

Density Functional Calculations of the Electronic Band Structure and Optical Properties of KCaF_3

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ABSTRACT

The electronic band structure and optical properties of cubic KCaF_3 are studied using the density functional theory. The calculated band structure of cubic KCaF_3 shows an indirect band gap with two values of 5.95 eV and 5.94 eV at the $M \rightarrow \Gamma$ and $\Gamma \rightarrow R$ lines of Brillouin zone, respectively. The structural optimization has been performed using the generalized gradient approximation (GGA). The calculated structure optimization of KCaF_3 has been compared with experimental results. Good agreement between theoretical and experimental results was observed. Moreover, some optical constants such as energy-loss functions for volume and surface, coefficients of extinction, reflectivity and absorption, refractive index and effective number of valence electrons per unit cell participating in the inter-band transitions and the linear photon-energy-dependent dielectric functions have been calculated.

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1. INTRODUCTION

ABO_3 and ABF_3 have similar crystal structures and are abundantly used in many areas of scientific and technological because of their interesting electro-optic and electro-mechanic properties, nonlinearities, large dielectric constants, and fundamental interest in the physics of their phase transitions. Since they undergo phase transitions as a result of rotations of the F_6 octahedral around one of the major crystallographic axes of high temperature cubic symmetry phase, these Perovskite-type crystals having chemical formula ABF_3 , of which KCaF_3 is an example, have been attracting serious attention. The ideal structure of perovskite fluoride KCaF_3 crystal compound has a simple cubic lattice, where the monovalent K atom lies in the center of the cube, the divalent Ca atom lies at the corners of the cube and the fluorine F atoms lie in the axes of the cube.

Demetriou *et al.* [1] determined the nature of high conductivity of KCaF_3 using single crystal neutron diffraction experiments. Daniel *et al.* [2] presented a

thorough investigation by Raman scattering of KCaF_3 depending on temperature, and obtained useful information on high temperature structural instabilities occurring in this compound. Flocken *et al.* [3] made a priori theoretical study of the potential-energy surface for KCaF_3 and examined the relative stability of the various lower-symmetry structures generated from cubic perovskite phase by rotations of the octahedral CaF_6 . Chomodolsky *et al.* [4] investigated the electronic calculations for ABX_3 ($A = \text{K, Rb, Cs}$; $B = \text{Ca}$; $X = \text{F}$) by the pseudo-potential method taking into account the gradient corrections for the exchange-correlation energy. Watson *et al.* [5] presented the results from constant-pressure and constant-temperature molecular dynamics simulations on the fluoride-perovskites (KMnF_3 , KZnF_3 and KCaF_3). His prediction was that KCaF_3 is super-ionic conductor. Rousseau *et al.* [6] investigated the unusual mechanism of phase transition occurring in KCaF_3 by inelastic neutron scattering.

As seen from the discussion above, an important number of experimental data on the physical properties exist, but

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there are almost no theoretical studies done on the electronic and optical properties of KCaF_3 crystal. Moreover, no detailed *ab-initio* general potential calculations of the electronic band structure and optical properties of KCaF_3 crystal have been reported as far as we know.

In this study, the self-consistent norm-conserving pseudo-potentials with the Troullier-Martins scheme [7] have been used in all calculations. To consider the exchange-correlation effects, the Perdew-Burke-Ernzerhof GGA functional (PBE-GGA-96) [8] was used. 4s electron for potassium atom, 4s electron for calcium atom, and 2s and 2p electrons for fluorine atom were studied as true valence and plane waves were used as the basic set for electronic wave functions. To solve the Kohn-Sham equations [9], the conjugate gradient minimization method [10] was used by the ABINIT code [11]. All the calculations included cubic unit cells containing one molecule. A good convergence for the bulk total energy calculation was achieved with choice of cut-off energies at 50 Hartree using an $8 \times 8 \times 8$ Monkhorst-Pack mesh grid [12].

