Electronic and Optical Properties of Dy_2O_3: ab initio calculation

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Abstract

In this work, we have investigated the electronic and optical properties of the technologically important rare earth oxide compound – Dy_2O_3 using the density functional theory within the GGA. The band structure of Dy_2O_3 has been calculated along high symmetry directions in the first Brillouin zone. The real and imaginary parts of dilectric functions and the other optical responses such as energy-loss function, the effective number of valence electrons and the effective optical dielectric constants of the rare earth sesquioxide - Dy_2O_3 were calculated.

Keywords: rare earth oxide, ab initio calculation, electronic structure, optical properties

1. Introduction

Dy_2O_3 is the interesting material from both fundamental and industrial perspectives and has a wide range of applications. It is thermodynamically stable, making it useful for corrosion resistive coating [1-5]. Additionally, its high refractive indices lead to applications in optics, such as antireflection coatings, switches, filters and modulators [1,4]. The most recent interest of Dy2O3 is due to its high dielectric constant and electrical stability, making it good candidate for a new class of gate oxides in metal-oxide semiconductor field-effect transistors [1]. In addition, many properties of rare-earth sesquioxides are determined by their semicore *f* - levels. While being mainly localized on the rare-earth atoms and usually not participating in bonding and electronic conduction, *f* –shell electrons are available for optical transition and can establish strong magnetic order [1]. So far as we know, no ab initio general potential calculation of the optical properties of the rare-earth sesquioxides have been reported. The main purpose of this work is to provide some additional information to the existing features of Dy_2O_3 by using density functional theory. Therefore, in this work, we have investigated the electronic and optical properties of Dy_2O_3 compound.

2. Method of Calculation

In the present paper, all calculations have been carried out using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Faculty of Physics of the University of Vienna[6-9] within the density functional theory (DFT) [10]. The exchange-correlation energy function is treated within the GGA (generalized gradient approximation) by the density functional of Perdew et al. [11]. We get a good convergence using a $5 \times 5 \times 5$ Monkhorst-Pack [12] mesh grid for the total-energy calculation with a cutoff energy of 510 eV for Dy_2O_3. The electronic iterations convergence is 1.0×10^{-5} eV using the Normal (blocked Davidson) algorithm and reciprocal space projection operators. These values were found to be sufficient for studying the electronic and optical properties of Dy_2O_3 crystals.

3. Results and Discussion

3.1 Structural and Electronic Properties

In the first step of our calculations, we have carried out the equilibrium lattice constants of Dy_2O_3, by minimizing the ratio of the total energy of the crystal to its volume using the experimental data [13]. We have compared the present result for lattice parameters of Dy_2O_3 with previous experimental values [13-28] and are given in Table 1. This result are within the accuracy range of calculations based on density functional theory.

Table 1. The calculated equilibrium lattice parameters and direct band gaps together with the available experimental values for Dy_2O_3.

Material	Reference	a=b=c (Å)	E_g(eV)	Space Group
Dy_2O_3	Present (GGA-VASP)	10.674	3.90	$Ia\bar{a}3(No: 206)$
	Ref.[13]	10.630		
	Ref.[14]	10.662		
	Ref.[15]	10.669		
	Ref.[16]	10.665		
	Ref.[17]	10.620		
	Ref.[18]	10.670		
	Ref.[19]	10.668		
	Ref.[20]	10.670		
	Ref.[21]	10.668		
	Ref.[22]	10.666		
	Ref.[23]	10.653		
	Ref.[24]	10.672		
	Ref.[25]	10.667		
	Ref.[26]	10.665		
	Ref.[27]	10.668		
	Ref.[28]	10.670		

The investigation of electronic band structure for understanding the electronic and optical properties of Dy_2O_3 is very useful. The band structure of the Dy_2O_3 was calculated using GGA. The electronic band structure was calculated along the special lines connecting the high-symmetry points Γ, H, N, and P for Dy_2O_3 in the k-space. The electronic band structure of Dy_2O_3 along the high symmetry directions have been calculated by using the equilibrium lattice constants and is given in Fig. 1.

