculated peaks are more prominent in the high energy range in both parallel and perpendicular components. As already suggested, a stronger relaxation would improve the agreement.

#### IV. CONCLUSIONS

Our calculation on  $\text{NdF}_3$  compound shows that the electronic structures, energy gaps are highly influenced by the  $f$ -states in these compounds. These  $f$ -states are well treated by inclusion of on-site coulomb interaction with LSDA+U approximation. The shifting of  $f$ -states away from  $E_F$  by using LSDA+U approximation shows the correct insulating nature of both compounds in agreement with experimental observations. Our calculated BS and DOS using LSDA+U approximation show that the  $d$  states of both R and F atoms constitute the broad conduction band while the  $F-p$  states constitute the broad valence band. The  $R_{\parallel}$  and  $R_{\perp}$  for both compounds are in fair agreement with the experiment. Low values of reflectivity

clearly indicate the transparency of these compounds in the visible and ultra violet region of spectrum in agreement with experimental observations. Thus LSDA+U results are able to explain the optical properties of  $\text{NdF}_3$  compound well.

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