The dielectric function, that is known to be mainly connected to the electronic response, was calculated in the momentum representation, which required the matrix elements of the momentum \vec{P} between occupied and unoccupied eigenstates. The imaginary part, $\varepsilon''(\omega)$, of the dielectric function, $\varepsilon(\omega)$, is given by

$$\varepsilon''(\omega) = \frac{Ve^2}{2\pi\hbar m^2 \omega^2} \int d^3k \sum_{n,n'} \left| \langle \vec{k}n | \vec{p} | \vec{k}n' \rangle \right|^2 \times f(\vec{k}n) (1 - f(\vec{k}n')) \delta(E_{\vec{k}n} - E_{\vec{k}n'} - \hbar\omega), \quad (1)$$

where e is the charge of the electron, m is the mass of the electron, V is the volume, ω is the frequency of an electron, $|\vec{k}n\rangle$ is a crystal wave function, \vec{p} is the momentum operator, $f(\vec{k}n)$ is the Fermi function, and $\hbar\omega$ is the energy of the incident photon. The summation over the Brillouin zone (BZ) is calculated using a linear interpolation on a mesh of uniformly distributed points. Matrix elements, eigenvalues, and eigenvectors are calculated in the irreducible part of the

BZ. The correct symmetry for the dielectric constant was obtained by averaging the calculated dielectric function. The real part, $\varepsilon'(\omega)$, of the dielectric function $\varepsilon(\omega)$ was evaluated from the imaginary part, $\varepsilon''(\omega)$, by using the Kramer-Kronig transformation. Non-linear optical response for cubic KCaF_3 single crystal has not been investigated in this work.

As it is known, properties of ground-state are determined by Kohn-Sham equations. Since the unoccupied conduction bands have no physical importance and a band gap problem appears at energy values that are too low, the self-energy effects should be taken into account when the optical response calculations are made. The scissor approximation [13] was used in order to include the self-energy effects, and it was chosen at 2.5 eV in the present work using the experimental energy gap (6 - 13 eV) for KCaF_3 by Chornodolskyy *et al.* [4].

The present study focuses on the electronic and optical properties of KCaF_3 crystal using density functional theory under the GGA, which is absent in the literature.

2. RESULTS AND DISCUSSION

As it is known, all physical properties are related to total energy. For example, equilibrium lattice constant of a crystal is the lattice constant that minimizes total energy. If total energy can be calculated, then any physical property, related to total energy, can be determined. For theoretical calculation of lattice constant, basic state energy of cubic KCaF_3 crystal is calculated for different volumes around the experiment balance volume. Figure 1 shows the total energy as a function of the volume of KCaF_3 by the GGA. Table 1 presents the experimental and calculated volume values.

Various techniques have been used to study the structure of KCaF_3 crystal experimentally [1-3, 14]. The KCaF_3 crystal is cubic and belongs to the space group Pm-3m (No. 221). The studied KCaF_3 contains one molecule with five atoms per unit cell, as shown in table 1. K is located at the central position (1/2,1/2,1/2), Ca is located in the position (0,0,0), and F is located in the positions: (1/2,0,0), (0,1/2,0) and (0,0,1/2). Calculations were carried out using the lattice constant $a = 4.4584$ (Å) for KCaF_3 [1]. Table 1 gives the crystal data of KCaF_3 obtained from the structure optimization.

Table 1. Crystal structure data of cubic KCaF_3 .

Space group	Pm-3m						
KCaF_3	Experimental	Calculated	Atom	Wyckoff	x	y	z
a (Å)	4.4584	4.5293	K	1b	0.5	0.5	0.5
E_g (eV)	6 - 13	5.94 - 5.95	Ca	1a	0.0	0.0	0.0
Volume (Å ³)	88.62	92.92	F	3d	0.5	0.0	0.0

Pseudo-potential method, based on density functional theory under the GGA, was used to obtain the lattice parameter of cubic KCaF_3 crystal. That is, via minimizing the crystal total energy to crystal volume ratio (volume optimizing), the theoretical lattice constant has been calculated as $a = 4.5293 \text{ \AA}$. Experimental and calculated

values of the lattice parameters for the lattice which is at equilibrium are given in table 1. As can be seen from table 1, the deviation of the calculated equilibrium volumes for GGA calculation is 4.85% of the experimentally determined value.