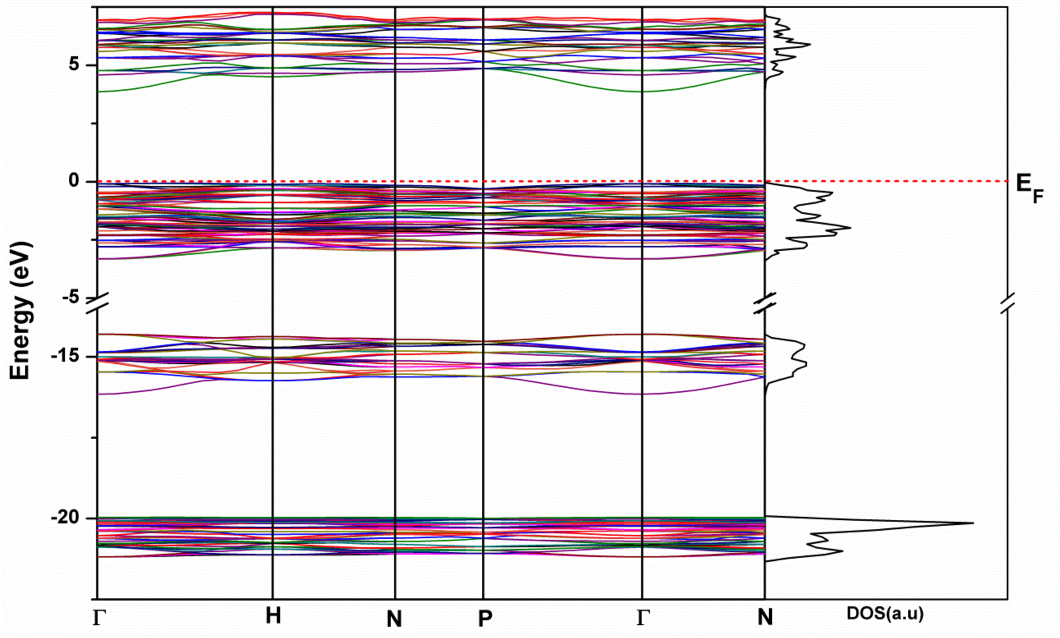

Figure 1. The calculated electronic band structure and Density of State for Dy_2O_3.

As can be seen in Fig.1, the Dy_2O_3 compound has a direct band gap semiconductor with the value 3.90 eV (in Γ-high symmetry point). The band gap value obtained for Dy_2O_3 is good agreement with the earlier theoretical resuts, but is less than the estimated experimental results [1,3,5]. In Fig. 1, the lowest valance bands that occur between 0 and -3.5 eV (72 energy states) are dominated by O 2p states while the valence bands that occur between -14 eV and -16.5 eV (24 energy states) are dominated by Dy 6s states. The lowest occupied valance bands are essentially dominated by O 2s (-19 eV and -21.5 eV and include 48 energy states).

3.2. Optical Properties

At the level of a linear response, the polarization can be calculated using the following relation [29]:

$$P^i(\omega) = \chi_{ij}^{(1)}(-\omega,\omega)E^j(\omega) \tag{1}$$

Where $\chi_{ij}^{(1)}$ is the linear optical susceptibility tensor [30]

The dielectric function $\varepsilon_{ij}(\omega) = 1 + 4\pi\chi_{ij}^{(1)}(-\omega,\omega)$ and the imaginary part of $\varepsilon_{ij}(\omega)$, $\varepsilon_2^{ij}(\omega)$ is given by

$$\varepsilon_2^{ij}(\omega) = \frac{e^2}{\hbar\pi}\sum_{nm}\int d\vec{k}\, f_{nm}(\vec{k})\frac{v_{nm}^i(\vec{k})v_{nm}^j(\vec{k})}{\omega_{mn}^2}\delta\left(\omega - \omega_{mn}(\vec{k})\right) \tag{2}$$

where n, m denote energy bands, $f_{mn}(\vec{k}) \equiv f_m(\vec{k}) - f_n(\vec{k})$ is the Fermi occupation factor. The real part of $\varepsilon_{ij}(\omega)$, $\varepsilon_1^{ij}(\omega)$, can be obtained by using the Kramers-Kroning transformation [30]. Because the Kohn-Sham equations determine the ground state properties, the unoccupied conduction bands as calculated, have no physical significance.

