
Investigation of structural, electronic and optical properties of KCdF_3

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Abstract: The structural, electronic and optical properties of KCdF_3 are investigated using the density functional theory (DFT) within the generalized gradient approximation (GGA). The calculated lattice parameters have been compared to experimental results and demonstrated to be in good agreement with them. The calculated electronic band structure of cubic KCdF_3 shows that crystal has a indirect forbidden band gap with value of 2.95 eV from the high symmetry point R to gamma point in the first Brillouin Zone (BZ). The optical spectra are investigated under the scissor approximation in the photon energy range, up to 30 eV. The dielectric function and some optical constants such as energy loss functions, reflectivity, extinction, and absorption coefficients, effective number of valance electrons and refractive index are calculated.

Keywords: Density Functional Theory, Electronic Structure, Optical Properties

1. Introduction

In recent years, extensive researches devoted to the experimental and theoretical study of structural phase transitions occurring in some fluoride compounds have let us to understand the physical properties of solids. Crystal structures of fluorides are prevalent in scientific and technological areas due to their electro-optic and electro-mechanic properties, nonlinearities, large dielectric constants, and fundamental interest of phase transitions. These structures undergo phase transitions as a result of rotations of the F_6 octahedral around one of the major crystallographic axes of the high temperature cubic symmetry phase. Therefore, the electronic structure and optical properties of fluorides are very important. The energy gap of these compounds lies in the ultraviolet region of the spectrum [1] that makes these crystals interesting for researchers. Among these important fluorides, KCdF_3 crystal structure is particularly attractive due to luminescent property, laser medium and applications in radiation [2, 3]. The KCdF_3 crystal was found to have three temperatures of the phase transitions at 485, 471 and 243 K [4]. The ideal structure of KCdF_3 crystal compound has a simple cubic lattice where the potassium atom (K) lies in the center of the cube, the cadmium atom (Cd) lies at the corners of the cube and the fluorine atoms (F) lie in the middle point of sides of the cube.

Moreover, KCdF_3 crystal structure has been studied in detail. Huang et al. reported the preparation of KCdF_3 nanocrystal [5]. Hidaka et al. presented the procedure of structural analysis of the phase III of KCdF_3 containing six kinds of domains and discussed the results in terms of the successive condensation of soft phonon modes, using a full matrix least-squares method [4, 6]. Hidaka et al. studied the successive structural transitions of KCdF_3 by means of thermal diffusivity, polarized light scattering and X-ray diffraction [7]. Rousseau et al. considered the possible existence of phase transitions due to rotations of CdF_6 octahedral in the KCdF_3 compound using a simple model of force constants [8]. Darlington investigated the structures of two non-cubic phases of KCdF_3 [9]. Chun-gang Duan et al. predicted that several fluoride MCdF_3 ($M = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$) compounds could be formed in a ferroelectric crystal structure based on first-principle total energy calculations [1]. Kleemann et al. observed two weakly discontinuous structural phase transitions on single domains of KCdF_3 in the temperature dependence of the linear birefringence [10]. Geguzina detected the nature and temperatures of the phase transitions of fluorides with the perovskite structure [11].

In our knowledge, no detailed first principle calculations of the physical properties of KCdF_3 have been reported. In the present paper, the detailed calculations of the electronic and optical properties of KCdF_3 are carried out using the

pseudopotential method based on the DFT within GGA.

2. Details of the Calculations

KCdF₃ has cubic structure at room temperature and belongs to the space group Pm-3m (No. 221). KCdF₃ contains one molecule with five atoms per unit cell. The experimental lattice constant of KCdF₃ crystal is 4.293 Å [12]. At room temperature, K, Cd, and F ions are located at (0.5, 0.5, 0.5), (0.0, 0.0, 0.0), and (0.5, 0.0, 0.0), (0.0, 0.5, 0.0), (0.0, 0.0, 0.5) in the unit cell of KCdF₃, respectively.

The computer calculations were performed in the ABINIT code. After optimization process, the electronic and optical properties were calculated. The calculated results were obtained using GGA included the exchange-correlation effects [13] of DFT. The self-consistent norm-conserving pseudopotentials of FHI-type with a Troullier-Martins scheme [14] for all atoms of KCdF₃ crystal were used. 4s electron for K atom, 5s and 4d electrons for Cd atom, and 2s and 2p electrons for F atom were considered as the true valence. The basis set for the electronic wave functions were chosen to be plane waves. The conjugate gradient minimization method [15] was used to solve Kohn-Sham equations [16] in the ABINIT code [17]. A good convergence for the total energy calculation with 50 Hartree cut off energy has been achieved using a 8 x 8 x 8 Monkhorst-Pack mesh grid [18]. On the other hand, the irreducible BZ was sampled with 10 x 10 x 10 Monkhorst-Pack mesh grid to calculate the optical properties of KCdF₃.