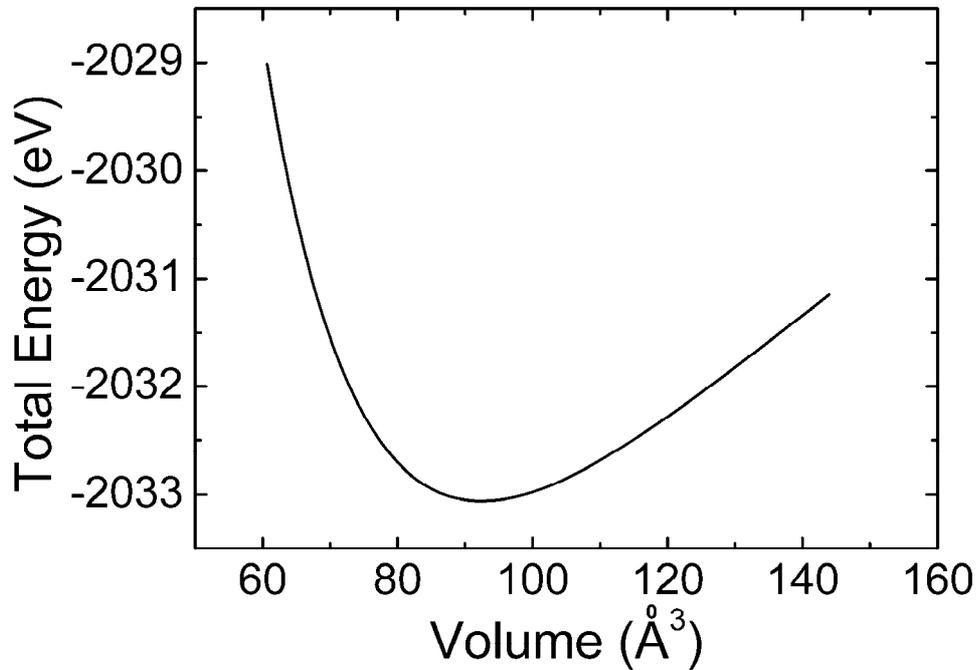


Figure 1. Dependence of total energy on unit cell volume for cubic KCaF_3 crystal.

The investigation of electronic band structure of cubic KCaF_3 is very useful in understanding the electronic and optical properties of the material better. At this point, we need firstly to describe our calculated electronic structure. Figure 2 shows the energy-band structure calculated using the GGA for cubic KCaF_3 . There, the origin of energy was arbitrarily set to be at the valence band maximum.

The band structure calculations have been done in the high-symmetry directions of the first BZ. The band structure of KCaF_3 has been calculated and plotted on surface of the BZ. The k points showing the corners of irreducible BZ are marked with letters in figure 2, where the Fermi level is set to zero. The maximum of valence

band and minimum of conduction band are placed at the $M \rightarrow \Gamma$ and $\Gamma \rightarrow R$ lines of the BZ.

An indirect band gap at $M \rightarrow \Gamma$ and $\Gamma \rightarrow R$ symmetry lines of the BZ is observed at the calculated band structure for cubic KCaF_3 crystal. The indirect band gaps computed by GGA are 5.95 eV and 5.94 eV at $M \rightarrow \Gamma$ and $\Gamma \rightarrow R$ lines, respectively. The found band gap is smaller than experimental result of 6 - 13 eV [4], probably because of a discrepancy in the GGA method. Good agreement with the experimental result can be obtained by adding a correction factor to this band gap. Moreover, total density of states (DOS) for cubic KCaF_3 crystal is also studied and the calculated DOS are shown in figure 3.