The known sum rules [30] can be used to determine some quantitative parameters, particularly the effective number of the valence electrons per unit cell N_{eff}, as well as the effective optical dielectric constant ε_{eff}, which make a contribution to the optical constants of a crystal at the energy E_0. One can obtain an estimate of the distribution of oscillator strengths for both intraband and interband transitions by computing the $N_{eff}(E_0)$ defined according to

$$N_{eff}(E) = \frac{2m\varepsilon_0}{\pi\hbar^2 e^2 Na} \int_0^\infty \varepsilon_2(E) E dE \tag{3}$$

Where N_a is the density of atoms in a crystal, e and m are the charge and mass of the electron, respectively, and $N_{eff}(E_0)$ is the effective number of electrons contributing to optical transitions below an energy of E_0.

Further information on the role of the core and semi-core bands may be obtained by computing the contribution that the various bands make to the static dielectric constant, ε_0. According to the Kramers-Kronig relations, one has

$$\varepsilon_0(E) - 1 = \frac{2}{\pi} \int_0^\infty \varepsilon_2(E) E^{-1} dE \tag{4}$$

One can therefore define an ‘effective’ dielectric constant, that represents a different mean of the interband transitions from that represented by the sum rule, Eq. (4), according to the relation

$$\varepsilon_{eff}(E) - 1 = \frac{2}{\pi} \int_0^{E_0} \varepsilon_2(E) E^{-1} dE \tag{5}$$

The physical meaning of ε_{eff} is quite clear: ε_{eff} is the effective optical dielectric constant governed by the interband transitions in the energy range from zero to E_0, i.e. by the polarization of the electron shells. We first calculated the real and imaginary parts of the linear dielectric function of the Dy_2O_3 compound (Fig. 2). In order to calculate the optical response by using the calculated band structure, we have chosen a photon energy range of 0-65 eV and have seen that a 0-50 eV photon energy range is sufficient for most optical functions. We first calculated the real and imaginary parts of linear dielectric function of the Dy_2O_3 compound (Figs. 2). The Dy_2O_3 compound studied so far have ε_1 are equal to zero in the energy region between 9 eV and 50 eV for decreasing $(d\varepsilon_1/dE < 0)$ and increasing of $(d\varepsilon_1/dE > 0)$ ε_1 (see, Table 2). Also, values of ε_1 versus photon energy have main peaks in the energy region 4 eV and 50 eV. Some of the principal features and singularities of the ε_{ij} for Dy_2O_3 investigated compound is shown in Table 2.

Tablo 2. The energy values at the zero point of real part of dielectric function and the maximum peak values of the imaginary part of the dielectric function for Dy_2O_3.

zero points of ε_1 (eV)					
W	X	Y	Z	T	U
10.277	13.957	28.539	34.928	44.302	45.760

maximum peak values of ε_2 (eV)					
A	B	C	D	E	F
7.2921	9.652	27.081	28.331	30.381	44.163

The peaks of ε_2 correspond to the optical transitions from the valence band to the conduction band and are in agreement with the previous results. The maximum peak values of ε_2 for Dy_2O_3 is around 9.65 eV.

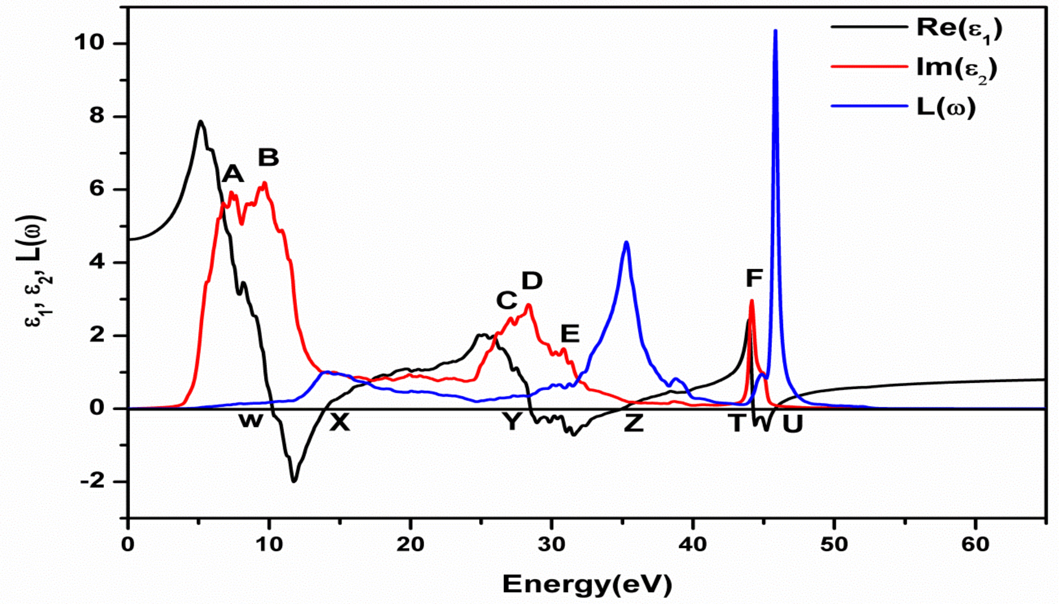

Figure 2. The real and imaginary parts of the linear dielectric function and Electron energy–loss spectrum of Dy_2O_3.