The electronic excitation spectrum of a material is usually defined in terms of frequency dependent complex dielectric function. The real and imaginary parts of the frequency dependent dielectric function contain all required response information. Since optical properties of a solid are the response of the solid to electromagnetic perturbation occurring from incoming light to solid, the calculation of optical properties means computation of optical response function, namely dielectric function. If the imaginary component of dielectric function is known, the real part of the dielectric function can be obtained using the Kramers-Kronig relations. Rest of optical constants of the solid can be also calculated via imaginary dielectric function.

The Kohn-Sham equations determine the ground-state properties. Because the unoccupied conduction bands have no physical importance and a band gap problem appears at too low energy values, the self-energy effects must be included when the optical response calculations for semiconductors and insulators are made. In the GGA calculations, in order to include the self-energy effects, the scissor approximation [19] was used. In the approximation, we have shifted theoretical values of band gap by 4.5 eV in order to match the experimental [20] and the theoretical band gap values.

3. Result and Discussions

In general, if total energy of a solid is known, one can

determine the physical properties of the solid. As shown in Fig. 1, the theoretical lattice constant was calculated as 4.497 Å by minimizing the total energy as a function of volume for the KCdF₃ crystal. Comparing calculated lattice constant to experimental result [12], it is seen that they are in good agreement. For the rest of the calculations, the calculated lattice constant was used.

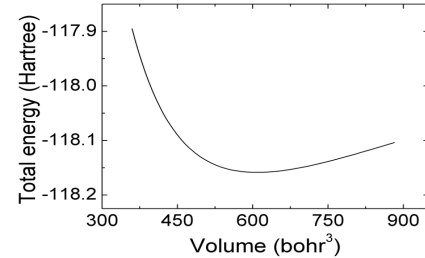


Figure 1. Dependence of total energy on unit cell volume for cubic KCdF₃.

The investigation of energy band structure is very useful to be understood the electronic and optical properties of a material. Therefore, the calculated energy band structure of KCdF₃ was obtained and demonstrated in Fig. 2, covering a wide range of energy from -21 to 12 eV, along high symmetry directions in the first BZ. The Fermi level is set as zero energy level and indicated by a horizontal dashed line in Fig. 2.

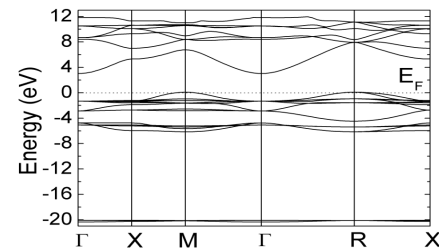


Figure 2. Calculated electronic band structure for cubic KCdF₃.

The high symmetry points of irreducible BZ are marked with letters in Fig. 2. The maximum of valence band and the minimum of conduction band are located at the high symmetry points R and Γ , respectively, in the BZ. Therefore, the band structure for cubic KCdF₃ shows indirect forbidden band gap from R to Γ .

The value of calculated indirect forbidden band gap is 2.95 eV. It is seen that the obtained band gap is less than the experimental band gap [20]. It is well known that the calculated band gap in DFT is always smaller than the experimental band gap. Probably, the underestimation of the band gap is due to the generic nature of the DFT. Thus, a scissors operator applied to the calculation of optical parameters is needed to shift all the conduction levels in order to agree with the measured value of the band gap.

Next, the optical properties of cubic KCdF₃ were also studied. The optical properties can be obtained from the complex dielectric function which is usually connected with the electronic structure [21, 22]. The frequency dependent imaginary part of complex dielectric function was calculated. Using the imaginary component of dielectric function, the

real part of the dielectric function can be obtained by the Kramers-Kronig relations. The calculated optical functions neglecting all lattice vibrational effects and pertaining to only the electronic transitions were shown in Fig. 3. The optical response was chosen in the photon energy range of 0-30 eV considering the calculated band structure in Fig. 2. As a result of all the calculations, it is seen that the 0-30 eV photon-energy range was sufficient for optical response of KCdF_3 .

The KCdF_3 compound has a cubic structure which is

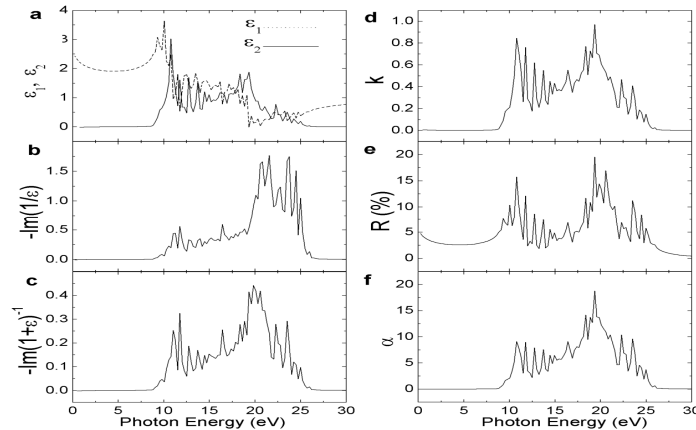


Figure 3. Calculated a) Real (ϵ_1) and imaginary (ϵ_2) parts of optical dielectric functions, b) energy loss function for volume, c) energy loss function for surface, d) extinction coefficient (k), e) Reflectivity spectrum, e) absorption (α) coefficient for KCdF_3 .