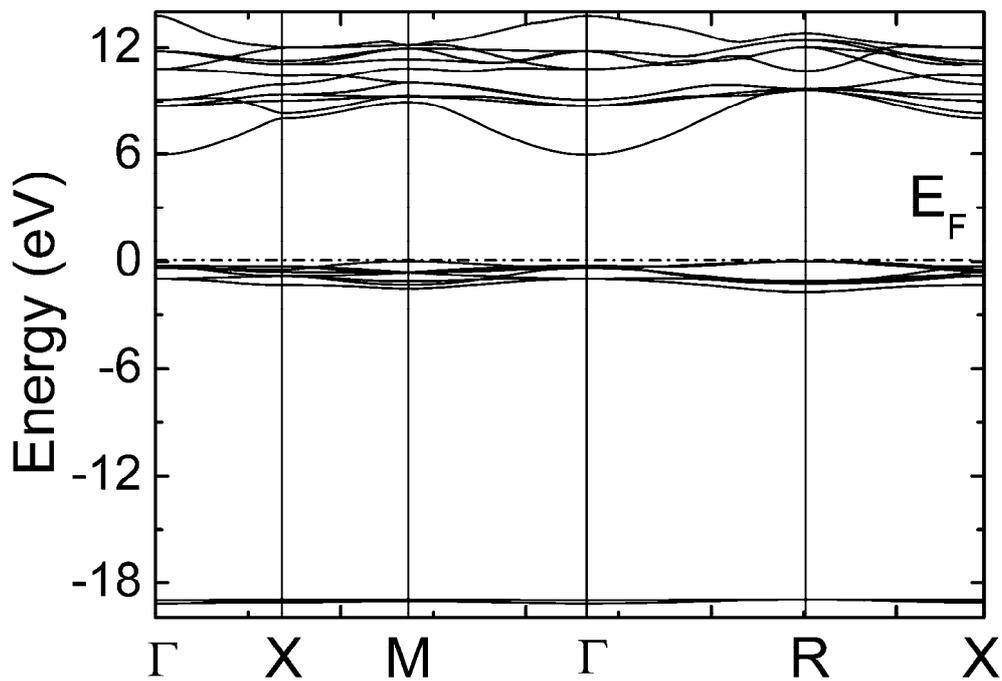


Figure 2. Calculated band structure for cubic KCaF_3 crystal.

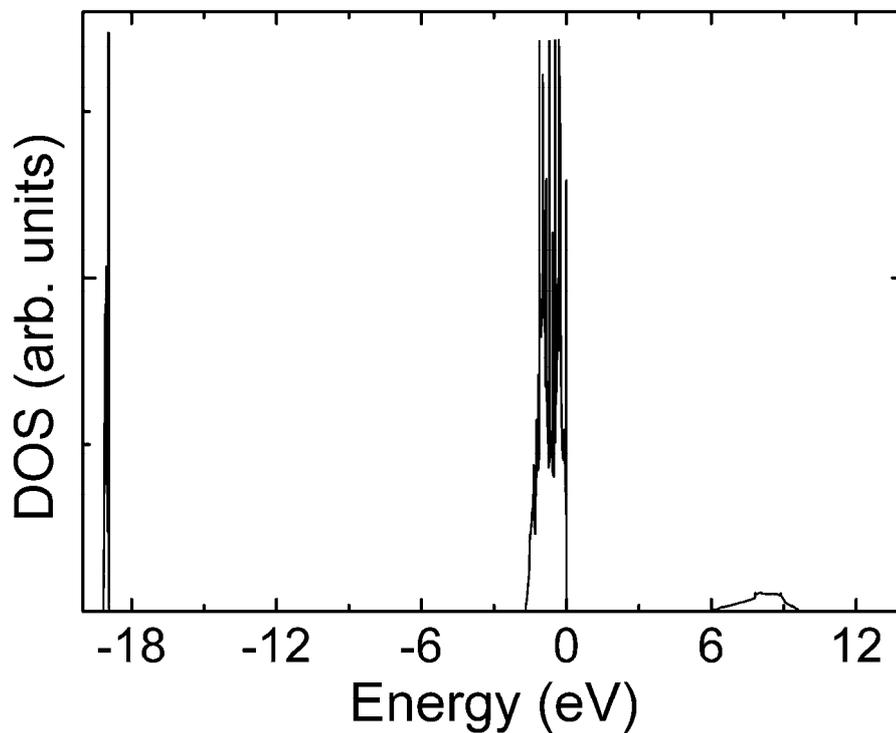


Figure 3. Total density of states for cubic KCaF_3 crystal.