The corresponding energy-loss functions, $L(\omega)$, were calculated using eq.(6) and is also presented in Fig. 2. The $L(\omega)$ describes the energy loss of fast electrons traversing the material. The sharp maxima in the energy loss function are associated with the existence of plasma oscillations [30]. The curve of L has a maximum near 45 eV for Dy_2O_3.

$$L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} \tag{6}$$

The calculated effective number of valence electrons N_{eff} is given in Fig 3(a). The effective number of valence electron per unit cell, N_{eff} up to 5 eV is zero (below the band gap) then reaches saturation values at about 50 eV for Dy_2O_3. This means that deep-lying valence orbitals participate in the interband transitiond as well (see Figs. 1). The effective optical dielectric constant, ε_{eff}, is shown in Fig. 3(b).

The curves of ε_{eff} can be arbitrarily divided into two parts. The first part is characterized by a rapid growth of ε_{eff} and extends up to 12 eV. The second part shows a smoother and slower growth of ε_{eff} and reaches a saturation values at about 30 eV. This means that the largest contribution to ε_{eff} is made by transitions corresponding to the bands at ~5 eV and ~12 eV.

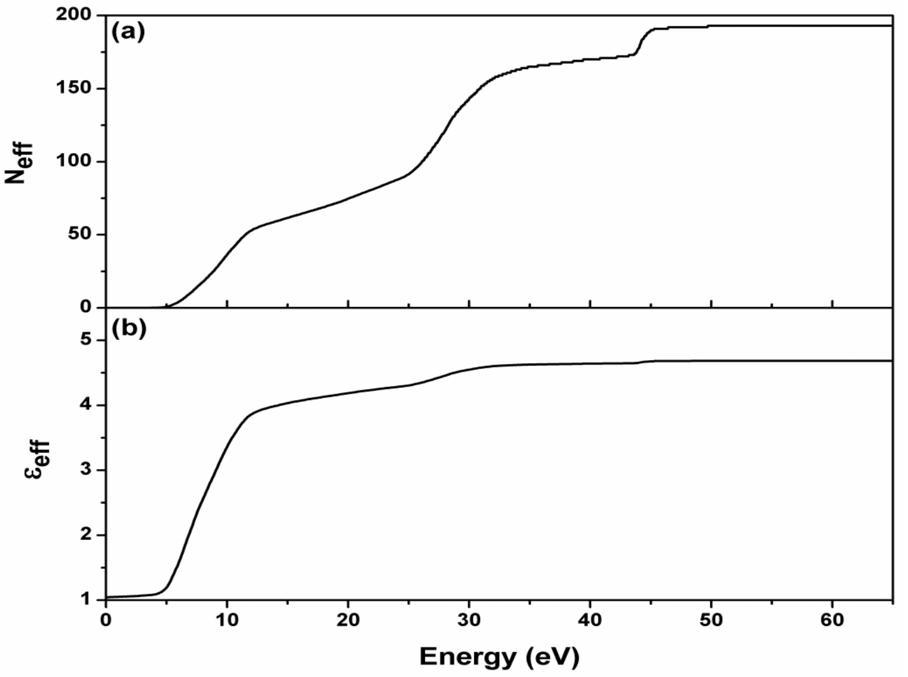

Figure 3. The calculated (a) effective number of electrons participating in the interband transitions and (b) effective optical dielectric constant.

4. Conclusion

In the present work, we have made a detailed investigation of the electronic, and frequency-dependent linear optical properties of the Dy_2O_3 crystal using the density functional methods. The result of the structural optimization implemented using the GGA are in good agreement with the experimental and theoretical results. We have examined photon-energy dependent dielectric functions, some optical properties such as the energy-loss function, the effective number of valance electrons and the effective optical dielectric constants for Dy_2O_3.

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