From the Fig. 3, while the 0 - 9.50 eV photon-energy range is characterized by high transparency, no absorption and a small reflectivity which explains the origin of the peak structure in the reflectivity and absorption coefficient spectra, 9.50 - 10.75 eV photon-energy range is characterized by strong absorption and appreciable reflectivity which means that optical absorption increases more quickly in this photon-energy range. Moreover, the photon-energy range of 10.75 - 25.00 eV is characterized by high reflectivity. As can be seen from Fig. 3a, the static dielectric constant for KCdF_3 was calculated as 2.44. The real part of dielectric function equals to zero at 19.31 and 19.43 eV.

The calculated energy-loss functions of volume and surface for KCdF_3 were illustrated in Figs. 3b and 3c, respectively. The volume loss function gives a description about the energy loss of the fast electrons passing through the material. One can see from these figures, the energy-loss functions for volume and surface shows mainly many intense maximum peaks. The sharp maxima in the volume-loss function are associated with the excitation of plasma. The energy values corresponding to peaks of volume loss function coincide with the energy values corresponding to zero values of real part of dielectric function.

Moreover, the extinction coefficient, reflectivity spectrum, and absorption coefficient are shown in Figs. 3d, 3e and 3f, respectively.

The sum rule can be used to determine the effective number of valence electrons contributing to optical transitions [21, 22]. An estimate of distribution of oscillator strengths can be obtained for both intraband and interband

optically isotropic (anaxial) system. Therefore, the linear dielectric tensor for KCdF_3 has one independent component. The calculated real and imaginary parts of the frequency dependent dielectric function were presented in Fig. 3. The peaks of the imaginary part of dielectric function in Fig. 3a correspond to the optical transitions from the valance band to the conduction band. As seen from the Fig. 3a, the KCdF_3 exhibits two fundamental oscillator bands at 9.50 and 10.74 eV.

transitions. As can be seen from Fig. 4a, the effective number of valence electrons is zero up to photon energy values of 9.5 eV, then rises rapidly and reaches a saturation value at about 25.00 eV. This shows that the interband transitions do not include deep-lying valence states.

The calculated refractive index was shown in Fig. 4b. For the calculation of the refractive index, 0-3 μm photon-wavelength range was taken and it was sufficient enough for the calculations. This figure represents spectral dependence of the calculated main refractive index for cubic KCdF_3 in a wide wavelength range and reveals the decreasing behavior of refractive index (n) with the transition from the intrinsic absorption region towards long wavelengths where a normal dispersion takes place. Using $n = n(\lambda)$ dependence, the maxima were obtained at $\lambda = 0.12 \mu\text{m}$ with the values of n as 1.92.

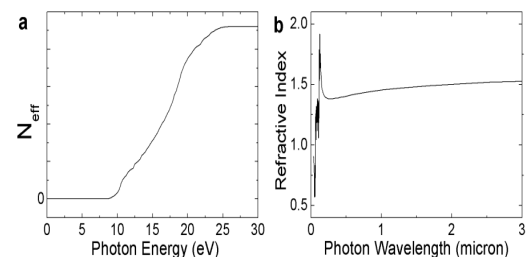


Figure 4. a) Effective number of valence electrons vs photon energy b) Refractive index vs photon wavelength for KCdF_3 .

4. Conclusions

The aim of the present work is to investigate electronic

and optical properties of cubic KCdF₃ compound using the DFT under the GGA. As a result of calculations, it was found that the forbidden band gap of cubic KCdF₃ is indirect character in the symmetry direction from R to Γ in the BZ. The calculated value of forbidden band gap is 2.95 eV and is smaller than its experimental value due to the generic nature of the DFT. The photon energy dependent dielectric functions as well as related quantities such as energy-loss functions for volume and surface, extinction and absorption coefficients, reflectivity and refractive index were investigated. Moreover, the effective number of valence electrons per unit cell participating in the interband transitions was studied. The results of implemented structural optimization by using the GGA are in excellent agreement with the available experimental data. For optical and electronic properties, the calculated results cannot be compared with any data due to the lack of any experimental or theoretical work previously performed.

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