We also studied the linear optical properties of cubic KCaF_3 in the present work. The optical functions calculated by ignoring all lattice vibrational effects and concerning only the electronic transitions are shown in figure 4. The optical response was calculated in the photon energy range of 0 - 30 eV using the calculated band structure. As a result of calculations, we saw that a 0 - 20 eV photon-energy range is enough for most optical

functions. Thus, we have deduced the values of real and imaginary parts of the dielectric function as a function of the photon energy.

The calculated real and imaginary parts of frequency-dependent linear dielectric function are shown in figure 4(a). Imaginary part of dielectric constant, \mathcal{E}_2 , shows several main peaks at 9.10, 9.77, 10.18, 10.67, 12.07,

13.45, 14.08, and 14.52 eV along the crystallographic *c*-direction. These peaks correspond to the transitions from valence to conduction band. KCaF_3 exhibits two fundamental oscillator bands at 9.10 and 9.77 eV, which correspond to optical transitions from valence to conduction band. For the 0 - 9 eV photon-energy range, there is high transparency, no absorption and a small reflectivity. These remarks explain origin of the peak structure in reflectivity and absorption coefficient spectra. The 9.0 - 12.0 eV photon-energy range is characterized by strong absorption and appreciable reflectivity. That is, optical absorption increases more quickly in this photon-energy range. In 12.0 - 17.0 eV photon-energy range there is a high reflectivity.

The real part of the frequency-dependent linear dielectric function found from imaginary part by Kramers-Kronig conversion is also presented in figure 4(a). The calculated static dielectric constant of KCaF_3 crystal is $\epsilon_0 = 1.54$. Figure 4(a) shows that the function ϵ_1 is equal to zero at 12.38, 13.07, 15.09, and 15.78 eV along the crystallographic *c*-direction. The inter-band transitions at these lines, which consist mostly of plasmon excitations, the scattering probability of volume and surface losses are directly connected to energy loss function.

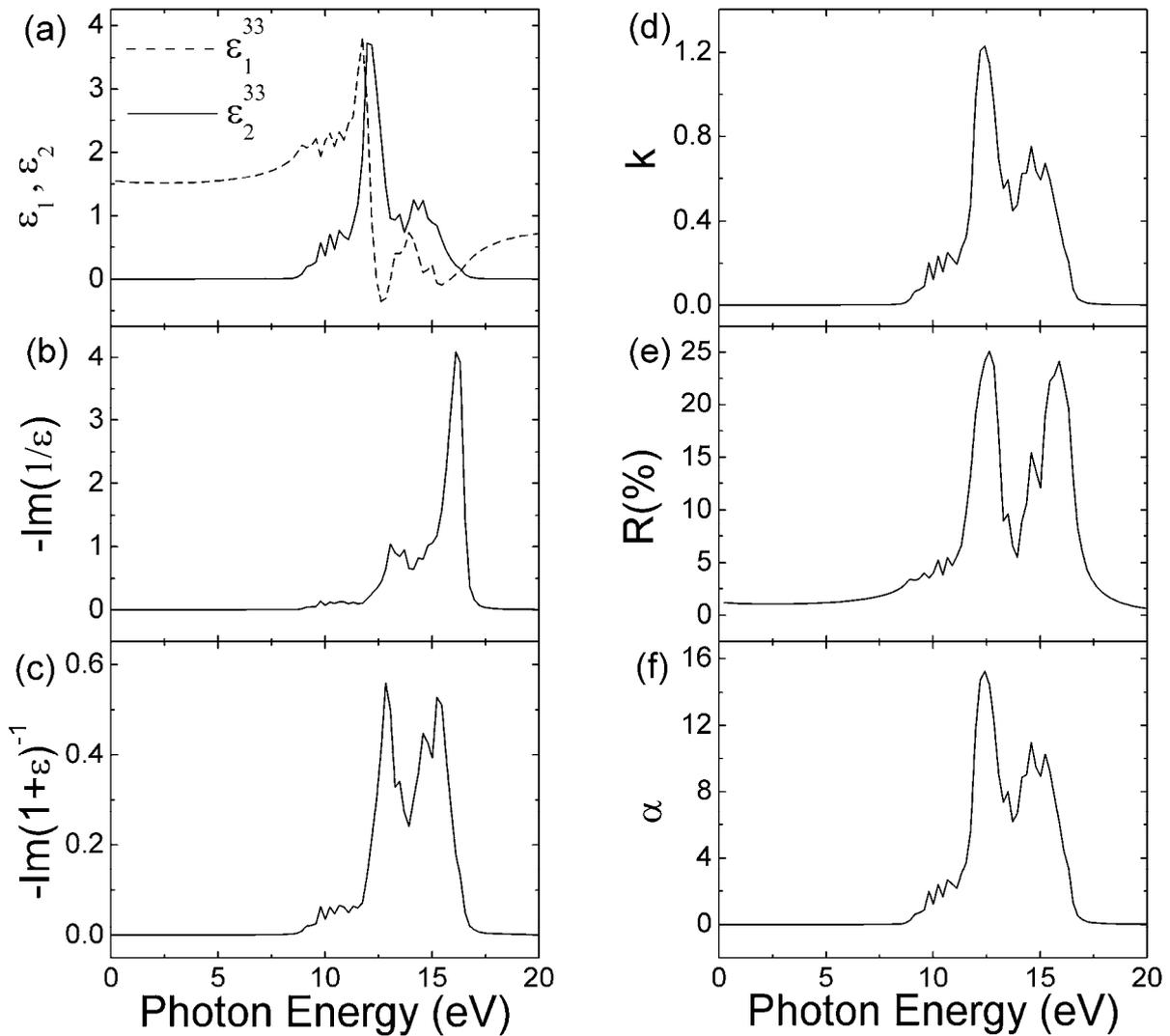


Figure 4. Optical spectra for cubic KCaF_3 crystal. Calculated real and imaginary parts of optical dielectric function, energy-loss functions for volume and surface, extinction coefficient, reflectivity spectrum and absorption coefficient.

For KCaF_3 , the calculated energy-loss functions, $-\text{Im}\epsilon^{-1}$ for volume and $-\text{Im}(1+\epsilon)^{-1}$ for surface, are plotted in figures 4(b) and 4(c) corresponding to crystallographic *c*-direction, respectively. The Energy-loss functions describe energy loss of fast electrons

transversing the material. The calculated energy-loss function for volume shows intense maximum peaks at 13.07 and 16.05 eV because of excitation of plasmons. The calculated energy-loss function for surface shows mainly intense maximum peaks at 12.75, 14.52, and

15.75 eV. The peak values of volume loss coincide with one of zero values of real part of dielectric function. The sharp maxima in the energy-loss functions are associated with existence of plasma oscillations or the energy $\hbar\omega_p$ of volume and surface plasmons. The calculated extinction coefficients, reflectivity spectrum and absorption coefficients along crystallographic c -direction are shown in figures 4(d), 4(e), and 4(f), respectively.

An initial choice of photon-wavelength range of 0 - 3 μm was made for the calculation of the refractive index. It

was noticed that a 0 - 1 μm photon-wavelength range is sufficient for the calculations, as seen from figure 5(a). The spectral dependence of the calculated main refractive index for cubic KCaF_3 crystal in a wide wavelength range is shown in figure 5(a). It is seen from figure 5(a) that the value n decreases with transition from intrinsic absorption region towards long waves, *i.e.* a normal dispersion takes place. A maximum value in the dependence, $n = n(\lambda)$, have been obtained at $\lambda = 0.106$ μm . The maximum value of n is 2.007.

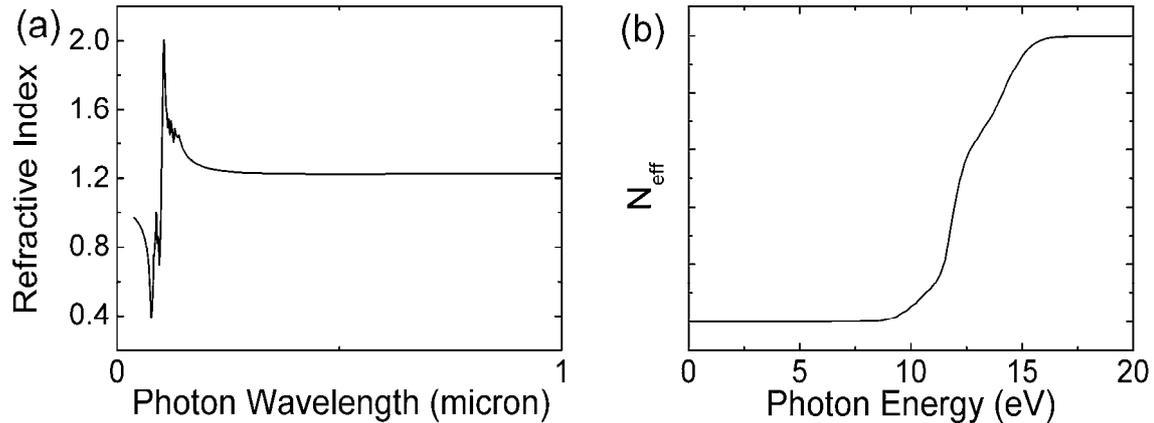


Figure 5. Dispersion of the refractive index and effective number of valence electrons for cubic KCaF_3 crystal.

The sum rule [15] can be used to calculate the effective number of valence electrons per unit cell contributing to the optical constants in the inter-band transitions. For both intra-band and inter-band transitions, an estimate of the distribution of oscillator strengths can be obtained by computing the $N_{eff}(E_0)$ defined according to

$$N_{eff}(E_0) = \frac{2m\epsilon_0}{\pi\hbar^2 e^2} \frac{1}{N_0} \int_0^{E_0} \epsilon_2(E) E dE \quad (2)$$

where $N_{eff}(E_0)$ is the effective number of electrons contributing to optical transitions below an energy of E_0 . In equation 2, E_0 denotes the upper limit of integration, the quantities m and e are the electron mass and charge, respectively, and N_0 stands for the electron density. As can be seen from figure 5(b), the effective electron number, $N_{eff}(E_0)$, is zero up to 8.50 eV, then rises rapidly and reaches a saturation value above 16.50 eV. This shows that the deep-lying valence states are not involved in the inter-band transitions.

3. CONCLUSIONS

In the present work, the electronic and linear optical properties of cubic KCaF_3 crystal have been examined in detail using the density functional methods under the GGA. The fundamental gap of KCaF_3 crystal was found to be indirect at the $M \rightarrow \Gamma$ and $\Gamma \rightarrow R$ points of the BZ as a result of calculations. The calculated band gaps by GGA are 5.95 and 5.94 eV at the $M \rightarrow \Gamma$ and $\Gamma \rightarrow R$ points. These values are smaller than the experimental

results of 6 - 13 eV due to the discontinuity in the GGA. We have examined the photon energy-dependent dielectric functions and related quantities such as energy-loss functions for volume and surface, extinction and absorption coefficients, reflectivity and refractive index. Besides these, a very important optical parameter, the effective number of valence electrons per unit cell participating in the inter-band transitions, was studied and calculated. The results of applied structural optimization by the GGA and experimental results agree with each other well.

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